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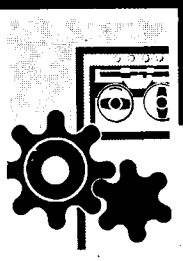

TECHNICAL REPORT

Extent of Exposure Survey of Benzyl Chloride

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

EXTENT OF EXPOSURE SURVEY OF BENZYL CHLORIDE

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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
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ABSTRACT

The National Institute for Occupational Safety and Health (NIOSH), under PL 91-596 is responsible for criteria development and epidemiological research of occupational exposures to toxic materials or harmful physical agents. Thus, NIOSH has sponsored SRI International to investigate occupational exposure to benzyl chloride. A suitable worker population could not be located for use in a retrospective mortality study, so a limited, cross-sectional extent of exposure survey was conducted to document the current exposure pattern of benzyl chloride production and use.

The purpose of this report is to summarize the industrial hygiene surveys of two chemical plants in the eastern United States. The major emphasis of these studies was to determine the extent of worker exposure to benzyl chloride. The report describes the workplace, job type, and industrial practices involved in the production and use of benzyl chloride, sampling procedures used, and a summary of sampling results and conclusions that can be drawn from the surveys.

Results of all but one of the 60 full-shift personal monitoring samples taken were in the range of .01-.14 ppm. Short-term personal monitoring samples taken in the benzyl chloride manufacturing facility and during drum loading procedures ranged from .02 - .27 ppm.

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.

INTRODUCTION

The Williams-Steiger "Occupational Safety and Health Act of 1970" (P1 91-596) was passed into law "to assure safe and healthful working conditions for working men and women...." The act established the National Institute for Occupational Safety and Health (NIOSH) in the U.S. Department of Health, Education, and Welfare. NIOSH has been given the authority and responsibility under the act to conduct field research studies in industry and develop needed information regarding potentially toxic substances or harmful physical agents. Section 20(a)(7) states that 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.

NIOSH has selected chlorinated hydrocarbons for study because vinyl chloride has been shown to be a human carcinogen and because current research indicates that a growing number of these compounds are known animal carcinogens and suspected human carcinogens. Based on their toxicity or possible carcinogenicity, the industry in which the compound is used or produced, the history of their production and use, the process and related raw materials involved, and the number of workers potentially exposed, the list of potential carcinogens might also include benzyl chloride, monochlorobenzene, methylene chloride, and methyl chloride. Epidemiologic investigation on these compounds will be helpful in resolving the question of whether the agents are carcinogenic in humans. This study, "Extent of Exposure Survey on Benzyl Chloride," which focuses on benzyl chloride, was conducted by SRI International under contract to NIOSH to investigate one of the agents identified in the "Industrial Hygiene Assessment of Selected Chlorinated Hydrocarbons" (Contract No. 210-76-0158). However, a suitable study population of benzyl chloride workers does not currently exist (as determined during walk-through surveys). Therefore, a limited cross-sectional extent of exposure survey was conducted to document exposure resulting from production and use of benzyl chloride.

The objectives of this study were to:

- Review and summarize the toxicological effects of benzyl chloride.
- Document and describe selected workplaces, including information on the production and use of benzyl chloride.
- Identify job types and describe specific jobs.
- Describe current industrial hygiene and safety practices.

- Document work exposures to benzyl chloride and document relevant process or production changes occurring during the survey that may affect the evaluation of job function exposures. Company sampling results are included for Plant A.
- Describe sampling and analytical recovery studies of benzyl chloride and toluene-contaminated air.

Industrial hygiene walk-through surveys were conducted at five plants during the week of October 4, 1976 to assess the feasibility of an epidemiological investigation. It was determined during these visits that measurable amounts of airborne benzyl chloride were present in the in-plant atmospheres. Work practices and general plant information were investigated. Furthermore, detailed industrial hygiene surveys to quantify worker exposures to benzyl chloride were conducted in two of the plants during the week of February 13, 1977.

BACKGROUND

Benzyl chloride is produced commercially by the photo-chlorination of toluene. Ninety-five million pounds of benzyl chloride were reported to have been produced in the United States during 1975.[1] Usually benzyl chloride is produced and used as a chemical intermediate within the same manufacturing facility. It is reported that 65-70% of the benzyl chloride productuion is used to manufacture butyl benzyl phthalate, 20-25% to produce benzyl alcohol and benzyl dimethyl alkyl ammonium, and 5-15% to produce other organic compounds, including pharmaceuticals, dyes, leather tanning, perfumes, and photography.[2] This study focuses on occupational exposures resulting from benzyl chloride production and use in the production of butyl benzyl phthalate, benzyl alcohol, and benzyl cyanide.

Benzyl chloride has been demonstrated to be an extreme lacrimator (an irritant to the eyes, nose and throat), and capable of causing lung edema.[3] It is believed that benzyl chloride, like other chlorinated hydrocarbons, is metabolized chiefly in the liver, thus causing liver and kidney damage in high concentrations. In addition, severe corneal damage with permanent disability has been caused by benzyl chloride liquid contacting the eye. Typical signs and symptoms from benzyl chloride exposure are irritation of the eyes and respiratory tract. Weakness, headaches, irritability, insomnia, anorexia, and finger tremors may also occur.[4] The Threshold Limit Value of 1 ppm for benzyl chloride has been established because of its irritating effect to the eyes.[5]

In a test for mutagenicity, it was shown that benzyl chloride was slightly mutagenic when applied directly onto an open plate with strain TA100 of Salmonella typhimurium. However, when the test was repeated in a desiccator that would retain the benzyl chloride vapor, it was reported that benzyl chloride was highly mutagenic.[6,7] It has also been shown that benzyl chloride is a primary carcinogen in rats, causing sarcomas at the point of subcutaneous injections, although no excessive tumors were reported from intraperitoneal injections of mice.[8,9] Although benzyl chloride is included in the suspected carcinogen list, there are no references involving humans.[10]

DESCRIPTION OF PLANTS SURVEYED

PLANT A

This facility contains a continuously operating benzyl chloride manufacturing unit. In another area of the plant, benzyl chloride is used as raw material to produce butyl benzyl phthalate on a continuous basis. Both of these operations were investigated. However, a batch unit operation uses benzyl chloride to produce a special solvent was not surveyed because it was not using benzyl chloride at the time of the visit.

The facilities that manufacture benzyl chloride and benzyl phthalate were constructed in 1961 as one unit. This single building is a relatively open structure, four stories in height. Potential worker exposures to benzyl chloride or other hazardous substances are kept to a minimum with this type of building design. The published total capacity of benzyl chloride production for the manufacturing unit is 75 million pounds per year. It was estimated by company officials that the normal operation yield is somewhat higher than the published capacity. Production rates during the time of the survey were reported to be at normal capacity.

Process and Control Operations

Plant A produces benzyl chloride by the continuous photo-chlorination of toluene. Toluene and chlorine are pumped to the manufacturing area from storage tanks and rail cars, respectively. Chlorine is vaporized at the manufacturing site and fed to a series of chlorinators where it is reacted with toluene to produce crude benzyl chloride. The output of the chlorinators, which contain quantities of unreacted toluene and benzal chloride (also known as benzyl dichloride, $C_6H_5CHCl_2$), along with the crude benzyl chloride, is pumped to the toluene stripper. Here the unreacted toluene is removed and recycled back to the chlorinators. Hydrogen chloride, a by-product of the benzyl chloride manufacturing process, is removed from the crude product and pumped to a storage tank. From the stripper column, the crude benzyl chloride is pumped to the two refining columns where the product is further separated from the reaction residue. The residue is pumped to a storage tank for final disposal. The refined benzyl chloride is cooled and pumped to either the benzyl phthalate use area, or to one of several storage tanks. A block diagram of the benzyl chloride production process is shown in Figure 1.

