

#### IV. ENVIRONMENTAL DATA AND BIOLOGIC EVALUATION

##### Environmental Concentrations

Environmental data derived from the manufacture and use of chloroform are very scarce. The only industrial environmental data available are from surveys of the pharmaceutical industry where the chloroform consumed is less than 10% of the total produced. Although fluorocarbon refrigerants and resins account for almost 90% of the chloroform used in the United States, [96] there are no studies on workroom concentrations of chloroform used in their production.

Challen et al [67] in 1958 studied chloroform concentrations in a confectionery manufacturing plant in England, in which chloroform vapor were given off during the production of medicinal lozenges. Employees had complained about exposure to chloroform and subsequently a system of exhaust ventilation was installed. An air sample was taken continuously in the breathing zone of the operator during a period of 20 minutes coinciding with the duration of the ingredient mixing process. The sample was drawn through 2 U tubes containing dried silica gel at the rate of 1 liter/min. Additionally, at a point in the operation where a peak concentration was expected, a 6-liter grab sample was taken. Air samples of 30-minute durations were also taken in the breathing zones of cutting room operators performing 3 different operations during 2 periods of production on the same day under the current ventilation conditions. For purposes of allowing a comparison, the original conditions in the cutting room were simulated by closing the doors and windows and shutting off the ventilation system. On the day of the simulated conditions, air samples of 30-minute

durations each were taken during 3 periods of production in the breathing zone of operators performing the 3 different operations and in the general room air. All samples were analyzed by the alcohol KOH combustion method (alkali hydrolysis).

Under the current conditions of ventilation, the continuous sample taken during the mixing operation contained 128 ppm, and a peak value of 1,163 ppm of chloroform lasting 1 1/2 minutes was found in the grab sample of air adjacent to the emptying of the mixer. The mixing operation occurred no more than 4 times daily for a total of about 2 hours. In the cutting room, the environmental concentrations were: feeding operation, 71 and 57 ppm; dusting operation, 35 and 31 ppm; and tray removal, 23 and 29 ppm.

Chloroform concentrations in the air found by Challen et al [67] during the simulation of the original conditions were as follows: feeding operation, 219, 237, and 161 ppm; dusting operation, 110, 158, and 155 ppm; removing trays, 77 and 92 ppm; general atmosphere at the center of the room, 82 and 92 ppm.

Concentrations of chloroform during the years 1968-72 in a plant manufacturing film were supplied by the Department of Labor and Industries, Commonwealth of Massachusetts. [LD Pagnotto, written communication, December 1973] A solvent mixture containing 75% methylene chloride, 22% chloroform, and toluene was used in the operation. Samples were collected by drawing air at a rate of 0.5 liters/min for 90-120 minutes through a U-tube filled with 7 g of silica gel and desorbed by soaking in isopropyl alcohol for 2 hours. Aliquots of this solution were hydrolyzed by

potassium hydroxide (KOH) for 17 hours, and for 65 hours in order to estimate both chloroform and methylene chloride.

To differentiate between the amounts of chloride recovered from chloroform and methylene chloride, it was necessary to use empirical chloride recovery factors determined from control samples analyzed in parallel. During the first 17 hours of hydrolysis, averages of about 4% of the methylene chloride and about 80% of the chloroform were hydrolyzed. During hydrolysis an average of about 20% of the methylene chloride, but virtually no additional chloroform was hydrolyzed. It was necessary to run methylene and chloroform controls for each determination.

Over the 5 years of surveillance, a total of 79 samples were determined by this method. The measured concentrations of chloroform ranged from 7-170 ppm, with a mean of 47 ppm. On 2 consecutive days in 1973, samples were collected on charcoal and analyzed by GC. On these 2 days concentrations ranged from 30-585 ppm, and in general, appeared to be higher than concentrations previously observed by the silica gel-alkaline hydrolysis method.

