

IV. ENVIRONMENTAL DATA

Sampling and Analytical Methods

Colorimetric methods of analysis involving air sampling have generally used the following reagents: arsenous anhydride, [62] neutral and acidic iodide, [63] methyl orange, [64] and o-tolidine. [65]

Boltz and Holland [66] reviewed the o-tolidine method, the methyl orange method, and the Konig reaction method involving cyanogen chloride-pyridine and condensation of a glutaconic aldehyde with an aromatic amine. For the o-tolidine method, a 9-liter air sample filtered through 10 ml of absorber solution allowed the detection of 0.05 ppm chlorine [67]; for methyl orange, a 3-liter air sample filtered through 10 ml of absorber solution allowed detection of 0.05 ppm chlorine. [64] Both methods were pH-dependent and neither was specific for chlorine only; other oxidizing agents will produce the same effects. [66] These authors [66] found that iron(III), manganese(III), manganese(IV), and nitrite interfered with the determination by o-tolidine, although Johnson and Overby [68] introduced a stabilized, neutral, o-tolidine reagent which effectively eliminated these interferences. Oxidizing agents such as bromine were reported to interfere with determination by methyl orange, [64] although iron(III) and substances containing available chlorine such as chloramine did not. [66] Laitinen and Boyer [69] developed a methyl orange method for visible-UV spectrophotometric determination of chlorine in the presence of bromine. Microliter aliquots of bromine solution and chlorine solution were simultaneously injected into a nitrogen stream which was dispersed into 25

ml of methyl orange solution. Individual halogen mole fractions were determined with an 8% relative error and a $\pm 11\%$ relative standard deviation. The cyanogen chloride-pyridine method [66] was observed to be fairly specific, detecting chlorine, bromine, and substances containing available chlorine or bromine, but it suffered from decreased sensitivity (50% of that of the o-tolidine method [66]), the use of noxious reagents, and lengthy color development (2 hours at room temperature, 40 minutes at 60 C). [66]

The color reaction of the methyl orange-chlorine system was seen immediately (bleaching) with color stability lasting at least 24 hours. [64] The o-tolidine system [66] developed maximum color with chlorine almost immediately; the color intensity decreased thereafter at a moderate rate. [66]

Instrumental methods have been primarily gas chromatography, [70-77] UV spectrophotometry, [69,78] colorimetry, [79] amperometry, [80] mass spectrometry, [81] catalytic combustion, [82] and the use of direct reading detector tubes. [83] Bethea and Meador [71] listed 15 gas chromatographic methods for chlorine including one for an on-line analyzer. The gas chromatographic methods were particularly suited to trace analyses but required specialized equipment and expertise. Measurements of absorbance of UV radiation may be useful for singular halide components [69] but are difficult with mixtures. [78] Analogous potential complicating effects occur with mass spectrometric and catalytic combustion procedures.

Sampling of air by syringe followed by a colorimetric analysis using permeation tube standards has been developed [84] but reproducibility

depends on operator technique.

Currently, certain chlorine-specific tubes have been evaluated and certified by NIOSH in accordance with the provisions of 42 CFR 84 (1974). In order to be certified, detector tubes must exhibit (1) accuracy within $\pm 35\%$ at half of the NIOSH test concentration (NTC) and within $\pm 25\%$ at 1, 2, and 5 times the NTC (for chlorine, the NTC was 1 ppm); (2) channeling (beveled stained-unstained interface) of less than 20%; and (3) tube reader deviation (standard deviation estimate of three or more independent readers) of less than 10% of the average of the readers.

A method has been developed which uses an electrolytic cell through which chlorine-laden air passes. Chlorine oxidizes the bromide ions in the electrolyte; this causes an increase in current in the amperometric measuring circuit of the cell. Current is measured directly by the concentration of chlorine in the range of 0-50 ppm. [80] A procedure was developed [70] which used the combination of a gas chromatograph, an ion-selective electrode, and a combustion furnace. It detected as little as 36 ng chloride after conversion from chlorine. A combination pyrolysis-furnace/microcoulometric cell was found to be accurate to $\pm 2.5\%$ with a detection limit of 3 ng but it was sensitive to chlorinated hydrocarbons. [79] Other electrometric methods, [85-87] continuous colorimetric methods, [88, 89] and sensitized test paper methods are mentioned in the literature. [90] In general, automatic and continuous monitoring methods are effective for a narrow range of specific industrial applications, eg, process or fixed position area monitoring, but they are not suited for typical work situations where breathing zone concentrations must be determined.

