

IV. ENVIRONMENTAL DATA AND ANALYTICAL METHODS

Environmental Data

Hausler and Lenich [11] reported environmental levels of 1-113 ppm of allyl chloride in a manufacturing plant. The concentrations for the different processing areas are given in Table IV-1. No information on the sampling and analytical method or on the number of samples taken from each area was given.

TABLE IV-1

ALLYL CHLORIDE LEVELS
IN AN EAST GERMAN MANUFACTURING PLANT

Plant Area	Concentration (ppm)
Laboratory	1
Filling	6
Production	17- 19
Tank storage	14-100
Pumproom	61-113

From Hausler and Lenich [11]

Dow Chemical USA [19] reported personnel monitoring data by job classification for its allyl chloride-manufacturing plant and provided a description of the sampling and analytical methods used. Sampling was conducted using a calibrated, battery-operated pump, and personal monitoring collection columns containing 20-ml volumes of Westvaco Nuchar

WVH charcoal. Quintuplicate samples were taken for each job classification at a rate of 2 liters/minute for 7 hours. Allyl chloride and other chlorinated hydrocarbons were extracted with 30 ml of carbon disulfide and analyzed in a gas chromatograph equipped with a hydrogen flame detector. Average allyl chloride levels ranged from 0.05 to 3.05 ppm. The range and average concentrations by job classification are given in Table IV-2.

TABLE IV-2
 ALLYL CHLORIDE PERSONNEL MONITORING
 DOW CHEMICAL USA, 1975

Job Classification	No. of Samples	Concentration* (ppm v/v)		
		High	Low	Av**
At Allyl Chloride-Manufacturing Site No. 3				
Control room, Operator "A"	6	0.91	0.19	0.45
Control room, Operator "C"	8	0.94	0.24	0.57
Instrument	4	4.72***	0.12	2.16
Laboratory	4	0.71	0.23	0.40
Shift foreman	4	4.03***	0.12	1.30
Maintenance	4	6.09***	0.78	3.05
Class 2 operator	5	6.13***	0.005	1.73
Head packaging operator	2	0.09	0.02	0.05
Chief material-handling technician	2	0.31	0.13	0.22

TABLE IV-2 (CONTINUED)

ALLYL CHLORIDE PERSONNEL MONITORING
DOW CHEMICAL USA, 1975

Job Classification	No. of Samples	Concentration* (ppm v/v)		
		High	Low	Av**
At Epichlorohydrin Unit No. 1				
Control room, Operator "A"	5	1.11***	0.04	0.49
Instrument	2	1.24***	0.31	0.78
Laboratory	6	3.42***	0.04	1.60
Shift foreman	3	4.67***	0.39	1.89
"Epi" helper	4	2.71***	0.05	0.88
Control finisher	2	1.42***	0.27	0.85
Maintenance	13	0.51	0.05	0.20

*High values for allyl chloride possibly caused by acetone interference

**Numerical average between high and low values, not the TWA value

***Potential exposure; protective equipment worn during sampling operations and process upsets

From Dow Chemical USA [19]

Similar data were also provided by Shell Chemical Company [20] for various job classifications at its allyl chloride-manufacturing plant. Analysis was similar to the Dow Chemical [19] procedure, but plastic bags were used in place of charcoal for sampling. [21] Results of this monitoring are summarized in Table IV-3.

TABLE IV-3

SUMMARY OF ALLYL CHLORIDE MONITORING RESULTS

Job Classification	8-Hour TWA			Peak (Up to 15 minutes)			Comments
	No. of TWA's	Range (ppm)	Mean* (ppm)	No. of Samples	Range (ppm)	Mean* (ppm)	
Loading (T/C, T/T, and Drum)	8	0.4-3.2	1.9	5	6.2-39.5	19.5	Loading operators wear breathing masks when loading allyl chloride. Drum-loading measurements were taken prior to installation of ventilation system. No allyl chloride has been drum loaded since ventilation system was installed. Tank car and tank truck loading rate is each 2-3 hr/d.
Marine cargo inspection	-	-	-	5	Less than 0.1- 2.7	0.9	Gauging and inspecting crude epichlorohydrin barges. Exposure is limited to about 15-20 min/barge, 2-3 barges/mon. Allyl chloride is a contaminant (10-15%) in crude epichlorohydrin.
Dockman	1	Less than 0.1	-	7	Less than 0.1- 6.0	1.5	Connecting and disconnecting barge loading lines on crude epichlorohydrin barges
Operators, except for G-300	70	Less than 0.1-3.6	0.47	15	0.1-30.7	11.3	Evaluations are for routine operations and do not include shutdown or start-up periods. Full breathing apparatus is worn during shutdown or start-up.
G-300 operators	5	0.1-5.3	**	-	-	-	"
Shift foreman	16	0.1-3.4	0.61	-	-	-	"