Bomski et al, [55] while investigating the health of workers in a pharmaceutical plant in Poland, repeatedly measured chloroform concentrations in the air of the production rooms. No information was given about the time span covered by the investigation, the number of air samples collected, or the duration of individual sampling times. The range of concentration reported was between 2 and 205 ppm (0.01-1.0 mg/liter) determined by the method of Grabowicz. [68] This method is a modification of the Fujiwara colorimetric method which is explained in detail in the following section.

## Environmental Sampling and Analytical Method

### (a) Collection Methods

Most of the analytical methods are dependent on the effectiveness and reproducibility of the sorption of chloroform on or in different collecting media.

Air samples should be collected and transported to a laboratory, then desorbed or chemically treated, and finally analyzed quantitatively. Silica gel has been used extensively in the past as a collection medium. [67,97] Silica gel is a polar adsorbent and shows pronounced selectivity in adsorbing polar molecules, particularly water. Hence, when sampling large volumes, the atmospheric moisture may compete for the adsorption sites and displace the chloroform being sought. When sampling large volumes (more than 3 liters), the silica gel adsorption tube may become saturated with water thus impairing the retentive properties of the collection medium. [98]

Activated charcoal as a collection method has been used in conjunction with gas chromatography. [99] Activated carbon is nonpolar and will consequently adsorb organic vapors in preference to water vapor so that sampling of volumes higher than 3 liters can be accomplished without noticeable moisture interferences. [98]

Williams and Umstead [100] have developed a collection method in which atmospheric samples are concentrated on porous polymer beads. The same column utilized for sample collection is subsequently used for GC analysis. The advantage of this method is that it integrates collection and

analysis into one operation. However, it has not yet been developed for field use.

Liquids have been used as collection absorbers of chloroform contaminated atmospheres. Impingers containing m-xylene [101] were used as collectors for gas chromatographic analysis and bubbler bottles containing a pyridine solution were also used as the collection method in conjunction with colorimetric analysis. [97] The use of liquid impingers and bubblers poses problems in field measurements due to difficulties in collecting breathing zone samples without spilling of liquid and the added problem of transporting liquid samples for laboratory analysis.

Other investigators have collected the contaminated atmospheres directly by grab samples using a variety of containers ranging from plastic bags to hypodermic syringes. [99] However, the small amounts collected do not accurately represent the atmosphere in a plant location during a work shift.

#### (b) Desorption Methods

When solid collection media are used it is necessary to desorb the contaminant collected on the medium. Isopropyl alcohol and heat were used by the Massachusetts Department of Labor and Industries to desorb chloroform from silica gel. Desorption from charcoal was studied by Otterson and Guy. [99] They recommended the use of different desorbing agents depending upon the comparative gas chromatograph retention times for the desorber and the contaminant. Carbon disulfide was determined to be the best desorbent for chloroform.

(c) Analysis

Several methods have been used to determine the concentration of chloroform in the air. The analytical methods can be divided in 2 broad categories: 1) methods based on chloroform chemical reactions; and 2) methods based on chloroform physicochemical characteristics.

The 3 chemical methods that have been used extensively are: 1) dechlorination of collected vapor samples with strong alkalis followed by titration of the chloride ion (alkali hydrolysis) [34,67]; 2) colorimetric measurement of the reaction products of chloroform and pyridine heated in alkali solution (Fujiwara reaction) [102]; and 3) direct reading colorimetric indicators. [103]

The dechlorination method (alkali hydrolysis) requires collection of the chloroform contaminated atmosphere over a suitable collection medium followed by hydrolysis in isopropyl alcohol. Solid KOH is added and the mixture is allowed to sit overnight (about 20 hours). After neutralization the liberated chloride ion is titrated with silver nitrate. [97] The percentage of chlorine hydrolyzed is determined by comparison between samples and known controls. This method has the disadvantage of a long and elaborate procedure in which the amount of chloride ion liberated depends on the duration of the process of alkali dechlorination. When a mixture of chlorinated hydrocarbon vapors is analyzed, there is the additional problem of specificity; it is necessary then to differentiate the contribution of each chlorinated compound to the total amount of chloride ion liberated. [LD Pagnotto, personal communication, 1973]

