IV. ENVIRONMENTAL DATA

Environmental Concentrations and Engineering Controls

Reports of workroom air levels of phosgene in industrial processes utilizing phosgene as a starting material have not been published in the United States. In contrast, the formation of phosgene by decomposition of chlorinated hydrocarbons and the resulting occupational exposures have been extensively studied. In evaluating ventilation plans for the control of phosgene in a plant conducting "phosgenation," the Bureau of Engineering Safety, Department of Labor and Industry, State of New Jersey, [24] reported briefly on workroom air concentrations of phosgene. Air sampling in the breathing zones of chemical operators during routine phosgenations showed concentrations of phosgene "well within the TLV of 0.1 ppm" at the time of this investigation. Details of the sampling and analysis procedures were not given, nor were individual sampling results reported. Although management had filed plans for canopy hoods over the reactors, the ventilation actually consisted of flexible ducts, 4 inches in diameter, to each kettle. Engineering controls did not conform to the applicable MCA Chemical Safety Data Sheet. [1] Over a 2-year period prior to this investigation, at least 6 employees had been acutely exposed to unknown concentrations of phosgene. [24] Four of these were not able to return to work the day after exposure. One death had occurred and was attributed to phosgene inhalation. No details were reported. After the fatality, the Bureau of Engineering Safety ordered all phosgene operations stopped because of deficient controls. Subsequently, management of the plant discontinued the use of phosgene.

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In 1962, Filatova et al [58] investigated health hazards occurring in the manufacture of diisocyanates utilizing phosgene as one of the raw materials. The authors commented favorably on the isolation of hazardous sections of the plant as a method of control. Local exhaust ventilation was utilized extensively. Ninety-one workroom air samples were taken and analyzed for phosgene by undescribed methods. Units of analytical results were not stated but are assumed to be mg/liter. Results showed phosgene concentrations ranging from a reported 0 to 0.013 mg/liter (0-3.25 ppm), with the most frequently observed concentrations ranging from a reported 0 to 0.0004 mg/liter. Of the 91 samples, 31 were negative for phosgene. However, an unspecified number exceeded the Maximum Permissible Concentration (MPC) of 0.5 mg/cu m (0.125 ppm) during such operations as cleaning vats or distillation apparatus. Recommendations for control included mechanization of manual procedures, provision of independent ventilation systems for each floor, limiting the number of hoods for each system to 10-12, and providing an intake velocity of at least 1-1.5 meters/second (197-296 feet/minute) for hoods with movable sash and louvers.

In 1966, Filatova [59] reported industrial hygiene evaluations of phosgene in the production of isocyanates. A continuous-flow method was used, involving the use of remote control equipment and the mechanization of unspecified operations, and so-called hermetization which was assumed to mean enclosure or sealing of equipment, particularly that operating under pressure. Under these conditions, 91% of air samples were below maximum permissible concentrations for phosgene. Filatova did not further report the results of air sampling.

Also in 1966, Levina et al [36] reported on industrial hygiene problems and worker health in monuron production. Monuron was defined as 3-(p-chlorophenyl)-1,1-dimethylurea and was used as an agricultural pesticide. Monuron was produced by the interaction of parachlorophenylisocyanate and dimethylamine. Synthesis of the isocyanate involved the use of phosgene. The authors criticized the plant layout because units using materials of high toxicity (eg, phosgene) were located throughout the general work area rather than being isolated. Local exhaust ventilation placed at sources of contaminant escape, in addition to general ventilation, provided some control. Makeup air inlets were considered by the authors [36] to be wrongly placed. Workroom air samples analyzed for phosgene (503 samples) showed concentrations commonly ranging from 1.0 to 2.0 mg/cu m (0.25-0.5 ppm). The maximum permissible concentration in Russia at that time was 0.5 mg/cu m (0.125 ppm). Most phosgene was released during disassembly and repair of pumps, which often became clogged. This operation, as well as repair of other phosgene equipment, the transmission of phosgene under pressure, and the taking of samples for quality control were carried out by workers wearing gas masks. Released phosgene was said to be neutralized with ammonia. Control recommendations included replacement of equipment with improved hermetically sealed pumps and revamping of the makeup air system to provide uniform air supply at low velocities. Mechanization of systems, relocation in areas removed from the general workrooms, and use of remote controls were also recommended.

