

IV. ENVIRONMENTAL DATA AND BIOLOGIC MONITORING

Environmental Concentrations

There is an abundance of information on the concentrations of carbon disulfide at which workers have been routinely exposed. Most of the reports discussed in Chapter III include measurements of the workplace environment. These measurements are exclusively from the viscose rayon industry, where there is concomitant exposure to hydrogen sulfide. Workplace concentrations of carbon disulfide ranged from less than 9 mg/cu m (3 ppm) [54,60,67,75] to peaks exceeding 6,200 mg/cu m (2,000 ppm) [9]. Hydrogen sulfide concentrations were rarely measured or reported.

A thorough environmental investigation was conducted by Rosensteel et al [9] in 1973, as a Health Hazard Evaluation and Determination Report for NIOSH. Carbon disulfide and hydrogen sulfide samples were collected in the workers' breathing zones and in the general workroom areas of the spinning and cutting rooms of a viscose rayon plant. Air samples of carbon disulfide in workers' breathing zones were obtained using a midjet bubbler-impinger, and 12 of 36 samples were determined to contain concentrations in excess of 20 ppm (62 mg/cu m) as an 8-hour TWA concentration. In seven samples, the TWA concentrations of carbon disulfide exceeded 100 ppm (310 mg/cu m). General workroom samples of air drawn through a midjet impinger, with sampling times of 20-176 minutes, contained concentrations of hydrogen sulfide ranging from 0.74 to 3.37 ppm (1.03 to 4.68 mg/cu m). Breathing-zone samples for workers in cutting and spinning operations contained concentrations of hydrogen sulfide of around 1 ppm (1 mg/cu m). A hydrogen sulfide concentration of 6.47 ppm (8.99 mg/cu m) was determined in a sample

taken at head height, 6 inches inside a spinning hood. However, 13 of 15 hydrogen sulfide detector tubes found no measurable level (less than 1 ppm) of hydrogen sulfide in the aisles between the machinery of the spinning and cutting areas. The two measurable readings were 1 and 5 ppm (1 and 7 mg/cu m). It was therefore concluded that hydrogen sulfide did not present a health problem in that plant, but that exposures to carbon disulfide required further study. Eight workers in the cutting area and six in the spinning area were selected for more comprehensive monitoring and analysis, which was performed on a return visit.

Measurements of carbon disulfide concentrations in 10- to 20-minute air samples from the breathing zones of the eight cutters ranged from less than 20 to more than 2,000 ppm (less than 62 to more than 6,200 mg/cu m) [9]. The concentrations of carbon disulfide exceeded 100 ppm (310 mg/cu m) in more than one-half of the 196 samples taken. Similar measurements of the spinners' exposures showed that carbon disulfide concentrations were far lower in the spinning areas than in the cutting areas. The TWA concentration for all measurements was 11.2 ppm (34.7 mg/cu m) with a range of 0.9-127 ppm (2.8-394 mg/cu m). These data were combined with the general room exposure measurements to obtain TWA concentrations for the entire work shift for the 14 workers. Weighting was done on the basis of length of exposure in heavily contaminated, general, and nonexposed work areas. For cutters, shift TWA concentrations ranged from 9.5 to 129 ppm (29.5 to 400 mg/cu m); seven of the eight workers were exposed at concentrations higher than the OSHA standard of 20 ppm (62 mg/cu m) for an 8-hour day. Seven of eight were exposed to spot concentrations above the peak limit of 100 ppm (310 mg/cu m); concentrations in four of the eight

general room samples exceeded the 30-ppm (93 mg/cu m) ceiling limit. The spinners did not have environmental exposures in excess of the OSHA standard; TWA concentrations ranged from 4.3 to 11.1 ppm (13.3 to 34.4 mg/cu m).

Hernberg et al [8] reported the results of extensive environmental monitoring from 1945 through 1967 in a Finnish viscose rayon plant. Plant chemists took up to 36 air samples (5-10 minutes) each year from each of 10-40 different sites. The concentrations of carbon disulfide and hydrogen sulfide were determined separately by a titrimetric method [42]. A total of approximately 3,000 measurements were available [8]. The concentrations reported were totals of carbon disulfide plus hydrogen sulfide, with carbon disulfide concentrations estimated to be 10 times those of hydrogen sulfide. The combined concentrations were generally 10-30 ppm in the 1960's, 20-40 ppm in the 1950's, and higher than 40 ppm before 1950. In 1976, Hernberg et al [46] reported that concentrations dropped during 1967-1975, with levels falling to below 5 ppm by 1972.

Environmental concentrations of carbon disulfide in a US viscose rayon plant were reported to be between 10 and 15 ppm (31 and 47 mg/cu m) in the churn and spinning rooms, determined by personal sampling equipment and colorimetric analytic procedures [6 (pp 25-28)]. Hydrogen sulfide concentrations usually remained near 1 ppm (1 mg/cu m), as measured by colorimetric methods.

