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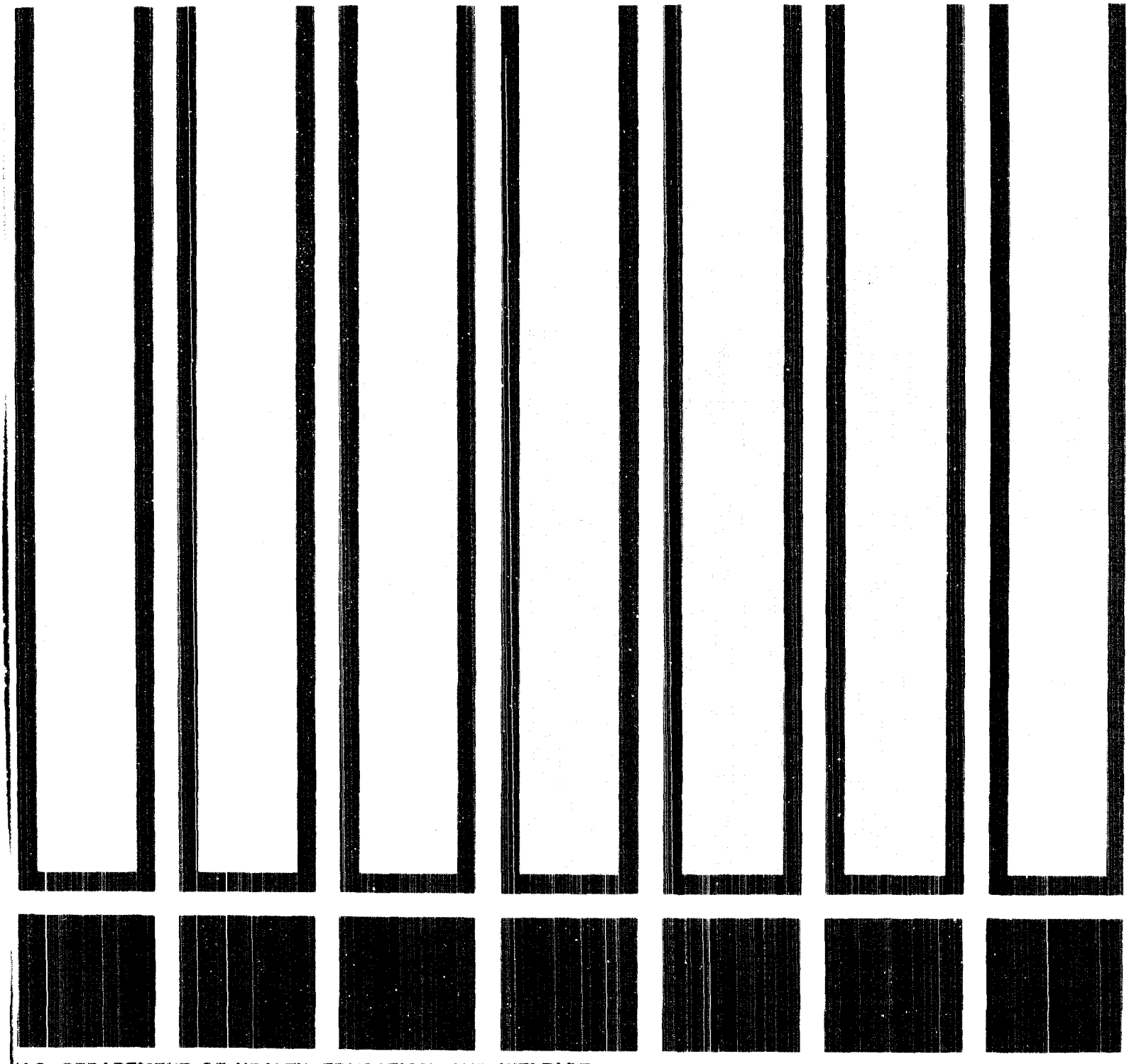

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service / Center for Disease Control
National Institute for Occupational Safety and Health

criteria for a recommended standard....

OCCUPATIONAL EXPOSURE TO

ALLYL CHLORIDE

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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SEPTEMBER 1976

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

HEW Publication No. (NIOSH) 76-204

CRITERIA DOCUMENT:
RECOMMENDATIONS FOR AN OCCUPATIONAL
EXPOSURE STANDARD FOR ALLYL CHLORIDE

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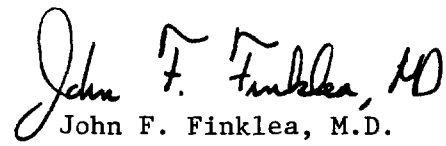
PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. The National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived. Recommended standards for occupational exposure, which are the result of this work, are based on the health effects of exposure. The Secretary of Labor will weigh these recommendations along with other considerations, such as feasibility and means of implementation, in developing regulatory standards.

It is intended to present successive reports as research and epidemiologic studies are completed and as sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contribution to this report on allyl chloride by members of my staff and the valuable constructive comments by the Review Consultants on Allyl Chloride, by the ad hoc committee of the American Industrial Hygiene Association, and by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine. The NIOSH recommendations for standards are not necessarily a consensus of all the consultants and

professional societies that reviewed this criteria document on allyl chloride. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.



John F. Finklea, M.D.
Director, National Institute for
Occupational Safety and Health

The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and recommended standard for allyl chloride. The Division review staff for this document consisted of Herbert E. Christensen, D.Sc., Howard L. McMartin, M.D., and Douglas L. Smith, Ph.D., with Hervey B. Elkins, Ph.D., (consultant) and Seymour D. Silver, Ph.D., (consultant).

Stanford Research Institute developed the basic information for consideration by NIOSH staff and consultants under contract No. CDC-99-74-31. Sonia Berg had NIOSH program responsibility and served as criteria manager.

REVIEW COMMITTEE
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

Harry M. Donaldson
Division of Surveillance, Hazard Evaluations,
and Field Studies

Robert A. Glaser
Division of Physical Sciences and Engineering

Russel H. Hendricks, Ph.D.
Western Area Laboratory for Occupational
Safety and Health

Harry B. Plotnick, Ph.D.
Division of Biomedical and Behavioral Sciences

Robert A. Rinsky
Division of Surveillance, Hazard Evaluations,
and Field Studies

Shiro Tanaka, M.D.
Division of Surveillance, Hazard Evaluations,
and Field Studies

Joseph R. Williams
Appalachian Laboratory for Occupational
Safety and Health

Department of Labor Liaison:

George W. Ozga, Ph.D.
Office of Standards

REVIEW CONSULTANTS ON ALLYL CHLORIDE

Dennis Chamot, Ph.D.
Assistant to the Executive Secretary
Council for Professional Employees, AFL/CIO
Washington, D.C. 20005

David A. Fraser, Sc.D.
Professor of Industrial Health
School of Public Health
University of North Carolina
Chapel Hill, North Carolina 27514

Howard L. Kusnetz
Manager, Safety and Health--Manufacturing
Shell Oil Company
Houston, Texas 77001

Carl A. Nau, M.D.
Professor of Clinical Toxicology
School of Medicine
Texas Tech University
Lubbock, Texas 79406

Doris H. Thompson, M.D.
Director
New Orleans City Health Department
New Orleans, Louisiana 70112

J. R. Venable, M.D.
Medical Director
Department of Industrial Medicine
Texas Division, Dow Chemical U.S.A.
Dow Chemical Company
Freeport, Texas 77541

I. RECOMMENDATIONS FOR AN ALLYL CHLORIDE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to allyl chloride in the workplace be controlled by adherence to the following sections. The standard is designed to protect the health and safety of employees for up to a 10-hour workday in a 40-hour workweek over a working lifetime. Therefore, compliance with all sections of the standard should prevent adverse effects of allyl chloride on the health and safety of employees. The recommended standard is measurable by techniques that are valid, reproducible, and available to industry and governmental agencies. Sufficient technology exists to permit compliance with the recommended standard. Although the workplace environmental limits are considered to be safe levels based on current information, they should be regarded as the upper boundary of exposure and every effort should be made to maintain the exposure at levels as low as is technically feasible. The criteria and standard will be subject to review and revision as necessary.

"Allyl chloride" is the common synonym for the compound 3-chloropropene, also referred to as 3-chloro,1-propene. Other synonyms appear in Table XI-1. The term allyl chloride will be used throughout this document. The recommendations in this chapter apply to all places of employment where allyl chloride is manufactured, used, stored, or handled and where employees may be exposed by dermal or eye contact, inhalation, or ingestion. "Overexposure" to allyl chloride vapor is defined as known or suspected exposure above the time-weighted average (TWA) environmental level or ceiling limit. If exposure to other chemicals also occurs, for

example from contamination of epichlorohydrin with allyl chloride, provisions of any applicable standards for the other chemicals also shall apply. The "action level" is defined as half the recommended TWA environmental limit. When environmental concentrations are at or below the action level, adherence to Section 8 (a) and (b) is not required. "Emergency" is defined as any disruption in work process or practice such as, but not limited to, equipment failure, rupture of containers, or failure of control equipment, which is likely to result in unexpected exposure to allyl chloride vapor or liquid in quantities which may cause physical harm.

Section 1 - Environmental (Workplace Air)

(a) Concentration

Exposure to allyl chloride vapor shall be controlled so that employees are not exposed at a concentration greater than 1.0 part per million parts of air (ppm) by volume (approximately 3.1 mg/cu m of air) determined as a TWA concentration for up to a 10-hour workday in a 40-hour workweek, or at a ceiling concentration of 3.0 ppm (9.4 mg/cu m) for any 15-minute sampling period.

(b) Sampling, Collection, and Analysis

Procedures for collection and analysis of environmental samples shall be as provided in Appendices I and II or by any methods shown to be equivalent in accuracy, precision, and sensitivity to the methods specified.