Although the o-tolidine method is the most sensitive procedure for determining trace amounts of chlorine, [66] the methyl orange method is not affected by iron III or compounds containing available chlorine such as chloramine, and yet has 70% of the sensitivity of o-tolidine. [66] In addition, o-tolidine has been mentioned as a suspected carcinogen. [91,92]

The method of choice for atmospheric sampling and analysis of elemental chlorine in working environments is the methyl orange procedure. [64] In this procedure, 10 ml of methyl orange sampling solution is placed in a fritted bubbler, and a volume of air is drawn through at a rate of 1-2 liters/minute for 15 minutes. Absorbance is then measured with a spectrophotometer. This procedure is designed to cover the range of 5-10 mg of free chlorine/10 ml of sampling solution. For a 30-liter air sample, this corresponds to approximately 0.05-1.0 ppm in air. The method has an accuracy of $\pm 5\%$. Reagent stability is good and preparation is not lengthy. Samples remain stable for 24 hours (see Appendix II). Equipment and apparatus needed are uncomplicated, and sampling and analysis are straightforward and easily interpreted.

Minimal performance criteria required for this recommended method and for any proposed alternative method should provide at least one-half the recommended environmental limit as a level of reliable detection. This is required for the purpose of identifying work areas subject to periodic air sampling.

Environmental Levels and Engineering Controls

Few studies have been published concerning workroom airborne

concentrations of chlorine and the extent of engineering controls required to reduce exposures. In 1964, this scarcity of information prompted the environmental health study of a chlorine plant described by Pendergrass.

[93] In the plant studied, chlorine was produced by the electrolysis of brine in 180 Hooker-type cells. The chlorine unit consisted of a cell house, a purification area, a compressor area, and a cell renewal building. The cell house and purification areas were of primary concern in this study. The building housing the cells was about 60 x 300 feet with a high ceiling and partial side walls. The purification area was about 25 feet from the cell house and was not enclosed. In normal operations, exposure could occur when chlorine was released to the workroom atmosphere during routine replacement of cells, replacement of connectors between cells and headers, discharge of caustic and brine from cells, and from leaks in old cells. Release of chlorine in the purification area was most likely to occur at the primary cooler. Larger amounts of chlorine were occasionally released to the work area when increased gas pressure blew a water seal in a header. Over a 5-month period, 2,785 air samples of 8 hours' duration each were collected and analyzed. The 8-hour average levels at various locations ranged from less than 0.1 ppm to greater than 6.0 ppm. Of the 2,785 samples, 91.2% were less than 1.1 ppm chlorine and 98.9% were less than 1.0 ppm chlorine. The concentrations of chlorine in those samples which exceeded 1.0 ppm were not given. Controls were not mentioned, but the system described by Pendergrass apparently was essentially an enclosed system.

Ferris et al [47] used detector tubes to determine chlorine concentrations in the workplace air of a pulp and paper mill that manufactured its own chlorine. Thirty-three samples indicated the existence of workplace airborne concentrations of chlorine that ranged from "trace" to 64 ppm. (Mean concentrations ranged from "trace" to 7.4 ppm.) No sampling locations were given and no samples were related to any specific job category. Existence of controls was not mentioned.

Concern with the possible long-term effects of exposure to chlorine at low airborne concentrations resulted in an epidemiologic study by Patil et al [52] of diaphragm cell workers in 25 chlorine plants. Each plant was surveyed every 2 months throughout the study-year. TWA exposures to chlorine ranged from 0.006 to 1.42 ppm with a mean of 0.15 ppm. Of the personnel studied, 98.2% were exposed to chlorine at TWA levels below 1.0 ppm. Controls were not mentioned, nor were sampling locations designated.

Feiner and Marlow, [94] reporting on industrial hygiene in pulp mills, stated that the need for control of chlorine by ventilation in pulp mill-bleaching plants was minimal when chlorine was accurately metered in proportion to the volume of stock to be bleached. However, they recommended covers for bleach chests, hoods for rinse washers, and exhaust ventilation of the enclosures as precautionary measures. The authors did not provide air sampling data to support their statement.

Elkins [95] reported one sample of "hazardous concentration" out of four samples taken in textile- and paper-bleaching processes. "Hazardous concentration" was assumed to indicate that the threshold limit value of 1 ppm was exceeded. No further data were given.