*This represents the arithmetic mean which is an overestimate of the central tendency of distribution. The data appear to follow a log-normal distribution with a lower geometric mean.

**Four of five samples were less than 0.3 ppm.

Adapted from Shell Chemical Company [20]

The environmental data provided by Dow Chemical USA [19] and Shell Chemical Company [20] give an indication of the air concentrations that currently exist in US plants manufacturing and using allyl chloride. However, this information by itself should not be considered complete enough to provide the basis for a firm conclusion regarding the feasibility of the recommended standard.

Sampling and Analysis

Allyl chloride may be measured in the field with a calibrated combustible gas indicator [22,23] or with a calibrated halogenated hydrocarbon (halide) indicator. [23] To obtain quantitative results with the former, meter readings must be compared with standard curves for allyl chloride, which can be constructed by graphically plotting known allyl chloride concentrations against instrument readings. The combustible gas indicator measures flammable organic vapor concentrations by recording changes in the resistance of an electrically charged wire induced by the combustion of vapors in contact with the wire. [24] The halide indicator is used to determine the concentration of halogenated hydrocarbons by comparing the color of the flame with a predetermined color standard. [24] These instruments are not specific for allyl chloride. They are subject to interference from the presence of other combustible compounds or of other halogenated organic compounds, respectively.

Plastic bags have been used by a number of investigators in the collection of organic compounds. [25,26] Personal sampling for allyl chloride has been conducted at Shell Chemical Company [21] with a specially modified pump to draw the air sample into the plastic bags. These bags

were lightweight, inexpensive, nonbreakable, and easy to use; they were subject to sample losses (bag loss) through reactions between the sample and the bag material and through the permeation of the bag by the sample. Bag loss in 24 hours for allyl chloride was reported by Shell Chemical Company [21] to be 9% using Teflon and 3% with aluminized polyester. Bag memory (the presence of sample residuals following repeated and thorough flushing after usage) is also a problem. Shell Chemical Company [21] reported bag memory levels after 1 day of 1.9 ppm v/v using Teflon and 1.6 ppm v/v using aluminized polyester. Following a daily schedule of thorough flushing, the 5-day levels were 0.02 and 0.05 ppm v/v for Teflon and aluminized polyester, respectively. The initial allyl chloride air concentration was 67 ppm for both materials.

Activated charcoal tubes have been designed for sampling allyl chloride [27] and other halogenated hydrocarbons. [28-30] Charcoal is an ideal collecting medium because of its electrical nonpolarity and its high adsorption of organic gases and vapors. However, adsorption and desorption efficiencies may vary with different batches of charcoal and with the laboratory. Therefore, recovery rates should be determined for each batch of charcoal within each laboratory. Desorption efficiency can also vary with changes in the characteristics of the desorption solvent. It is, therefore, necessary to determine the desorption efficiency (DE) for each batch of charcoal or change in type of desorption solution. An equation for the desorption efficiency calculation is presented in Appendix II.

Other sampling procedures used for the collection of organic solvents and certain halogenated hydrocarbons may be adaptable to allyl chloride. These include sampling bottles, [31] silica gel, [32-34] and bubblers.

[35,36] No reports were found on their specific uses in sampling for allyl chloride. Therefore, controlled laboratory experiments need to be conducted to determine the practicality and effectiveness of these procedures before actual field use.

Chemical analyses that are dependent upon the isolation and determination of the chloride ion produced by hydrolysis or pyrolysis may be used for quantitative analysis of allyl chloride, provided no other source of chloride ions is present. [37] Appropriate methods [38] include gravimetric determination of the chloride by precipitating silver chloride and volumetric determinations such as the micro-Volhard method, [6] Mohr method, [39] or methods using adsorption indicators. [40,41] None of these procedures is specific for allyl chloride because of interference from other chlorinated compounds.