Control of Exposure

In a NIOSH environmental and medical evaluation of a viscose rayon plant, Rosensteel et al [9] made recommendations for engineering and

administrative control of carbon disulfide exposure. Having found toxic effects in workers exposed to carbon disulfide at excessively high concentrations, they recommended implementation of a comprehensive ventilation program for control of exposures near the cutting machines and in the general work areas. A strict respirator program and regular environmental and medical monitoring were also recommended.

Hernberg et al [46], in 1976, reported a large drop in the incidence of coronary heart mortality in the last 3 years of an 8-year prospective study on a cohort of 343 viscose rayon workers. The authors suggested that this return to "normal" mortality resulted from engineering and administrative controls in the viscose rayon factory. Engineering improvements, employee transfers to areas without carbon disulfide exposure, and use of personal protective equipment in operations with peak exposures were part of the improvement program.

Nurminen [47], in 1976, mentioned several factors which possibly contributed to the decreased risk of death from coronary heart disease in the same cohort of viscose rayon workers. Improved hygienic conditions, eg, better ventilation, increased awareness of hazards, and the use of personal protective equipment during peak exposures, all may have affected the decreased risk of coronary death in workers formerly exposed to carbon disulfide at excessive levels.

Flesch and Lucas [89], in a 1974 NIOSH Health Hazard Evaluation Report on a cellophane production plant, recommended several methods to decrease employee exposure to carbon disulfide. Frequent maintenance of machinery, proper use of ventilation control systems, implementation of administrative controls such as operator rotation, and assignment of

additional personnel were suggested to help increase safety, ensure proper monitoring, and alleviate employee anxiety. Respirator use was recommended at times of peak exposure.

The Manufacturing Chemists' Association [1] suggested that downdraft or lateral-type ventilation be used around equipment from which the vapor may escape. The vapor must be drawn away from workers' breathing zones. Ventilation must be designed to prevent accumulation of carbon disulfide vapor in pockets or enclosed areas.

Oppl [90], in 1967, suggested that the use of air forced downward from the ceiling (approximately 2.5 meters above the floor) through vents located between carbon disulfide-generating machinery, would effectively limit carbon disulfide exposure in the workers' breathing zones. The use of this method has been rare.

Environmental Sampling and Analytical Methods

(a) Collection Methods

Most analytical methods depend on the efficiency and reproducibility of carbon disulfide uptake by collection media. Air samples are usually collected and transported to a laboratory, where they are desorbed or chemically tested and finally analyzed quantitatively.

Viles [91], in 1940, suggested four methods of carbon disulfide vapor collection. The first was the use of a bubbler containing glass beads connected to the intake section of a water reservoir. Water is decanted out of the reservoir, drawing air through the bubbler. The second method uses a hand-operated exhausting pump to bubble the air sample through a reagent. The other two methods are grab-sampling procedures, one using a

citrate of magnesia pressure bottle and the other an evacuated gas collecting tube.

Absorption bottles with fritted glass bubbler tubes have been used in the viscose rayon industry to collect carbon disulfide from samples of air drawn through sampling lines that open at various sites throughout a factory [92].

The American Industrial Hygiene Association (AIHA) Analytical Abstracts [93], in 1965, recommended collection of carbon disulfide with a bubbler containing glass beads wetted with a solution of diethylamine and copper acetate.

The use of a glass bubbler attached to a bulb-type hand aspirator has been recommended in the United Kingdom as the collection method for carbon disulfide [94]. Lead acetate-impregnated filter paper is used to remove interfering hydrogen sulfide. Hunt et al [95], in 1973, also recommended the use of a glass bubbler with an attached rubber-bulb aspirator. The efficiency of absorption of carbon disulfide was found to vary from 100% at a flow rate of 50 ml/minute to 89% at a flow rate of 200 ml/minute. Higher temperatures also decreased absorption efficiency.

Rosensteel et al [9] described the collection method used by NIOSH in an evaluation of a viscose rayon plant. The sampling train consisted of a midget bubbler and impinger, with a battery-operated personal sampling pump.

Truhaut et al [96], in 1972, determined that carbon disulfide is fully adsorbed onto activated charcoal with virtually no hydrogen sulfide interference. McCammon et al [97], in 1975, recommended using tubes containing activated coconut-shell charcoal to adsorb carbon disulfide.

The carbon disulfide can then be effectively desorbed with benzene or xylene.

(b) Analysis

Several methods have been used to measure carbon disulfide in samples. The two major analytical methods are based on colorimetric determination and gas chromatography.

Matuszak [98], in 1932, developed an analytical procedure for carbon disulfide which involved condensing it with alkali and alcohol and then estimating the concentration by titrating the resulting xanthate. Interferences by hydrogen sulfide, mercaptans, and unsaturated hydrocarbons were described as potential problems with this method, although treatment of the xanthate solution with dilute aqueous alkali was an adequate remedy. Tischler [99], also in 1932, devised an analytical method using colorimetry. Carbon disulfide in ethanol, diethylamine, and copper acetate were combined, and the color of the solution was compared with those of standard solutions. This copper-diethylamine method has been very widely used. Numerous other reports [91,94,95,100-103] have affirmed its effectiveness or described its use.