Joyner and Durel [25] reported on a spill of about 6,000 gallons of liquid chlorine. Three hours after the spill, the contaminated area was approximately 200 yards in length along a highway. Chlorine at concentrations of 10 ppm was found in the fringes of this area. About 7 hours after the spill, chlorine at a concentration of 400 ppm was found in more heavily contaminated areas 75 yards from the spill. Two and one-half hours later, after treatment of the spill had begun, the airborne chlorine levels dropped to 8 ppm. Joyner and Durel stated [25] that minor first-degree burns of the facial skin resulted from exposure to the gaseous chlorine. In a verbal communication of July 1974, Joyner stated that there was no opportunity for persons to contact the liquid; therefore, he was certain that the skin irritation was caused by gaseous chlorine.

Capodaglio et al [49] investigated the respiratory function of workers engaged in chlorine production by means of the electrolysis of brine in mercury cells. They noted that no special precautions were taken to control chlorine in the plant air, although ventilation was present to minimize mercury exposure. Presumably this would have also prevented exposure to chlorine. The authors [49] stated that natural and forced ventilation "assured 40 hourly exchanges" in a 40,000-cu m shed. Under these conditions, 18 samples taken for an unspecified period of time showed the average airborne chlorine concentration to be 0.298 ppm. Sixteen spot samples showed an average chlorine concentration of 0.122 ppm.

Smith et al [96] reported that most chlorine cell rooms had airborne chlorine levels well below 1 ppm, usually in the 0.1 to 0.3-ppm range. No supporting data were given.

The TI-2 Chemical Industry Committee of the Air Pollution Control Association [97] mentioned that chlorine-manufacturing and processing equipment was normally operated with a slightly negative gauge pressure, thus preventing leaks of chlorine into cell room atmospheres. Pressure fluctuations occurring in the system from power outages or compressor failures could have caused chlorine leakage until cells were shutdown.

Connell and Fetch [98] described vacuum-operated systems for water chlorination. These systems removed much of the hazard which could result from leaks in pressurized chlorine piping.

Many references recommend ventilation of chlorine storage and handling rooms. [98-105] Several of these [99,102,104] recommend a ventilation rate of one air change every 1-4 minutes. Ventilation for bleach mixing rooms and rooms for storage of chlorine containers in pulp, paper, and paperboard mills is required by 29 CFR 1910.261. It has been recommended that chlorine be used only in fully or partially enclosed systems. [99]

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In order to obtain data on industrial contaminants which might affect Massachusetts' workers, Elkins [106] prepared in 1939 a list of existing threshold concentrations or maximum allowable concentrations (MAC's), added some tentative proposals for Massachusetts, and sent the list to 19 American and 8 foreign experts. Suggestions and criticisms were received from all but two of the American and four of the foreign experts. The results were tabulated and considered in detail by the Massachusetts Dust and Fume Code Committee. One ppm was proposed for chlorine as a maximum allowable concentration. There was no written explanation provided to determine if this was intended as a TWA or as a ceiling value.

In 1945, Cook [107] compiled a list of standards and recommendations for MAC's of industrial atmospheric contaminants. The author noted that 1 ppm was the MAC value for exposure to chlorine in the workplace air in California, Connecticut, Massachusetts, New York, Oregon, and Utah. According to Cook, 2 ppm was the standard promulgated by the American National Standards Association (now the American National Standards Institute Inc). The American National Standards Institute Inc order department, however, has no record of a standard prior to 1945 (written communication, March 1976).

Cook [107] reported that early work had indicated 1 ppm should be the maximum allowable concentration for chlorine, and that this recommendation had been generally followed in industry. However, Cook [107] proposed 5

ppm rather than 1 ppm based on data referred to in the US Bureau of Mines technical paper 248. [39] This paper described research conducted by the Chemical Warfare Service, American University Experiment Station, and purportedly showed that 15.1 ppm chlorine was necessary to cause throat irritation and 30.2 ppm was necessary to cause coughing, while the chlorine concentration least detectable by odor was 3.5 ppm. This value was likely a TWA concentration since Cook stated that in every case the concentrations given were considered allowable for prolonged exposures, usually assuming a 40-hour week.

In 1947, the American Conference of Governmental Industrial Hygienists (ACGIH) [108] adopted an MAC for chlorine of 2 ppm. It was not stated whether this MAC was intended as a ceiling concentration or as a TWA concentration. The April 1948 meeting of this same organization [109] adopted 1 ppm as a threshold limit value (TLV). This TLV for chlorine was clearly specified as a TWA concentration.