In 1967, Levina and Kurando [38] described exposures to phosgene and other chemicals in the manufacture of isopropyl phenylcarbamate, used as a herbicide. Totally enclosed equipment kept under reduced pressure

prevented the escape of toxic chemicals to a large degree. Equipment and connections were made of corrosion-resistant materials, with special attention to flanges and valves. Atmospheric pollution was prevented by trapping gases and returning them to process. However, where manual labor was substituted for mechanization or total enclosure, some gas escape was possible. Hazardous processes were separated, and ventilation was reported to be correctly designed and located. Makeup air was supplied. Phosgene was detected in 30% of all air samples taken; of the samples where phosgene was detected, the usual concentration was 0.5 mg/cu m (0.125 ppm), the maximum permissible concentration. Methods of sampling and analysis were not described. During operations such as quality control sampling, pressure transfer of phosgene, and pump repair, the concentration of phosgene in the workroom air was 1.0 mg/cu m (0.25 ppm). However, these concentrations were described as transient, because the premises were cleared by release of ammonia whenever the odor of phosgene became discernible. Gas masks were worn by personnel engaged in these tasks. Recommendations for further control included improved sealing of equipment, elimination of manual operations by maximum automation, use of protective clothing, and good personal hygiene.

Rispoli [60] reported 1 and 5 ppm phosgene in a plastics-manufacturing plant. No details of sampling or analysis were given, but ventilation was described as insufficient.

Reporting on 109 cases of phosgene inhalation over a 12-year period, Thiess and Goldmann [19] selected the 3 most severe cases for more detailed discussion. None of the exposures reported were long-term inhalation of low concentrations but were acute accidental exposures at relatively high

concentrations. No determinations of workroom air concentrations were reported, but in 2 of the severe cases some assumptions and calculations were made which might have defined the exposure level involved.

One case described by Thiess and Goldmann [19] involved a worker removing brick lining, presumably saturated with phosgene, from a reaction vessel. The chemical process for which the reactor was constructed was the chlorination of aluminum oxide in the presence of carbon monoxide for the production of aluminum chloride. Phosgene was a byproduct of this reaction. Contrary to instructions, the brick lining was removed with a jackhammer from the inside of the furnace and without respiratory protection. Instructions had been given to remove the brick from the outside of the vessel and to wear respiratory protection. The exposure lasted about 30 minutes, during which the worker was presumed to have inhaled dust particles with adsorbed phosgene. Again, assumptions and calculations based on porosity measurements of the brick indicated that a total volume of 2.5 liters was available for absorption of gas by the lining material. This exposure terminated fatally. There is at least a suggestion that the effect of phosgene was enhanced because of its association with particulate matter, but this was not proved.

Unpublished data show that air concentrations of phosgene were generally low in a chemical manufacturing unit where phosgene was used as a raw material. (AF Myers, written communication, November 1974) Air samplers placed on operators showed concentrations on analysis ranging from nondetected to 0.08 mg/cu m. Samples taken in fixed locations ranged from nondetected to 0.52 mg/cu m. During the 2-month period of fixed location sampling, there were 5 instances of off-scale measurements (greater than

0.55 mg/cu m) reportedly due to leaks. In summary, the workroom air measurements of phosgene in a manufacturing unit showed that, about 25% of the time, operators were exposed to very low but measurable concentrations of phosgene. Sampling procedures used did not determine individual peaks. Details of controls or of fixed sampling locations were not given. The plant surveyed was reportedly old and built with out-of-date technology.

The decomposition of chlorinated hydrocarbons by means of heat or ultraviolet radiation with the formation of phosgene has been blamed for a number of incidents involving respiratory tract damage in humans. [5,6,7,21,61,62,63,64, written communication from DR Parker, Oregon State Board of Health, November 1964] This has stimulated a great deal of investigation of the decomposition products formed when chlorinated hydrocarbons are exposed to ultraviolet radiation and heat, such as open flames and burning cigarettes. The following exemplify these investigations.