The benzyl phthalate area is a continuously operating facility that receives the needed benzyl chloride either directly from the benzyl chloride manufacturing area or from one of the benzyl chloride storage

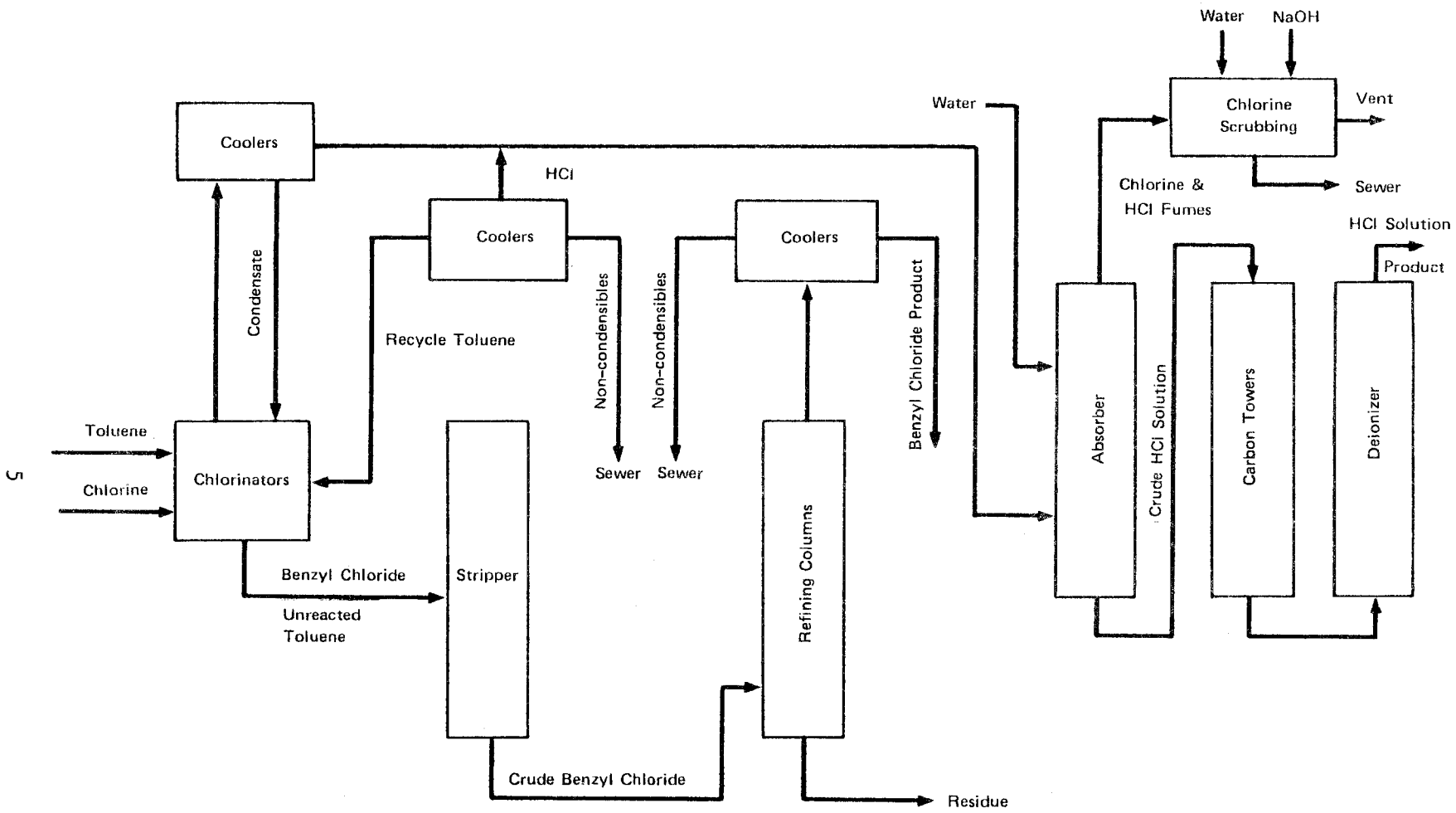

Figure 1. Benzyl Chloride Production Process Block Diagram — Plant A

tanks. Benzyl chloride is charged with other chemicals (disodium phthalate*) in a series of reactors to produce benzyl phthalate. An insignificant quantity of benzyl chloride is present in the final product.

Drumming is normally conducted during the day shift. A worker first prepares the area for drumming by feeding benzyl chloride to a storage tank located on the roof of the shipping building. After a proper amount of benzyl chloride has been pumped to the tanks, an inhibitor (propylene oxide) is added. The line is then flushed with nitrogen to ensure that all of the inhibitor has entered the tank. The benzyl chloride/inhibitor mixture is mechanically mixed in the storage tank for about 30 minutes. A sample of the finished product is collected and taken to the laboratory for quality analysis. Once the laboratory approves the product, drumming can begin.

Benzyl chloride drumming is performed near the center of a one-floor enclosed structure, with full-width doors on each side of the complex. A worker places a pallet of empty drums (four drums) upon a scale and inserts the feed hose from the benzyl chloride storage tank (located on the roof) into one of the drum bung openings.

A four-inch diameter, flexible point-of-source type exhaust hose is then placed next to the drum filling point. Using a Velometer, the survey team measured the inlet velocity of the exhaust system to be greater than 800 feet of air per minute. The exhaust system is connected to a four-inch diameter stack that rises about eight feet above the top of the building. The worker maintains the benzyl chloride fluid flow until the drum reaches full weight. The feed hose is then turned off and the hose is removed from the drum opening. Good control of benzyl chloride vapors was achieved with this type of system.

Personnel

The plant employs about 170 non-union workers, approximately 100 of whom are hourly employees. The plant is in operation seven days a week on a rotating shift schedule, i.e., three shifts per day on four-week cycles, averaging 46 hours per week. The work force is supplemented by contract labor who in general are not assigned to one fixed work area, but may work in any number of areas, including production facilities. These workers assist in the maintenance of the building and are not involved with the production equipment.

A total of 20 employees work within the three benzyl chloride areas. The manufacturing area and benzyl phthalate use area employ the following types of workers each shift:

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*Plant A did not specify which chemical is used, but the Merck Index (p. 151, 4th edition, 1976) indicates that disodium phthalate is typically the reactant in this process.

- One chief operator.
- One benzyl chloride manufacturing operator.
- One crude plasticizer operator.
- One refining plasticizer operator.
- One second-level supervisor (day shift).
- Two first-level supervisors (day shift).
- Material-handling operator (day shift).

The chief operator remains in the control room, an enclosed area in the manufacturing and use area, for the greater part of the shift. This worker functions as manager of the manufacturing and use area. He routinely checks the control board and oversees the work of the three operators. The chief operator may go into the work areas if an operator needs assistance or a problem exists that cannot be resolved by an operator alone. The average exposure duration for this worker is less than one hour per shift.

The three operators who work in the manufacturing and use facility perform essentially the same tasks. They obtain quality control samples at various times during the shift and hand carry them to the laboratory for analysis. The sample locations and frequency of sampling are shown in Table 1. These operators also read the process control meters (flow, pH, etc.) and make adjustments in those processes if necessary. The operators will respond to making changes in the operation if deemed necessary by the chief operator. It is also the responsibility of the operator to solve any problem that may develop. If needed, the operator may call upon the chief operator or maintenance personnel for assistance. Under extreme conditions when a severe problem exists, the operator may shut down the operation completely. The average exposure duration to benzyl chloride for each of these workers is about four hours per shift.

The material handling operator is assigned several tasks during the workday, including the drumming of benzyl chloride for shipment. This worker's exposure to benzyl chloride is limited to the drumming operation that may be required for a complete shift if orders demand. While the survey team was visiting the plant, drumming was being performed about six hours a day.