In their documentation of TLV's [110] published in 1962, the ACGIH cited reviews by Heyroth [111] and Henderson and Haggard [112] to explain its selection of 1.0 ppm as the TLV for chlorine. Heyroth [111] cited data from an unpublished dissertation that men could work without interruption in air containing 1-2 ppm chlorine. A translation of this dissertation by Matt [38] has been reviewed in Chapter III under Effects on Humans. Heyroth listed 1 ppm as a "maximum permissible" limit in 13 states and 5 ppm in Ohio and Washington. Heyroth [111] also referred to the Principles of Exhaust Hood Design, [113] in which DallaValle suggested that the limit be less than 0.35 ppm. The basis for this limit was not identified.

Henderson and Haggard [112] recommended a maximum concentration of 0.35-1.0 ppm for prolonged exposure. The only reference cited by either Heyroth [111] or Henderson and Haggard [112] which gave any support to the TLV of 1 ppm was Matt, [38] as quoted by Heyroth. [111]

Henderson and Haggard [112] and a more recent edition of Heyroth [114] were used as a basis for the 1966 documentation [115] of the 1-ppm chlorine TLV. It was recommended as a ceiling value "to minimize chronic changes in the lungs, accelerated aging, and erosion of the teeth," but no data were given to document the occurrence of these chronic changes.

Between 1965 and 1968, [116-119] the 1-ppm TLV was considered a ceiling value by the ACGIH. A revised second edition of the Documentation citing Heyroth [114] listed a threshold limit of 1 ppm as adopted by the ACGIH and deleted its discussion of concentrations proposed by different states and its reference to DallaValle. [113]

The 1971 documentation of threshold limit values [120] acknowledged that relatively few studies provided data useful in developing a TLV and proceeded to give a general review of proposed limits without specifically supporting its TLV as a TWA concentration of 1 ppm. Thus it stated that Heyroth [114] and Flury and Zernik [121] had proposed 1 ppm, Henderson and Haggard [112] had suggested 0.35-1 ppm, Cook [107] had suggested 5 ppm, and Rupp and Henschler [16] had proposed 0.5 ppm. This documentation [120] discussed the results of studies by McCord, [36] Ferris et al, [47] and Kowitz et al [28] in which adverse effects were found in humans after exposure to chlorine. However, the exposure levels in these studies [36,47] varied from negligible to 15 ppm and did not give support to the

TLV of 1 ppm. The Kowitz et al report [28] concerned a chlorine accident and did not quantify exposures.

In 1971, the Pennsylvania Department of Environmental Resources [122] adopted a 1-ppm TLV which was a TWA concentration and it also adopted a short-term limit of 3 ppm for 5 minutes. [123] Heyroth [114] and Imperial Chemical Industries, Great Britain, (no specific reference listed) were cited as a basis for the documentation of these short-term limits. Heyroth [114] reported that chlorine at 3-6 ppm caused a reaction, but that men could work without interruption at 1-2 ppm. The Imperial Chemical Industries recommendation [123] stated that exposure to chlorine at 4 ppm for more than a short time might lead to symptoms of illness.

A number of occupational airborne chlorine limits have been set by foreign countries and international groups. East Germany, Hungary, Poland, [124] and Bulgaria [125] recommended a permissible concentration of 1 mg/cu m (about 0.3 ppm) while West Germany [124] recommended 2 mg/cu m (0.5 ppm) and Czechoslovakia, Great Britain, Yugoslavia, [124] Finland, [125] and Japan [126] recommended 3 mg/cu m (about 1 ppm). The Czechoslovak limit of 3.0 mg/cu m was a suggested mean value and was asserted to be "considerably lower than the concentration which molests unaccustomed persons." A peak concentration (MAC) of 6 mg/cu m (about 2 ppm) was also established which was stated to be low enough to prevent lung edema after short exposure. Documentation was not given for the suggested MAC.

In the Soviet Union, [127] a mandatory maximum permissible concentration of 0.001 mg/liter (about 0.3 ppm) in the workroom air was established by the Main State Health Inspector of the USSR, January 10,

1959, Regulation No. 279-59. Maximum permissible concentrations were considered ceiling values, and they could only be exceeded with the permission of the State Sanitary Inspection of the USSR if the workers were in an industrial area for an "unspecified short period."

Rupp and Henschler [16] investigated the relevant literature and conducted studies on the effects of chlorine at low concentrations on man. Exposures to chlorine at concentrations of 0.5 ppm and higher were reported to be disturbing. The authors proposed an MAK value of 0.5 ppm to the Committee for Testing of Industrial Substances Injurious to Health of the German Research Association. It is not clear whether this MAK value was intended to be a TWA or a ceiling concentration. This value was accepted by the committee in November 1961. Prior to 1961, the MAK value in Germany had been 1 ppm. [16]

In 1971, the Japanese Subcommittee on Permissible Concentrations of Hazardous Substances [126] recommended the continued acceptance of the 1961 TWA concentration of 1 ppm chlorine. The recommendation was based on reports and data from human and animal experiments as well as from experience in the industry. No documentation was provided.