In the colorimetric analytical method based on the Fujiwara reaction, [102] a stream of air containing chloroform is passed through a

washer bottle containing pyridine at a rate of 0.5 liter/min. After collection in pyridine, methylethyl ketone and NaOH are added to an aliquot of the sample. A control and an aliquot of the former solution are heated in a boiling water bath, and cooled during a fixed time period. The absorption is then determined with a suitable spectrophotometer. This method requires less time than the dechlorination method, but the problem of specificity in the presence of mixtures of other chlorinated hydrocarbons remains.

The third chemical method consists of direct reading indicators, [103] which are glass tubes packed with solid chemicals that change colors when measured and controlled flow of air containing chloroform passes through the packed material. There are 2 types of sampling procedures: 1) direct passing of the test vapor through the tube followed by comparison with a calibration chart; 2) drawing the test vapor into a pyrolyzer accessory prior to detection. [104] Both methods are nonspecific for chloroform since the liberated halogen ion produces the stain to be read and any halogen or halogenated compounds will interfere. Regulations on detector tubes are found in 42 CFR Chapter I, subchapter G, Part 84, Subpart B, paragraph 84.20 (e). These regulations provide that measurement with colorimetric indicator tubes should be correct within  $\pm 25\%$  of the values read. There are commercially available detector tubes which fulfill this criterion.

The category of analytical methods, based on the physicochemical properties of chloroform, includes: gas chromatography (GC), [105] infrared spectrometry (IR), [106] and photodetector analyzers (Davis Halide Meter). [107] The gas chromatographic method of analysis provides a specific

quantitative analytical method. [105] Gas chromatographic analysis is specific for different chlorinated hydrocarbons since every compound has a specific retention time in a given chromatograph column. However, there is the possibility that several compounds in a mixture may have similar retention times. This problem is easily overcome by altering the stationary phase of the chromatograph column by changing the column temperature or other analytical parameters. Altering conditions will usually change the retention times and separate the components.

A mass spectrometer in conjunction with the gas chromatograph could be used to identify unknown chemicals passing through the chromatograph column. A charcoal capillary tube is employed to trap and transfer the observed unknown GC peak to a mass spectrometer for qualitative identification as described by Cooper et al. [108]

The use of an infrared spectrophotometer [106] provides the advantages of an instantaneous reading of exposure levels of vapors and, in conjunction with a recorder, can document concentration levels during a complete operation cycle. The IR spectrophotometer eliminates the necessity of collecting and transporting samples to a laboratory for analysis. This analytical method has been used for continuous monitoring of industrial operations with chlorinated hydrocarbon exposures. [106] However, complicated instrumentation is necessary to draw the samples and record the data continuously. There is also the need to assure that the atmosphere of relevant working stations is sampled and that such samples correspond to the breathing zone of the workers at the working stations. [106] There are also possibilities of interferences with other air contaminants which are



not easy to detect or resolve without expertise in infrared spectrophotometry.

Halide meters (Davis Halide Meters and modifications) are based on the detection of the increased brightness of an a-c arc (metal electrode) when enveloped by an atmosphere contaminated with halogenated hydrocarbons. [107] The instrument is sensitive to all halogens and halogenated compounds and consequently is nonspecific for chloroform. The Halide meter seems suitable for continuous monitoring if there is only chloroform present as the air contaminant.

(d) Conclusions and Recommendations

(1) Compliance Method

On the basis of the review of the analytical methods it is recommended that gas chromatography be chosen as the compliance method. The method is recommended in conjunction with activated charcoal tubes as a collection method and the use of carbon disulfide as a desorbent.