A worker involved in the tank truck loading of benzyl chloride was also included in the survey. Although tank truck loading requires about two hours to complete, potential exposure to benzyl chloride is limited to the time required for taking quality control samples and the initial equipment setup, i.e., about one half hour.

Medical and Safety Programs

Plant A has extensive medical and safety programs. Pre-employment and annual physicals are required of all workers.[10] Biological testing

Table 1. Quality control sampling points in the benzyl chloride manufacture area, Plant A

Sampling Point	Number of Samples (per shift)
Toluene dryer after filter	1
Finished goods, benzyl chloride north column	2 per day
Finished goods, benzyl chloride south column	2 per day
Chlorination mass	1
Crude feed to refining column	1
Refining column residue--north tank	1
Refining column residue--south tank	1
Residue tank	1
Benzyl chloride storage tank	1 per day

including blood and urine analysis is performed under contract with a special medical service. This service administers all required tests from a mobile van brought onto the plant property. In addition, two men working on each shift are trained in first aid. Smoking is permitted only in designated areas.

Plant A requires that each employee wear company supplied work clothing and safety shoes, glasses, and hats. During tank truck loading, quality control sampling, and drumming, additional personal protection equipment, such as goggles or face shields and rubber gloves, aprons and overshoes, are supplied. Respirators are available for potential high risk exposures, such as during system breakdown. Respirators used will vary in type, depending on the risk, from a NIOSH-approved cartridge type to Scott Air Pacs®. Emergency showers are provided throughout the plant site. This equipment is inspected by an operator once each shift.

PLANT B

Plant B manufacturers benzyl chloride for use as an intermediate in the production of benzyl alcohol on a semi-continuous basis. Another area uses benzyl chloride in a batch operated benzyl cyanide process. All three facilities were surveyed during this visit.

The facility that manufacturers benzyl chloride operates on a part batch, part continuous basis. The manufacturing of benzyl chloride began in 1934 and has been operating to date without major interruptions. Production was reported to be at capacity during the time of the survey.

Process and Control Operations

The manufacture of benzyl chloride is conducted in two buildings. Chlorine and toluene are fed by pipe to the first building, a four-flour enclosed structure, from a tank car and storage tank, respectively. Chlorine is vaporized at the first building and fed to a number of continuously operating chlorinators. Here the chlorine is reacted with toluene to produce the crude product. The output of the last chlorinator also contains quantities of unreacted toluene and benzal chloride. This product is transferred by pipe to the continuously operating toluene stripper located in the second building. The second building is a four-floor, relatively open structure located a short distance away from the chlorinators. The building design limits worker exposures to benzyl chloride or any other potentially hazardous substances that may be present in the in-plant air. The stripper removes, cools, and recycles the toluene back to the storage tanks. The benzyl chloride is then further separated from the process residue and piped to one of two batch feed refining columns. The columns work in tandem and are switched or recharged about once every forty hours. The switching of the refining columns requires approximately three to four hours to complete and can occur up to twice a day. The refining unit further separates the benzyl chloride from the process residue. At this point only small quantities of toluene are present in the product. From the refining columns the benzyl chloride is piped to one of two 15,000-gallon storage tanks where the chemical is either transferred to one of the use areas or is packaged in drums and tank trucks for sale. An additional 25,000-gallon storage tank for benzyl chloride is located near the two main storage tanks. The entire system is a relatively closed operation except during the quality control sampling.

Benzyl chloride is used in the first use area for the manufacture of benzyl alcohol. This process, which is located in an enclosed structure, combines benzyl chloride with a soda ash solvent in a continuously operating reactor. The material is refluxed for several hours, then transferred to a separator that removes the process residue and dibenzyl ether from the crude benzyl alcohol. The benzyl alcohol is stored in its crude state until needed by the batch feed refining unit. The refining process reduces the benzyl chloride present in the benzyl alcohol to less than 0.1%. The refined product is transferred by pipe to the shipping area for packaging.

Benzyl cyanide is manufactured in the second area that uses benzyl chloride. This facility is located in an enclosed structure and operates on a batch basis. The process combines sodium cyanide, aqueous methanol, and benzyl chloride in a reactor for approximately 12 hours of refluxing. Methanol is removed by distillation and water is added to the balance. A brine is formed along with the crude benzyl cyanide. The crude product is piped to a refining unit that further separates the noncombustible bottoms from the 99+% pure benzyl cyanide.

Drumming and tank car loading of benzyl chloride are performed by one worker on the day shift. Drumming is conducted at one end of the ground floor of an open structure. The employee places an empty drum on a scale and adds an inhibitor to extend the shelf life of the product. The worker then inserts the feed hose into the bung opening. The worker places a flexible point-of-source exhaust hose next to the drum opening. The exhaust system draws the benzyl chloride vapors away from the worker to a stack located on the opposite side of the room that rises above the building. The worker releases the benzyl chloride fluid flow until the drum reaches full weight. The feed hose is turned off and the hose is removed from the drum opening. Due to the exhaust system and the building design (relatively open), exposures to potentially hazardous substances are kept to a minimum.

Personnel

The total plant employs about 150 persons of whom 28 are in maintenance, 46 are operators, 55 are administrators and managers, and approximately 20 are technical persons (e.g., quality control chemists, technicians). Low employee turnover and absenteeism were reported by plant management. The plant is in operation seven days a week on a rotating shift schedule, i.e., three shifts in two-week cycles.

A total of 15 employees work within the three benzyl chloride areas. The manufacturing and use areas each employ the following types of workers:

- One chief benzyl chloride operator (day shift).
- One benzyl chloride operator.
- One benzyl chloride drumming operator (day shift).
- One benzyl alcohol operator.
- One chief benzyl cyanide operator (day shift).*
- One benzyl cyanide distillation operator.
- One benzyl cyanide reaction operator.
- Two maintenance workers (day shift).

In the benzyl chloride manufacturing facility, a chief operator is present only during the day shift. During the first three hours of his shift, the chief operator assists in changing the distillation columns. The balance of the shift is spent transferring the refined benzyl

*During the survey there were four benzyl cyanide operators working the day shift.

chloride from the receiver to either the storage facility or to one of the two use areas. The chief operator spends most of this time working in the process area making routine process adjustments and quality control sampling, but his greatest potential for exposure to benzyl chloride is limited to those times quality control samples are taken (see Table 2). Personal sampling results indicate that the 6-hour time-weighted average (TWA) exposure to benzyl chloride is 0.07 ppm with short-term exposures up to 0.27 ppm during quality control sampling for workers not using respiratory protection.

The operators who work in the manufacturing facility perform essentially the same tasks:

- They assist the chief operator in the first part of the shift when changing of the distillation columns is performed.
- They make routine adjustments on process flows and temperatures.
- They perform quality control sampling.
- They respond to any problems that may occur during this shift.

The average exposure duration to benzyl chloride for each of these workers is at least half the work shift.

The drumming and tank truck loading of benzyl chloride are performed by one worker on the day shift. Drumming is performed nearly every day, averaging one-half of this worker's workday. Tank truck loading requires about two hours per truck. The exposure to the worker does not extend throughout this two-hour period. The exact exposure duration was not determined since this operation was not performed during the time of the survey.

The benzyl alcohol use area employs one operator each shift. It is the responsibility of these operators to combine the needed materials in the reactor and take quality control samples of the crude benzyl alcohol, soda ash, and line samples to and from this reactor. These workers make all process adjustments and routinely check the process area. The sampling results indicate that a TWA exposure duration to benzyl chloride for these workers is 0.02 ppm.

The benzyl cyanide use area employs one chief operator and two operators on the day shift and two operators on the evening and night shifts. The chief operator is responsible for assigning tasks to the two operators as well as other line management type duties. He takes three quality control samples of the benzyl cyanide finished product each day. The chief operator performs the drumming and tank truck loading. Drumming is performed only when there are orders demanding them; these occur on the average about four to five times per month and require less than two hours of the chief operator's time. Tank trucks are loaded two to three times per week, averaging three hours to complete. It is the

Table 2. Quality control sampling points in the benzyl chloride manufacture and use areas, Plant B.