Infrared spectrophotometers equipped with long-path gas cells can be used in continuous-air monitoring. [37] This method is specific for allyl chloride, but interferences may occur. Quantitative analysis by infrared spectrophotometry is beset with practical problems, including difficulties in reproducing narrow cell widths, the high probability of overlap in absorption spectra of the components in the sample, and the narrowness of the peaks, any or all of which may lead to deviations from Beer's Law. Infrared spectrophotometers are also affected by moisture, which absorbs broad regions of radiation and may thus interfere with the sample's spectrum. [42]

The recommended sampling and analytical methods are described in detail in Appendices I and II. [27] The procedure involves the use of charcoal tubes for sampling the employee's breathing zone, with subsequent

gas chromatographic analysis. The gas chromatograph possesses adequate sensitivity to allow for allyl chloride quantitation at concentrations in the low ppm range. [27] Its versatility allows for the simultaneous separation and quantitation of organic compounds in a mixture. [28] Gas chromatographic procedures which are specific for allyl chloride are available. [27,43,44] The sampling method has the advantage of using a small, portable, collecting device which involves no liquid. The analytical procedure is rapid and subject to minimal interference. Existing interferences can be eliminated by changing chromatographic conditions. Disadvantages include limitations in the amount of sample that can be taken and in precision, the latter caused by difficulties in reproducing the pressure drop across the tube. The combined sampling and analytical procedure has a useful range of 0.16-3.20 ppm; the coefficient of variation over this range is 0.071. The coefficient of variation is a measure of accuracy as well as precision of the combined sampling and analytical method. This value corresponds to a 0.07-ppm standard deviation at 1 ppm.

Control of Exposure

Engineering design and work practices should have as their primary goals the control of vapor concentration, the prevention of skin contact with the liquid, and the prevention of fires. The achievement of these three goals can best be accomplished by the use of a properly constructed and maintained closed-system operation. Where such systems cannot be adequately designed, local exhaust ventilation should be provided to direct vapor away from employees and to prevent the recirculation of exhaust air.

Guidelines for designing a local exhaust ventilation system can be found in Industrial Ventilation--A Manual of Recommended Practice, [45] or in ANSI Z9.2-1971. [46] Respiratory protective equipment is not considered an adequate substitute for engineering controls; however, respirators must be readily available to all workers for emergency purposes and for maintenance and repair operations.

Liquid splash or heavy vapor concentrations of allyl chloride may have deleterious effects on the eyes. [7] Whenever complete eye protection is needed, carefully fitted full-facepiece respirators or chemical safety goggles shall be worn. Face shields may be used in addition to chemical safety goggles in operations where the employee's duties increase the possibility of facial contact with the liquid. Face shields alone are inadequate substitutes for chemical safety goggles, because of the danger of liquid striking the eyes from underneath or around the sides of the face shield. [22]

Protective equipment, including gloves, aprons, shoes, face shields, and other apparel, must be worn whenever contact with liquid allyl chloride is likely. [38] Protective apparel should be made of materials that prevent penetration of allyl chloride through the material and that will not deteriorate during usage. Industrial practice indicates that leather is unreliable for protection from skin contact (HL Kusnetz, written communication, July 1976). Contaminated leather goods are to be removed immediately and discarded. [22] Results of a test conducted by Dow Chemical USA showed that neoprene, nitrile, and natural rubber are rapidly penetrated by allyl chloride when in continuous contact with the liquid. [19] Penetration occurred in 2-4 minutes for 0.015-inch nitrile, in 4-6

minutes for 0.02-inch neoprene, and 8-10 minutes for 0.03-inch natural rubber. These data indicate that rubber is permeable to allyl chloride. However, synthetic or natural rubber may be used if care is taken to prevent permeation during use. Other materials which are available for protection of various areas of the body include polyvinyl chloride and polyethylene. The penetration rate of allyl chloride through these materials should be determined before use. All protective clothing should be thoroughly washed after use to remove residual traces of allyl chloride. [8,38] Showering or cleansing of the contact area of the skin with soap and water is necessary immediately after contact with liquid allyl chloride.