Morehead [104] slightly altered the copper-diethylamine method by using 2-methoxyethanol as the reaction medium (replacing ethanol). This modification improved sensitivity by increasing color intensity and stability, permitting determination of smaller carbon disulfide concentrations. AIHA Analytical Abstracts [93] recommended this improved copper-diethylamine method, noting that a concentration of less than 2 ppm (6 mg/cu m) could be detected in a 1-liter sample.

A NIOSH Health Hazard Evaluation [9] used the basic copper-diethylamine method, but with a slight technical improvement. The absorbance of the solution at 420 nm on a spectrophotometer was measured, and the carbon disulfide concentration was determined from a calibration curve prepared from known concentrations. Others [6 (pp 5-8),105] have also reported the use of spectrophotometry in industrial situations.

Kneebone and Freiser [105], in 1975, reported two methods of analyzing carbon disulfide. The first method, a potentiometric procedure, depended on the reaction of carbon disulfide with pyrrolidine to form dithiocarbamate which was then chelated by addition of copper. The disappearance of Cu^{++} was monitored with a cupric-ion electrode. The method could detect as little as 7 μg of carbon disulfide. The error of carbon disulfide detection in this method was about 5%, and the precision of replicate measurements was 3%. The second method was based on the same reaction, but the chelate was extracted into isoamyl acetate and atomic-absorption spectrophotometry was used to determine the concentration of the copper, from which the concentration of carbon disulfide was calculated. The sensitivity of this method was also found to be 7 μg , but, according to the authors, sensitivity in the range of 1-5 μg would have been attainable with more sophisticated equipment. The average error of detection was less than 2%, and the precision of replication was 1-2%. The authors felt that the atomic-absorption method allowed detection at a lower concentration than other analytical methods.

McCammon et al [97], in 1975, found that gas chromatography with a flame photometric detector could accurately and efficiently analyze carbon disulfide collected in charcoal tubes. This method is very sensitive,

capable of detecting 1 μg of carbon disulfide in a charcoal tube. They reported the accuracy of the method to be 6% with a relative standard deviation (coefficient of variation) of 9%. Interference was caused by high humidity but the use of a desiccant, calcium sulfate, effectively reduced this problem.

(c) Recommendations

NIOSH recommends that carbon disulfide in air be collected with activated coconut-shell charcoal, desorbed with benzene or xylene, and analyzed by gas chromatography. Although several other collection methods have been used for carbon disulfide, the charcoal-tube method has many advantages. Charcoal tubes are relatively simple to prepare, ship, and store; personal sampling is easily achieved; interference from hydrogen sulfide is minimal; high temperatures do not affect sampling efficiency; and sampling tubes and pumps are commercially available. The gas chromatography method has been demonstrated to be reproducible, widely accepted, and more accurate than other methods. Charcoal-tube sampling and analysis by gas chromatography are methods approved by NIOSH and validated at 20 ppm (62 mg/cu m). Work on validation of the method at lower concentrations is in progress. The recommended sampling and analytical methods are described in Appendices I and II.

The copper-diethylamine method of carbon disulfide detection has been widely used since 1932. However, the sensitivity and accuracy of this method are not adequate to monitor carbon disulfide at concentrations below the NIOSH-recommended TWA concentration limit of 3 mg/cu m (1 ppm). The potentiometric method and, especially, the atomic-absorption method are capable of accurately detecting carbon disulfide at low concentrations.

However, the difficulty of operation, the cost, and the lack of supportive data are arguments against the recommendation of these methods.

Biologic Monitoring

Yoshida [106], in 1955, determined that a carbon disulfide metabolite found in the urine of test animals catalyzed the iodine-azide reaction, in which iodine is reduced by sodium azide. The rate of color disappearance of the iodine was proportional to the concentration of the metabolite.

Vasak et al [107], in 1963, studied the relationship of the iodine-azide reaction in human urine to the concentrations of carbon disulfide inhaled. An unspecified number of men and women, 20-40 years old, not exposed to carbon disulfide in their daily work, inhaled carbon disulfide from face masks for 8-hour periods at measured concentrations of 50-200 $\mu\text{g/liter}$ (16-64 ppm). Control subjects were indicated in the authors' graphs but were not described. Urine samples were collected at 20-hour intervals, and the iodine-azide test was performed to determine the amount of carbon disulfide metabolites present. To correct for differences in urine volume, which would affect the concentration of metabolites and hence the iodine-azide reaction time, the authors developed a coefficient of exposure (E); this was determined by the formula $E = C(\log t)$, where C is the creatinine concentration in the urine in mg/ml and t is the time in seconds required for the iodine to disappear. The creatinine concentration was used to correct for dilution of the urine because the authors determined that the amount of creatinine excreted during 2-hour periods was constant "to a significant degree."

A nearly linear relationship was found between the coefficient of

exposure and the carbon disulfide concentration in the inhaled air. Vasak et al [107] concluded that persons exposed to carbon disulfide at concentrations below 50 $\mu\text{g}/\text{liter}$ (16 ppm) had coefficients of exposure of 6.5 or higher, while greater exposures were reflected in lower E values. Exposure at a concentration of 200 $\mu\text{g}/\text{liter}$ (64 ppm) produced an E value of 1.