The combined collection-desorption analytical method was first evaluated in laboratory trials by Otterson and Guy. [99] Fraust and Hermann [109] evaluated the optimal charcoal granule size, sampling rates and total volume for charcoal sampling tubes. White et al [110] applied the findings of Fraust and Hermann [109] and in addition determined the optimal cross section of the charcoal tubes and the optimal number of collecting sections. The tubes were further modified for use as personal samplers for chlorinated hydrocarbon vapor exposures. [111]

The reasons for the choice of gas chromatography - activated carbon collection as the compliance method are:

(A) Charcoal tubes are easy to prepare, ship, and store.

(B) Estimation of exposure with personal samplers is easily achieved.

(C) Desorption with carbon disulfide is efficient and reproducible.

(D) Gas chromatography identifies chloroform in combination with many other compounds.

(E) At the sample volumes recommended, interference by moisture is minimal.

(F) The sampling tubes and personal pumps are commercially available.

However, a disadvantage of the method is the indirect system of measurement requiring collection and desorption prior to analysis.

## (2) Monitoring Methods

It is also recommended that direct reading colorimetric tubes (gas detection tubes) be used as an inexpensive way to determine whether exposure, as defined in Chapter I, exists. The tubes must be used with manufacturer's instructions and for monitoring purposes only.

For situations in which there is a continuous and constant chloroform use (fluorocarbon refrigerants and resins production, manufacture of chloroform, and some pharmaceutical uses), the establishment of a continuous monitoring system of the working location is suggested. The work place should be monitored by a multiprobe continuous air sampler in different working locations, at the breathing zone of the workers

involved. An appropriate motion-time study at the different probe locations will determine the worker TWA exposure.

The analytical apparatus for continuous monitoring should be a calibrated infrared spectrophotometer or, if the only halogenated hydrocarbon present is chloroform, a halide meter. If various other halohydrocarbons are present a gas chromatograph should be used. The continuous monitoring findings should be corroborated with the compliance method described in Appendix I.

#### Biologic Evaluation of the Environment

Lehmann and Hasegawa [34] are the only investigators who have studied concentrations of chloroform in exhaled air of persons with known exposures. The data are presented in Table X-3. One subject was exposed to 4,400 ppm (21.5 mg/liter) for 30 minutes, and the concentrations in the exhaled air were followed during the first 30 minutes after the end of exposure. The average concentrations in the exhaled air collected during the 3 immediately consecutive 10-minute postexposure periods were 1.70, 0.97, and 0.85 mg/liter, respectively.

The other subject was exposed by Lehmann and Hasegawa [34] for 15 minutes to chloroform at 7,200 ppm (35.3 mg/liter) and the concentration in the exhaled air was followed for 20 minutes after the end of exposure. The average concentrations in the exhaled air collected during the 3 immediately consecutive 5-minute postexposure periods were 2.31, 1.48, and 1.04 mg/liter, respectively. These data show that exhaled breath concentrations of chloroform are dependent upon exposure concentration, exposure time, and the time after exposure that the air is sampled. In order to

evaluate exposure to chloroform, data are needed which take these 3 factors into consideration.

Chloroform concentrations in the blood have been measured during and following anesthesia. [44,50] These data show that chloroform in the blood is eliminated rapidly at first but that some remains for at least 8 hours after exposure to anesthetic concentrations. These data are inadequate for evaluating industrial exposure.

## V. DEVELOPMENT OF A STANDARD

### Basis for Previous Standards

In 1946, the Sub-Committee on Threshold Limits of the ACGIH published a list entitled "Maximum Allowable Concentrations of Air Contaminants for 1946", with the understanding that the list would be revised each year. [112] The list of values was compiled from 3 sources:

(a) The list reported by the Sub-Committee on Threshold Limits at the 5th Annual Meeting of the ACGIH in 1942.

(b) The then comprehensive list published by Cook in Industrial Medicine. [113]

(c) Published values of the Z-37 Committee of the American Standards Institute.

The value proposed for chloroform by the ACGIH [112] was 100 ppm.