Allyl chloride is a volatile, flammable liquid in the Class IB category of the National Fire Protection Association's (NFPA) "Standard on basic classification of flammable and combustible liquids." [47] The flammable limits are 3.3-11.2% in air. [1] Because of its volatility, care should be exercised to ensure that the vapor concentrations do not reach the flammable limits in enclosed spaces. Electrical wiring should be installed in accordance with section 500 of the National Electric Code, NFPA No. 70, Class 1, Group D. [48] All equipment must be explosion-proof and designed to avoid static accumulation. Metal piping and equipment should be bonded and grounded so that the resistance to ground does not exceed 1 megohm. [22] To reduce the possibilities of fire, all structures used in operations dealing with the manufacturing, handling, and storage of allyl chloride should comply with NFPA No. 30, Flammable and Combustible Liquids Code. [49]

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

Previous occupational standards for allyl chloride have been based primarily on two experiments. Adams et al [15] conducted acute inhalation toxicity studies on rats and guinea pigs at concentrations of 290-29,300 ppm for exposure periods of from 10 minutes to 9 hours. Torkelson et al [5] performed extended studies on rats, rabbits, guinea pigs, and dogs at exposures of 8 ppm and 3 ppm for 7 hours/day, 5 days/week.

A tentative standard for allyl chloride prepared in 1950 by Elkins [35] recommended a maximum allowable concentration (MAC) of 5 ppm. As defined by Elkins, the MAC was the highest concentration that should be tolerated continually. The MAC was based on vapor exposure data by Adams et al. [15] At the Seventeenth Annual American Industrial Hygiene Association (AIHA) Meeting held in April 1956, Smyth [50] reported that the American Conference of Governmental Industrial Hygienist (ACGIH) had proposed 5 ppm as the TLV for allyl chloride. The ACGIH [51] adopted a TLV for allyl chloride of 5 ppm in 1957. The ACGIH value was based on the work conducted by Adams et al [15] and on an analogy with chloroprene, a structurally related compound. [50] In 1963, the AIHA Hygienic Guide Series [37] listed a maximum atmospheric concentration of 5 ppm for an 8-hour workday based on the ACGIH recommendation. At the same time, however, the AIHA cited the more recent work of Torkelson et al [5] as indicative of the need for a ceiling concentration of 2 ppm for people repeatedly exposed to allyl chloride. The ACGIH TLV was reduced to 1 ppm in 1963. [52] In the 1971 Documentation of the Threshold Limit Values for

Substances in Workroom Air, [53] the ACGIH reported that the reduced TLV for allyl chloride was based on the findings of Torkelson et al [5] of liver and kidney damage in rats and guinea pigs exposed at a concentration of 8 ppm and of reversible liver damage in female rats exposed at 3 ppm.

The American National Standards Institute (ANSI) has no recommended standards for allyl chloride. No standards set by foreign countries could be found.

The present federal standard, 29 CFR 1910.1000, for occupational exposure to allyl chloride is a 1-ppm 8-hour TWA limit and is based on the 1968 ACGIH TLV.

Basis for the Recommended Standard

In the one epidemiologic study of occupational exposure to allyl chloride, where exposure duration was 16 months, Hausler and Lenich [11] suggested that abnormal liver function test findings followed exposure to allyl chloride at concentrations of 1-113 ppm measured in different areas of a plant manufacturing allyl chloride. Individual liver function test results were not provided, so the degree of variation from the authors' stated normal could not be determined. However, when measured concentrations were reduced to 0.5-36 ppm (generally 1 ppm or less), the authors [11] reported that liver function test results returned to normal in the employees studied. Hausler and Lenich [11] concluded that the initial, abnormal liver function test results were indicative of liver damage caused by chronic exposure to allyl chloride.

Shell Chemical Company [7] reported eye irritation at concentrations of 50-100 ppm and thresholds for nasal irritation and pulmonary discomfort

at less than 25 ppm. Deep-seated pain was produced by skin contact with very small amounts of the liquid. Pain persisted for up to 8 hours after exposure.

