EXTENT-OF-EXPOSURE SURVEY OF METHYL CHLORIDE

Joel M. Cohen
Robert Dawson
Masao Koketsu

SRI International
Menlo Park, CA 94025

Contract No. 210-76-0158

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations, and Field Studies
Cincinnati, Ohio 45226

September 1980

DISCLAIMER

NIOSH Project Officer: Michael S. Crandall
SRI International Project Leader: Masao Koketsu

DHHS (NIOSH) Publication No. 80-134

PREFACE

NIOSH has been granted the authority and responsibility under the "Occupational Safety and Health Act of 1970" to conduct field research studies in industry, evaluate findings, and report on these findings. Section 20(a)7 of this Act states the NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in aging adults. Section 22(e) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. For this purpose NIOSH established a contractual agreement with SRI International to perform an extent-of-exposure study of methyl chloride. The funding for this work was provided by the Division of Cancer Cause and Prevention, National Cancer Institute, through the Interagency Agreement on Research on Occupational Carcinogens (Y-01-CP-60605).

ABSTRACT

Following preliminary, walk-through, industrial hygiene surveys of U.S. plants in which methyl chloride is used, four facilities were selected for further surveying of human exposures to the chemical. Ninety-five full-shift personal samples for methyl chloride covering workers in 21 job classifications, and 28 area samples of 18 different sites at these four facilities were collected and analyzed. The findings were reported separately for the four plants. This report consolidates the findings for the individual plant surveys.

The report includes--in addition to background information on production and uses, toxicity and human exposure standards, and production processes--descriptions of operations and jobs, exposure control efforts, health and safety programs, air sampling data collected, summary tables of worker exposure levels to methyl chloride, sampling and analytical procedures and methods, evaluation of findings, and recommendations.

All of the time-weighted-average personal exposures for normal operations, ranging from <0.1 to 21.4 ppm, at the four facilities surveyed were below current permissible levels.

This report was submitted in partial fulfillment of Contract No. 210-76-0158 by SRI International under the sponsorship of the National Institute for Occupational Safety and Health.

CONTENTS

FIGURES

TABLES

INTRODUCTION

Under the terms of the authority and responsibility given to the National Institute for Occupational Safety and Health (NIOSH) to develop needed information regarding potentially toxic substances in industry (see Preface), NIOSH contracted with SRI International to conduct an industrial hygiene study of exposure to four chlorinated hydrocarbons. Chlorinated hydrocarbons were selected as an area for study because vinyl chloride has been shown to be a human carcinogen and because a growing number of the compounds have been shown by research to be known animal carcinogens and suspected human carcinogens. The four compounds selected for study--benzyl chloride, monochlorobenzene, methylene chloride, and methyl chloride--were chosen on the bases of: the industry in which the compound is produced or used; history of production and use; processes and related new materials involved; and numbers of workers potentially exposed. The report that follows concerns industry exposures to methyl chloride.

OBJECTIVES AND SCOPE OF THIS STUDY

The objectives of this industrial hygiene study were to:

- Review and summarize the toxic effects of methyl chloride.
- Document and describe selected workplaces, including information on the production and use of methyl chloride.
- Identify job types and describe specific jobs.
- Describe current industrial hygiene and safety practices, including engineering controls, work practices, administrative controls, and biological and environmental sampling and control procedures.
- Document (1) job-function exposures to methyl chloride and (2) relevant process or production changes occurring during the survey that could affect the evaluation of job-function exposures.
- Describe analytical procedures for collection and analysis of methyl chloride.

Detailed industrial hygiene surveys reflecting these objectives were made at four U.S. facilities where methyl chloride is used. These detailed surveys, all of which had been preceded by preliminary surveys, were conducted during the period December 1978 to June 1979.

LIMITATIONS OF STUDY

The industrial hygiene surveys represent singular evaluations of worker exposures to methyl chloride and do not reflect possible variations in exposure due to seasonal or operational changes. An attempt was made to evaluate exposures for each type as encountered during all work shifts. These studies were made during periods of normal production. The possibility of encountering a highly unusual exposure situation during a sampling period of several shifts was remote; therefore, the resulting exposure measurements can be considered to represent only those exposures that are associated with the usual and normal operating conditions.