In 1959, the Threshold Limit Value (TLV) for chloroform was reduced to a time-weighted average of 50 ppm for a normal working day by the ACGIH [114] in their annual review of the TLV values.

In 1962, the ACGIH [115] published its Documentation of Threshold Limit Values (TLV's) in which it cited the recommendations of Cook [113] that exposures to chloroform be kept below 50 ppm, and the study of Challen et al. [67] The 1968 TLV, which was unchanged from the 1962 recommendation, was promulgated as a regulation by OSHA. This was published, apparently in error, as a ceiling value of 50 ppm, in the Federal Register, volume 39, page 23541, dated June 27, 1974.

In 1969, the ACGIH changed the time-weighted average limit to a ceiling and documented this in 1971. [116] This ceiling limit of 50 ppm

was considered adequate to prevent any serious short-term effects on the liver, but it was recommended that chloroform be used with close medical surveillance, particularly with those workers who consume alcohol. The recommendation was based in part on the studies of Challen et al, [67] Bowski et al, [55] and unpublished data from the Massachusetts Division of Occupational Hygiene. A notice of intended change for chloroform from 50 (ceiling) to 25 ppm (time-weighted average) was made by the ACGIH in 1972 [117] and 1973. [118]

The AIHA Hygienic Guide Series of 1965 for Chloroform [95] suggested that a time-weighted average (TWA) of 10 ppm be used with a ceiling of 25 ppm. This recommendation was based on unpublished experimental animal data.

In 1970, the International Labour Office in Geneva published tables of Permissible Levels of Toxic Substances in the Working Environment for many countries. [43] The chloroform standards for 8 different countries are listed below; it is not clear from the reference whether these are time-weighted averages or ceiling concentrations.

<u>Country</u>	<u>Standard, ppm</u>
Bulgaria	10
Czechoslovakia	10
Czechoslovakia	50*
Finland	50
Hungary	4
Hungary	20*
Japan	50
Poland	10
Rumania	10
Yugoslavia	50
*for brief exposures	

#### Basis for Recommended Environmental Standard

The major exposure to chloroform has been as an anesthetic [33,44,50,58] and most experiments have been related to this use. Cardiac arrhythmias have occurred, especially when chloroform anesthesia has been prolonged beyond 30 minutes. [56,57] Liver and kidney injuries have also been found, sometimes resulting in death several days after anesthetic exposure. [30,36,44,46,47,53,94]

It is difficult to evaluate the total exposure to chloroform during anesthesia since concentrations frequently were not reported. However, it should be noted that the concentrations in anesthesia are extremely high and are not constant throughout the exposure period. Whipple and Sperry

[30] demonstrated in experiments with dogs that chloroform anesthesia for a period of 1-2 hours caused central liver necrosis. At autopsy of a woman who had died from delayed chloroform poisoning, they found liver changes that resembled changes found in dogs. The only other experimental study of liver changes after inhalation of chloroform was that by Kylin et al [78] in 1963 who exposed 20 mice to 100, 200, 400, and 800 ppm for 4 hours. In this study, the mice exposed to 100 ppm did not develop demonstrable liver necrosis, however, moderate fatty infiltration of the liver was noted. In mice exposed to 200 ppm, some necrotic areas appeared in the liver and there was an increase in serum ornithine-carbamoyl transferase. Exposures to 400 and 800 ppm resulted in increasing necrosis and serum enzyme activity.

Although Schwetz et al [83] did not report detailed studies of liver changes in female rats exposed to chloroform 7 hours/day for 10 days, they did report that liver weights, both absolute and relative, increased as a result of exposure to 100 and 300 ppm but not to 30 ppm. However, embryo and fetal anomalies, including delayed skull ossification and the formation of wavy ribs, were found in the offspring of the rats exposed to 30 ppm.