Djuric et al [108], in 1965, used the iodine-azide test to analyze the urine of workers exposed to carbon disulfide in a viscose rayon plant. As a control, 35 healthy persons not exposed to carbon disulfide were tested; all had E values between 10 and 6.5, ie, normal. Urine samples were also obtained from workers in various viscose rayon operations. The urine was collected three times daily: before, during, and after work. Three exposure classes of workers were recognized from the test results. The first group had normal E values, greater than 6.5, both before and after exposure. The authors considered it unlikely that these workers were exposed to carbon disulfide at concentrations above 50 $\text{mg}/\text{cu m}$ (16 ppm). A second group had normal values prior to the work shift, but E values were below 6.5 after work; they recovered overnight and had normal values again the next morning. The third group had abnormal E values during and after work and failed to recover by morning, possibly an early indication of carbon disulfide poisoning. Djuric et al concluded that the iodine-azide test was a simple and reliable method of evaluating the average exposure to carbon disulfide and determining whether workers have recovered from previous exposure.

Stokinger and Mountain [109] suggested this test for use as an indicator of employee susceptibility to carbon disulfide. If test values at

the beginning of the workweek have not returned to normal (preexposure) values, the employee would be considered hypersusceptible, and signs of carbon disulfide intoxication would be expected to appear with continued exposure. However, the iodine-azide test is not sensitive enough to detect carbon disulfide in the urine of workers exposed at concentrations at or below the NIOSH-recommended TWA concentration limit of 3 mg/cu m (1 ppm). Also, this test has not been adequately investigated for use as an indicator of hypersusceptibility to carbon disulfide.

While the iodine-azide test cannot measure carbon disulfide exposures as accurately or sensitively as air sampling, the test can be of value as a measure of carbon disulfide body burden. Periodic use of this test may be useful in providing an additional method of monitoring employee exposure to carbon disulfide.

V. WORK PRACTICES

Work practices and safety precautions for handling carbon disulfide are the subjects of several reports [1,3,110-112]. Carbon disulfide is harmful to health when the vapor is inhaled or when there is prolonged or repeated skin contact. Occupational exposures to carbon disulfide can occur in several industries, but employees engaged in the production of viscose rayon have been the most frequently exposed. Workers are primarily exposed to the vapor of carbon disulfide but may occasionally come into contact with the liquid.

The lower and upper explosive limits for carbon disulfide in air at 20 C are 1% and 50% by volume, and the autoignition temperature is 100 C [110]. Carbon disulfide is designated as a Class 1A (the most flammable) liquid in 29 CFR 1910.106(a)(19)(i). Recommended work practices are intended to ensure that potential sources of ignition are prohibited in areas where carbon disulfide is stored or handled. Because contact with surfaces at temperatures above 80 C may be sufficient to ignite a mixture of carbon disulfide and air, smoking, open flames, spark-generating equipment, exposed steam lines, and even naked electric light bulbs must not be permitted in areas containing carbon disulfide liquid or vapor [111]. To minimize fire and explosion hazards, precautions must be taken to ensure that airborne carbon disulfide does not accumulate to concentrations of 0.1% (3,100 mg/cu m; 1,000 ppm).

Special precautions (eg, testing the concentration of carbon disulfide and making sure there is no oxygen deficiency) are necessary before workers enter vessels or other enclosed spaces that may contain

carbon disulfide [1].

Skin protection is necessary for workers who may be exposed to carbon disulfide in liquid form. Carbon disulfide is a fat solvent, and contact between the liquid and the skin can cause dryness and cracking of the skin; prolonged dermal contact can cause chemical burns. Synthetic-rubber gloves are recommended to protect the hands, but, since no gloves have been shown to be completely impervious to carbon disulfide, employees should be cautioned to avoid prolonged immersion of even gloved hands in carbon disulfide solutions. Gloves must be washed and dried thoroughly every day. Carbon disulfide must not be allowed to accumulate and remain under gloves, clothing, or shoes [1]. Goggles or face shields also should be worn by employees working with liquid carbon disulfide.

Small amounts of carbon disulfide may be stored in drums in cool, well-ventilated areas. Bulk carbon disulfide should be stored in tanks and covered with water. Further work practices recommended for the safe handling, storage, and use of carbon disulfide are described in the Chemical Safety Data Sheet [1].

If carbon disulfide is spilled, potential sources of ignition should be eliminated immediately, spark-proof ventilation should be provided, and the spill should be cleaned up. A small spill should generally be allowed to evaporate under conditions of good air circulation. However, a large spill (one that will not quickly evaporate) should be covered with water and flushed into a retention basin under a water layer; it should not be drained into a sewer system because of the possibility of an explosion. Disposal of carbon disulfide should be in accordance with relevant local, state, and federal regulations.

If a carbon disulfide fire occurs, it should be extinguished with a water spray. In addition to dousing the flames, this will prevent reignition by cooling the equipment. Carbon dioxide and dry chemical extinguishers may be used on small fires. Proper firefighting and personal protective equipment must be readily accessible to all workers potentially exposed to carbon disulfide [1].