In 1933, the Underwriters Laboratories [65] reported the results of decomposition of a number of chlorinated hydrocarbons (ie, chloroform, carbon tetrachloride, a number of halocarbon compounds, dichloroethylene, methylene chloride, and others) exposed to gas flames, hot electric range units, oil fires, wood fires, and hot metal surfaces. The temperatures of these heat sources were not specified. Decomposition products were analyzed for hydrogen chloride, phosgene, chlorine, and others. The analytical method for phosgene involved the reaction of phosgene with aniline to form diphenylurea. The influence of relative humidity and initial concentration of chlorinated hydrocarbon was studied. The major decomposition product found was hydrogen chloride measured as total acids,

which ranged from nondetected to 8.86 volume percent, followed by phosgene with concentrations ranging from a reported zero to 0.143 volume percent. Chlorine was found in the concentration range of a reported zero to 0.164 volume percent.

In 1936, Yant et al [66] found significant quantities of phosgene in the decomposition products of carbon tetrachloride exposed to excelsior fires and heated steel surfaces. The analytical method used was based on the formation of diphenylurea which was found by Yant et al [66] and the Underwriters Laboratories [65] to be essentially free from interference by hydrogen chloride and chlorine. More recent research has shown that hydrogen chloride and chlorine do significantly interfere with the diphenylurea analytical method. [67]

Elkins and Levine [68] investigated the decomposition of halogenated hydrocarbons when passed through burning cigarettes and cigars. Analytical methods used were for total chloride and therefore not specific for phosgene. However, based on the small amounts of total chloride found in the samples, the authors [68] concluded that phosgene was not a hazard when cigars or cigarettes were smoked in the presence of chlorinated hydrocarbon vapor.

In 1955, Little, [20] using the p-dimethylaminobenzaldehyde and diphenylamine method, confirmed the conclusions of Elkins and Levine [68] that phosgene was not formed in sufficient quantities by smoking to present a hazard. He also found that various chlorinated hydrocarbons in contact with a heated silica tube did not produce significant quantities of phosgene below 400 C. Even in atmospheres containing small amounts of phosgene, finding no detectable phosgene in effluent gas from cigarettes

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led to the conclusion that, if any phosgene were formed, it was subsequently decomposed when passed through the combustion zone of the cigarette. It was also hypothesized that the phosgene was absorbed by the tar fraction of the tobacco combustion product.

Crummett and Stenger [69] found that, in contact with heated metals, methyl chloroform (1,1,1-trichloroethane) produced relatively small amounts of phosgene, but much more hydrogen chloride than did carbon tetrachloride.

Dahlberg, [70,71] Dahlberg et al, [72] and Dahlberg and Myrin [73] extensively investigated the interaction of ultraviolet radiation with chlorinated hydrocarbons. These studies indicated that relatively lower amounts of phosgene were formed compared to the quantities of dichloroacetyl chloride formed simultaneously. Although there have been no environmental limits recommended for dichloroacetyl chloride, it seems likely that it would be a strong irritant to skin and eyes. Actual measurements of decomposition products of trichloroethylene in welding shops confirmed their experimentally derived conclusions. In 10 welding shops under varying conditions of ventilation and trichloroethylene concentration, phosgene was found in concentrations ranging from 0.003 to 3.0 ppm, while dichloroacetyl chloride concentrations ranged from less than 0.01 to 13.0 ppm.

In a more recent investigation, Andersson et al [74] experimentally studied phosgene formation from perchloroethylene (PCE) during welding. Welding was carried out in a closed chamber, into which varying concentrations of PCE had been introduced by evaporation of the solvent in front of a fan. Analysis for both perchloroethylene and phosgene were done by gas chromatograph with an electron-capture detector. The authors

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concluded that welding in air containing PCE below its threshold limit value of 100 ppm was more hazardous than welding in air containing trichloroethylene or methyl-chloroform because of the much faster formation of phosgene from PCE. Levels of perchloroethylene ranged from 2.1 to 30 ppm, while phosgene formed after 5 or 10 seconds ranged from 0.2 to 1.7 ppm.

Noweir et al [75] found that, at very high temperatures, phosgene itself decomposes, perhaps accounting for concentrations lower than expected. However, phosgene decomposition was greatly reduced in the presence of carbon tetrachloride, indicating that, at least for this chlorinated hydrocarbon, phosgene formed by its decomposition should be relatively stable as long as some carbon tetrachloride remained.