Sampling Points	Number of samples (per day)
Benzyl Chloride Manufacturing	
Chlorinator	2 (per shift = 3 samples)
First cut on distillation	1
Tech cut (at receiver)	1
Line sample	1
Toluene stripper	1
Crude product from chlorinator	1
Benzyl Alcohol Manufacturing	
Crude product	1 (per shift)
Finished product	1 (per shift)
Benzyl Cyanide Manufacturing	
Crude product	1
Finished product	3

chief operator's job to change the process filters, a task performed about three times per week.

The benzyl cyanide operators are responsible for charging the reactors with the needed raw materials. They make all process adjustments and check the reaction temperatures. The operators control the output of the reaction vessel, sending the crude product to a holding tank and the process residue to an area for disposal. Every morning one operator cleans the charging stills by blowing out the lines with compressed air.

Medical and Safety Programs

Pre-employment and annual physicals have been required for all employees for the past four years. These physicals include blood and urine analysis, chest x-ray, and audiogram. The plant physician, who is not located on the plant site, reviews these records. The plant has at least one person per shift qualified in first-aid. Other medical assistance is available from nearby city-owned facilities. A formalized safety program exists and is administered by two workers.

Plant B requires that each employee wear safety shoes, hardhat, and safety glasses. Rubber aprons, overshoes, goggles and gloves are required in all drumming operations. During the addition of sodium cyanide to the benzyl cyanide process, a NIOSH-approved mechanical filter respirator is worn.

SAMPLING AND ANALYTICAL PROCEDURES

Personal and area environmental air samples of benzyl chloride manufacturing and use were taken during the course of the surveys. Personal sampling employed monitoring pumps which were attached to the belts of the workers. Tygon tubing connected the pump to the sampling medium. Charcoal tubes were used as the collecting medium. The sample layer of the tube contained 100 mg of charcoal that was separated from the 50 mg backup charcoal layer by a 3 mm portion of urethane foam separator of uniform and exact porosity. A plug of silylated glass wool was placed in front of the absorbing section. The pressure drop across the tube was about two inches of water at the 200 ml/min flow rate. (See Appendix A, Section 6.2 for a detailed description of the sampling apparatus.)

The sampling pumps were used to draw air through charcoal tubes at a nominal rate of 200 ml/minute. The calibration of the pump was performed with a bubblemeter (buret set in an inverted position) using a charcoal tube assembly in line between the pump and buret. The pumps were adjusted for 200 ml/min by checking the time required for the soap bubble to traverse the distance from the 0 to 200 mark on the buret.

Flow calibrations in the field were made using a precision rotameter that was calibrated using the soap film (primary standard) measurement technique as described above. A batch representative charcoal tube was used to adjust and read the flow rates. As the humidity and level of contaminants were not significant, it can be assumed that no change in resistance resulted. The precision rotameter was used to check the flow rates before and after each pump was used. These readings were then noted. The flow rates were validated with the soap bubble technique after returning to the laboratory. The average flow (average of starting and final flow) for the total sampling period was used in calculating exposure concentrations.

Both personal and general area sampling for presence of benzyl chloride was performed. Personal sampling was conducted on workers during their total working shift; thus, TWA exposure for each job was calculated. This calculation is necessary under the Occupational Safety and Health Administration (OSHA) standards, which are based on an eight-hour TWA basis. The TWAs (as parts of benzyl chloride vapor per million parts of air) were calculated as follows:

$$\text{TWA (ppm)} = \frac{24.450 \times \text{mg per liter}}{\text{MW}}$$

where

MW = molecular weight (benzyl chloride = 126.58)

mg per liter = mg of benzyl chloride in one liter of air sample collected.[11]

The calculated concentrations of benzyl chloride were not corrected for temperature and pressure because these corrections were considered to be insignificant. Each job type was sampled separately. When a task was to be performed that would expose the worker to a potentially high concentration of benzyl chloride (e.g., quality control sampling), an additional sample was taken for the full length of time of the task so that ceiling concentrations would be determined.

The analysis of the samples for total benzyl chloride concentration was accomplished using the NIOSH-approved analytical technique, Method S115* (see Appendix A). Once the samples have been collected, the technique requires the desorption of charcoal using carbon disulfide. Desorption was done for 30 minutes. Next, a portion of the sample was injected into a gas-liquid chromatograph (GLC) with a flame ionization detector (FID). The area under the sample peak was measured and integrated. The preliminary results were read directly from a standard curve that was prepared earlier from injection of known quantities of benzyl chloride. Each section of the charcoal tube (i.e., front and back sections) was analyzed separately.

Recovery tests were performed using charcoal tubes from the same batch as those used on the field visit. Both liquid and vapor phase spiking (adding of known quantities) were performed. The standard NIOSH-approved analytical technique* used with tubes spiked with either benzyl chloride or a mixture of benzyl chloride and toluene or hexane in both the liquid and vapor phase. Toluene is used in the benzyl chloride production process and was shown from an earlier survey to be a contaminant likely to be present in the employee's breathing zone.

The results of this study indicated good precision and accuracy (no samples outside of ±25% if a sample that was apparently not spiked is ignored) in the collection and analysis of benzyl chloride alone, or in combination with toluene from either the liquid or vapor phase. The average desorption efficiency for benzyl chloride was 0.96 ±.01 (for 18 samples) in the presence of toluene. As shown in Table 3, average recovery was 106% for benzyl chloride and 103% for toluene from six samples spiked from the vapor phase. The coefficient of variation for the analysis of benzyl chloride at a level of 66μg/tube was 5.9%. This level was approximately three times the concentration of benzyl chloride found in air samples obtained at both plants' manufacturing facilities. (Complete results obtained from the spiking experiment are shown in Appendix B.)

*Method No. S115 was previously validated 4/11/75 under a NIOSH contract in the range 2-8 mg/m^3 (0.4-1.6 ppm) with a precision ($\overline{CV_T}$) of 0.096.

Table 3 Analysis of charcoal tubes spiked from vapor phase

	Benzyl chloride		Toluene	
Sample	Micrograms added	Micrograms found	Milligrams added	Milligrams found
1.	66	72	4.28	4.32
2.	66	66	4.28	4.44
3.	66	65	4.28	4.35
4.	66	72	4.28	4.45
5.	66	71	4.28	4.45
6.	66	76	4.28	4.44
	Average	70		4.41
	Standard deviation	4.1		0.06
	Average recovery	106%		103%

METHODOLOGY

WALK-THROUGH SURVEYS

In October 1976 a walk-through survey was conducted at Plant A and Plant B to determine if these plants are suited for a more detailed industrial hygiene survey to quantify worker exposures to benzyl chloride. Preliminary determination in the manufacturing and use facilities with a J-W® TLV Sniffer, Century Systems organic vapor analyzer, Wilks MIRAN® 1A gas analyzer, and charcoal tube area samples indicated relatively low background concentrations of organic vapors in the in-plant air. Charcoal tube short-term area samples taken indicated TWA benzyl chloride concentrations ranging from .01 to .04 ppm. Continuous sampling from a single location near the benzyl chloride control room of Plant B with the MIRAN® 1A at the specified wavelength and pathlength for benzyl chloride indicated instantaneous background airborne levels of up to 4 ppm. Table 4 shows the results of the charcoal tube area sampling that was performed during the walk-through survey.

IN-DEPTH SURVEYS

To obtain the most information possible from the detailed visit, the survey team sampled every employee at each plant that had any potential benzyl chloride exposure. Thus, over 200 man-hours of benzyl chloride exposure time was sampled at Plant A and over 150 man-hours of exposure time at Plant B. Breathing zone samples were taken for eight hours on all shifts with additional samples taken for short duration during selected operations (e.g., 15 minutes of a drumming operation). Area monitoring was performed using a Century Systems Total Organic Vapor Analyzer and a MIRAN® 1A gas analyzer.