Good sanitation and personal hygiene in conjunction with recommended work practices will minimize the risk of inadvertent ingestion of carbon disulfide. Employees should wash their hands before drinking, eating, or smoking. If carbon disulfide comes into contact with the eyes, they should be flushed with copious amounts of water. Emergency showers, eyewash fountains, and handwashing facilities must be accessible, and changes of clothing (including gloves and shoes) must be readily available.

As described in Chapter IV, engineering controls should be used to keep levels of airborne carbon disulfide below concentrations hazardous to the health of workers, but certain situations, such as vessel entry, nonroutine maintenance or repair operations, or emergencies, may require respiratory protection. The selection of proper respiratory devices is discussed in Chapter I. These respirators shall be immediately accessible to employees in emergency situations.

Appropriate posters and labels should be displayed, and the US Department of Labor form OSHA-20, "Material Safety Data Sheet," or a similar OSHA-approved form, should be filled out and kept accessible to employees. Effective employee education and supervision are necessary to ensure the safety and health of employees potentially exposed to carbon disulfide.

VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

Exposure to carbon disulfide was first regulated in Germany for workers in the rubber industry [13]. Terms of a 1902 ordinance stipulated a maximum continuous working period of 2 exposure hours, in a workday with not more than 4 exposure hours, for workers in departments with high carbon disulfide levels; there was to be at least a 1-hour interval between the two exposure periods. Persons under the age of 18 were not permitted to work in carbon disulfide departments. The employer was responsible for providing overalls, lockers, and washrooms and was required to have the employees examined every 4 weeks by a physician. Workers showing signs of carbon disulfide intoxication were not permitted to work in hazardous departments during their convalescence and were permanently excluded from any hazardous work if they were found to be oversensitive to carbon disulfide. Included in this regulation were specifications for worker airspace and ventilation. Great Britain issued a similar ordinance in 1922; other European countries and the USSR enacted similar regulations soon thereafter [13].

In a "Survey of Carbon Disulfide and Hydrogen Sulfide Hazards in the Viscose Rayon Industry," issued by the Pennsylvania Department of Labor and Industry [13] in 1938, Lewy stated: "The standards of the viscose rayon industry in America differ so widely that in one plant insomnia and bad dreams are regarded as alarming signs, while in another, more than half of the workers show objective signs of degenerative changes of the peripheral nerves, apparently without causing any concern to the management." Based

on surveys of occupational disease in viscose plants, the Industrial Board of the Pennsylvania Department of Labor and Industry established a "permissible limit" of 10 ppm (31 mg/cu m) in the breathing zone 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 a 1938 report on six cases of occupational carbon disulfide intoxication in viscose rayon workers, Gordy and Trumper [113] suggested a maximum air concentration "preferably around 10 ppm." In 1939, Elkins [114], 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 previous standards. Carbon disulfide was considered "extremely toxic," and an MAC of 15 ppm (47 mg/cu m) in workplace air was proposed [114]. No justification for this figure was given.

In 1940, Bowditch et al [115] 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 against possible effects. A value of 15 ppm (47 mg/cu m) for carbon disulfide was recommended, but no basis was cited for the standard.

A list of MAC's for industrial atmospheric contaminants published by Cook [116] in 1945 included those of the American Standards Association, of the US Public Health Service, and of the States of California, Connecticut, Utah, Oregon, Massachusetts, and New York. The values for the last two

states were to be used as guidelines rather than as mandatory standards. A limit of 20 ppm (62 mg/cu m) was recommended for carbon disulfide. No explanation was given for the increase in the Massachusetts MAC for carbon disulfide from the value of 15 ppm (47 mg/cu m) proposed by both Elkins [114] and Bowditch et al [115]. In substantiating the proposed level of 20 ppm (62 mg/cu m) for carbon disulfide, Cook [116] cited a study by Barthelemy [28] on conditions in a viscose rayon plant. Barthelemy reported that when carbon disulfide levels were below 0.1 mg/liter (less than 32 ppm) "no trouble whatever was experienced." As additional support for his proposed carbon disulfide limit, Cook [116] referred to studies by Wiley et al [117] which, stated Cook, showed "no significant toxic effects" in animals exposed to carbon disulfide at 30 ppm (93 mg/cu m) over a long period. However, Wiley et al [117] had reported that exposure of mice and rats to a mixture of carbon disulfide and air at a concentration of 0.114 mg/liter (about 37 ppm) for 8 hours/day over a period of 20 weeks "gave definite evidence of toxic effects." They recommended that carbon disulfide concentrations in industrial atmospheres be kept below 0.1 mg/liter (less than 32 ppm) and that, if exposures to higher concentrations occurred, working hours be shortened and employees be transferred periodically to operations with no carbon disulfide exposure hazards.