A number of occupational exposures to decomposition products of chlorinated hydrocarbons have been reported. In 1947, Hill [64] briefly reported an investigation of complaints of workers exposed to fumes arising from a carbon arc-welding operation. A presumably adequate exhaust ventilation system existed, but the fumes causing the complaints were sometimes strong enough to be detected at some distance from the arc. The workers had not complained prior to the relocation of the operation to a room near a trichloroethylene degreaser. Qualitative tests indicated the presence of phosgene presumably caused by breakdown of trichloroethylene vapor by the ultraviolet radiation of the arc. It was recommended that the degreaser be replaced with alkaline wash equipment and that the use of chlorinated hydrocarbons in the welding room be prohibited.

Spolyar et al [5] investigated the circumstances causing the death of an employee who had installed a trichloroethylene degreaser and had

operated it without the condensing coils functioning. A strong odor of solvent was present in the room when the employee's body was discovered. An investigation by the authors [5] took place 3 weeks later, disclosing the following:

(1) Trichloroethylene had been used in a degreaser designed for higher-boiling perchloroethylene, causing excessive loss of solvent.

(2) A fuel-oil-burning space heater was located in the degreaser room, and all windows and doors had been closed on the day of the accident.

(3) Under test conditions, 225-450 ppm trichloroethylene were found near the degreasing tank.

The trichloroethylene vapor passing through the firebox of the space heater could be decomposed with the possible formation of phosgene. A re-creation of the situation at the time of the accident, described in Effects on Humans, was undertaken, during which it was noted that one of the solvent heaters in the degreaser became red-hot. Samples taken at that time in the approximate location of an operator's breathing zone showed much higher levels of trichloroethylene and 15 ppm phosgene. The authors [5] suggested that the decomposition of the trichloroethylene was caused by the degreaser heating element rather than by the space heater, although a back pressure in the smoke pipe of the latter could occur under adverse weather conditions because of the configuration of the stack.

Although some effects due to trichloroethylene were apparent, the authors concluded that the cause of death was consistent with phosgene exposure.

In 1951, Wulfert [62] reported the results of an investigation of the manufacturing of hard metal drills (presumably with tungsten carbide drill

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inserts). Drills were washed in trichloroethylene after which the solvent was blown off with compressed air into the shop atmosphere prior to brazing. Brazing was completed with an induction coil or gas brazing, depending on the size of the drill. Results of workroom air sampling for phosgene were reported only as exceeding 1 ppm. The author [62] concluded that local exhaust ventilation was required.

An investigation of worker complaints was reported by Challen et al [76] in 1958. The workers involved were employed in a welding shop fabricating aluminum milk churns. Upper respiratory symptoms were thought to have been caused by phosgene from decomposition of trichloroethylene originating from a tank of the solvent located in an adjacent bay. Air samples were taken and analyzed for trichloroethylene, ozone, and phosgene. All phosgene samples contained less than 0.1 ppm, although the trichloroethylene concentrations ranged from a reported 0.0 to 238 ppm and the ozone concentrations ranged from 0.9 to 1.7 ppm. The authors [76] concluded that ozone rather than phosgene was the source of the complaints. Exhaust ventilation was installed in the degreasing shop and at the welding positions and operating procedures to prevent solvent drag-out were implemented, resulting in improved working conditions.

In a November 1964 letter from DR Parker to J Boyer, the Oregon State Board of Health reported finding a phosgene concentration in air of 4.86 mg/cu m (1.2 ppm) in the vicinity of welders who had complained of noxious odors. Two other samples indicated no phosgene. Decomposition of perchloroethylene vapor from a recently installed degreaser was considered to be the source of the phosgene. The perchloroethylene concentration on the day of the high phosgene sample was as much as 37 ppm. Remedial

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recommendations included relocation and isolation of the degreaser from the welding area. A ventilated booth was suggested for this purpose.

In summary, the earlier experimental studies [65,66] clearly indicate phosgene produced by decomposition of chlorinated hydrocarbons could present a hazard; there are cases that clearly show phosgene present in sufficient quantity to be a health hazard. [5,65,66] It should be noted that the various methods of heating, different temperatures used when producing the chlorinated hydrocarbon decomposition products, and the different analytical methods probably accounted for much of the variation from study to study.

Sampling and Analytical Methods

Detection methods for phosgene prior to the mid-1950's met minimal demands for sensitivity and detection limits. Soon after this, however, large-scale industrial use of the gas in polymer manufacturing processes prompted increased emphasis on potential industrial hygiene problems associated with its use. Linch et al [77] reviewed most of the analytical methods for phosgene used prior to 1965 and classified them into (1) physical measurement, (2) determination of chloride ion after hydrolysis, (3) iodometric procedures, (4) gravimetric procedures, and (5) colorimetric procedures.