Section 2 - Medical

Medical surveillance, as outlined below, shall be made available to employees subject to exposure to allyl chloride.

(a) Preplacement examinations shall include at least:

(1) Comprehensive medical and work histories with special emphasis directed toward the respiratory system, liver, kidneys, skin, and eyes.

(2) A physical examination.

(3) Specific clinical tests, including, but not limited to, a 14- x 17-inch chest x-ray, pulmonary function tests including the forced vital capacity (FVC) and the 1-second forced expiratory volume (FEV 1), a complete blood count, a complete urinalysis with microscopic examination, and liver function tests, including at least serum glutamic oxaloacetic transaminase (SGOT) and serum glutamic pyruvic transaminase (SGPT) determinations.

(4) An evaluation of the employee's ability to use negative or positive pressure respirators.

(b) Periodic examinations shall be made available at least annually. These examinations shall include at least:

(1) Interim medical and work histories.

(2) Liver function tests and urinalyses as described for the preplacement examination.

(c) During examinations, applicants or employees having medical conditions which would be directly or indirectly aggravated by exposure to allyl chloride shall be counseled on the increased risk of material impairment of their health from working with allyl chloride.

(d) Initial medical examinations shall be made available to all workers within 6 months after the promulgation of a standard based on these recommendations.

(e) In the event of an overexposure to allyl chloride vapor, a physical examination, liver function tests, urinalysis, and pulmonary function tests as described for preplacement examinations, as well as other tests as determined by the attending physician, shall be made available within a reasonable period of time. If contact with the liquid has occurred, skin and eye irritation shall also be considered in the examination.

(f) In an emergency involving allyl chloride, all affected personnel shall be provided with immediate first-aid services, especially with regard to the respiratory tract, skin, and eyes. In the event of skin or eye contact with liquid allyl chloride, immediately flush eyes and skin with water for at least 15 minutes. Contaminated clothing and shoes shall be removed. In all cases of eye contact or inhalation of vapor causing marked irritation of the nose or throat, a physician shall be consulted. Because of the possibility of delayed reactions in the lungs and eyes, persons so exposed to allyl chloride shall be observed for a minimum of 24 hours following exposure. Tests as described in paragraph (e) of this section should be made available as warranted by results of the 24-hour observation period.

(g) Pertinent medical records shall be maintained for all employees exposed to allyl chloride in the workplace. Such records shall be kept for at least 20 years after termination of employment. These records shall be made available to the designated medical representatives

of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee.

Section 3 - Labeling and Posting

(a) Labeling

Containers of allyl chloride shall carry a label stating:

ALLYL CHLORIDE

(3-CHLOROPROPENE)

HIGHLY FLAMMABLE

DANGEROUS IF INHALED OR SWALLOWED

ABSORBED THROUGH SKIN

IRRITATING TO SKIN AND EYES

Keep away from heat, sparks, and open flames.
In case of fire, use foam, dry chemical, or carbon dioxide fire extinguisher.
Avoid contact with eyes, skin, and clothing.
Keep container closed.
Use with adequate ventilation.

First aid: In case of skin or eye contact, immediately flush affected area with water for at least 15 minutes. Consult physician.

(b) Posting

Areas where allyl chloride is present shall be posted with a sign reading:

ALLYL CHLORIDE

HIGHLY FLAMMABLE

DANGEROUS IF INHALED OR SWALLOWED

ABSORBED THROUGH SKIN

IRRITATING TO SKIN AND EYES

Avoid heat, sparks, or open flames.
No smoking permitted.
In case of fire, use fire extinguishers located at (location).
Avoid breathing vapor.
Avoid contact with skin, eyes, and clothing.
Provide adequate ventilation.

First aid: In case of skin or eye contact, immediately flush affected area with water for at least 15 minutes. Consult physician.

This warning sign shall be printed both in English and in the predominant language of non-English-reading employees. All employees shall be trained and informed of the hazardous areas with special instructions for illiterate employees.

Section 4 - Personal Protective Equipment

(a) Respiratory Protection

(1) Engineering controls shall be used to maintain allyl chloride vapor concentrations below the permissible exposure limits. Compliance with the permissible exposure limits may be achieved by the use of respirators only:

(A) During the time necessary to install or test the required engineering controls.

(B) For nonroutine operations, such as maintenance or repair activities, in which concentrations in excess of the permissible exposure limits may occur.

(C) During emergencies when air concentrations of allyl chloride may exceed the permissible limits.

(2) When a respirator is permitted by paragraph (a)(1) of this section, it shall be selected and used pursuant to the following requirements:

(A) The employer shall establish and enforce a respiratory protective program meeting the requirements of 29 CFR 1910.134.

(B) The employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the respirator provided. The respiratory protective devices provided in conformance with Table I-1 shall comply with the standards jointly approved by NIOSH and by the Mining Enforcement and Safety Administration (formerly Bureau of Mines), as specified under the provisions of 30 CFR 11.

TABLE I-1

RESPIRATOR SELECTION GUIDE

Air Concentration	Respirator Type
Less than or equal to 50 ppm	(1) Any supplied-air respirator with full facepiece operated in demand (negative pressure) mode (2) Any self-contained breathing apparatus with full facepiece operated in demand mode (3) In instances where brief exposures, 5 minutes or less, are encountered, a gas mask, full facepiece with chin-style, front- or back-mounted organic vapor canister may be used.
Less than or equal to 300 ppm (concentration considered to be immediately dangerous to life or health)	(1) Type C supplied-air respirator with full facepiece operated in continuous-flow or pressure-demand (positive pressure) mode (2) Type C supplied-air respirator with hood, helmet, or suit
Greater than 300 ppm (with impermeable protective clothing)	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode (2) Combination Type C supplied-air respirator with full facepiece operated in the pressure-demand mode and an auxiliary self-contained air supply
Emergency (entry into an area of unknown concentration for emergency purposes, eg, firefighting; worn with impermeable protective clothing)	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode (2) Combination Type C supplied-air respirator with full facepiece operated in the pressure-demand mode and an auxiliary self-contained air supply
Escape (from an area of unknown concentration)	(1) Gas mask, full facepiece, with front- or back-mounted organic vapor canister (2) Self-contained breathing apparatus with full facepiece operated in either the demand or pressure-demand mode

(C) Respirators specified for use in higher concentrations of allyl chloride may be used in atmospheres of lower concentrations.

(b) Eye Protection

Full-facepiece respirators or chemical safety goggles shall be provided and worn for operations in which allyl chloride may splash into the eyes. Face shields may be used to augment chemical safety goggles where full facial protection is needed, but face shields, used alone, are not adequate for eye protection. Eye protection shall be selected and used in accordance with 29 CFR 1910.133.

(c) Skin Protection

Appropriate protective apparel, including gloves, aprons, suits, boots, or face shields (8-inch minimum) shall be provided and worn where needed to prevent skin contact with liquid allyl chloride. Protective apparel shall be made of materials which most effectively prevent skin contact under the conditions for which it is deemed necessary. Since leather articles cannot be effectively decontaminated, they shall be prohibited for use as protective apparel. Rubber articles may be used provided care is taken to ensure that permeation does not occur during usage. Protective apparel should be discarded at the first sign of deterioration.

Section 5 - Informing Employees of Hazards from Allyl Chloride

(a) Each employee subject to allyl chloride exposure shall be informed at the beginning of his employment or assignment to an allyl chloride area, and on an annual basis thereafter, of the hazards, relevant

symptoms, appropriate emergency procedures, and proper conditions and precautions for the safe use of allyl chloride. People engaged in maintenance and repair shall be included in these training programs. Each employee shall be instructed about the availability of such information which shall be kept on file. Information kept on file shall include that prescribed in paragraph (b) of this section and shall be accessible to the worker at each place of employment where allyl chloride is present.

(b) Information as required shall be recorded on the "Material Safety Data Sheet," shown in Appendix III or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 - Work Practices

(a) Emergency Procedures

For all work areas where a reasonable potential for emergencies exists, the procedures specified below and any others appropriate for a specific operation or process shall be formulated in advance, and employees shall be instructed in their implementation.

(1) Procedures shall include prearranged plans for obtaining emergency medical care and for transportation of injured workers. These plans shall be reviewed by a responsible physician to ensure the adequacy of medical procedures and of training of first-aid personnel.

(2) Firefighting procedures shall be established and implemented. These shall include procedures for emergencies involving the release of allyl chloride vapor or its combustion products. In case of fire, allyl chloride sources shall be shut off or removed. Chemical foam, carbon dioxide, or dry chemicals shall be used for fighting allyl chloride

fires, and proper respiratory protection and protective clothing shall be worn.

(3) Approved eye, skin, and respiratory protection as specified in Section 4 shall be used by personnel essential to emergency operations.

(4) Eyewash fountains and emergency showers shall be provided in accordance with 29 CFR 1910.151.

(5) An emergency communication system shall be instituted and employees informed of its proper usage.

(6) Employees not essential to emergency operations shall be evacuated from exposure areas during emergencies. Perimeters of areas of hazardous exposures shall be delineated, posted, and secured.

(7) Only personnel properly equipped, trained in the procedures, and adequately protected against the attendant hazards shall shut off sources of allyl chloride, clean up spills, and repair leaks. All leaks shall be repaired immediately.

(8) Any spills of allyl chloride shall be cleaned up promptly by flushing with water or absorbing with materials such as vermiculite. Care shall be taken to prevent accumulation of explosive concentrations of allyl chloride vapor.