In 1963, the Second International Symposium on Permissible Limits for the Air of Workplaces [128] adopted an MAC of 1 ppm which was considered as a ceiling value. No basis or documentation was given to support the MAC.

ANSI [129] adopted an 8-hour TWA concentration of 1.0 ppm in 1974. At the same time, a maximum peak acceptable concentration of 3.0 ppm for 5 minutes and an acceptable ceiling of 2.0 ppm were established. In both cases, these concentrations were acceptable only insofar as the 8-hour TWA

was not exceeded. The primary references cited in support of the acceptable concentrations were: Patil et al, [52], Kowitz et al, [28] Weill et al, [26] Kaufman and Burkons, [35] and Heyroth. [114]

The present federal standard (29 CFR 1910.1000) for chlorine is an 8-hour TWA of 1 ppm and is based on the ACGIH TLV for 1968. [119]

Basis for the Recommended Environmental Limit

Exposure to high concentrations of chlorine can be fatal. The LC50 for dogs is approximately 800 ppm for 30 minutes. [53,55] Humans have died after accidental exposures to high chlorine concentrations. [19,23,24,29] These were accidental exposures and the chlorine concentrations were not reported.

Accidental massive exposures to chlorine have on occasion been associated with ECG changes. Four studies [22,27,31,34] mentioned ECG's of patients exposed to chlorine at high concentrations. Chasis et al (22) obtained serial tracings on 12 patients and found either no abnormality or evidence of preexisting heart disease. Uragoda's [31] patient had one PVC (premature ventricular contraction) every three normal beats when first examined with fewer PVC's on a subsequent examination, 27 days later. In 48 ECG's taken in cases of chlorine exposure, Leube and Kreiter [34] found several instances of significant sinus tachycardia, isolated ventricular extrasystoles, and signs of repolarization disturbance of the left ventricle. Gervais et al [27] found one instance of transient right-heart block. A lack of data made it impossible to estimate a possible dose-response relationship.

Chronic lung disease was reported in persons who had accidental exposure to chlorine at high concentrations. [24,28] Hoveid [24] relied on statements by exposed individuals about their health. These statements were made an unspecified time after exposure, without other confirmation. He assigned 20% of the persons to the category of those having "difficulties believed to be a reasonable consequence of the accident." Kowitz et al [28] performed a series of pulmonary function tests on 11 persons after they were discharged following hospitalization for exposure to chlorine and found that, even after 3 years, their lung volumes were still low. The study did not provide a quantitative estimate of the exposure, although the acute respiratory distress had been severe in 7 of the 11, and acute symptoms were documented in the remaining 4. [28]

Rupp and Henschler, [16] in exposing subjects to concentrations of chlorine increasing from zero to 1.3 ppm over 50 minutes, demonstrated that itching in the nose began at 0.06 ppm after approximately 4 minutes for one subject, cough began at 0.5 ppm within 25 minutes, and headache began at about 1 ppm,; beyond 1 ppm, all test subjects felt the stay was uncomfortable. Between 1.0 and 1.3 ppm, one subject had severe shortness of breath, cough, and a violent headache, the latter probably an individual variation in sensitivity to chlorine. When 20 subjects were exposed to concentrations of airborne chlorine averaging 0.027 ppm, tickling in the nose occurred; at concentrations averaging 0.058 ppm, tickling involved the throat as well, and at concentrations averaging 0.452 ppm conjunctival burning was present, which progressed to a feeling of pain in a few

subjects after 15 minutes. There were no data given for effects at concentrations of chlorine between 0.5 and 1.0 ppm.

In a similar study, Beck [17] found that 4 of 10 subjects, after exposures of up to 30 minutes, experienced some tickling and stinging in the nose at 0.09 ppm, and one had a weak cough. At 0.2 ppm, 7 of 13 had tickling and stinging in the nose and throat and 3 had slight conjunctival burning. At 1 ppm, 7 of 10 had symptoms of upper respiratory irritation. In one subject, the exposure had to be terminated in 20 minutes because it was unbearable. With gradually increasing concentrations of chlorine, three of four subjects exposed felt a stinging in the throat at 0.3 ppm, and at 1.4 ppm, one subject felt neck pain and conjunctival irritation.

Matt [38] experienced an unpleasant burning in the eyes and nose when he exposed one subject to chlorine at a concentration of 1.3 ppm. He concluded, however, that uninterrupted work was possible at this level.