Physical measurements were based on the olfactory or taste response imparted to tobacco smoke immediately after phosgene inhalation and was considered to be a very sensitive indicator [77] of the gas, although it suffered from the obvious disadvantage of depending on the exposed worker to determine his exposure.

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A method of analysis based upon chloride present after hydrolysis was reported [77,78] to depend on aqueous decomposition of phosgene in dilute alkali. Residual base was titrated or the chloride present was determined by the Volhard or the bichromate method; the hydrogen chloride gas produced upon hydrolysis could also be absorbed in ammoniacal silver nitrate and the resultant silver chloride determined gravimetrically. [79,80] However, these procedures were susceptible to physiologically inert, acid-reacting, or chloride-producing components occurring simultaneously with the phosgene. [77]

Iodometric procedures in anhydrous acetone with thiosulfate titration suffered from inherent field limitations due to the anhydrous conditions necessary and evaporation of the volatile solvent. [77]

Gravimetric procedures included (1) a method based on insoluble diphenylurea derived from phosgene and aniline, but which was sensitive to halogen interferences [80] and limited to a lower detection threshold of about 10 ppm [77]; and (2) a modified Kjeldahl nitrogen analysis of the diphenylurea which offered little improvement.[77]

Review of colorimetric analytical methods [81,82,83,84] that were developed indicated that the most sensitive and specific detector was 4-(4'-nitrobenzyl)pyridine (NBP) plus N-benzylaniline although it did not readily lend itself to a liquid reagent system. Later investigators [85] developed a method using diethylphthalate as an absorber with NBP and N-benzylaniline and easily determined phosgene at concentrations less than 0.1 ppm in air. Spot tests have been described [77,79,81] for phosgene which generally rely on colored complex formation between heavy metals and diphenylcarbazones.

Various detector papers and treated crayons have been described for determination of phosgene [86,87,88,89] with the most sensitive prepared from a benzene solution of 2% 4-(4'-nitrobenzyl)pyridine, 5% N-phenylbenzylamine, and a chalk matrix which was then dried and pressed into crayons and was capable of detecting 8 ppb phosgene in air after a 1-minute exposure. All of the crayon and detector paper methods suffer sensitivity loss from storage; color change sensitivity to oxygen, chlorine, hydrogen chloride, and daylight; and the inherent disadvantage of reliance on visual detection of small color differences. [88, 89]

Direct reading, colorimetric detector tubes are available for the measurement of phosgene. [1,2,90,91,92] They offer a quick and easy method of determining approximate quantities in the reported range of 0-50 ppm and of indicating the need for initiation of emergency procedures or for further, more accurate evaluation. Today, most detector tubes are of the "length of stain" type. A fixed volume of air is drawn through a glass tube containing a solid sorbent which reacts with phosgene. A color stain is produced which varies in length with the concentration measured. The length of stain is compared with a calibration chart provided by the manufacturer. Accuracy expected is only $\pm$ 30%.

An ultraviolet technique was developed [93] which uses the absorption at 254.5 nm of 1,3-diphenylurea formed when phosgene reacts with aniline-saturated water. A later refinement of the technique [67] was made using an extraction step with a 1:1 solution of n-hexane and 1-pentanol. The latter method allowed detection of 0.01 ppm phosgene in air with a 30-liter air sample. Collection efficiency was only about 90%.

A micromanometric method was described [94] which utilized measurement of gaseous reaction products resulting from hydrolysis of phosgene, but details as to sensitivity and specificity were lacking.

Gas chromatographic techniques provide the most specific and sensitive detection methods for phosgene. A silica gel column at 56.5 C with a hot wire detector was first used to detect phosgene in pyrolysis products on a semiquantitative basis. [95] The development of the electron capture detector for the gas chromatograph provided a high degree of specificity for phosgene. This detector was first tried [96] in conjunction with a dodecylphthalate column at 50 C with resultant 2% standard deviation and detection down to 1 ppb. The authors suggested that this method can possibly be used as the basis for an automatic, continuous monitoring system. A later refinement [97] used a column of "20% silicon oil DC 200" (probably silicone DC 200) on Chromosorb W at 25 C for detection from below 1 ppb to 0.1 ppm phosgene. Jeltes et al [98] confirmed detection below 0.005 ppm but pointed out inherent difficulties due to hydrolysis by trace amounts of moisture, leakage of transfer syringes, and problems in transporation and storage of the air samples. Basu et al [99] presented operational parameters, retention times, and response factors for gas mixtures including phosgene using a 3-column, 3-detector (thermal conductivity) gas chromatographic system with a resultant reproducibility represented by a ±1% standard deviation.