(b) Control of Airborne Allyl Chloride

Engineering controls, such as process enclosure or local exhaust ventilation, shall be used to maintain allyl chloride vapor concentrations within the recommended environmental limits. All such control equipment shall meet the requirements of subpart S of 29 CFR 1910 for hazardous locations. Ventilation systems shall be designed to prevent the

accumulation or recirculation of allyl chloride vapor in the workplace and to effectively remove allyl chloride vapor from the breathing zones of employees. Exhaust ventilation systems discharging into outside air must conform with applicable local, state, and federal air pollution regulations and must not constitute a hazard. Ventilation systems shall be subject to regular preventive maintenance and cleaning to ensure effectiveness, which shall be verified by airflow measurements taken at least quarterly.

(c) Storage

Containers of allyl chloride shall be kept tightly closed at all times when not in use. Because allyl chloride is a Class IB flammable liquid, containers shall be stored in accordance with the applicable provisions of 29 CFR 1910.106 and shall be protected from heat, mechanical damage, and sources of ignition. Allyl chloride shall be stored so as not to come in contact with strong oxidizers, acids, aluminum, zinc, amines, peroxides, chlorides of iron or aluminum, and other materials which react with allyl chloride.

(d) Handling and General Work Practices

(1) Use of allyl chloride as a maintenance solvent shall be prohibited.

(2) Prior to maintenance work, sources of allyl chloride and its vapor shall be eliminated to the extent feasible. If concentrations at or below the workplace air limits cannot be assured, respiratory protective equipment shall be used during such maintenance work.

(3) All piping systems and any equipment or metallic materials used in the transfer of allyl chloride must be electrically

bonded and grounded.

(4) An employee whose skin becomes contaminated with liquid allyl chloride shall immediately wash or shower to remove all traces of allyl chloride from the skin. Clothing contaminated with the liquid shall be cleaned before reuse or disposed of. Some materials which cannot be effectively decontaminated, such as leather, shall be discarded.

(e) Waste Disposal

Waste material contaminated with liquid allyl chloride shall be disposed of in a manner not hazardous to employees. Incineration, properly conducted to prevent the hazardous release of combustion products such as hydrochloric acid, may serve as a means of disposal.

(f) Confined Spaces

(1) Confined spaces which have contained allyl chloride shall be thoroughly ventilated, cleaned, neutralized, washed, inspected, and tested for oxygen deficiency and for allyl chloride and other contaminants prior to entry.

(2) Entry into confined spaces, such as tanks, pits, tank cars, barges, process vessels, and tunnels, shall be controlled by a permit system. Permits signed by an authorized representative of the employer shall certify that preparation of the confined space, precautionary measures, and personal protective equipment are adequate and that precautions have been taken to ensure that prescribed procedures will be followed.

(3) Individuals entering confined spaces where they may be exposed to allyl chloride shall wear a respirator as outlined in Section 4 and suitable harnesses with lifelines tended by another employee outside

the space who shall also be equipped with the necessary protective equipment.

(4) Accidental exposure to allyl chloride in confined spaces shall be prevented by disconnecting and blocking off allyl chloride supply lines.

(5) Confined spaces shall be ventilated while work is in progress to keep the concentration of any allyl chloride present below the workplace environmental limits and to prevent oxygen deficiency.

Section 7 - Sanitation

(a) Food preparation, dispensing (including vending machines), and eating shall be prohibited in work areas where allyl chloride is present.

(b) Employees who handle liquid allyl chloride shall be instructed to wash their hands thoroughly with soap or mild detergent and water before eating or using toilet facilities.

(c) Smoking shall be prohibited in areas where allyl chloride is used, transferred, stored, or manufactured.

Section 8 - Environmental Monitoring and Recordkeeping

Within 6 months of the promulgation of this standard, each employer, who has a place of employment in which allyl chloride vapor is released into the workplace air, shall determine by an industrial hygiene survey if exposure to airborne concentrations of allyl chloride above the action level may occur. Records of these surveys, including the basis for concluding that air levels are at or below the action level, shall be

maintained. Surveys shall be repeated at least once every 3 years and within 30 days of any process change likely to result in an increase of airborne allyl chloride concentrations. If it has been decided that the environmental concentration of allyl chloride vapor may exceed the action level, TWA environmental limit, or the ceiling level, then the following requirements shall apply:

(a) Personal Monitoring

(1) A program of personal monitoring shall be instituted to identify and measure, or permit calculation of, the exposure of all employees occupationally exposed to allyl chloride vapor above the action level. Source and area monitoring may be used to supplement personal monitoring.

(2) In all personal monitoring, samples representative of the exposure in the breathing zone of the employee shall be collected. Procedures for sampling, calibration of equipment, and analysis of allyl chloride samples shall be as provided in Section 1(b).

(3) For each TWA determination, a sufficient number of samples shall be taken to characterize the employee's exposure during each workshift. Variations in work and production schedules shall be considered in deciding when samples are to be collected. The number of representative TWA determinations for an operation or process shall be based on the variations in location and job functions of employees relative to that operation or process.

(4) Employees shall be observed along with the operation or process to determine when maximum exposure is expected. One or more 15-minute samples taken during the time of such maximum exposure shall be used

to determine the actual ceiling concentration to which an employee is exposed.

(5) If an employee is exposed above the action level, the exposure of that employee shall be monitored at least once every 3 months.

(6) If an employee is found to be exposed in excess of the recommended TWA environmental level or ceiling limit, control measures shall be initiated, and the employee shall be notified of the exposure and of the control measures being implemented. The exposure of that employee shall be measured at least once every 30 days. Such monitoring shall continue until two consecutive determinations, at least 1 week apart, indicate that employee exposure no longer exceeds the recommended environmental limits. Quarterly monitoring may then be resumed.

(b) Recordkeeping

Employers or their successors shall maintain records of environmental monitoring for each employee for at least 20 years after the individual's employment has ended. These records shall include: the dates of measurements; job function and location of the employee within the worksite at time of sampling; sampling and analytical methods used and evidence of their accuracy; number, duration, and results of samples taken; TWA determinations based on these samples; type of personal protective equipment in use, if any; name and social security number of the employee being monitored; dates of employment with the company; and information regarding changes in job assignment. Employees and former employees shall have access to information on their own exposures.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon that were prepared to meet the need for preventing occupational diseases arising from exposure to allyl chloride. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultation with others, formalized a system for the development of criteria on which standards can be established to protect the health of employees from exposure to hazardous chemical and physical agents. Any criteria and recommended standards should enable management and labor to develop better engineering controls resulting in more healthful work practices and should not be used as final goals.

These criteria for a standard for allyl chloride are part of a continuing series of criteria developed by NIOSH. The proposed standard applies only to the processing, manufacture, and use of allyl chloride in products as applicable under the Occupational Safety and Health Act of 1970. The standard was not designed for the population-at-large, and any extrapolation beyond occupational exposures is not warranted. It is intended to (1) protect against development of toxic effects on the respiratory tract, liver, and kidneys and against local effects on the skin

and eyes, (2) be measurable by techniques that are valid, reproducible, and available to industry and governmental agencies, and (3) be attainable with existing technology.

The major concern in occupational exposure to allyl chloride is its potential for causing liver and kidney damage at low concentrations and lung damage at higher concentrations. Irritation of the eyes and of other sensory organs, dermatitis, and chemical burns have also been associated with exposure to allyl chloride.

Present toxicologic information on allyl chloride is meager. Further epidemiologic research is desirable and experiments are also needed to investigate the possible carcinogenic, teratogenic, and mutagenic properties of allyl chloride. Such experiments should also be used to further elucidate the type and severity of damage associated with chronic exposure conditions. Possible synergistic effects with other chemicals such as epichlorohydrin should be investigated.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Allyl chloride is a volatile, highly reactive, liquid halogenated hydrocarbon. A number of its important properties are presented in Table XI-1. [1]

The high-temperature chlorination of propylene is believed to be the only production method used commercially although other reactions leading to allyl chloride formation are known. [2 (pp 1-2,26)] This synthesis involves the direct substitution of chlorine for a hydrogen atom on the saturated carbon at a minimum operating temperature of 300 C. In 1973, total allyl chloride production in the United States was about 300 million pounds. [3]

Commercially, allyl chloride is used as an intermediate in chemical reactions. [4] The major commercial derivative of allyl chloride is epichlorohydrin which is used in the manufacture of epoxy resins. [2 (pp 1-2,26)] Allyl chloride is also important in commercial glycerol production.

NIOSH estimates that approximately 5,000 workers are potentially exposed to allyl chloride in the United States.

Historical Reports

Allyl chloride has been known for over 100 years. The lack of an economical means of synthesis hampered its early commercial use. An economically feasible synthesis of allyl chloride by high-temperature

chlorination of propylene in the 1930's led to the commercial production of allyl chloride beginning in 1945.

Effects on Humans

In 1959, Torkelson et al [5] exposed 13 volunteers in groups of two or three to allyl chloride at a concentration of 3 ppm. The exposure chamber was a stainless steel, vault-like room with two hinged doors sealed with Silastic gasketing. The room was equipped with an air pump, circulating fan, and temperature-controlled metering equipment to deliver the toxicant. Air samples were drawn directly from the chamber using Saran plastic tubing. The allyl chloride was converted by pyrolysis to the chloride ion and measured with the micro-Volhard method. [6] The length of exposure ranged from 1 to 3 minutes. Of the 13 volunteers, 10 reported an awareness of a definite odor but no sensory irritation at 3 ppm. The exposure period was too short to draw any conclusions regarding other adverse effects from allyl chloride at this level.

Unpublished data from Shell Chemical Company [7] indicated that after exposure to allyl chloride at 3-6 ppm only half of an unsuspected number of volunteers could detect its odor, but at 25 ppm all detected its characteristic pungent odor. Eye irritation occurred in 50% of the people tested at a concentration of 50-100 ppm. Nasal irritation and pulmonary discomfort thresholds were reported at an allyl chloride concentration of less than 25 ppm (exact concentration not given). Tests were conducted on unconditioned personnel for 5 minutes. No further experimental details were provided.