The MIRAN® 1A was used in a single designated location continuously measuring the concentration of benzyl chloride; however, it had limited utility for the in-depth survey due to its size, weight, and power requirements and the location suitable for the operation of the MIRAN® proved to be unsatisfactory. These problems were compounded by the prevailing climatic conditions. All the benzyl chloride levels detected by the MIRAN were at or below the lower level of sensitivity of the instrument. Therefore, the use of this equipment was discontinued.

The Century was used in a portable fashion, measuring the presence of total hydrocarbons in several locations within the manufacturing and use facilities when there seemed to be a chance for benzyl chloride exposure. The Century proved to be especially helpful in pinpointing areas of potential exposure for short-term charcoal tube sampling. These two instruments were the only instruments used to characterize background

Table 4. Benzyl chloride charcoal collection tube area sampling results.*

	Location	Time (minutes)	Volume (liters)	Concentration (ppm)
Plant A	2nd floor rear benzyl chloride Q. C. sampling	220	38	.03
	2nd floor control room	180	22	.02
	1st floor near gateway entrance	190	38	.01
Plant B	1st floor benzyl chloride operators desk	120	24	.01
	2nd floor control room	155	31	.04
	2nd floor near control room	113	23	.01

*Walk-through survey conducted October 1976.

levels of benzyl chloride. Results from sampling with the Century are shown in Tables 5 and 6. Although not directly translated into exposure concentrations, the Century readings indicate the areas within a production facility where potential exposures to organic vapors are the greatest. Using the Century in this mode can be helpful in locating leaks as well as other breaks in the product lines at seals that need replacing. Table 5 shows that the concentrations throughout the two facilities are relatively uniform with the greatest exposures occurring around the quality control sampling points. In Table 6, higher meter readings were recorded at the benzyl chloride chlorination unit than at the other two manufacturing areas, primarily because the building is enclosed.

Charcoal tube monitoring was used as the primary sampling system to quantitate area (as determined by the Century) and personal exposure levels to benzyl chloride and other potentially hazardous substances (e.g., toluene). Charcoal tube sampling is considered the most reliable and effective sampling procedure for determining airborne levels of the chemical agents that may be present.

Table 5. Results of environmental sampling, Plant A.

	Sample Location	Century Meter Reading*
Manufacturing Area	Entrance, ground floor	5.0 - 6.0
	Sampling point--crude feed to column	2.0 - 2.5
	First floor landing	0.6 - 0.8
	Sampling point-finished goods	1.8 - 2.5
	Second floor near chlorinators	0.4 - 0.6
	Second floor landing	0.2
	Third floor landing	0
Benzyl Phthalate Use Area	Second floor	0.8
	Sampling point--quality control point	0.0 - 0.5
	Control room-second floor	1.2

*These meter readings cannot be directly translated into benzyl chloride concentrations since other organic vapors (e.g., toluene) that also affect meter deflection were present in the in-plant atmosphere. It has been shown that the Century instrument can detect benzyl chloride vapor and indicate an equivalent meter reading of about 54 percent of the total quantity present. Therefore, 1 ppm of benzyl chloride would be shown on the Century Meter as .54.

RESULTS AND DISCUSSION

Plant A

Plant A responded to our request for their available benzyl chloride exposure data and a summary of monitoring information collected from April 1975 to May 1976 is shown in Table 7. Plant A has an excellent industrial hygiene group and these data were therefore considered reliable and included in the report. The levels found by Plant A are similar to results obtained in this survey for TWAs and individual tasks. Because the facilities apparently have not been substantially modified, indications are that exposure levels in the benzyl chloride and plasticizer areas have been the same since production began in 1961.

Table 6. Results of environmental sampling
Plant B

Sample location	Century meter reading*
Benzyl Chloride Manufacturing Area	
Chlorination Area (18C)	
First floor	12.
Second floor near stairway	6.2
Second floor near #4 chlorinator	10.
Second floor between #3 & #4 chlorinators	7.
Second floor between #1 & #2 chlorinators	7.6
Second floor near #1 chlorinator	12.
Third floor report station	8.4
Third floor center	8.6
Chlorination Area (18B)	12.
Refining Area (14)	
Fourth floor	0.4
Third floor	2.5
Third floor control room	0.8
Specific gravity station	0.6
Second floor	0.5
First floor (ground floor)	0.8
1. Peak reading	1.2
Benzyl Alcohol Manufacturing Area	
First floor (ground floor)	0.4
First floor drum cap station	0.2
Second floor	0.6
Second floor chart board	1.1
Second floor empty reactor	0.5
Second floor report station	0.4
Second floor desk	0.4
Third floor near columns, off reactor	0.3
Third floor by reactor	0.2
Third floor benzyl chloride tank	0.3
Benzyl Cyanide Manufacturing Area	
Drumming station	0.5 - 2.0
First floor (ground floor)	0.8
Report station	0.4 - 3.6
Sodium cyanide storage area (drums being opened during sampling)	35.
Near methanol tank	15.
Crude tank #1 & #2	8.
Second floor	
Sampling point	1.
Crude reactor area	1.1
Crude reactor #2	1.
Crude reactor #3	0.6
#4 still	0.8
#5 still	0.5
Second floor, Area B	0.2
#3 still	0.7
Control panel	0.5
Work station	0.4
Sample point by LB still #5	0.6
Walkway under benzyl chloride storage tank	2.
Breathing zone under benzyl chloride storage tank	1.

*These meter readings cannot be directly translated into benzyl chloride concentrations since other organic vapors (e.g., toluene) that also affect meter deflection were present in the in-plant atmosphere. It has been shown that the Century instrument can detect benzyl chloride vapor and indicate an equivalent meter reading of about 54 percent of the total quantity present. Therefore, 1 ppm of benzyl chloride would be shown on the Century meter as .54.

Table 7. Plant A benzyl chloride charcoal collection tube air sampling results*

Location	Sample description†	Group affected	Time (min)	Concentration of benzyl chloride (ppm)
Benzyl Chloride Department (April 1975)	General operation of benzyl chloride process	Benzyl Chloride Operator	247	<0.02
			233	<0.02
			240	<0.02
			275	<0.01
Shipping and Traffic Department (April 1975)	Drumming benzyl chloride	Material Handler	173	<0.02
	Bulk loading of benzyl chloride		150	0.02
Benzyl Chloride User #1 Department (April 1975)	General operation of user #1 process	User #1 Operator	270	<0.02
			233	<0.02
			265	<0.01
Quality Control Laboratory (April 1975)	Analysis of benzyl chloride samples	Lab Technician	250	<0.02
Benzyl Chloride Unit (Nov. 1975)	Operator sampling benzyl chloride to storage, toluene dryer, N&S residues and refining column feeds, chlorination mass	Benzyl Chloride Operator	10	1.2
			8	0.3
			8	0.8
			8	0.3
	Operator sampling various streams plus one change of refining column screen		10	4.7
Benzyl Chloride Unit (May 1976)	General operation of benzyl chloride process	Benzyl Chloride Operator	240	<0.1
			240	0.1
			240	<0.1
			240	<0.1
	Changing screen on crude column by operator		10	0.4

*As reported by Plant A.
†Samples were collected on porous polymer packing and analyzed by GC/FID of the thermally absorbed material.

Benzyl chloride TWA exposure concentrations from the survey of Plant A are shown in Table 8. All these concentrations are well below the permissible exposure limit of 1 ppm. The range of eight-hour exposures varies from <.01 ppm to .08 ppm with an average exposure of .03 ppm. Those workers with the highest group average exposure are the benzyl chloride manufacturing operators. Material handlers and maintenance workers had exposures comparable to the 15 operators. As expected, the greater benzyl chloride exposures recorded occurred during quality control sampling. These samples are taken by the benzyl chloride manufacturing operator and last about 20 minutes. Although the short-term levels are higher than this normal TWA exposure, they are still well below the threshold limit value (TLV).