BACKGROUND

Methyl chloride, also known as chloromethane and monochloromethane, at ordinary temperature and pressures, is a colorless gas with an ethereal nonirritant odor and a sweet taste. The chemical is handled commercially as a liquid. The chemical formula and some chemical and physical properties of the compound are given in Table 1.

Table 1. Chemical and physical data for methyl chloride

Synonyms: chloromethane, monochloromethane	
Chemical formula: CH_3Cl CAS No. 74-87-3 NCI-C 55629	
Some chemical and physical properties:	
Freezing point	-97.6°C
Boiling point (760 mm Hg)	-23.8°C
Specific gravity	
Liquid (20/40C)	0.920
Gas (0°C, air = 1)	1.74
Molecular weight	50.49
Vapor density (Air =1)	1.785
Diffusivity in air	
(25°C, Air = 1)	0.105 cm^2/sec
Critical temperature	143.1°C
Auto-ignition temperature	632°C
Flash point	below 0°C
Flammability limits (in air)	10.7 - 17.4%
Solubility (H_2O, 25°C)	0.48 g/100g

Sources: Compiled from Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 5. New York, Wiley-Interscience, 1979, P.678, and Manufacturing Chemists Association. Chemical Safety Data Sheet SD-40. Methyl Chloride. Washington, D.C, 1970.

PRODUCTION AND USES

The volume of methyl chloride produced in the United States in 1977 (latest year for which firm data are available) was approximately 216,000 metric tons (238,000 short tons). The chemical is used mainly in the production of silicone resins, tetramethyl lead (anti-knock agent in gasoline), and synthetic rubber, and as an extractant and refrigerant. Almost two-thirds of the methyl chloride consumed is in the production of silicone intermediates; about one-fifth is used in producing tetramethyl lead.[1] The chemical is used much less as a refrigerant (and as an aerosol propellant) than it once was. (The major source of methyl chloride intoxication was once due to leakage of refrigeration systems.)

TOXICITY AND HUMAN EXPOSURE STANDARDS AND EXPERIENCE

The current Occupational Safety and Health Administration (OSHA) standard for methyl chloride is 100 parts per million (ppm) as an eight-hour time-weighted average (TWA). The acceptable ceiling concentration for 15 minutes is 200 ppm, and the maximum acceptable peak concentration for five minutes in any three-hour period is 300 ppm.[2]

The American Conference of Governmental Industrial Hygienists (ACGIH) recommends threshold limit value (TLV) of 100 ppm for exposure to methyl chloride and a short-term exposure limit (STEL) of 125 ppm. (The STEL is a maximum concentration to which workers can be exposed continuously for a period of up to 15 minutes for no more than four times in any one work day.) The ACGIH has proposed that the TLV be lowered from its current recommendation of 100 ppm to 50 ppm.[3]

It was more than 20 years ago when methyl chloride was first implicated as a potentially toxic substance. At that time it was foumd that the compound produces harmful effects to the central nervous system with secondary injury to the kidney, liver, lungs, and cardiovascular system.[4]

Reported signs and symptoms of chronic exposure include weakness, drowsiness, staggering gait, thickness of the tongue, memory lapse, headache, dizziness, and blurred vision. Vomiting may also occur. These effects tend to begin several hours after exposure.[5,6] Acute exposures are much like the chronic. The primary route of entry into the body is by inhalation, but the substance can be absorbed percutaneously as well.[6,7]

A limited amount of mutagenic testing has been conducted on methyl chloride. In one experiment, methyl chloride was found to be highly mutagenic in Salmonella typhemurium using the Ames bacterial mutagenicity test.[8]

In 1976, NIOSH studied the behavioral and neurological effects of methyl chloride on 122 workers who had been occupationally exposed to the substance in fabricating procedures. The study showed no significant differences in the presence of abnormal neurological symptoms between experimental and control groups, although there were indications that exposure did adversely affect performance of cognitive time-sharing tasks and that it increased finger tremor.[9]

There are many difficulties in attempting to quantify air concentrations of methyl chloride that constitute a threat to human life. Much of the data reported in the literature are for cases where individuals have either died or experienced severe illness as a result of acute accidental exposure. In some situations, it is difficult to establish that the workers suffered from exposure to methyl chloride, because many of them reported symptoms that could be associated with exposure to other chemicals that may have been present.