Bloomfield [118], in 1947, reviewed the reports of an American Conference of Governmental Industrial Hygienists' (ACGIH) committee which was attempting to develop a list of MAC's for adoption by all the states. He reported that, of 24 states and 3 cities responding to an inquiry on carbon disulfide, 3 reported an existing MAC of 15 ppm (47 mg/cu m), 20 reported a value of 20 ppm (62 mg/cu m), and 4 listed no established value.

In 1955, Kleinfeld and Tabershaw [119], citing cases they had seen and the "experience of others," recommended that the 20-ppm (62 mg/cu m) carbon disulfide MAC be reduced to 10 ppm (31 mg/cu m).

For carbon disulfide, the ACGIH [120] adopted an MAC of 20 ppm (62 mg/cu m) in 1946, and this value remains in effect as the threshold limit value (TLV). The 1961 ACGIH listing [121] included the notation "skin" along with the recommended TLV, indicating that cutaneous absorption of carbon disulfide must be prevented if the TLV is to protect employees from the toxic effects of exposure to the compound. The 1971 ACGIH Documentation [122] listed a TLV of 20 ppm (62 mg/cu m) with the following statement: "The limit of 20 ppm, although protecting against serious systemic effects, would appear to have little margin of safety, especially for those with mineral-deficient diets." Moreover, 2 of the 17 studies cited in the Documentation [122] supported a lowering of the TLV for carbon disulfide to 10 ppm (31 mg/cu m). In 1976, ACGIH [123] retained the TLV of 20 ppm (62 mg/cu m) for carbon disulfide but introduced a tentative value of 30 ppm (93 mg/cu m) as a short term exposure limit (STEL). The STEL is the maximum concentration at which workers can be exposed for a period of up to 15 minutes.

In 1968 [124], the American National Standards Institute (ANSI) adopted an 8-hour TWA value of 20 ppm (62 mg/cu m) for carbon disulfide based on the 1967 ACGIH-recommended TLV [125]. In addition, ANSI adopted an "acceptable ceiling concentration" of 30 ppm (93 mg/cu m) for an 8-hour/day, 5-day workweek, provided that the TWA was at or below 20 ppm and that an "acceptable maximum peak" of not more than 100 ppm (311 mg/cu m) for 30 minutes did not occur more than once during an 8-hour workday.

For carbon disulfide in the working environment, the following permissible levels have been set by foreign countries: Hungary, Japan [126], and the Federal Republic of Germany [127], 60 mg/cu m (about 19 ppm); German Democratic Republic [127], 50 mg/cu m (about 16 ppm); Yugoslavia [126], Czechoslovakia, and Sweden [127], 30 mg/cu m (about 10 ppm); Romania [126], 15 mg/cu m (about 5 ppm); USSR and Poland [126], 10 mg/cu m (about 3 ppm). The Soviet standard, established in the early 1920's [13], is a maximum permissible concentration, never to be exceeded.

The current federal standard for carbon disulfide (29 CFR 1910.1000) incorporates the values recommended by ANSI in 1968 [124]. This specifies an 8-hour TWA value of 20 ppm (62 mg/cu m), with an acceptable ceiling concentration of 30 ppm (93 mg/cu m) for an 8-hour day, 5-day workweek, and an acceptable maximum peak during any 8-hour work shift of not more than 100 ppm (311 mg/cu m) for 30 minutes.

Basis for the Recommended Standard

(a) Workplace Environmental Limits

Human studies have shown that exposure to carbon disulfide affects the cardiovascular system [8,33,41,43-46,48], the nervous system [54-57,63,64], the eyes [65-67], the reproductive organs [58,60,61], and several other systems and organs [10,75,128]. All occupational data used as the basis for the recommended occupational environmental exposure limit for carbon disulfide are from the viscose rayon industry and therefore include effects induced by exposure to hydrogen sulfide also; however, most investigators have measured and reported only the carbon disulfide concentrations. The ratio of the concentrations of evolved carbon

disulfide to hydrogen sulfide in viscose rayon manufacture has been estimated at 2:1 [6], 4:1 [7], 5:1 [28], and 10:1 [8-10].

There are reports of apparent synergism of toxic effects when the two compounds are found together [85-87,129]. Several investigators [85-87] have concluded that environmental limits developed for each compound independently should not be applied to situations in which a mixture of hydrogen sulfide and carbon disulfide is present. Rosensteel et al [9], in a 1973 NIOSH Health Hazard Evaluation of a viscose rayon plant, concluded that the potentially hazardous conditions in the production of rayon staple fiber resulted from the presence of carbon disulfide and not from that of hydrogen sulfide. Tiller et al [41] discounted the role of hydrogen sulfide in the increased coronary mortality rate of viscose rayon workers. In support of these observations, animal experiments have shown that health effects similar to those reported in viscose rayon workers resulted from exposure to carbon disulfide alone [78-80].

Seppalainen et al [55] and Seppalainen and Tolonen [56] reported polyneuropathy, slowed conduction velocities, and abnormal EMG's and EEG's in workers exposed to carbon disulfide at concentrations of approximately 10-30 ppm (31-93 mg/cu m). Vasilescu [57] found that young men exposed to carbon disulfide at approximately 5 ppm (16 mg/cu m) had diminished muscular power, markedly weakened knee and ankle reflexes, and a slowing of motor conduction velocities. However, because peaks of up to 225 ppm (700 mg/cu m) of carbon disulfide were measured, the 5 ppm (16 mg/cu m) figure may not accurately reflect the true environmental conditions.