In contrast, subjective responses of industrial hygienists from the Dow Chemical Company [CB Kramer, written communication, June 1974] suggested that chlorine at a higher concentration was required to produce a respiratory response or eye irritation. During air sampling periods of 10 minutes or more, average chlorine concentrations of 1.92-41.0 ppm produced a "minimal", "easily noticed," or "strong" respiratory response. Eye irritation was considered "minimal" at an average concentration of 7.7 ppm (one air sample) and "easily noticed" at concentrations of 8.7-41.0 ppm (4 samples). The above values were qualified, however, by the observation that a previous exposure of the same individual on the same day resulted in a less discerning response subsequently.

Several epidemiologic studies [46-52] have attempted to relate previous industrial exposure to the frequency of pulmonary abnormalities and symptoms found. The study by Ferris et al [47] indicated that no specific adverse effects resulted from repeated exposures to chlorine at concentrations ranging from 0 to 64 ppm over a period averaging 20.4 years. Insufficient data were provided, however, to determine TWA exposures. The most extensive prevalence study, which was conducted by Patil et al [52] and which was the only one reporting time-weighted averages, reported TWA concentrations of chlorine were 0.44 ppm or less for all but 21 of 332 workers. For these 21, the TWA concentrations ranged from 0.52 to 1.42 ppm; 15 were 0.52-1.00 ppm and 6 were 1.00-1.42 ppm, and their durations of exposure ranged from 2 to 14 years. No dose-response relationship (extent of exposure to chlorine vs pulmonary symptoms or signs) could be established for any of the 332 workers. There are no prospective epidemiologic studies relating the degree of exposure to chlorine in industry with the incidence of either mild chronic symptoms or chronic disability.

It is concluded that the existing federal standard should be lowered. Exposures to chlorine at concentrations of 1.3 ppm for 7 minutes, [38] 0.2-1.0 ppm for 30 minutes or less, [17] and 0.5 ppm or more for 1 hour or less [16] have resulted in the development of symptoms of both ocular and respiratory irritation. Exposure to chlorine at concentrations of approximately 0.5 ppm resulted in conjunctival pain in several subjects after 15 minutes. On the other hand, it was reported [52] that 311 workers exposed to chlorine TWA concentrations of 0.44 ppm or less for an average

of 11 years did not show any significant dose-related pulmonary or ocular effects when compared with a control group. Considering this evidence as well as the fact that further research is needed (see Appendix III) to clarify the relationship between chlorine dose and effect, a ceiling concentration of 0.5 ppm chlorine, measured over a sampling period of 15 minutes, is recommended as an environmental limit.

It is recognized that many workers handle small amounts of chlorine or work in situations where, regardless of the amounts used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with many of the provisions of this recommended standard, which has been prepared primarily to protect worker health under more hazardous circumstances. 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 chlorine" has been defined as exposure at or above one-half of 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. One-half of 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, because of nonrespiratory hazards such as those leading to skin burns or irritation or eye contact, it is recommended that appropriate work practices, training, and other protective measures be required regardless of concentrations of chlorine in air.

VI. WORK PRACTICES AND ENGINEERING CONTROLS

Safety precautions for the manufacture, storage, transportation, handling, and use of chlorine are well-defined and are the subject of a considerable body of literature. [40,99, 101-105,130-136] These references are concerned primarily with prevention and control of hazards arising from emergency situations involving escape of relatively large amounts of chlorine from leaks or accidentally ruptured containers or pipelines. Reports of work practices written specifically for the prevention of low-level exposures are limited. The type of ventilation needed for the control of chlorine in storage areas and in the workplace depends upon vapor density, dead air spaces, temperature, convection currents, and wind direction. [99] Use of fully or partially enclosed processes is recommended. [99,137] If full enclosure of the process cannot be used for control, good engineering practices, such as those recommended in Industrial Ventilation--A Manual of Recommended Practice, [138] should be followed in order to control continuous low-level exposures and to minimize excursions.

Emergency Assistance

If in-plant emergency teams cannot cope with chlorine emergencies, the nearest supplier, manufacturer, or designated source of information must be called for assistance. [102,134,139] Phone numbers of persons for such assistance must be prominently posted in areas where emergencies are likely to occur. Information to be furnished to the supplier, manufacturer

or other information source when assistance is requested should include:

User company name, address, telephone number, and persons to contact for further information.
Travel directions to emergency site.
Type and size of container or other equipment involved.
Nature, location, and extent of emergency.
Corrective measures being applied. [102]

Standardized kits for the control of leaks have been designed and manufactured. The Chlorine Institute maintains current listings of the locations of these kits. [139,140] The Chlorine Institute should be contacted for the nearest location if chlorine emergency kits are not readily available locally.