Although the gas chromatographic methods display excellent analytical capabilities, field use is hampered by the lack of an adequate personal sampling method. Recent investigations by Barrett et al [100] of a number of solid sorbents indicated that phosgene can be efficiently collected with

activated carbon, alumina, and porous glass, but no satisfactory desorption technique was found.

Methods have been reported for automatic or continuous monitoring of phosgene in air. [77,90,96,101,102,103, RW Miller, written communication, May 1975] The instrumentation requirements make the methods impractical for field use. In-plant applications may be possible but the lower limit of detection may be questionable.

One continuous-sensing instrument which has been found to be generally reliable below 0.1 ppm of phosgene is the Army's M8 portable alarm device for toxic chemical agents. It uses an electrochemical cell as the sensing unit and is designed to give a warning signal when the concentration of phosgene exceeds a certain value. The instrument is therefore not ideally suited for measurement of varying concentrations, but may well have some application as a monitoring or safety device. The device has been tested at concentrations of 0.074 ppm, 0.185 ppm, 0.443 ppm, and 0.625 ppm. The response was found to be linear over this range. [100]

The method of choice for detection of phosgene in the workroom air should provide for a minimum limit of detection of less than 0.05 ppm, reasonable freedom from interference from commonly expected chemicals (see Appendix II) and should permit relatively easy sample collection. The method which best meets these requirements is described in an Analytical Guide by the American Industrial Hygiene Association [104] and is an improved nitrobenzylpyridine colorimetric method. It involves drawing air through a midget impinger containing 10 ml of a solution of 0.25% 4-(4'-nitrobenzyl)pyridine and 0.5% N-phenylbenzylamine in diethylphthalate and

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measurement of the subsequent color development at 475 nm. Sampling efficiency is at least 99%, [85,104] and the range 0.05-1.0 ppm can be measured if a 25-minute sample at 1 liter/min is collected in 10 ml of reagent. No statistically significant interferences were observed [85,104] from carbon tetrachloride, chloroform, perchloroethylene, trichloroethylene, dichlorodifluoromethane, chlorine, hydrogen chloride, or chlorine dioxide. Color stability is good (only 10-15% loss in color density after 8 hours), sampling and analysis equipment needed is simple and readily available, and operator expertise required is minimal.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1940, Bowditch et al [105] listed a maximum concentration of 1 ppm (4 mg/cu m) phosgene which was in effect in Massachusetts as a guide to manufacturers interested in maintaining satisfactory working conditions. In 1945, Cook [106] compiled a list of maximum allowable concentrations (MAC) of industrial atmospheric contaminants. Cook noted that 1 ppm (4 mg/cu m) was the MAC value for exposure to phosgene in the workroom air adopted by California, Connecticut, New York, Oregon, Utah, and the US Public Health Service. Cook referred to Fieldner et al [107] and Flury and Zernik [108] as a basis for the accepted value of 1 ppm (4 mg/cu m). Fieldner et al [107] indicated that 3 ppm of phosgene in air was irritating to the throat. Flury and Zernik [108] indicated that 1 ppm was the highest tolerable amount in man, with 1.25-2.5 ppm termed as dangerous to life if the exposure was prolonged.

In 1947, Bloomfield [109] reviewed the efforts of a committee within the American Conference of Governmental Industrial Hygienists to develop an MAC which could be adopted by all the states. Bloomfield [109] cited unanimous agreement on a phosgene MAC value of 1 ppm (4 mg/cu m) among 23 respondents.

In 1947, the American Conference of Governmental Industrial Hygienists [110] adopted an MAC value for phosgene of 1 ppm (4 mg/cu m). It was not stated if this MAC was intended as a ceiling value or as a TWA concentration. The April 1948 meeting of this same organization [111] adopted 1 ppm as a recommended limit and changed the name to Threshold Limit Values (TLV's).