The only account of liver abnormalities among industrial workers exposed to chloroform is a report by Bowski et al. [55] These investigators found 17 cases of hepatomegaly in a group of 68 workers exposed to chloroform in concentrations ranging from 2-205 ppm for 1-4 years in a pharmaceutical firm. Three of the 17 workers with hepatomegaly were judged by the authors to have toxic hepatitis on the basis of elevated serum enzymes, and elevated serum gamma globulin. This group of workers was also considered to be much more susceptible to viral hepatitis than the



inhabitants of the city in which the plant was located, but the basis for this inference is tenuous, since no information was given on possible contributions to the problem by poor sanitation, for example the incidence of viral hepatitis in other plant workers was not mentioned.

In the study by Challen et al [67] no liver abnormalities were found among 17 workers exposed to chloroform. Nine workers were exposed to chloroform at TWA concentrations ranging from 23-71 ppm, but for only 4 hours/day. These workers had been working under these conditions for 10-24 months. Another group of workers who had previously been exposed to chloroform in concentrations estimated to have ranged from 77-237 ppm for up to 8 hours/day, also had no abnormal liver findings. However, it had been many months since this latter group had been exposed to chloroform.

These studies indicate that liver damage may occur in workers from exposure to chloroform in varying concentrations up to 205 ppm. [55] The studies with mice showed some liver cell necrosis from 4 hours' exposure to 200 ppm and fatty infiltration of the liver from 100 ppm for 4 hours. [78] The studies with rats showed increased liver weights from 10 consecutive 7-hour daily exposures to 100 ppm, but not to 30 ppm exposures. [83] The studies by Challen et al [67] indicated no liver injury from 4 hours per day exposure of workers to 23-71 ppm chloroform.

While the exposure conditions studied by Challen et al [67] (23-71 ppm chloroform for 4 hours/day) seem below the threshold for liver injury, they are not adequate to protect workers from other undesirable responses such as dryness of the mouth and throat at work, and lassitude in the evening, which occurred among the workers exposed to 23-35 ppm chloroform for 4 hours a day. It seems reasonable to infer from these observations

that the lassitude reflects central nervous system depression and that dry mouth and throat and the digestive tract symptoms reflect a local irritant action in those areas.

It can be interpreted from the study of Challen and co-workers [67] that a safe level to exposure for workers lies somewhere between 23 and 35 ppm for 4-hour workdays, or about 10 to about 18 ppm for 8-hour workdays. The appropriate limit within this range is not clear, but because of mild effects in this group (mouth and throat dryness and evening fatigue) and because of the fetal abnormalities found in rats exposed to 30 ppm, [83] it is concluded that the environmental limit to be recommended should be the lowest in this range, namely 10 ppm, as a time-weighted average.

The absorption of chloroform resulting from exposure to a given time-weighted average concentration for 8 hours a day, 5 days a week, would be about the same as that absorbed for 10 hours a day, 4 days a week. Thus, the same time-weighted average limit is applicable whether the 40-hour workweek is applied over 5 8-hour days or 4 10-hour days.

It is likely that a central nervous system depressant, such as chloroform, might at briefly high concentrations affect attention, judgment or perception sufficiently so that if an emergency were to occur the worker might not take appropriate action. This suggests the need for a ceiling concentration to be observed, as a limitation on excursions above the time-weighted average and as a limit applicable to occasional and brief use of chloroform. However, after detailed consideration of the data applicable to derivation of such a ceiling, no basis from the scientific data appears. The ceiling proposed by American Industrial Hygiene Association [95] in its Hygienic Guide Series is based on animal data that seem more applicable to

development of a time-weighted average limit. Thus, a ceiling limit of 50 ppm based on a 10-minute sampling period is proposed on the basis of good practice.

It is recognized that many workers handle small amounts of chloroform or are working in situations where, regardless of amounts used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with all provisions of this recommended standard, which has been prepared primarily to protect worker health under hazardous circumstances. On the other hand, concern for worker health requires that protective measures be instituted below the enforceable limit to ensure that exposures stay below that limit. For these reasons, "exposure to chloroform" has been defined as exposure above half the environmental limit, thereby delineating those work situations which do not require the expenditure of health resources for environmental and medical monitoring and associated recordkeeping. Half the environmental limit has been chosen on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas from areas in which a hazard may exist. However, it is recommended that appropriate work practices and protective measures to prevent skin and eye contact and to prevent exposure to pyrolysis products be required, regardless of air concentrations of chloroform.