Animal inhalation studies have shown extensive pulmonary and renal damage from exposure to allyl chloride at concentrations of 290-72,600 ppm. [14,15] Only one published account of effects from allyl chloride at low concentrations and chronic exposures was found. This study [5] showed extensive liver and kidney damage in both sexes of rats, guinea pigs, and rabbits after exposure at a concentration of 8 ppm. At 3 ppm, the authors concluded that slight, reversible liver damage occurred in female rats only.

Based on tests with rats, rabbits, and guinea pigs at 8 ppm and 3 ppm, Torkelson et al [5] suggested a ceiling standard of 2 ppm with a 1-ppm TWA concentration. The 2-ppm ceiling was selected because of the borderline effect of reversible liver damage noted at the 3-ppm concentration in female rats. A TWA concentration of 1 ppm was believed necessary to provide additional protection because of the small safety margin afforded by the ceiling.

Available animal and human studies do not provide adequate data to justify an alteration of the current OSHA standard of a 1-ppm TWA concentration. NIOSH, therefore, recommends that the present standard be maintained.

Animal studies reported or summarized in the available literature [7,14,15] indicate that acute pulmonary irritation or damage, as well as central nervous system effects, occur at levels well above the recommended TWA environmental limit. However, pulmonary discomfort in humans has been

reported for 5-minute exposures at concentrations of less than 25 ppm of allyl chloride. [7] Concentrations producing this effect may be proportionally lower for longer exposure periods. NIOSH, therefore, recommends a ceiling limit of 3 ppm of allyl chloride for any 15-minute period.

As an additional safeguard, medical surveillance and environmental monitoring to detect liver, kidney, and lung damage in the early stages are to be provided for all employees subject to occupational exposure to allyl chloride. Medical and other pertinent records, which are of importance in assessing a worker's exposure, must be maintained for the duration of employment plus 20 years. This will allow enough time for future detection of chronic sequelae which may be related to the employee's known occupational exposure.

VI. RESEARCH NEEDS

Epidemiologic Studies

A review of the literature yielded only one epidemiologic study [11] on allyl chloride. Results indicated that allyl chloride may cause liver damage at concentrations between 1 and 113 ppm. More studies are needed to provide additional information on occupational exposure to allyl chloride and to determine the relationship of airborne concentrations and observed effects in humans.

Chronic Animal Inhalation Experiments

Chronic inhalation experiments have been conducted only at concentrations of 3 and 8 ppm. [11] At 8 ppm, extensive liver and kidney damage were observed in guinea pigs and rats, while at 3 ppm only reversible liver damage in female rats was observed. Between 3 and 8 ppm, there appears to be a great difference in the severity and type of damage, suggesting that the slope of the response curve for allyl chloride is very steep. Therefore, a small fluctuation in allyl chloride concentration may have a great effect on the degree of damage. To clarify this point, further inhalation experiments are needed to determine a dose-response relationship and to establish a threshold for allyl chloride-induced liver, kidney, and lung changes. Additional toxicologic experiments on a variety of species would serve to further characterize, both functionally and histologically, the nature of the lung, kidney, and liver changes produced

by allyl chloride. These results may then provide insight into human susceptibility to the effects of the compound.

Carcinogenic, Mutagenic, and Teratogenic Experiments

Because allyl chloride is structurally similar to vinyl chloride, a compound with known carcinogenic effects, research aimed at studying the potential carcinogenic effects of allyl chloride over a wide range of concentrations is particularly important. Mutagenicity and teratogenicity should also be investigated because of the absence of information in these areas.

Biochemical Experiments on Animals

Strusevich and Ekshtat [17] have shown that allyl chloride affected pancreatic lipase, trypsin, and amylase activities. Further work is necessary to clarify the significance of these findings as they relate to the adverse health effects of allyl chloride and to the concentrations at which these effects first manifest themselves. Additional tests may be desirable to determine if other biochemical effects are present and to elucidate basic metabolic pathways.

Combined Effects of Allyl Chloride and Epichlorohydrin

Allyl chloride is used primarily in the manufacture of epichlorohydrin. [2 (pp 1-2,26)] Employees may, therefore, be exposed to

a mixture of these compounds. An experimental investigation of the existence of additive or synergistic effects should be conducted.

Sampling and Analysis

Further studies are needed to develop sampling and analytical methods providing increased accuracy, sensitivity, specificity, and precision in the determination of allyl chloride at concentrations below 0.5 ppm.

VII. REFERENCES

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