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The TLV of 1 ppm was considered "sufficiently low to cause no more than minimal effects" by the ACGIH according to the 1962 Documentation of the Threshold Limit Values. [112] The Documentation [112] cited Fieldner et al [107] and Henderson and Haggard [113] to explain its selection of a TLV of 1 ppm (4 mg/cu m) for phosgene. Fieldner et al [107] reported that the Chemical Warfare Service at the American University Experiment Station, Washington, DC, considered 1 ppm of phosgene (4 mg/cu m) the maximal concentration safe for prolonged exposure. Henderson and Haggard, [113] in their review on phosgene, referred to Fieldner et al [107] and listed 1 ppm (4 mg/cu m) or less as a maximum concentration allowable for prolonged exposure. Both sources listed 3 ppm as the concentration at which throat irritation first occurs. The Documentation did not quote any other experimental or occupational data to support its recommended TLV.

A change to 0.1 ppm (0.4 mg/cu m) was proposed by the ACGIH in 1964 [114] and 1965 [115] and adopted in 1966. [116] A TLV of 0.1 ppm (0.4 mg/cu m) was supported in the 1966 Documentation [117] because of the "seriousness of the response at the experienced levels of phosgene and by analogy with edemagenic agents of similar activity." The Documentation cited Gross et al [42] who wrote that phosgene, which could produce fatal pulmonary edema or acute chemical pneumonia at a high concentration, could also produce chronic pneumonitis at a low concentration. Gross et al suggested that the chronic pneumonitis is reversible even though residual pneumonitis could be found three months later. [42] The alveolar epithelium in rats can become irritated after a single 120-minute phosgene exposure at 0.5 ppm. [42] Studies by Box and Cullumbine [40] indicated that preliminary nonlethal doses of phosgene produced a transitory effect of

increasing tolerance to the gas. It was necessary to damage the lungs of rats and mice to produce this effect. Stokinger et al [118] reported chronic lung injury of small animals after repeated exposure to ozone. They stated that this is a separate process from the development of tolerance to subsequent acute exposure. In reviewing Stokinger's article, [118] the Documentation [117] stated that "the development of tolerance, however, is believed to be the triggering mechanism of chronic, irreversible pulmonary changes of emphysema and fibrosis from prolonged daily exposure at concentrations that produce no ostensible acute response." The Documentation [117] assumed that both ozone and phosgene caused pulmonary edema.

The 1971 Documentation [119] was the same as the 1966 Documentation [117] with a few minor style changes and one additional sentence listing a recommendation for the USSR (1959) of 0.1 ppm and mentioning Elkins, [120] who recommended 0.5 ppm. There was no discussion of the additional recommendations nor were any new references cited in the bibliography. In 1974, it was recommended [121] that the TLV of 0.1 ppm be changed to a ceiling concentration of 0.05 ppm (0.2 mg/cu m). Documentation for this change was published in the 1974 ACGIH Transactions [122] and refers to Stokinger's article on ozone toxicity studies [118] which indicated that there were chronic, irreversible pulmonary changes from prolonged daily exposure even though there was no acute response. None of the references cited specifically supported the ceiling limit of 0.05 ppm (0.2 mg/cu m) which was recommended because of the irritating effect of phosgene on the respiratory tract.

In 1971, Pennsylvania [123] adopted an environmental limit of 0.1 ppm (0.4 mg/cu m) for phosgene. It was a maximum average atmospheric concentration for an 8-hour day. A short-term maximum average exposure limit of 1 ppm (4 mg/cu m) for 5 minutes was established. Henderson and Haggard, [124] Imperial Chemical Industry, and Patty [125] were cited as the basis for the short-term limit in the Pennsylvania documentation. [126]

Phosgene is suspected to be formed by the decomposition of fluorochlorocarbons in submarine atmospheres. Webb [127] listed a maximum limit of 0.1 ppm (0.4 mg/cu m) exposure for a 90-day dive. He reported that an interim limit of 1 ppm (4 mg/cu m) for a 1-hour exposure was recommended by the Navy's Bureau of Medicine and Surgery. The limit was for a single exposure and not a permissible limit for repeated short-term exposures.