## VI. WORK PRACTICES

The principal method for the manufacture of chloroform is chlorination of methane, [1] and suitable controls for safe use of methane and chlorine should be used. Engineering controls required for the safe handling of chlorine are available. [119]

Further information concerning specific work practices for chloroform such as engineering controls, preventive measures, medical management, first aid, training, safety, etc, can be found in the Manufacturing Chemists' Association Safety Data Sheet SD-89. [120]

### (a) Bulk Handling

Of primary concern in bulk loading or unloading operations is the possibility that an emergency situation may arise as a result of equipment breakdown or failure to follow proper work procedures. All piping and valves at the loading or unloading station should be carefully inspected prior to connection to the transport vehicle and periodically during the operation. Personal protection must be provided during both inspection and connection. Eye wash and safety shower installations should be readily available in the immediate area. Unloading areas must be posted "Danger: loading or unloading chloroform".

### (b) Storage and Use

Although chloroform is noncombustible, decomposition to toxic compounds including phosgene, tetrachloroethylene, hydrogen chloride, chlorine and carbon dioxide may occur in case of a fire. [1]

Protective measures include use of closed systems whenever feasible, personal protective equipment, protective clothing, purging of equipment

prior to and during servicing and maintenance, and well designed and properly functioning laboratory hoods and exhaust systems. In general, good engineering practices should be used to control continuous low-level exposures and to minimize excursions. For example, good ventilation practices are recommended in Industrial Ventilation-A Manual of Recommended Practice [121] published by the American Conference of Governmental Industrial Hygienists. Special handling and disposal procedures are also required because of the ability of chloroform to undergo chemical reactions with other materials. For example, chloroform reacts violently with acetone in the presence of alkali and also with alkali metals. It reacts less violently with caustic. For these reasons, chloroform should not be disposed of along with other waste solvents. The ability of some chlorinated solvents to react with aluminum producing anhydrous aluminum chloride suggests that chloroform should not be stored in aluminum containers.

Safety showers and eye wash fountains are necessary in areas where accidental exposure is likely to occur.

(c) Maintenance of Equipment

All equipment used for handling chloroform must be emptied and purged prior to entry or disassembly. Under conditions where it is necessary to enter or otherwise work with chloroform contaminated equipment maintenance personnel must use either a self-contained breathing apparatus, pressure demand type, with an impervious protective suit; or a combination supplied air suit with auxiliary self-contained air supply. Safety precautions for emergency rescue require that all maintenance personnel be informed of wearing personal protective equipment. [2]

(d) Emergencies

Spills must be anticipated. Storage tanks should be diked to contain the contents of the tank. Drum storage areas must also be diked to contain the volume of chloroform present in the drums so as to prevent release to other areas. Areas where major spills are likely to occur should be constructed so that they may be closed until properly protected personnel can enter, clear and ventilate the area. Normal work should not be continued until the concentration of chloroform has been reduced to that prescribed by this standard. Sewering of chloroform should be done in compliance with local, state, and federal waste disposal regulations. Consideration should be given to pumping the diked spill to another tank. In addition, it is advisable to have facilities for transfer of the contents of a leaking tank to another suitable tank.

(e) Respiratory Protection

For adequate respiratory protection against the multiplicity of conditions which may be encountered in individual operations, many types of respirators have been developed and approved. Each has a particular field of application and limitations from the viewpoint of protection, as well as advantages and disadvantages from the viewpoint of operational procedures and maintenance. Detailed information on the selection and use of respirators can be obtained from the respiratory protection devices manual [122] published by the AIHA and the ACGIH in 1963. The American National Standards Practices for Respiratory Protection, ANSI Z88.2-1969, [123] also classifies, describes, and gives the limitations of respirators.