Shell Chemical Company [7] has reported no evidence of chronic intoxication or acute pulmonary irritation coincident with their manufacture of allyl chloride. However, data supporting this conclusion have not been made available. The most frequent complaint following suspected overexposure to allyl chloride vapor involved the eyes. Irritation of the conjunctivae and eyelids has been observed after exposure to relatively high vapor concentrations. Orbital pain, which generally occurred 2-6 hours after exposure, was relieved somewhat by limiting the patient's exposure to bright lights. Skin contact with liquid allyl chloride was responsible for dermatitis and blistering including damage to the subcutaneous tissues. Deep-seated pain (described as bone-ache type) beneath the point of skin contact was reported with very small amounts (exact quantity not given) of allyl chloride. Pain persisted for up to 8 hours after exposure. One case of first- and second-degree chemical burns of the skin reportedly was caused by the wearing of allyl chloride-contaminated clothing for protracted periods. All findings by Shell Chemical Company were based on industrial experience but were not correlated with any known environmental concentrations of allyl chloride.

Shell Chemical Company [8] reported in an industrial hygiene bulletin summarizing literature on allyl chloride that the compound may produce varying degrees of local irritation or injury to the tissues of the respiratory tract. Complaints of eye, nose, or throat irritation, and, in the more severe cases, sneezing and epistaxis have been reported among allyl chloride workers.

Dow Chemical USA [9] has conducted medical surveillance of employees exposed to allyl chloride and epichlorohydrin. Annual blood profile tests

included hemoglobin, hematocrit, red blood cell (RBC) and white blood cell (WBC) counts, platelet count, and lactic dehydrogenase (LDH), SGOT, SGPT, blood glucose, blood urea nitrogen (BUN), bilirubin, albumin, globulin, and other determinations. Chest X-rays and pulmonary function tests (FVC and FEV 1) were given every 2 years to employees over the age of 40 and every 4 years for those under 40. Results of these tests for all allyl chloride workers were not made available. However, the Texas Division of Dow Chemical USA has identified 33 employees who were stated to have been overexposed to allyl chloride, 7 by inhalation, 11 by eye contact, 11 from skin contact, and 4 by skin and eye contact. Followup SGOT and SGPT levels of these employees were reported to have been within the normal ranges of two testing laboratories.

Karmazin [10] reported that 50% of human volunteers detected allyl chloride dissolved in water by taste at a concentration of 0.75 mg/liter and by odor at a concentration of 0.33 mg/liter. Allyl chloride was tasted by all subjects at a level of 1.0 mg/liter and smelled by all subjects at a level of 0.66 mg/liter. Allyl chloride concentrations were estimated, not measured. The number of subjects and methods of testing employed were not given.

Epidemiologic Study

Hausler and Lenich, [11] in 1968, studied the effects of chronic allyl chloride exposure on 45 men and 15 women working in an allyl chloride-manufacturing plant. Allyl chloride concentrations varied within the plant depending on the types of processes in the immediate area. Measured levels ranged from a low of 1 ppm in the laboratory to a

high of 113 ppm in the pumproom. The extent of employee exposure during the 16-month exposure period was dependent upon their duties. Effects were determined during medical examinations as described in the East German "Medical Serial Examinations of the Workers" with additional urinalyses and liver function tests, including enzyme activity determinations. Liver function was measured by thymol, cadmium, and serum bilirubin tests. Enzyme activity tests included LDH, SGOT, SGPT, sorbose dehydrogenase (SDH), and glutamic acid dehydrogenase (GDH) determinations. The only unusual finding on physical examination was the presence of a garliclike odor of the body and in the exhaled air in 20 of the exposed workers. No similar complaints had been reported in serial examinations performed in 1965 and 1966.

Urine tests [11] disclosed that two individuals had passed traces of protein, a few erythrocytes, epithelial cells, and leukocytes. Five individuals had slightly elevated urobilinogen levels. According to Hausler and Lenich, [11] the presence of allegedly abnormal results in liver function tests, including enzymatic tests, was indicative of early stages of liver damage. Although individual test findings were not reported, the criteria used to judge these abnormal results along with the number of persons exhibiting each type of abnormal result were provided and are given in Table III-1. However, in the absence of preexposure control values, a definite conclusion that these results are indicative of abnormal liver function cannot be made. The plant subsequently was remodeled so that the allyl chloride level was 1 ppm or less in all areas except in the pumproom, where the concentration was 15-36 ppm. The authors stated that all individuals previously reported to have abnormal findings in the liver

function and urine tests returned to normal within 6 months, but the results of these tests were not presented to support their conclusion.

TABLE III-1

RESULTS OF LIVER FUNCTION TESTS
PERFORMED ON MALE AND FEMALE EMPLOYEES

Test Finding	Men (n=45)	Women (n=15)	Total (n=60)
Cadmium positive	6	1	7
Total bilirubin over 1 mg%	9	1	10
Thymol positive	7	3	10
SGOT above 45 U	5	-	5
SGPT above 17 U	19	6	25
LDH above 83 U	6	6	12
GDH positive	20	5	25
SDH positive	16	5	21

From Hausler and Lenich [11]

Animal Toxicity

Smyth and Carpenter [12] developed an acute range-finding procedure to determine the approximate lethal dose of toxic chemicals. This method was used to estimate the single-dose, oral and dermal LD50's for allyl chloride in rats and rabbits, respectively. [13] Mortality during a 14-day observation period after administration of the compound was reported. In the oral tests, single doses of allyl chloride were administered by stomach

tube to rats weighing 90-120 g, and the oral LD50 was estimated by a comparison of these results with the LD50 data of a structurally similar compound (not identified). Rubber cuffs described by the Food and Drug Administration were used in the skin absorption tests to ensure maximum contact of the material with the skin of the rabbits. An oral LD50 of 700 mg/kg in rats and a dermal LD50 of 1,900 mg/kg in rabbits were reported. Since range-finding LD50 studies provide approximate values, these values should be used only as preliminary laboratory data.

The range finding method has also been used to determine the approximate mortality rates of exposure to a variety of chemicals by inhalation. [12] Allyl chloride at a concentration of 2,000 ppm caused one death in a group of six rats within 4 hours. [13]

Using a stomach tube to administer allyl chloride in an unidentified oil solution, Karmazin [10] obtained oral LD50 values of 450 mg/kg for albino rats, 500 mg/kg for white mice, and 300 mg/kg for rabbits. Observation times were not reported. Microscopic examination of animal tissues disclosed mild degenerative changes in the myocardium, liver, and kidneys.

In unpublished data of experiments on mice, Shell Chemical Company [7] reported LC50's of 1,455 ppm for 60-minute and 24,633 ppm for 10-minute exposures. All mice exposed to allyl chloride at a concentration of 73,900 ppm for 10 minutes died within 24 hours. Two of four mice survived ten 60-minute exposures (sequence not stated) to allyl chloride vapor at a concentration of 129 ppm. All mice dying or killed after one or more exposures at 129 ppm showed "profound" pulmonary damage (details not given), considerable injury to the liver, and slight changes in the kidneys

and spleen. No other experimental data were provided.

In 1938, Silverman and Abreu [14] studied the toxic and anesthetic properties of allyl chloride (3-chloropropene) and three other monochlorinated compounds (1-chloropropene; 1-chloro,2-methylpropene; 3-chloro,2-methylpropene). Ten white mice in each of three groups were subjected to 10-minute exposures of allyl chloride at concentrations of 1.0 millimole/liter (24,200 ppm), 2.0 millimoles/liter (48,400 ppm), or 3.0 millimoles/liter (72,600 ppm) in a 2.5-liter glass bottle. The age, sex, and weight of the mice were not reported. After exposure, the animals were examined periodically for 48 hours. Necropsies were performed immediately on all animals dying within this time period. Animals were selected randomly from groups in which no deaths occurred, and killed for examination. Allyl chloride was highly injurious to pulmonary tissues and moderately so to the tissues of other organs, but the nature of the damage was not specified. All 10 mice exposed at 3 millimoles/liter died, some within 5 minutes from the start of exposure and the rest within 24 hours after termination of exposure. Nine of 10 mice exposed at 2 millimoles/liter died within 6-47 hours, and 4 of 10 mice exposed at 1 millimole/liter died within 26-46 hours. Anesthetic effects were noted in mice exposed at concentrations of 2 or 3 millimoles/liter. Onset of anesthesia was 2-8 minutes after the start of exposure at 2 millimoles/liter in 9 of 10 mice and 1-2 minutes at 3 millimoles/liter in all 10 mice. Recovery from anesthetic effects occurred 20 seconds-4 minutes after the termination of exposure at 2 millimoles/liter and 6 minutes at 3 millimoles/liter. No anesthetic effects were observed at 1 millimole/liter. In other tests on mice exposed at a level of 0.5

millimole/liter (12,100 ppm), allyl chloride caused prompt and profound mucosal irritation. From these findings, Silverman and Abreu [14] concluded that allyl chloride is potentially dangerous to persons working with it and estimated that in humans a single 10-minute exposure at a concentration of 22,000 ppm could result in death.