During the C-shift in one benzyl chloride use facility a product line became plugged in the amine stripping operation. The breakdown lasted about two hours and required the operators to wear cartridge type respirators. Personal sampling continued throughout the shift and was not interrupted or altered to account for the use of the respirators. The breakdown occurred in an area where benzyl chloride is generally not found.

A random sampling of charcoal tubes was checked for toluene concentration. In all cases, the toluene level was less than or equal to 20 ppm, well below the TLV of 100 ppm. These low exposure levels reflect the short periods of time the workers spend in the closed system processing area, which is located in a relatively open structure. Also, the workers (operators) spend much of their time in an enclosed room (control room), which is kept under positive pressure, thus eliminating significant levels of benzyl chloride, even during system breakdowns.

Plant B

Benzyl chloride TWA exposure concentrations from the survey of Plant B are shown in Table 9. The full-shift concentrations ranged from .01 ppm to .14 ppm with an average concentration of .04 ppm, well below the permissible exposure limit of 1 ppm. One sample contained a benzyl chloride level of 3.19 ppm (not included in the average benzyl chloride concentrations). This sample was from a benzyl chloride manufacturing operator. That high exposure to benzyl chloride was explained by what a company representative called a "benzyl chloride feed line backup" causing a catch feed basin to fill. It was reportedly necessary to open the line and then drain the basin. Although not observed by the survey team, it must be assumed that the worker did not wear respiratory protective equipment.

The range of eight-hour benzyl chloride concentrations from all other operations varied from .01 ppm to .14 ppm with an average exposure for the group of .04 ppm. The benzyl chloride manufacturing operators, as a group, had the highest average exposure of .10 ppm. Short-term sampling indicated that the benzyl chloride chief operators received an exposure above their normal TWA exposure when they were obtaining quality control

Table 8. Plant A benzyl chloride charcoal collection tube personal sampling results.

Job title	Date-Shift*	Time (min)	Volume (l)	Concentration (ppm)
Full-shift sampling				
Chief Operator for Benzyl Chloride and Use Area 1	14-A	293	63.7	.01
	14-B	464	111.4	.02
	15-C	480	116.4	.04
	15-A	454	123.7	.03
	15-B	456	106.0	.05
	16-C	478	124.3	.02
	16-A	456	111.7	.03
				.03±.01
Benzyl Chloride Operator	14-A	289	64.3	.01
	14-B	475	114.0	.01
	15-C	480	136.8	.04
	15-A	456	130.0	.03
	15-B	452	125.4	.08
	16-C	485	120.0	.02
	16-A	459	125.1	.06
				.04±.03
Crude Plasticizer Operator - Use Area 1	14-A	292	67.2	.01
	14-B	465	110.4	.02
	15-C	476	115.4	.03
	15-A	454	129.4	.02
	15-B	472	113.3	.04
	16-C	479	116.2	.03
	16-A	485	133.4	.03
				.03±.01
Refining Plasticizer Operator - Use Area 1	14-A	297	69.1	.01
	14-B	471	109.5	.03
	15-C	478	113.5	.04
	15-A	461	126.8	.02
	15-B	467	122.6	.05
	16-C	480	115.2	.03
	16-A	463	114.6	.03
				.03±.01
Material Handling Operator and Tank Car Loading	14-A	182	45.0	.03
	15-A	256	64.6	.03
	16-A	454	108.3	.03
	16-A	100	31.0	.03
Maintenance	14-A	275	63.3	<.01

Table 8. Plant A benzyl chloride charcoal collection tube personal sampling results (continued).

Job title	Date-Shift*	Time (min)	Volume (l)	Concentration (ppm)
Short-term sampling				
Benzyl Chloride	14-B	15	4.3	.09
Operator taking	15-B	27	7.6	.10
Quality Control Samples				.1±.01
Material Handling	14-A	25	7.1	<.02
Operator Filling One Pallet of Drums				
Blanks				t
				t
				t

*Shift "A" refers to day shift, i.e. 0800-1600.
Shift "B" refers to night shift, i.e. 1600-2400.
Shift "C" refers to evening shift, i.e. 2400-0800.

tBelow detectable limits

samples. Although this sample is higher than usual (three times normal TWA) it is still below the TLV.

During the addition of sodium cyanide to the benzyl chloride process, the operators wear a NIOSH-approved mechanical filter respirator. Personal sampling continued uninterrupted throughout this operation.

A random sampling of charcoal tubes was checked for toluene concentration. In all cases, the toluene level was less than or equal to 20 ppm, well below the TLV of 100 ppm. In general, these low exposure levels reflect the short periods of time the workers are active in the processing areas, the fact that the process is, in essence, a closed system and located in a relatively open structure.

Table 9. Plant B benzyl chloride charcoal collection tube personal sampling results

Job Title	Date-Shift*	Time (min)	Volume (l)	Concentration (ppm)
Full-shift sampling				
Benzyl Chloride Chief Operator	17-A	296	78.4	.07
	18-A	342	87.2	.06
				.07±.01
Benzyl Chloride Operator	17-A	287	74.6	.03
	17-B	442	126.0	3.19
	18-A	487	135.1	.09
	18-C	461	114.6	.14
				.10±.04†
Benzyl Chloride Drumming Operator	17-A	365	93.1	.03
	18-A	451	104.9	.03
				.03±.001
Benzyl Chloride Maintenance	17-A	330	88.3	.06
	17-A	327	89.1	.13
	18-A	424	105.4	.09
				.09±.04
Benzyl Alcohol Operator - Use Area 1	17-A	281	66.0	.02
	17-B	443	110.1	.02
	18-A	464	115.3	.03
	18-C	454	115.8	.02
				.02±.005
Benzyl Cyanide Operator - Use Area 2	17-A	267	66.3	.01
	17-A	271	65.7	.02
	17-A	283	67.5	.02
	17-A	226	55.4	.02
	17-B	437	114.7	.05
	17-B	423	117.4	.04
	18-A	495	123.0	.01
	18-A	441	119.1	.01
	18-A	434	117.2	.01
	18-A	458	116.8	.01
	18-C	457	113.6	.02
	18-C	456	120.8	.02
				.02±.01
Short-term sampling				
Benzyl Chloride Chief Operator Taking Quality-Control Samples	18-A	13	3.6	.27
Benzyl Chloride Operator Taking Quality Samples from Toluene Stripper	18-A	33	8.1	.02
Blanks				‡

*Shift "A" refers to day shift, i.e. 0700-1500,
Shift "B" refers to night shift, i.e. 1500-2300,
Shift "C" refers to evening shift, i.e. 2300-0700.

†In calculating this average, the concentration of 3.19 ppm was excluded.

‡Below detectable limits.