Respirators generally fall into the following classification according to their mode of operation:

- (1) Atmosphere-Supplying Respirators
  - (A) Self-contained.
  - (B) Hose mask.
  - (C) Airline.
  - (D) Combination self-contained and airline.
- (2) Air-Purifying Respirators
  - (A) Gas and vapor (gas mask and chemical cartridge).
  - (B) Particulate (dust, fog, fume, mist, smoke, and sprays).
  - (C) Combination gas, vapor, and particulate.
- (3) Combination Atmosphere-Supplying and Air-Purifying Respirators

The factors that affect the overall performance of an air-purifying respirator are the reliability of the face seal, the efficiency of the filters and/or absorbent canisters and other variables, such as leakage from exhalation valves. The performance of filters, canisters, and exhalation valves is predictable and controllable when test data are available. However, the current state of knowledge of the wearer's face size and shape and the respirator size and shape is such that the face seal is unpredictable and variable.

During the past several years, NIOSH has funded research and development projects to make quantitative respirators-man tests on all types of respirators to measure their performance and/or efficiency. The results of these tests made on half mask and quarter mask facepieces, operated with a negative pressure in the facepiece, show that the facepiece

leakage is the major limitation of these devices. From the test results, it has been demonstrated that the half mask or quarter mask facepiece may be used for protection up to 10X the TWA. The full facepiece, operated with a negative pressure, may be used up to 100X the TWA. The majority of the wearers can obtain a higher degree of protection. However, for purposes of uniform regulations, covering the many face sizes and shapes of the US working population, it is necessary to use these guides. These maximum use concentration guides do not take into account additional leakage from filters or canisters.

When providing respiratory protection against chloroform, the concentration immediately dangerous to life must be considered. In this document, it is assumed that any concentration of chloroform greater than 2,500 ppm is immediately dangerous to life.

In selecting and using gas masks and chemical cartridge respirators, the service life must be considered. The approval tests (under 30 CFR 11) for these 2 devices specify only carbon tetrachloride for the service life test. Based on recent tests by Nelson and Harder [124] who tested standard respirator cartridges against many types of industrial organic solvents, it is now possible to estimate the service life of approved organic vapor canisters or cartridges against chloroform. With a test concentration of 1,000 ppm of chloroform, they reported that the standard organic vapor cartridge has a service life of 33 min before a breakthrough of 10 ppm of chloroform. Under the same test conditions, a service life of 77 min for carbon tetrachloride was obtained. Since the approval test for organic vapor cartridges and canisters specifies carbon tetrachloride as a test atmosphere, it is possible to extrapolate or calculate service life at



various concentrations of chloroform. For example, the standard industrial size gas mask canister is tested against 20,000 ppm of carbon tetrachloride and it must have a service life of 12 min before a breakthrough of 5 ppm. Extrapolation indicates that the same canister would provide a service life of 4 hours against 1,000 ppm of carbon tetrachloride. However, the same organic vapor canister is much less efficient for chloroform. If it is assumed that carbon tetrachloride absorption is 100% efficient on activated charcoal, then chloroform absorption is only 43% efficient. From this, the service life against 1,000 ppm of chloroform for an industrial size canister is estimated at 2 hours. The chin-type canister with a much smaller volume of sorbent has a service life of 4 hours against 100 ppm of chloroform. The shortest service life is the chemical cartridge approved for use on chemical cartridge respirators. It has a service life of 3 hours against 100 ppm for chloroform.

NIOSH periodically issues a list of approved or certified respiratory protective devices. All devices approved by the Bureau of Mines are listed in Information Circular 8559 and supplements. All types of devices certified by the Testing and Certification Laboratory of NIOSH are listed in a separate publication. These are available from the Testing and Certification Laboratory, NIOSH, Morgantown, West Virginia, 26505.