In 1940, Adams et al [15] exposed guinea pigs and albino rats in groups of four or five for varying lengths of time to allyl chloride at concentrations of 290, 2,900, 5,800, 14,500, and 29,300 ppm to determine the shortest exposure producing 100% lethality of the group and the longest exposure permitting 100% survival of the group. Exposure times varied from 10 minutes at 14,500 ppm to 9 hours at the 290-ppm level. Initial concentrations were obtained by spraying the walls of the test chamber with a premeasured amount of allyl chloride. To maintain the desired levels, allyl chloride was introduced into the chamber by a continuous-flow system. The method of checking allyl chloride concentrations within the chamber was incompletely described, but levels were reported to be quite constant. The 100% lethal exposure times and 100% survival exposure times for rats and guinea pigs are listed in Table III-2. Gross reactions of the guinea pigs and rats to varying concentrations of allyl chloride are given in Table III-3. Microscopic examination showed significant lesions in the lungs and kidneys of animals that died or were killed after acute exposure to allyl chloride vapor at all concentrations tested. Renal lesions included prominent changes in the glomeruli showing distended capsular spaces, marked damage to the convoluted tubules characterized by distention of the lumina, and moderate congestion of the kidneys with hemorrhage of the intertubular capillaries. Pulmonary damage consisted of moderate-to-marked

congestion with frequent hemorrhage into the alveolar spaces, marked interstitial edema, thickening of the mucous membrane of the bronchioles, and desquamated epithelial cells, leukocytes, and erythrocytes in the lumina. Lesions were more severe in the kidneys than in the lungs. Only slight changes were recorded in the liver, the most prominent being congestion of the central vein and adjacent sinusoids. Renal damage was most severe under the conditions of low concentrations and long exposures. Higher concentrations were more irritating to the lungs. Animals allowed to recover for 4 weeks were essentially normal, with a few exhibiting slight-to-moderate fibrosis and scarring of the lungs and kidneys.

TABLE III-2

EXPOSURE TIMES (IN HR) FOR SURVIVAL AND LETHALITY IN RATS AND GUINEA PIGS EXPOSED TO ALLYL CHLORIDE VAPOR

Concentration		Rats		Guinea Pigs	
mg/l	ppm	100% Survival Exposure*	100% Lethal Exposure**	100% Survival Exposure*	100% Lethal Exposure**
100	29,300	0.25	0.50	-	-
50	14,500	0.50	1.25	0.25	0.75
20	5,800	0.50	2.00	-	-
10	2,900	1.00	3.00	1.00	2.00
1	290	3.00	8.00	1.00	4.00

*Observation period of 4 weeks
**Deaths within 24 hours

Adapted from Adams et al [15]

TABLE III-3

GROSS REACTIONS OF GUINEA PIGS AND RATS TO ALLYL CHLORIDE VAPORS

Animal	Conc (ppm)	Exposure Time	Effects
Guinea pigs	290	1 hr -4 hr	Drowsiness, unsteadiness, death in 24 hr
		6 hr	Eye irritation, unconsciousness, death in 24 hr
Rats	290	2 hr -9 hr	Similar to guinea pigs at 290 ppm, but more resistant to the narcotic action; death in 24 hr
Guinea pigs	2,900	30 min-2 hr	Slight eye and nose irritation in a few min; death shortly after exposure
Rats	2,900	30 min-2 hr	Same findings as for guinea pigs at 2,900 ppm; 6 of 10 rats exposed for 2 hr died
		3 hr -4 hr	Mortality 100% during exposure
"	5,800	30 min-2 hr	Rapid development of eye and nose irritation, death in 24 hr for 1- and 2-hr exposures
Guinea pigs, rats	14,500	10 min-1 hr 30 min-2 hr	Eye and nose irritation, drowsiness, weakness, instability, laboured breathing; some deaths in a few hr, all dead in 24 hr
Rats	29,300	15 min-1 hr	Eye and nose irritation, unconsciousness, death in 1 hr

Adapted from Adams et al [15]

Torkelson et al [5] repeatedly exposed 10 rats (5 of each sex), 4 male guinea pigs, and a female rabbit to allyl chloride at an average concentration of 8 ppm (range 7.9-10 ppm). Air samples drawn directly from

the chamber through Saran plastic tubing were heated at 1,000 C to form the chloride ion, which was collected in a solution containing 1% sodium formate and 1% sodium carbonate and was measured by the micro-Volhard method. [6] A total of twenty-eight 7-hour exposures in a glass-walled chamber was scheduled 5 days/week over a 35-day period. Matched controls were exposed daily to room air under similar conditions. Observations on general appearance, behavior, growth, and mortality failed to show any appreciable differences between the treated group and the controls. Microscopic examination of tissues from the lungs, heart, liver, kidneys, spleen, and testes showed definite tissue damage in the liver and kidneys of essentially all the exposed animals. Damage to the liver was characterized by dilation of the sinusoids, cloudy swelling, and focal necrosis; kidney damage included changes in the glomeruli, necrosis of the epithelium of the convoluted tubules, and proliferation of the interstitial tissues.

Further tests were conducted by Torkelson et al [5] on a larger scale using the same procedure as in the 8-ppm tests. Each of three groups of animals (selected by age and weight) was composed of 48 rats, 6 rabbits, 18 guinea pigs, and 2 dogs, with equal numbers of males and females. The study group was exposed to allyl chloride at an average concentration of 3 ppm (range 1.8-3.9 ppm), 7 hours/day, 5 days/week, for a total of 127-134 exposures over 180-194 days. One of two control groups was exposed to room air under conditions similar to those of the exposed animals. The other (unexposed) control group was held in the animal quarters. At the end of the exposure period, the rabbits, guinea pigs, and dogs were killed. Microscopic examinations revealed no abnormalities. The rats were divided

into two groups after the exposure period, and one group was allowed to recover for 2 months while the other was killed. In the latter group, BUN and blood nonprotein nitrogen determinations were within normal limits in all animals. No other measurements of kidney function were made. Microscopic examination of the kidney and liver tissues of rats killed immediately after exposure revealed only a slight central lobular degeneration in the livers of the female rats, but none in males. The number of female rats exhibiting this change was not given. This change was of a type normally seen in control groups. However, because of its absence in male rats and other animal species, the authors concluded that the effect was due to the allyl chloride exposure. The absence of this change in all rats allowed to recover for 2 months was interpreted as an indication that the damage was reversible.

Almeev and Karmazin [16] studied the effects of allyl alcohol and allyl chloride. They administered allyl chloride in a sunflower oil solution by gastric intubation to 84 albino rats at doses of 250, 300, 400, 750, 1,000, 1,500, or 2,000 mg/kg. Rats receiving allyl chloride at 2,000 mg/kg died within 2 hours, while rats subjected to doses of 1,500 and 1,000 mg/kg died on the first day. At doses of 250, 300, 400, or 750 mg/kg, all rats died by the third day, with most dying on the first. Results of macroscopic examination, described for allyl alcohol and stated to be similar for allyl chloride, revealed differing degrees of intumescence of the stomach and intestines, folded and swollen mucosa of the stomach, mucus in the lumen of the large and small intestines, and splenic hyperemia. The livers of these animals were flaccid and hyperemic with isolated small hemorrhages under the Glisson's capsules. The kidneys were hyperemic, and

the boundary between the cortical and medullary layers was smooth. The lungs were half-collapsed and pale red. Punctate hemorrhages were observed in some sections of the lungs. Microscopic tissue examination of the internal organs of these animals showed similar changes at the different dose levels and included mild degeneration of the myocardium, moderate hyperemia of the liver, degeneration of the connective tissues in the liver, hyperemic congestion of the stomach mucosa, and considerable edema in the submucosa. The kidneys exhibited cloudy swelling of the tubular epithelium and congestive hyperemia of the cortical- and medullary-layer vessels. The authors [16] provided only a qualitative description of organ damage produced by allyl chloride; therefore, the severity of the observed damage could not be related to the various doses.

In the subchronic portion of this study, Almeev and Karmazin [16] administered allyl alcohol or allyl chloride to rats in parallel experiments. The doses, equivalent to the LD50 or twice the LD50, were administered in 10 days by the procedures described above. For allyl alcohol, these doses were 14 or 28 mg/kg/day. The authors [16] stated that the macroscopic examination after allyl alcohol exposure included the stomach and the intestines, and no changes were apparent. The microscopic examination revealed hyperemia in the heart, liver, kidneys, and spleen, as well as degeneration of the myocardial fibrils and liver parenchyma. For allyl chloride, the doses were 45 or 90 mg/kg/day. Macroscopic examination of organs from rats given allyl chloride revealed tissue congestion. On microscopic examination, internal organs had noticeable hyperemia and mild degeneration. Although no further details were given for effects from allyl chloride, it is presumed that organs examined and changes noted were

similar to those described for allyl alcohol.

Strusevich and Ekshtat [17] determined the dynamics of activities of pancreatic lipase, amylase, and trypsin and its inhibitor in white rats after oral administration of four chlorinated compounds, including 2,3-dichloropropene and allyl chloride, at doses of 1/10, 1/50, or 1/250 of the LD50's. Because the LD50's were not identified, doses used cannot be determined. Enzymatic activities were studied on the 1st, 10th, and 20th days after each compound was administered. The administration of 2,3-dichloropropene at all dose levels changed the activities of trypsin and its inhibitor (not identified) by producing a significant increase in the level of the inhibitor with a drop in trypsin activity. These changes were most evident on the 10th and 20th days. One month after the administration of 2,3-dichloropropene, 0.05 mg of pilocarpine was given orally to each rat. There was no change in the activities of trypsin and its inhibitor at 1/10 the LD50. This may have indicated a state of inactivity of pancreatic excretory function. At the other dose levels, pilocarpine increased trypsin activity indicating that the functional activity of the pancreas was retained. The authors have reported that allyl chloride produced effects similar to those of 2,3-dichloropropene, but to a lesser degree. After the administration of allyl chloride at doses of 1/50 and 1/250 the LD50, those of lipase activity was increased when measured on the 1st and 10th days and was decreased when measured on the 20th day. At 1/10 the LD50, allyl chloride reduced lipase activity throughout the experiment. At all doses, stimulation of the pancreas with pilocarpine increased lipolytic activity. An increase in amylase activity was noted throughout the experiment with allyl chloride at 1/10 the LD50. No results were given for

amylase at the 1/50 and 1/250 dose levels.