CONCLUSIONS

From the data collected throughout this study, the following conclusions are made:

- It is documented in the literature that benzyl chloride is an irritant to the eyes and respiratory tract in concentrations above the TLV. Upon contact with the skin, the liquid benzyl chloride can cause a high degree of irritation.
- Measurable levels of benzyl chloride exist in the in-plant air averaging .03 ppm for Plant A and .04 ppm for Plant B. Levels are highest during quality control sampling or during system breakdown. During routine quality control sampling, benzyl chloride concentrations ranged from .02-.27 ppm. Buckets are occasionally placed underneath a quality control port in Plant A to capture the product as the samples are being taken. The buckets are not removed; thus, higher than usual benzyl chloride exposures are possible. On occasion (frequency not known to survey team), a feed line may become blocked (as in Plant B) requiring an operator to clear the line. Even though this procedure is reportedly not normal, it may expose the worker to excess benzyl chloride. During the survey, one worker was exposed to a daily level of 3.19 ppm of benzyl chloride during an eight-hour shift. Most likely, however, this exposure occurred for a short time span during the eight-hour shift, thus representing a short term, acute exposure level.
- The TWA exposure of workers to benzyl chloride during normal operations was found to be well below the present OSHA standard of 1 ppm, principally for the following reasons:
  - The process is performed in a closed system, which is only opened for repairs and quality control sampling.
  - The worker is not required to spend much time in the process area.
  - The process is located in a relatively open structure.
- The sampling and analysis protocol used in these surveys is an effective and reliable evaluation strategy. That is, using the hand-held Century Analyzer to note the presence of organic vapors and to pinpoint areas of potential short-term high exposure and using charcoal tube sampling for quantitating workers' short-term and full-shift daily TWA exposure levels proved to be an efficient and effective survey technique. The MIRAN had limited utility in the survey due to its lack of portability.

REFERENCES

1. Directory of chemical producers. 1976. Chemical Information Services, Stanford Research Institute. Menlo Park, California

2. Chemical economics handbook. 1976. Stanford Research Institute, Menlo Park, California

3. Smyth, H. F. Jr. 1956. Improved communication--hygienic standards for daily inhalation. Am. Ind. Hyg. Assn. Quart. 17: 129.

4. Plunkett, E. R. 1976. Handbook of industrial toxicology. Chemical Publishing Co., Inc., New York.

5. Documentation of threshold limit values. 1971. 3rd edition, p. 24. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.

6. McCann, J., et al., Detection of carcinogens as mutagens: bacterial tester strains with R factor plasmids. 1975. Proc. Nat. Acad. Sci. 72-3:979-983.

7. Personal communication between S. Henson, Stanford Research Institute, and V. F. Simmon, Stanford Research Institute, Menlo Park, California, 1976.

8. Poirier, L.A., Stoner, G.D., and Shimpin, M.B. 1975. Bioassay of alkyl halides and nucleotide base analogs by pulmonary tumor response in strain A mice. Cancer Res. 35:1411-15.

9. Preussman, R. 1968. Direct alkylating agents as carcinogens. Ed. Cosmet. Toxicol. 6:575-77.

10. Christensen, H.E. et al., Eds. 1975. Suspected carcinogens, a subfile of the NIOSH toxic substances list. U.S. Department of Health, Education, and Welfare, Public Health Service, Rockville, Maryland, (DHEW Publication No. 75-188).

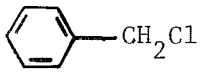
11. The industrial environment--its evaluation & control. 1974. U.S. Department of Health, Education, and Welfare, Public Health Service, Washington, D.C. (DHEW Publication No. 74-117).

APPENDIX A
ANALYTICAL METHODS WITH BACKUP DATA REPORTS

Table A-1. Benzyl Chloride chemical and physical data

Synonyms: Chloromethylbenzene; α - chlorotoluene

Chemical formula: $C_6H_5CH_2Cl$



Chemical and physical properties:

Description: Colorless, highly refractive and irritating liquid with a very pungent odor. The odor threshold limit has been established at 0.047 ppm.

Autoignition temperature:		585°C
Boiling point:		179.3°C at 760 mm Hg
		42.6°C at 10 mm Hg
Flash point:		
Open cup (anhydrous)		67°C
Closed cup (anhydrous)		60°C
Freezing point:		-39°C
Lower explosive limit:		1.1% (by vol.)
Melting point °C:		-43°C
Molecular weight:		126.58
Refractive index n_D^{15}		1.54124

Solubility: Soluble in both alcohol and ether. Although insoluble in cold water, benzyl chloride decomposes in hot water to give benzyl alcohol.

Specific gravity:	4.4°C	1.135
	15/15°C	1.10426
	20/20°C	1.1002
	25/25	1.090
Specific heat, 1 atm, 10-140°C, cal/(g)(°C):		0.000972

Stability: Unless stabilized, will undergo a Friedal-Crafts type condensation when exposed to certain metals.

Surface tension, dyn/cm:	15°C	38.43
	179.5°C	19.5
TLV:		1 ppm or 5 mg/m^3
Vapor density (air = 1)		4.34

Table A-1. Benzyl Chloride chemical and physical data (continued).

Temperature °C	Vapor pressure (mm Hg)
22	1
47.8	5
60.8	10
90.7	40
100.5	60
114.2	100
134.	200

Sources for Table A-1:

Kirk-Othmer. 1964. Encyclopedia of chemical technology. 5:281-3. 2nd. ed., Interscience Publishers, New York.

Leonardos, G., Kendall, D., Barnard, N. 1964. Odor threshold determination of 53 odorant chemicals. J. Air Pollution Control Assoc. 19(2):91-95.

Hawley, G. G. 1977. Condensed chemical dictionary. 9th ed. Van Nostrand Reinhold Co., New York.

American Conference of Governmental Industrial Hygienists. 1977. Threshold limit values for chemical substances in workroom air adopted by ACGIH for 1977. American Conference of Governmental Industrial Hygienists, Cincinnati.

Analyte:	Benzyl Chloride	Method No.:	S115
Matrix:	Air	Range:	2-8 mg/cu m
OSHA Standard:	1 ppm (5 mg/cu m)	Precision ($\overline{CV}_T$):	0.096
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 2-8 mg/cu m at an atmospheric temperature and pressure of 25°C and 744 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 0.5-15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a .05-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 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 the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least .39 mg of the analyte when a test atmosphere of 8.1 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 4 hours. Breakthrough did not occur at this time; the concentration of the analyte in the effluent was less than 2% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great the condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 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.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2-8 mg/cu m was 0.096. This value corresponds to a standard deviation of 0.48 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 6.3% less than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2.)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained

for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method of determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade).

7.2 Benzyl chloride (reagent grade).

7.3 Internal Standard: n-Heptadecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, break the ends of each tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method an 0.2% solution of internal standard in carbon disulfide is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 160°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and

reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for Determining Desorption Efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A 12.5 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent ot that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight 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 sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. (For the internal standard method use carbon disulfide containing 0.2% of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al. 1970. A convenient optimized method for the analysis of selected solvent vapors in the industrial atmosphere, Amer. Ind. Hyg. Assoc. J. 31: 225.

11.2 Documentation of NIOSH validation tests. Contract No. CDC-99-74-45.

11.3 Final report, NIOSH Contract No. HSM-99-71-31. September 15, 1972. Personal sampler pump for charcoal tubes.

Sampling Data Sheet No. S115

Substance

Benzyl Chloride

Standard

8-hour time-weighted average: 1 ppm (5 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

A known volume of air is drawn through a charcoal tube to trap the benzyl chloride vapors present. The analyte is desorbed from the charcoal with carbon disulfide, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 2-8 mg/cu m for a 10-liter sample at 25°C and 744 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined accurately, ±5%, over the range 0.05 to 0.2 liter per minute, plus charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam.

Sample Size

A sample size of 10 liters is recommended. Sample at a flow of 0.2 liter per minute or less.

Sampling Procedure

1. Immediately before sampling, the ends of the tube should be broken so as to provide an opening approximately one-half the internal diameter of the tube.

2. The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump. The charcoal tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of propylene dichloride.

3. Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere sampled. If the pressure reading is not available, record the elevation. If the pump is a low flow rate pump, set

the approximate flow rate and record the initial and final counter reading. The sample volume is obtained by multiplying the number of counter strokes times the cc/stroke factor.

5. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.

6. One charcoal tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank.

Special Consideration

1. Where 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.

2. Due to the high resistance of the charcoal tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without fully recharging the battery.

3. If high humidity or water mist is present, breakthrough volume can be severely reduced. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.

4. The desorption efficiency of charcoal varies from batch to batch. Therefore, all the tubes used to collect a set of samples should contain charcoal from the same batch. Several unused charcoal tubes should accompany the samples. Information on the batch number of the charcoal must be supplied.