Psychologic and behavioral abnormalities in workers exposed to carbon disulfide at concentrations around 20 ppm (62 mg/cu m) [63,64], periodontic

disorders at concentrations as low as 6 ppm (19 mg/cu m) [10], decreased immunologic reactivity below 3 ppm (9 mg/cu m) [75], and nervous excitability and hypotension below 3 ppm (9 mg/cu m) [54] have all been reported in the viscose rayon industry. However, the periodontic findings are of questionable importance and the reports of decreased immunologic reactivity and of nervous excitability and hypotension did not adequately describe measurements of carbon disulfide concentrations.

The most thoroughly documented studies on the health effects of carbon disulfide exposure have been on the cardiovascular system. In 1970, Hernberg et al [8,43] reported significantly elevated rates of coronary heart disease mortality, angina, and high blood pressure, as well as disturbances in plasma glucose and creatinine concentrations, in viscose rayon workers. In a 5-year followup of these workers, Hernberg et al [44,45] again reported increased coronary heart disease mortality and also higher than expected incidences of total infarctions, nonfatal infarctions, angina, and "coronary ECG's." The workers had been exposed to carbon disulfide plus hydrogen sulfide at mean combined concentrations of 10-30 ppm (31-93 mg/cu m) in the 1960's, 20-40 ppm (62-124 mg/cu m) in the 1950's, and higher but unspecified levels previously. The concentration of hydrogen sulfide was estimated to constitute 10% of the total concentration of the two compounds. In an 8-year followup in 1976, Hernberg et al [46] found no excess coronary heart disease mortality during the last 3 years of followup.

Tiller et al [41] described significantly higher than expected mortality from coronary heart disease in workers exposed to carbon disulfide plus hydrogen sulfide at a median combined concentration of about

20 ppm (62 mg/cu m). Also, "spinning" department workers exposed to carbon disulfide for more than 10 years had a death rate from coronary heart disease 2.5 times that of workers in other departments. Cirila et al [48] found that coronary disease increased linearly with exposure to increased carbon disulfide concentrations. Workers exposed at concentrations of about 20 ppm (62 mg/cu m) showed more ECG signs of coronary heart disease than did controls, and workers exposed at 40 ppm (124 mg/cu m) showed a very significant increase. Gavrilesco and Lilis [33] demonstrated that workers exposed to carbon disulfide at concentrations of 7-14 ppm (22-44 mg/cu m) for approximately 10 years developed atherosclerosis and arterial hypertension to a much greater degree than controls.

Signs of disturbed retinal vascular circulation were found by Raitta et al [65] and Raitta and Tolonen [66] in workers exposed to carbon disulfide at concentrations of approximately 10-30 ppm (31-93 mg/cu m). Szymankowa [67] noted conjunctival inflammation, temporary corneal opacities, and color-vision disturbances in workers exposed to carbon disulfide at reported concentrations of below 3 ppm (9 mg/cu m). Vigliani [31] described 43 cases of vascular encephalopathy which developed in viscose rayon workers exposed to carbon disulfide at concentrations of 10-48 ppm (31-149 mg/cu m).

Significantly greater frequencies of asthenospermia, hypospermia, and teratospermia were found in young men exposed to carbon disulfide at 13-26 ppm (40-81 mg/cu m) than in controls [58]. Vasilyeva [60] reported greater than expected frequencies of menstrual flow lasting more than 5 days, abundant and painful menstruation, and abnormal cellular composition of vaginal smears in women exposed to carbon disulfide at concentrations below

3 ppm (9 mg/cu m). Petrov [61] found that female viscose workers who had been exposed to carbon disulfide at concentrations around 9 ppm (28 mg/cu m) before and during pregnancy had significantly more difficulty than controls in bringing the pregnancies to term. Threatened pregnancy terminations, spontaneous abortions, and premature births were more common in exposed workers than in controls. Bezvershenko [62] found that dysmenorrhea, oligomenorrhea, irregular and delayed menstruation, infertility, and spontaneous abortions were more common in women exposed to carbon disulfide than in unexposed controls. While these studies report serious reproductive effects at concentrations as low as below 3 ppm (9 mg/cu m), the validity of the reported carbon disulfide concentrations is questionable because no sampling or analytical methods were identified and the results have not been corroborated. In contrast, reports by Finkova et al [35], Ehrhardt [34], and Jindrichova [36] did not show added risk to female workers at carbon disulfide concentrations as high as 64 ppm (199 mg/cu m).