In 1969, Dow Chemical Company conducted nine in-plant studies of methyl chloride manufacturing operations. Continuous monitoring devices were used for four months, and TWA exposures were determined for 54 job classifications. The range of concentrations was 5-78 ppm, with an average of 30 ppm. Peak concentrations were as high as 440 ppm. All of the study participants had routine physical examinations, and it was reported that no evidence of over-exposure to methyl chloride was found. (Personal communication: T.R. Torkelson, Dow Chemical Co. and D. Constine, SRI International, 1977.)

The ACGIH reports another study of worker exposure to methyl chloride. In this case, methyl chloride was used as a blowing agent in the manufacture of polystyrene foam, and the substance was released to the air during fabrication operations such as sawing, hot-wire cutting, drilling, and routing. The exposure experience is summarized as follows:[10]

- Exposure to methyl chloride associated with reported illness--nine plant surveys with a range of average exposures of 195-475 ppm.
- Exposure to methyl chloride <u>not</u> associated with reported illness--141 plant surveys with a range of average exposures of 15-195 ppm.

PROCESSES FOR PRODUCING METHYL CHLORIDE

Methyl chloride can be produced from the chlorination of methane through thermal, catalytic, or photochemical activation and by the hydrochlorination of methyl alcohol in the presence of a catalyst.[11] The latter process is the most widely used, and it is the process used at all four plants surveyed in this study. (Recently, processes for noncatalytic liquid-phase reactions of methanol with hydrogen chloride have been patented.[1])

In the process of producing methyl chloride by hydrochlorination of methyl alcohol, the methyl alcohol is combined with hydrogen chloride and a catalyst such as zinc chloride. Impurities in the reaction product that result are then removed to meet specifications desired for the final product. The basic reaction is as follows:

$$CH_3OH + HCl \xrightarrow{ZnCl_2} CH_3Cl + H_2O$$

Also present in the output of the reaction is unreacted methyl alcohol (which can be recovered and recycled) and unreacted hydrogen chloride, together with other impurities such as dimethyl ether. These byproducts (together with water) are removed--using such compounds as caustic and sulfuric acid--in refining, compression, and condensation stages which also liquify the methyl chloride vapors. The liquid methyl chloride is then pumped to storage. A simplified diagram of the basic process for producing methyl chloride by hydrochlorination of methyl alcohol is shown as Figure 1.

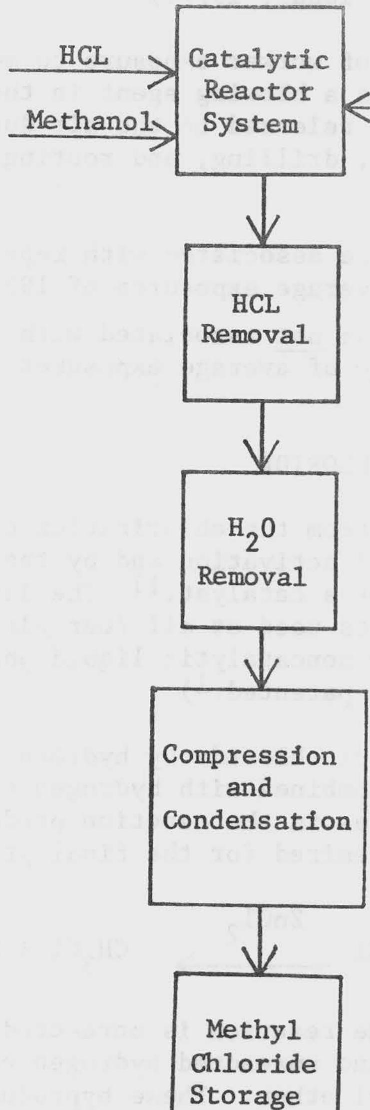

Figure 1. A diagram of the process for producing methyl chloride by hydrochlorination.