Kaye et al [18] administered 1 ml of allyl chloride solution (10% v/v in peanut oil) by subcutaneous injection into the lumbar region of male CFE-strain albino rats weighing 200-250 g. All rats had free access to water. To test for sulfur-containing metabolites, a group of rats was kept on a diet consisting of 5% sulfur-labeled yeast. The bile duct of one rat was cannulated and the upper part of the duct intubated to avoid contamination of the bile sample with pancreatic juice. Urine and bile were collected for 24 hours prior to the administration of allyl chloride and for two consecutive 24-hour periods after introduction of the compound. Samples were analyzed using paper chromatography with a radiochromatogram scanner and gas-liquid chromatography. The urine of rats given allyl chloride contained allyl mercapturic acid, allyl mercapturic acid sulfoxide, and 2- or 3-hydroxypropylmercapturic acid. To isolate these compounds, 1 ml of a 10% solution containing 12.7 g allyl chloride in peanut oil was administered subcutaneously to each of 137 rats. Allyl mercapturic acid in amounts corresponding to 1.7% of the administered allyl chloride was recovered. The other two compounds could not be isolated. To identify whether 2- or 3-hydroxypropylmercapturic acid was present, allyl chloride was administered subcutaneously to 21 rats. Their urine was collected over the 24-hour period immediately after doses were given. The presence of 3-hydroxypropylmercapturic acid was identified on a gas-liquid chromatograph using two different columns. Radiochromatograms of urine from rats fed 35S-labeled yeast confirmed the results in rats given allyl chloride.

Correlation of Exposure and Effect

Industrial exposure observations [7] have shown that liquid allyl chloride is a skin irritant responsible for dermatitis, damage to underlying tissues of the skin, deep-seated pain, and chemical burns.

As a vapor, allyl chloride at a concentration of 3 ppm had a definite odor for 10 of 13 volunteers. [5] Odor threshold experiments conducted by Shell Chemical Company [7] showed 50% of the human subjects could detect an odor at a concentration of 3-6 ppm; at 25 ppm, the odor was detectable by all subjects. At 50-100 ppm, 50% of the subjects tested reported eye irritation. Nasal irritation and pulmonary discomfort have been reported at a concentration of less than 25 ppm. [7]

Allyl chloride vapor had a narcotic effect on rats, mice, and guinea pigs over a concentration range of 290-72,600 ppm. [14,15] Susceptibility to the anesthetic effect was species-dependent, guinea pigs being the most sensitive. Such effects were not evident in humans at a vapor concentration of up to 113 ppm. [7,11]

In an epidemiologic study, Hausler and Lenich [11] suggested that changes in the results of liver function tests in 60 employees exposed to allyl chloride coincided with changes in allyl chloride levels. No preexposure values for the liver function tests were reported; however, the test results, reported by the authors as abnormal, did "return to normal" after a reduction in exposure, suggesting that the observed liver damage may have been related to allyl chloride exposure. Renal and pulmonary changes were not observed in any of the exposed employees. Twenty of the 60 exposed employees also complained of a garliclike odor of the body and in the exhaled breath.

Acute and chronic exposures to allyl chloride in animals have resulted in hepatic, renal, and pulmonary damage. [5,7,14,15] Tables III-4 and III-5 summarize the results of these experiments. Liver damage appeared to be more significant following chronic exposure [5] while pulmonary injuries followed acute exposures. [15] Animals were exposed to allyl chloride at a vapor concentration of 3 ppm, 7 hours/day, 5 days/week, for a total of 127-134 exposures over a 180- to 194-day period. [5] Slight liver damage was observed in female rats killed immediately after exposure. Female rats allowed to recover for 2 months after exposure, as well as male rats, rabbits, guinea pigs, and dogs, did not show this effect at this concentration. Torkelson et al [5] reported extensive liver damage in rats, rabbits, and guinea pigs exposed to allyl chloride at 8 ppm for 7 hours/day, 5 days/week, for 35 days. The authors also reported renal damage at this concentration. Extensive liver and pulmonary damage occurred in mice at a concentration of 129 ppm with ten 60-minute exposures, while only slight renal changes were observed. [7] Slight hepatic changes and significant pulmonary and renal lesions resulted in guinea pigs and rats exposed to allyl chloride at 290-29,300 ppm for periods of 10 minutes-9 hours. [15]

Carcinogenicity, Mutagenicity, and Teratogenicity

No reports which address the subject of carcinogenic, mutagenic, or teratogenic properties of allyl chloride were found. The Manufacturing Chemists Association is currently administering a research program to study the oncogenic and teratogenic effects of inhaled allyl chloride on rats and rabbits (AC Clark, written communication, February 1976).

TABLE III-4

EFFECTS FROM ALLYL CHLORIDE INHALATION ON ANIMALS

Animals	Concentration (ppm)	Exposure Time	Effects	References
Mice	73,900	10 min	Death	Anon [7]
White mice	72,605	"	Highly injurious to pulmonary tissues; moderate damage to other organs; onset of anesthesia in 1-2 min with recovery in 6 min; all mice dead within 24 hr	Silverman & Abreu [14]
"	48,403	"	Death in 9 of 10 mice in 6-47 hr; onset of anesthesia in 2-8 min with recovery in 20 sec-4 min; damage to organs same as at 72,605 ppm	"
Albino rats	29,300	15 min-1 hr	Significant lesions in lungs and kidneys; slight changes in liver; eye and nose irritation; death within 1 hr	Adams et al [15]
Mice	24,633	10 min	LD50	Anon [7]
White mice	24,202	"	Death in 4 of 10 mice within 26-46 hr; organ damage same as at 72,605 ppm	Silverman & Abreu [14]
Guinea pigs, albino rats	14,500	10 min-2 hr	Eye and nose irritation; drowsiness, weakness, instability, labored breathing; death within 24 hr; effects on lungs, liver, kidneys same as at 29,300 ppm	Adams et al [15]
White mice	13,300	10 min	Irritation of mucous membranes	Silverman & Abreu [14]
Albino rats	5,800	30 min	Rapid development of eye and nose irritation; death in 24 hr; lung, liver, and kidney damage same as at 29,300 ppm	Adams et al [15]
Guinea pigs, albino rats	2,900	30 min-2 hr	Slight eye and nose irritation; death in 24 hr; lung, liver, and kidney damage same as at 29,300 ppm	Adams et al [15]
Mice	1,455	1 hr	LD50	Anon [7]
Albino rats	290	6 hr	Eye irritation; unconsciousness; death in short time; no organ damage	Adams et al [15]
Guinea pigs, albino rats	290	1 hr-4 hr	Drowsiness; unsteadiness; no organ damage or deaths	"
Mice	129	1 hr x 10 exposures	Profound pulmonary damage; considerable liver injury; slight changes in kidneys and spleen	Anon [7]
Rats, rabbits, guinea pigs	8	7 hrs/d 5 d/wk x 28 exposures	Extensive tissue damage in liver and kidneys	Torkelson [5]
Rats, rabbits, guinea pigs, dogs	3	7 hrs/d, 5 d/wk x 180-194 exposures	Reversible liver damage in female rats; no effects in other animals	"

TABLE III-5

EFFECTS FROM ALLYL CHLORIDE IN
ORAL TOXICITY EXPERIMENTS ON ANIMALS

Animals	Concentration (mg/kg)	Effects	References
Albino rats	2,000	Death; flaccid and hyperemic livers, degeneration of liver connective tissue; swollen kidney tissue, swelling of canal epithelium of kidney, hyperemia of cortical and medullary layer vessels of kidney; half-collapsed and pale red lungs; effects on stomach, intestine, spleen	Almeev & Karmazin [16]
"	1,000-1,500	Death on 1st day; other effects same as at 2,000 mg/kg	"
"	750	Death within 3 days with most deaths on 1st day; other effects same as at 2,000 mg/kg	"
"	700	LD50 for 14-day observation period	Smyth & Carpenter [13]
Albino mice	500	LD50, observation time not provided	Karmazin [10]
Albino rats	450	"	"
Rabbits	300	"	"
Albino rats	250	Death within 3 days with most deaths on 1st day; other effects same as at 2,000 mg/kg	Almeev & Karmazin [16]
"	45, 90	Hyperemia of organ (nature of damage and organ affected not provided)	"

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.

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VIII. APPENDIX I

SAMPLING METHOD FOR ALLYL CHLORIDE

Atmospheric Sampling

Breathing zone samples should be taken as near as practical to the employee's breathing zone without interfering with his movement. A description of the sampling location and conditions, equipment used, date, time, and rate of sampling, and any other pertinent information shall be recorded at the time of sample collection. A sufficient number of samples should be taken to accurately characterize the employee's exposure during a work shift.

(a) Equipment

The sampling train consists of a charcoal tube and a vacuum pump.

(1) Charcoal tubes: Glass tubes with both ends flame-sealed, 7 cm long with a 6-mm OD and a 4-mm ID, containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of polyurethane foam. The primary adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of polyurethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool or polyurethane foam is placed in front of the adsorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flowrate of 1 liter/minute. Tubes with the above specifications are commercially available.

(2) Pump: A battery-operated pump, complete with clip for

attachment to the employee's clothing, capable of operation at 1 liter or less/minute.

(b) Calibration

Since the accuracy of an analysis can be no greater than the accuracy with which the volume of air is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the volume indicated. The frequency of calibration is dependent upon the use, care, and handling to which the pump is subjected. Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. Pumps should be recalibrated if they have been misused, or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary. Regardless of use, maintenance and calibration should be performed on a regular schedule and records of these kept.