Training and Drills

The value of drills and training in handling emergencies and in using equipment for personal protection and control of escaping chlorine was emphasized in the literature. [99,101,102,105, 134,141,142] Danielson [143] reported on a chlorine spill caused by a rail car bumping into a tank car discharging chlorine. A total of 55 tons of chlorine could have been released into the atmosphere; however, only a few tons escaped because of quick action by employees and supervisory personnel. Danielson [143] credited the quick action to rigorous and thorough training and drills.

Leaks

Studies by the Bureau of Mines [144] indicate that pinhole leaks in chlorine containers are rapidly enlarged by corrosion if moisture is

present. Furthermore, the control of chlorine leaks or spills by the use of water is not effective because of the limited solubility of chlorine in water. [144] Even the coldest water will supply sufficient heat to cause an increase in the evaporation rate of chlorine. [134] Therefore, water must never be used on leaking containers of chlorine, or to control spills. It is illegal to ship a leaking container of chlorine. [136]

Daily checks must be made for leaks in pressurized chlorine systems and containers. [134] Leaks may be detected by using the vapor from strong ammonia water. A white cloud will be formed near leaks. [99, 105,130,134] If leaking chlorine cannot be removed through regular process equipment, it may be absorbed in alkaline solutions. [99,130,134,136] These solutions can be prepared as described in Table XIII-3. [130] The quantities listed in the table are chemical equivalents and it is desirable to provide excess over these amounts in order to facilitate absorption.

Emergency leak kits designed for standard chlorine containers are available at various locations throughout the country. These kits operate on the principle of capping off leaking valves or, in the case of cylinders and ton containers, of sealing off a rupture in the side wall. [130] A record of kit locations is maintained by the Chlorine Institute. [139,140] If possible, users of chlorine should have their own appropriate emergency leak kits readily available for use at the process location. It should be noted, however, that the use of leak kits requires some training prior to use in an emergency situation.

Chlorine containers must be used on a first-in, first-out (FIFO) basis, [99] because valve packings may harden during prolonged storage and

cause leaks when containers are finally used.

Because of the potential danger of excessive hydrostatic pressure in chlorine containers, such containers are filled only partially with liquid chlorine, leaving sufficient gas-filled space to act as an expansion chamber. [40,100] Accordingly, gaseous chlorine is discharged from a cylinder if the cylinder is in the upright position, and liquid chlorine is discharged if the cylinder is inverted. Gaseous chlorine is discharged from the upper valve and liquid chlorine from the lower valve in a ton container. To minimize a leak in a container, the container should be oriented so that gaseous chlorine is discharged instead of liquid. The volume of gaseous chlorine formed by vaporization of liquid chlorine is about 450 times its original volume as a liquid. [99,102,134,137]

Protective Clothing and Equipment

Whenever liquid or gaseous chlorine is handled or used, it may come in contact with the skin and eyes, or be inhaled. For this reason, personal protective clothing and equipment are necessary. While not specific for chlorine, safety glasses or goggles, hard hats, and safety shoes should be worn or be available as dictated by the special hazards of the area or by plant practice. [130] Personnel working in areas where chlorine is handled or used should be provided with suitable escape-type respirators. Supplied-air and self-contained breathing apparatus should be used when the concentration of chlorine is not known, as in an emergency. [130]

Canister-type gas masks have limitations. In chlorine concentrations

of 2% (20,000 ppm), a canister will protect the user for about 10 minutes. [145, 30 CFR 11] Canisters should be discarded and replaced whenever they are used, or when the shelf life, as indicated by the manufacturer, expires. Canister masks do not protect in atmospheres deficient in oxygen and should not be used except for escape in chlorine concentrations exceeding 1%. [99,102,134,136,146] Self-contained breathing apparatus or supplied-air full-face respirators should be worn when atmospheres contain more than 1% chlorine or where oxygen deficiency may exist. Workers required to use respiratory protection must be thoroughly trained and drilled in its use. [99,105,136,146] When the concentration of chlorine is not known, as in an emergency, canister masks must not be used.

Fire and Explosions

Chlorine is classified as nonflammable and nonexplosive. However, it will support combustion of certain materials, [99,102,134] reacting explosively in some cases. At elevated temperatures, it reacts vigorously with most metals. [102] Carbon steel, for example, ignites in an atmosphere of chlorine at 483 F (250 C). [102] Fusible plugs are placed in chlorine containers to prevent rupturing of containers from excessive hydrostatic pressure caused by high temperatures. The fusible metal is designed to melt between 158 F and 165 F (70-74 C). [102] For these reasons, it is important to avoid application of heat to chlorine containers.