FACILITIES AND PERSONNEL SURVEYED

Four facilities at which methyl chloride is produced and used were surveyed for this report. In an attempt to provide as much of an exposure cross-section as possible, the plants were selected on the basis of such criteria as: number of persons potentially exposed; number of years involvement with the substance; level of substance concentrations as determined by preliminary area sampling; continuous operations and therefore relatively constant exposure levels; exposure situations limited primarily to the target chemical; unique use of the substance; and process representative of a major use of the substance.

The facilities are designated as Plants A, B, C, and D in this report. The plants are briefly described below, followed by description of their process and control operations, personnel and jobs in which potential exposure to methyl choride occurs, and health and safety programs that have been established.

DESCRIPTION OF FACILITIES

Following are brief overviews of the four facilities at which in-depth exposure surveys were made for purposes of this report.

Plant A--Overview

Plant A is on the site of a large, multi-chemical production facility located in an industrial area of the East. Production of methyl chloride at the Plant began in 1972. Use of the chemical began in 1959, however, in the formulation of tetramethyl lead (TML), and methyl chloride for this use was purchased from other suppliers until the Plant's own production facility became operational. Areas where the chemical may be encountered are at this production facility, at the TML production facility, and at a methyl- chloride-recovery facility that adjoins the TLM production area. The recovery facility was not surveyed for this study, since the operation is highly automated and no workers are regularly assigned to it.

Plant B--Overview

Plant B is a major producer of methyl chlorine occupying approximately one acre of land on the operating company's chemical complex in the South. Production of the chemical began in 1961, and the Plant's capacity has increased five times since then.

Plant C--Overview

Methyl chloride is both produced and used at Plant C, which is located on a multi-chemical production site in the Midwest. The chemical is used at the Plant for the production of methyl chlorosilanes and as a direct-contact-refrigerant--which latter use was not included in this survey. All methyl chloride used prior to the construction of the facility in 1952 was purchased (some is still purchased).

Plant D--Overview

At Plant D, which is located at a large, Midwest chemical-producing and -using facility, methyl chloride is used as a blowing agent in the production of polystyrene foam. Foam has been produced at the plant since 1949. The Plant D site covers an area of 2 acres at the chemical facility.

PROCESS AND CONTROL OPERATIONS

A general description of the basic process for producing methyl chloride by hydrochlorination of methyl alcohol, the process used at all four of the plants surveyed for this study, is given in the preceding chapter ("Background").

Plant A--Process and Control

The methyl chloride production facility at Plant A is housed in a four-floor enclosed building. The production building is equipped with an exhaust ventilation system that is designed to reduce worker exposures to potentially hazardous airborne substances. Ventilation throughout the facility appeared to be adequate for normal operating conditions. A room on the first floor, in which the control operator for the process spends the majority of his work shift, is air-conditioned.

The facility for manufacturing tetramethyl lead is in a six-floor enclosed building. In the TML production process, methyl chloride, flaked sodium lead alloy, and aluminum chloride (a catalyst) are introduced to a batch-operated reactor, or autoclave (there are 16 of them). The addition of methyl chloride is a fully automatic process and is performed with the reactor completely sealed. When the reaction is complete, excess methyl chloride is vented to a recovery system, and the reaction mass is dropped to a still, where the TML product is recovered by steam distillation. Residual aqueous sludge is emptied into a pit for eventual recovery of the excess lead it contains. A diagram of the TML production process is shown in Figure 2.