Although serious health effects have been found at low concentrations and a no-effect level has not been demonstrated, a recommended environmental limit for carbon disulfide should be based on studies that use documented, reproducible, and accurate environmental monitoring procedures and that report significant health effects. The cardiovascular [8,31,33,41,43-46,48,65,66] and neurologic studies [55-57] are therefore of primary importance in developing a standard, and 10 ppm (31 mg/cu m) appears to be the lowest concentration causing demonstrated adverse health effects. As coronary heart disease frequently results in sudden death, a safety factor should be applied to the lowest concentration shown to be

associated with such cardiovascular disorders. Therefore, NIOSH recommends that carbon disulfide concentrations in workplace air not exceed 3 mg/cu m (1 ppm) as a 10-hour TWA concentration during a 40-hour workweek. To avoid acute toxicity by carbon disulfide, a ceiling of 30 mg carbon disulfide/cu m of air (10 ppm) based on a 15-minute sampling period has been added to the recommended standard. Although several papers [58,60,61,62] document reproductive effects of carbon disulfide at concentrations at or near the recommended limits, their conclusions must be considered tentative because of shortcomings in their sampling, analytical, or experimental methodologies. If, however, additional information is obtained and these or other reports confirm effects at the reported concentrations, the recommended standard must be reviewed and serious consideration given to lowering the TWA and ceiling concentration limits.

Concern for worker health requires that protective measures be instituted below the recommended environmental limit to ensure that exposures stay below that limit. Therefore, environmental monitoring and recordkeeping are required for work areas where there is exposure to carbon disulfide above 1.5 mg/cu m (0.5 ppm) as a TWA concentration for a 10-hour workday, 40-hour workweek.

Because less hydrogen sulfide than carbon disulfide is evolved in viscose rayon manufacture [6-10], compliance with the recommended environmental limit for carbon disulfide will also minimize exposure to hydrogen sulfide.

(b) Sampling and Analysis

To monitor the concentration of carbon disulfide, the employees' breathing-zone air must be sampled periodically. NIOSH recommends sampling

with activated, coconut-shell charcoal tubes and analysis by gas chromatography. These methods are presented in Appendices I and II, although other methods of comparable reliability and accuracy are acceptable. The relative merits of various methods of sampling and analysis are discussed in Chapter IV.

(c) Medical Surveillance

In view of the documented effects of human exposure to carbon disulfide, NIOSH recommends that comprehensive preplacement and annual examinations, including ECG's, blood pressure tests, and neurologic tests, be made available to all workers occupationally exposed to carbon disulfide. The worker should be informed that disorders of the cardiovascular, nervous, and reproductive systems and of the eyes may result from exposure to carbon disulfide. In certain cases, an individual may exhibit symptoms warranting more frequent and more specialized examinations. Biologic monitoring, using the iodine-azide urine test as presented in Appendix III, may assist in detecting exposures at high concentrations that may not be detected by air monitoring. All pertinent medical records, with supporting documents, must be kept for at least 30 years after termination of employment.

(d) Personal Protective Equipment and Clothing

Personal protective equipment must be used in accordance with 29 CFR 1910, Subpart I. Because of the vesicant action of liquid carbon disulfide on the skin, synthetic rubber gloves must be used when work with liquid carbon disulfide is necessary. Employees working with liquid carbon disulfide must use face shields with goggles to protect against possible eye damage. Clothing that is contaminated with carbon disulfide must be

immediately replaced. In accordance with Tables I-1 and I-2, respiratory protection should be used to protect against harmful concentrations of carbon disulfide vapor but should not be used as a substitute for ventilatory and other engineering controls of the concentration of carbon disulfide in the air of the workplace.

(e) Informing Employees of Hazards

Employers must inform employees of the toxic and explosive hazards of carbon disulfide. A continuing education program, conducted at least annually, must be instituted by employers. This program should include instruction on the use of respiratory equipment, emergency procedures, and proper work practices.

(f) Work Practices

The extreme flammability and toxicity of carbon disulfide necessitate conformance to proper work practices. Procedures for emergency situations, control of airborne carbon disulfide, sanitation, and maintenance must be understood and followed by employees occupationally exposed to carbon disulfide. Carbon disulfide must be stored in cool, fire-resistant, well-ventilated areas. Conformance with all applicable local, state, and federal regulations is necessary when disposing of carbon disulfide. Carbon disulfide must not be allowed to enter sewer systems. Employee entry into confined spaces must be controlled by a permit system, or equivalent, and these areas should not be entered until the atmosphere has been tested for oxygen deficiency, carbon disulfide, or other contaminants. When necessary, however, proper respiratory protection should be used in entering these areas. Use of standby personnel is required when an employee enters confined spaces.

(g) Monitoring and Recordkeeping Requirements

Employers must determine by an industrial hygiene survey whether employees are exposed to carbon disulfide in excess of 1.5 mg/cu m (0.5 ppm) as a TWA concentration. If this survey reveals that exposure in these areas is below 1.5 mg/cu m (0.5 ppm) then such a survey need be made once every 3 years, supplemented by semiannual personal employee sampling. If exposure is found to be above 1.5 mg/cu m (0.5 ppm) as a TWA more frequent sampling will be required.

Comprehensive records of environmental monitoring must be kept for each employee occupationally exposed to carbon disulfide. These records must be kept for 30 years after the individual's employment has ended and must be made available upon request to the appropriate federal agencies and to the employee or his authorized representative.