The accuracy of calibration is dependent upon the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or soapbubble meter are recommended, although other standard calibration instruments such as a wet test meter or dry gas meter can be used. The actual setups will be similar for all instruments.

The calibration setup for personal sampling pumps using a soapbubble meter is shown in Figure XI-1. If another calibration device is selected, equivalent procedures should be used. Since the flowrate given by a pump is dependent on the pressure drop of the sampling device, in this case a

charcoal tube, the pump must be calibrated while operating with a representative charcoal tube in line. Calibration instructions using the soapbubble meter follow.

(1) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration; charge the battery as needed.

(2) Break the tips of a charcoal tube to produce openings of at least 2 mm in diameter.

(3) Assemble the calibration train as shown in Figure XI-1.

(4) Turn on the pump and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and drawing bubbles up the inside until they travel the entire buret length without bursting.

(5) Adjust the pump rotameter to provide the desired flowrate.

(6) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 13 inches of water at 1 liter/minute or 2.5 inches of water at 200 ml/minute.

(7) Start a soapbubble up the buret and measure the time it takes the bubble to move from one calibration mark to another. A stopwatch should be used for this measurement.

(8) Repeat the procedure in (7) above at least twice, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance. If, for the pump being calibrated, the volume of air sampled is calculated as the product of the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the

quotient of the volume between the two preselected marks divided by the number of strokes.

(9) Record the following data: the volume measured, elapsed time or number of strokes, pressure drop, air temperature, atmospheric pressure; manufacturer, model, and serial number of the pump; date, and name of the person performing the calibration.

(c) Sampling Procedure

The following procedure is applicable except when condensation occurs in the tube during sampling. Under this condition, the efficiency of the method would be impaired.

(1) Break both ends of the charcoal tube to provide openings of at least one-half the ID (2 mm) of the tube. A smaller opening causes a limiting orifice effect which reduces the flow through the tube. Place the smaller section of charcoal, which is used as a backup section, nearest the sampling pump. Use tubing to connect the back of the tube to the pump. Support the tube in a vertical position in the worker's breathing zone.

(2) Sample a maximum of 100 liters of air at a flowrate of 1 liter or less/minute. For example, to determine 8-hour TWA concentrations, two 4-hour or four 2-hour samples are suggested.

(3) Measure and record the temperature and pressure of the atmosphere being sampled.

(4) Treat one charcoal tube (the analytical blank) in the same manner as the sample tubes (break, seal, ship) except that no air is drawn through it.

(5) Immediately after sampling, cover the ends of the charcoal tubes with polyethylene or polypropylene caps. Under no circumstances should rubber caps be used. To minimize breakage during transport, capped tubes should be padded and packed tightly in a shipping container. If needed, a bulk sample (usually no more than 1 oz) of the suspected compound should be submitted to the laboratory in a glass container with a teflon-lined cap. Label the bulk sample so that it can be identified with the proper air samples. The bulk sample should not be transported, mailed, or shipped in the same container as the air sample or blank tubes. If the bulk sample is to be mailed, it should be packaged so as to prevent breakage.

IX. APPENDIX II

ANALYTICAL METHOD FOR ALLYL CHLORIDE

Principle of the Method

Allyl chloride vapor trapped on charcoal from a known volume of air is desorbed with benzene. Carbon disulfide is a suitable substitute for benzene but, if the desorption solvent is changed, modification of this method is needed. An aliquot of the desorbed sample is injected into a gas chromatograph. The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

Range and Sensitivity

This method was validated over the range of 1.80-7.19 mg/cu m (0.58-2.29 ppm) with a 100-liter sample at 24 C and 759 mmHg. With a sample size of 100 liters, the probable useful range of this method is 0.5-10 mg/cu m (0.16-3.20 ppm). The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of allyl chloride and other substances in the air. The first section of the charcoal tube was found to hold 1.5 mg of allyl chloride when a test atmosphere containing 7.56 mg/cu m (2.42 ppm) of allyl chloride in air was sampled at a flowrate of 0.945 liter/minute for 210 minutes. Under these conditions, 3% of the total allyl chloride sampled

was found on the backup section of the charcoal tube. If a particular atmosphere is suspected of containing a large concentration of contaminant, a sampling volume smaller than the suggested maximum of 100 liters should be taken.

Interferences

When the amount of water in the air is so great that condensation actually occurs in the charcoal tube, organic vapors will not be trapped. The capacity of the charcoal tube for allyl chloride may also be reduced by the presence of other organic vapors in high concentrations.

Any compound which has the same retention time as allyl chloride under the gas chromatographic conditions described in this method will interfere with the analysis. Substances suspected of being present in the sample should be injected to determine their retention time and, thus, the likelihood of interference. This type of interference may be overcome by changing the operating conditions of the instrument, the packing material of the column, or the column temperature. Retention time data on a single column cannot be considered proof of chemical identity. A mass spectrometer, a minimum of two different columns, or other suitable methods must be used to determine chemical identity.

When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

Precision and Accuracy

The coefficient of variation for the total analytical and sampling method in the range of 1.80-7.19 mg/cu m was 0.071. This value corresponds to a 0.071-ppm (0.21-mg/cu m) standard deviation at 1 ppm (3.13 mg/cu m).

Advantages and Disadvantages of the Method

The sampling device is small, portable, and involves no liquids. Interferences are minimal and most can be eliminated by altering the chromatographic conditions. The analysis is accomplished by using a rapid instrumental method, which also can be used for the simultaneous analysis of two or more compounds present in the same sample.

One disadvantage of the sampling method is that the sample amount is limited by the capacity of the charcoal tube before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. In the analytical method, the presence of other compounds with the same retention time may either mask the allyl chloride peak or increase the size of the peak. However, this can generally be overcome by altering the operating conditions of the gas chromatograph.

The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flowrate and cause the volume to be imprecise because the pump is usually calibrated for one tube only.

Apparatus

(a) Gas chromatograph equipped with a flame ionization detector.

(b) Column (4 feet x 1/4 inch, stainless steel) packed with 50/80 mesh Porapak, Type Q. Other columns which achieve the desired separation may also be used.

(c) An electronic or mechanical integrator for determining peak areas.

(d) Small glass-stoppered test tubes or equivalent.

(e) Syringes: 10-μl, and other convenient sizes for preparation of standards.

Reagents

(a) Benzene, chromatoquality.

(b) Hexane, chromatoquality

(c) Allyl chloride, reagent grade.

(d) Purified nitrogen.

(e) Purified hydrogen.

(f) Purified air.

(g) Compressed air (industrial grade), if needed as dictated by instrument design.

Analysis of Samples

(a) Wash all glassware in detergent and rinse thoroughly in distilled water.

(b) Score each charcoal tube, including the blank from field samples, with a file and break open in front of the first section of charcoal. Remove and discard the glass wool. Transfer the charcoal in the first (larger) section into a small, stoppered test tube. Remove and discard the separating foam section, and transfer the second section of charcoal to another test tube. The two charcoal sections are then analyzed separately.

(c) Prior to analysis, pipet 1.0 ml of benzene into each test tube to desorb the allyl chloride from the charcoal. Desorption is complete in 30 minutes if the sample is stirred occasionally.

CAUTION MUST BE EXERCISED AT ALL TIMES WHEN USING BENZENE BECAUSE OF ITS HIGH TOXICITY AND FLAMMABILITY. ALL WORK WITH BENZENE MUST BE PERFORMED UNDER AN EXHAUST HOOD.

(d) Typical gas chromatographic operating conditions:

(1) 50 cc/min (60 psig) nitrogen carrier gas flow.

(2) 65 cc/min (24 psig) hydrogen gas flow to detector.

(3) 500 cc/min (50 psig) airflow to detector.

(4) 185 C injector temperature.

(5) 250 C manifold temperature (detector).

(6) 160 C isothermal oven or column temperature.

(e) Inject the sample into the gas chromatograph using the solvent flush injection technique. This eliminates difficulties arising from blowback or distillation within the syringe needle, thus increasing the accuracy and reproducibility of the injected sample volume. Flush the 10-

μl syringe with solvent several times to wet the barrel and plunger, then draw 3.0 μl of solvent into the syringe. Next, remove the needle from the solvent and pull the plunger back about 0.2 μl to separate the solvent flush from the sample with an air pocket to be used as a marker. Then immerse the needle in the sample and withdraw a 5.0-μl aliquot. After removing the needle from the sample and prior to injection into the gas chromatograph, pull back the plunger a short distance to minimize sample evaporation from the needle tip. Make duplicate injections for each sample and for the standard. There should be no more than a 3% difference in the peak areas.

(f) Determine the area of the sample peak with an electronic integrator or some other suitable form of area measurement, and read the preliminary sample results from a standard curve prepared as outlined below.

Determination of Desorption Efficiency

The desorption efficiency of a particular compound can vary from one batch of charcoal to another and also from one laboratory to another. Thus, it is necessary to determine the percentage of allyl chloride recovered in the desorption process at least once. This procedure should be repeated for each new batch of charcoal used.

Activated charcoal, equivalent to the amount in the first section of the sampling tube (100 mg), is measured into a 5-cm, 4-mm ID glass tube, flame-sealed at one end. This charcoal must be from the same batch as that used for the samples and can be obtained from unused charcoal tubes. The open end is capped. A known amount of hexane solution containing a known

amount of allyl chloride is injected directly into the activated charcoal with a microliter syringe, and the tube is capped. The known amount injected is usually equivalent to that present in a 100-liter air sample at the selected level.

At least six tubes are prepared in this manner and allowed to stand overnight or longer to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The samples and blanks are desorbed and analyzed in exactly the same manner as described above for unknown air samples.