A system has been installed for capturing and removing methyl chloride vapors from the reactors. This system utilizes automatically controlled pressure to vent the vapors to a recovery unit (in a separate building), where they are liquified and where low-boiling impurities are removed (and vented to the atmosphere through a flame arrestor). The methyl chloride is pumped to storage tanks for reuse in the TML process.

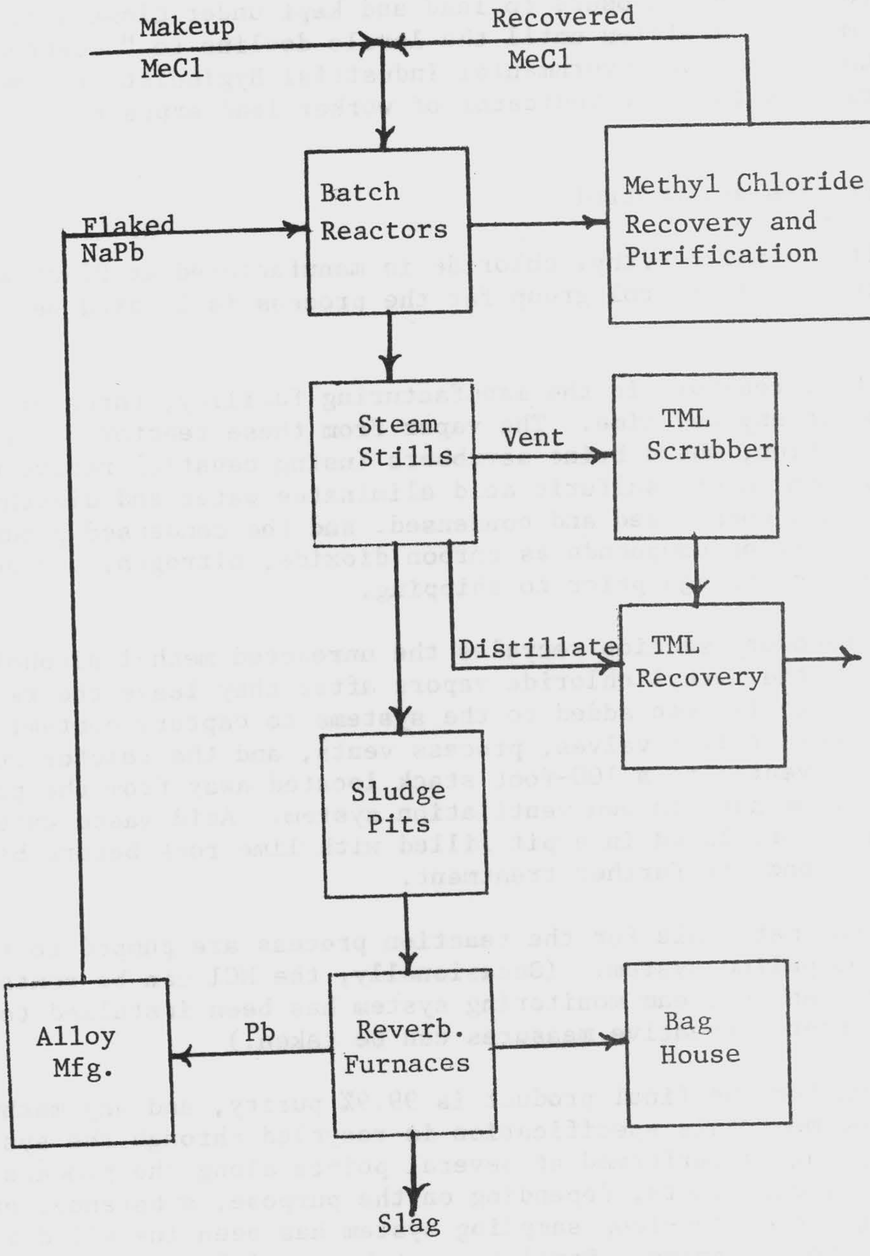

Figure 2. A diagram of the process for producing tetramethyl lead at Plant A.

Environmental sampling for the presence of methyl chloride in the production