A safe concentration zone of 0.4-0.5 mg/cu m (0.1 ppm to 0.125 ppm) was recommended for international adoption in 1968 by the Joint ILO/WHO Committee on Occupational Health. [128] The Joint ILO/WHO Committee [129] prepared a survey of legislation and practices concerning permissible limits and listed MAC values for the following foreign countries:

TABLE V-1

MAXIMUM ALLOWABLE CONCENTRATION VALUES IN SEVERAL COUNTRIES

Country	Standard	
	mg/cu m	ppm
Bulgaria	0.5	0.125
Czechoslovakia	2	0.5
Czechoslovakia	4*	1*
Finland	4	1
Hungary	0.5	0.125
Poland	0.5	0.125
Rumania	0.5	0.125
United Arab Republic	4	1
Yugoslavia	0.4	0.1

* for short single exposure

From reference 129

The USSR [37] cited a permissible phosgene concentration of 0.5 mg/cu m (0.125 ppm) as established by the Main State Health Inspector of the USSR on January 10, 1959, No 279-59. If workers are in an industrial area for a brief, unspecified period, deviations are permitted with the authorization of the USSR State Health Inspectorate.

Great Britain, [130] Japan, [131] and the Federal Republic of Germany [132] based their environmental limits for phosgene of 0.1 ppm (0.4 mg/cu m) on the ACGIH value. These environmental limits were TWA concentrations for a normal working day.

The present federal standard (29 CFR 1910.1000) for phosgene is an 8-hour TWA concentration of 0.1 ppm (0.4 mg/cu m) based on the 1968 ACGIH recommendation.

Basis for the Recommended Environmental Standard

At the present time, there are no definitive data in the scientific literature concerned with long-term effects of phosgene on humans exposed at low concentrations. Human exposure to phosgene reported in the literature (see Table III-5), for the most part, consists of instances of acute overexposure, often involving a mixture of pulmonary irritants. Those epidemiologic studies [36, AF Myers, written communication, November 1974] involving exposures at low levels of phosgene suffer from a number of defects, including exposures to multiple irritants and limited analytical or medical data. In spite of the weaknesses noted, these studies are at least suggestive that the present federal standard is safe for long-term exposures. Therefore, until more conclusive evidence is developed, NIOSH recommends that the present federal standard of 0.1 ppm as a TWA concentration be maintained.

In addition, since phosgene is an acute-acting, irritant gas, it is essential to control the short-term excursions above this average. Animal experiments have demonstrated a threshold for the development of pulmonary lesions after short-term exposure to phosgene. Gross et al [42] reported

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that exposure of rats to phosgene at a concentration of 3 ppm for 5 minutes resulted in slight to moderate chronic pneumonitis, while rats exposed at 1.3-1.5 ppm for 10 minutes showed no evidence of recognizable pulmonary lesions. Similarly, rat experiments conducted by Rinehart and Hatch [41] revealed that exposures to phosgene at a concentration of 1.5 ppm for 20 minutes or less did not result in any evidence of functional respiratory impairment as measured by carbon monoxide or ether uptake. In both studies, [41,42] deleterious effects were found at the lowest concentration used, 0.5 ppm, when duration of exposure was 120 minutes or greater. Although no data are available to substantiate the pulmonary effects of brief exposures to phosgene at low concentrations in humans, these studies suggest that a single exposure of 10-15 minutes' duration at concentrations of or below 1.5 ppm are likely to be safe. It is felt, however, that imposing further limitations on the degree of excursion permitted during a 10-hour workday will provide an additional margin of safety to ensure protection of the worker from the consequences of brief exposures to concentrations of phosgene above the recommended TWA limit. NIOSH is therefore proposing a ceiling limit of 0.2 ppm for any 15-minute period.

In view of the development of pulmonary edema and evidence of chronic lung changes as a result of exposure to phosgene, medical monitoring, including chest X-rays and pulmonary function tests, is required for the protection of the worker.

Professional judgment indicates that local contact with liquid phosgene is likely to cause severe tissue damage which could in part be due to the low temperature of liquid phosgene. Thus skin and eye protection, in addition to respiratory protection, is recommended for those likely to be in contact with liquid phosgene.

It is recognized that many workers are exposed to phosgene at concentrations considerably below the recommended occupational limits. Under these conditions, it should not be necessary to comply with many of the provisions of this recommended standard. However, concern for worker health requires that protective measures be instituted below the enforceable limits to ensure that exposures do not exceed the standard. For this reason, "occupational exposure to phosgene" has been defined as exposure above half the recommended TWA, thereby delineating those work situations which do not require the installation of unnecessary controls and the expenditure of health resources for provisions such as environmental and medical monitoring and associated recordkeeping.