Explosions have occurred during the chlorination of synthetic rubber, [147,148] during the manufacture of chlorine, [149,150] and in chlorine absorption systems. [151] The last two incidents [150,151] were caused by

a mixture of hydrogen and chlorine which was in excess of the explosive limits. Determination of the explosive limits of chlorine-hydrogen mixtures indicates variations of from 3% hydrogen in pure chlorine to 8% hydrogen in a pressurized gas mixture containing 19% chlorine. [152] It is important that precautionary measures be taken to prevent chlorine from coming into contact with materials with which it may react.

Hydrostatic Rupture of Containers and Systems

Liquid chlorine has a very high coefficient of thermal expansion. [102,146] A 50 F (28 C) rise in temperature causes a volume increase of about 6%. [145] If liquid chlorine is trapped in a pipeline between two valves, increasing temperature will cause very high pressures, leading to possible hydrostatic rupture of the line. Accordingly, precautions must be taken to avoid this. It is important that liquid chlorine lines be at the same or higher temperature as the chlorine being fed into the line to prevent condensation, and that the lines be equipped with adequate expansion chambers, pressure relief valves, or rupture discs discharging into a receiver or a safe area. [102,153-155] Some expansion chambers are heated to ensure that chlorine does not condense therein and destroy the effectiveness of the vapor cushion. [154] Should it become necessary to evacuate a chlorine line equipped with expansion chambers, it is important that the vacuum not be broken with liquid or gaseous chlorine, a procedure which would render the expansion chambers ineffective. Dry air or nitrogen must be used for breaking such vacuums. [153]

Warning Properties

The readily identifiable odor of chlorine and the attendant disagreeable reactions it produces appear to be one means by which workers are warned of impending excessive exposure. [40,99,101-103,105,137,141,156] However, determinations of the threshold of odor have given varying results. For example, Ryazanov [15] found the threshold of odor of chlorine to be 0.3-0.45 ppm, while Fieldner et al [39] and Leonardos et al [14] reported it to be 3.5 ppm and 0.314 ppm, respectively. The variation of these results probably reflects differences in methods of determination, and possibly differences in the development of odor adaptation. [16-18,99,101] While a noticeable odor of chlorine may indicate a potentially hazardous exposure, it should not be relied on as a quantitative indication.

Specific Gravity of Chlorine Gas

Gaseous chlorine is about 2.5 times as heavy as air. [102] Therefore, in the absence of air currents, [99] leaking chlorine tends to accumulate in low spots. Storage areas should be constructed with this property in mind, eliminating low spots unless they are specifically engineered for the purpose of chlorine collection. Personnel evacuation plans should consider the slope of the terrain and the prevailing wind direction when describing evacuation routes and sites. [99,134] Ventilation systems should remove contaminated air at the lower levels of rooms and replacement air should enter at the higher levels. [99,102]

Unmanned Chlorinators

Chlorinators used for water treatment are often unattended. [90] Allen and Angvik [90] described an alarm system based on the use of sensitized paper at remote unmanned chlorination stations which darkened upon contact with escaping chlorine gas. When the chlorine concentration reached 3 ppm, a visual warning signal appeared in a central manned station. Remedial personnel with proper emergency leak kits and respiratory protection equipment were then dispatched to the site of the leak. All chlorination stations were equipped with ventilation to clear the building of excessive chlorine. Consideration should be given to the installation of such alarm systems for unmanned areas where chlorine is stored or used.

Materials of Construction

Materials which will come into direct contact with liquid or gaseous chlorine in storage, conveying, process, or other systems must be carefully selected to avoid excessive corrosion or more serious consequences. Dry chlorine may be handled in a wide variety of materials but moist chlorine is extremely corrosive. Chlorine will vigorously react with many metals at elevated temperatures. [98,99,102,104,131-134,137,155] Ventilation has been used to prevent airborne chlorine from corroding equipment. [157] Ventilation systems for transporting chlorine should be constructed of corrosion-resistant materials.

Unusual Sources

Excessive exposure to chlorine may occur when solutions of hypochlorites are mixed with materials such as toilet bowl cleaners [4,158] or vinegar. [5] Maintenance and custodial personnel should be warned of this possibility and instructed not to mix hypochlorites with any other material. Chlorine exposure may also occur when chlorinated hydrocarbons are decomposed thermally [6] or by ultraviolet radiation from electric arcs. [7,8]