Two or three standards are prepared by injecting identical volumes of allyl chloride into 1.0 ml benzene with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$DE = \frac{\text{average weight recovered (mg)}}{\text{weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. The desorption efficiency versus the weight of the analyte found should be plotted.

Calibration and Standards

It is convenient to express the concentration of standards in terms of mg allyl chloride/1.0 ml benzene, because samples are desorbed in this amount of benzene. The density of the allyl chloride is used to convert

milligrams into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml benzene versus average peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed when the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day because of changes in instrument sensitivity and column response.

Calculations

The weight in mg, corresponding to the total peak area, is read from the standard curve. No volume corrections are needed, because the standard curve is based on mg allyl chloride/1.0 ml benzene and the volume of sample injected is identical to the volume of the standards injected.

Corrections for the blank from the field sampling are made for each sample by subtracting the amounts of allyl chloride found on the front and back sections of the blank from the amounts found in the respective sections of the sample:

corrected amount = amount on sample - amount on blank

The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total amount of allyl chloride in the sample. This total amount is divided by the desorption efficiency to obtain the adjusted total amount of allyl chloride in the sample:

$$\text{adjusted total amount} = \frac{\text{total amount}}{\text{desorption efficiency}}$$

The concentration of allyl chloride in the air sampled, expressed in mg/cu m (which is numerically equal to μg/liter of air), is given by the quotient of the adjusted amount in μg divided by the volume of air sampled in liters:

$$\text{concentration (mg/cu m)} = \frac{\text{adjusted amount (mg)} \times 1{,}000 \text{ liter/cu m}}{\text{volume (liters)}}$$

Another method of expressing concentration is ppm:

$$\text{concentration (ppm)} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

24.45 = molar volume (liter/mole) at 25 C and 760 mmHg

MW = molecular weight of allyl chloride (g/mole)

760 = standard pressure

P = pressure (mmHg) of air sampled

T = temperature (degrees C) of air sampled

298 = standard room temperature (degrees K)

or

$$\text{concentration (ppm)} = \frac{\text{mg/cu m} \times 0.815 \ (T + 273)}{P}$$

X. APPENDIX III

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or

competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "100 ppm LC50 rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity,

or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flashpoint and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50, if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

> Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.
>
> Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

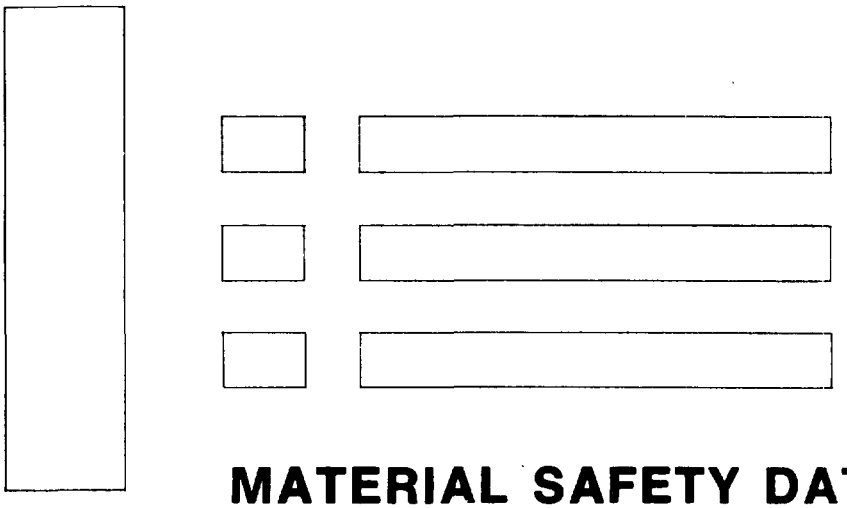
(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.



MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION	
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.
ADDRESS	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA			
BOILING POINT, 760 MM HG		MELTING POINT	
SPECIFIC GRAVITY (H_2O=1)		VAPOR PRESSURE	
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % BY WT	
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)	
APPEARANCE AND ODOR			

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE	

FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER	

EXTINGUISHING MEDIA	
SPECIAL FIRE FIGHTING PROCEDURES	
UNUSUAL FIRE AND EXPLOSION HAZARD	

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA

ROUTES OF EXPOSURE

INHALATION

SKIN CONTACT

SKIN ABSORPTION

EYE CONTACT

INGESTION

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

EYES

SKIN

INHALATION

INGESTION

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

OTHER HANDLING AND
STORAGE REQUIREMENTS

PREPARED BY

ADDRESS

DATE

XI. TABLES AND FIGURE

TABLE XI-1

CHEMICAL AND PHYSICAL PROPERTIES OF ALLYL CHLORIDE

Synonyms	3-chloropropene; 3-chloro,1-propene; chlorallylene; 1-chloro, 2-propene; 3-chloropropylene
Chemical formula	CH2CHCH2Cl
Molecular weight	76.53
Specific gravity (20/4 C)	0.938
Vapor density (air = 1)	2.64
Freezing point	-136.4 C
Boiling point	45.0 C
Flammable limits (% in air)	3.3-11.2
Vapor pressure (mmHg) at 25 C	368
Flashpoint (open cup)	-28.9 C
Solubility (in water) at 20 C	0.30 g/100 g
Conversion factors (760 mmHg and 25 C)	1 ppm = 3.13 mg/cu m 1 mg/cu m = 0.32 ppm

Adapted from references 1, 22, and 54

TABLE XI-2

OCCUPATIONS WITH POTENTIAL ALLYL CHLORIDE EXPOSURE

Allyl chloride manufacturers
Epichlorohydrin synthesizers
Glycerol synthesizers
DADM (diallyldimethyl ammonium chloride) synthesizers
Allyl alcohol producers
Medicinal product producers

Adapted from reference 4

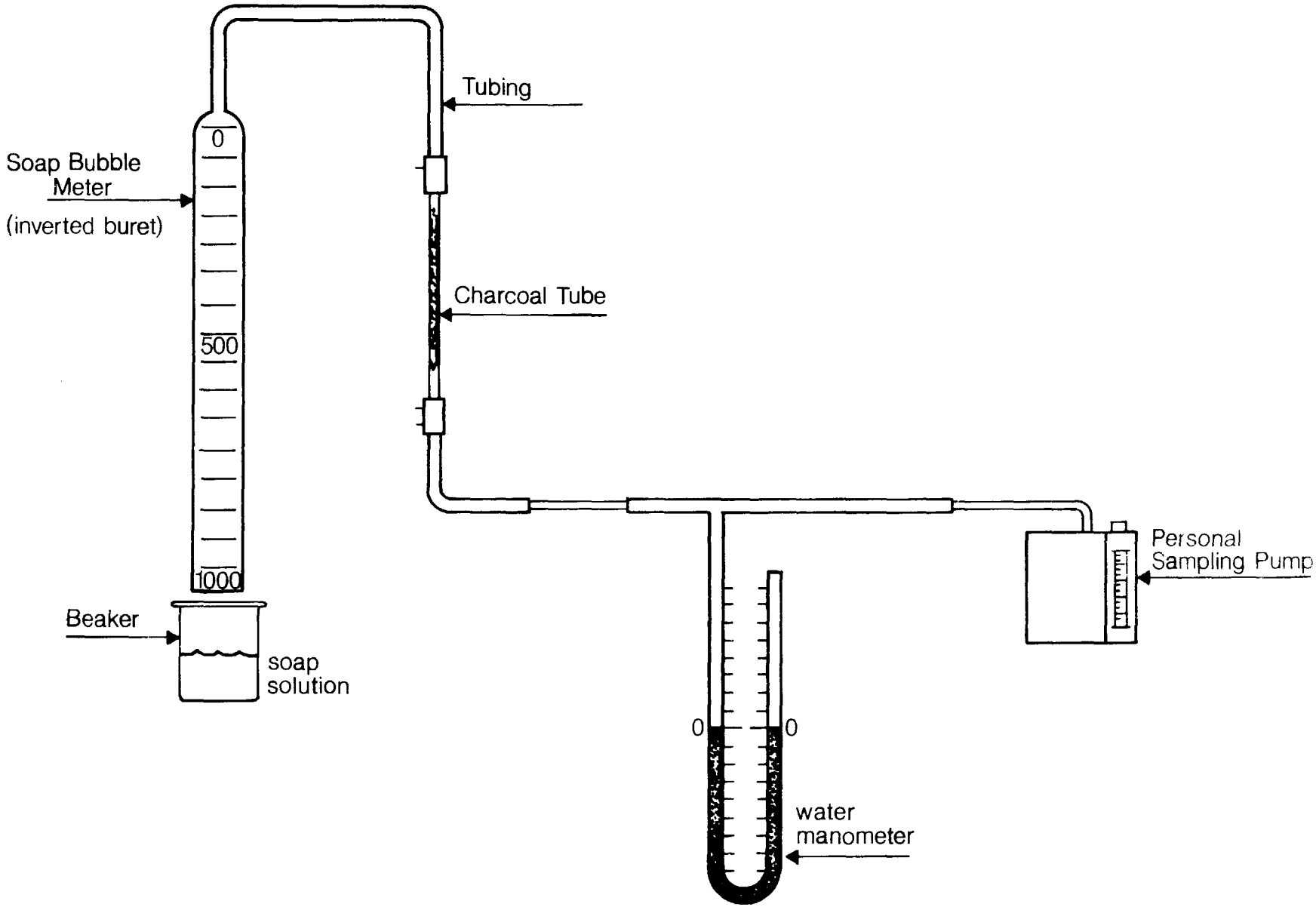


FIGURE X-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH CHARCOAL TUBE

☆ U.S. GOVERNMENT PRINTING OFFICE: 1977—757-057/5725

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HEW Publication No. (NIOSH) 76-204