Bulk Samples

A bulk sample of the suspected compound should be submitted to the laboratory in a glass container with a Teflon®-lined cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tube.

Reference

Benzyl chloride, NIOSH Method No. S115.

BACKUP DATA REPORT

Substance: Benzyl chloride, No. S115

OSHA Standard: 1 ppm (5 mg/cu m)

Chemical used for validation: Benzyl chloride, 97%
Aldrich Chemical Company, Inc.

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of benzyl chloride in air is described in NIOSH Method S115, which has been adapted from P&CAM 127. For determination of desorption efficiency 100 mg samples of charcoal were placed in 2-ml Hewlett Packard Automatic Sample Injector vials and were spiked with a 12.5 mg/ml solution of benzyl chloride in heptane injected with a 10-µl syringe. The amount of solution added was 2, 4, and 8 µl respectively for 0.5, 1, and 2 times the OSHA standard level, and was the same as the amount present in a 10-liter air sample at the respective level. The eluting solvent was carbon disulfide.

To study the change of desorption efficiency with varying time of standing before desorption a number of desorption samples at the OSHA standard level were prepared as described above. Groups of four samples were analyzed after 1, 2, and 7 days. The results, tabulated below showed no significant decrease in the period studies.

Time Before Desorption (Days)	Desorption Efficiency (%)
1	86.5
2	85.5
7	84.1

Samples of benzyl chloride in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pennsylvania. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of benzyl chloride in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 50 minutes). The "true" concentrations of benzyl chloride in the generated samples were determined by gas chromatographic analysis using a 5-ml sampling loop. The analysis was standardized by comparison with "bag" samples. The bag samples were prepared in 4-liter Teflon® bags by metering 4 liters of nitrogen into the bag, followed by injecting the required amount of benzyl chloride. Details of the analytical procedures are given in the Analytical Procedures section of Reference 1. In this case the desorption efficiencies at the three levels did not increase with increasing concentration and differed by less than one standard deviation. Therefore, the average desorption efficiency was used for all three levels.

Modifications

The P&CAM 127 method was used with one modification. An internal standard was added for improved accuracy.

Generation

The test atmosphere was generated by a syringe injection technique. Simultaneous three-stage dilution was employed so that the three concentrations were generated and sampled simultaneously. The details of the atmosphere generation equipment and operations are presented in the Atmosphere Generation section of Reference 2. The total gas flow rate of the first stage was 23.6 liters per minute, and the rate of benzyl chloride injection was 0.0114 g/hr. Sampling time was 50 minutes with a nominal flow rate of 200 ml/min for each charcoal tube.

Breakthrough

In order to test the capacity of the charcoal tubes an experiment was conducted at two times the OSHA standard level (actual concentration was 8.1 mg/cu m). Breakthrough is defined as the time at which the effluent concentration from the tube reaches 5% of the concentration in the test gas mixture. The volume of sample to be used must be such that the volume of test air sampled at the time of breakthrough is greater than 1.5 times the volume of sample to be collected for analysis. In this breakthrough experiment, eight tubes containing one section of 100 mg of charcoal were used to sample the test air, which was pumped through the eight tubes simultaneously through individual critical orifices. The combined effluent from the tubes was monitored continuously to detect breakthrough. After 4 hours the effluent concentration had reached only 2% of the test atmosphere concentration. Thus, the capacity of this lot of charcoal exceeds 0.39 mg of benzyl chloride and at the recommended sampling rate, the breakthrough volume is greater than 48 liters. This meets the above requirement.

Precision and Accuracy

The statistical procedures used are described in Reference 3.

$$\overline{CV}_1 = 0.031 \qquad \overline{CV}_2 = 0.081 \qquad \overline{CV}_T = 0.096$$

The average recovery of the generated samples over all levels was:

93.1%

References

1. Backup data report for camphor, No. S10, NIOSH Contract No. CDC-99-74-45.

2. Backup data report for ethyl alcohol, No. S56, ibid.

3. Documentation of NIOSH validation tests, ibid.

4. Sarkan, A. E., and Breenburg, B. G. 1962. Contributions to order statistics. New York, John Wiley & Sons, p. 302.

Data Sheet: Benzyl Chloride S115 Analysis

0.5S			1S			2S		
mg Added	mg Found	DE	mg Added	mg Found	DE	mg Added	mg Found	DE
.0250	.0224	0.898	.0500	.0458	0.917	.1000	.0929	0.929
.0250	.0224	0.895	.0500	.0461	0.921	.1000	.0942	0.942
.0250	.0230	0.921	.0500	.0461	0.923	.1000	.0931	0.931
.0250	.0235	0.939	.0500	.0452	0.904	.1000	.0874	0.874
.0250	.0222	0.886	.0500	.0438	0.876	.1000	.0881	0.881
.0250	.0212	0.848	.0500	.0445	0.890	.1000	.0874	0.874
n =		6			6			6
mean		0.898			0.905			0.905
std dev		0.0312			0.0187			0.0320
CV_1		0.0348			0.0207			0.0354

CV_1 0.031

$\overline{CV}_{A+\overline{DE}}$ 0.0335

Data Sheet: Benzyl Chloride S115 Sampling and Analysis

Test Level	Found				Taken	
	mg	Corr mg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	0.0166	0.0183	9.60	1.911	1.8	106.2
	0.0166	0.0183	9.60	1.911	1.8	106.2
	0.0147	0.0162	9.25	1.756	1.8	97.6
	0.0155	0.0172	9.60	1.791	1.8	99.5
	0.0137	0.0151	8.90	1.701	1.8	94.5
	0.0130	0.0143	9.40	1.526	1.8	84.8
			n = 6			
			mean	1.766		98.1
			std dev	0.145		
			CV_2	0.0819		
1S	0.0319	0.0353	9.15	3.859	3.9	98.9
	0.0361	0.0400	10.25	3.905	3.9	100.1
	0.0346	0.0383	10.05	3.812	3.9	97.8
	0.0272	0.0301	9.10	3.307	3.9	84.8
	0.0291	0.0323	9.55	3.380	3.9	86.7
	0.0211	0.0234	9.10	2.567*	3.9	65.8*
			n = 5			
			mean	3.65		93.66
			std dev	0.285		
			CV_2	0.0780		
2S	0.0760	0.0842	10.85	7.756	8.1	95.8
	0.0673	0.0746	9.70	7.686	8.1	94.9
	0.0620	0.0687	9.40	7.310	8.1	90.2
	0.0560	0.0620	9.30	6.669	8.1	82.3
	0.0578	0.0640	10.15	6.303	8.1	77.8
	0.0610	0.0675	9.85	6.857	8.1	84.7
			n = 6			
			mean	7.10		87.6
			std dev	0.583		
			CV_2	0.0821	$\overline{CV}_2$	0.081

*Deleted as an outlier, because this value did not pass the Grubb's outlier test at the 1% confidence level as described in Sarkan and Breenburg. 1962. Contributions to order statistics. New York, John Wiley & Sons.

APPENDIX

RESULTS OF CHARCOAL TUBE SPIKINC EXPERIMENTS

The results of our charcoal tube spiking experiments indicate that toluene does not affect either the collection of or analysis for benzyl chloride under the conditions tested. From Table B-1, the average desorption efficiency for benzyl chloride was 0.963 (standard deviation of 0.011 for 18 samples) in the presence of toluene; its desorption efficiency was 0.977 (standard deviation of 0.029 for 9 samples) when applied from a hexane solution. Average recovery was 106% for benzyl chloride and 103% for toluene from 6 samples spiked from the vapor phase, as is shown in Table B-6.

Table B-1. Desorption efficiency (D.E.) -- benzyl chloride

Samples spiked with benzyl chloride from hexane solution		Samples spiked with benzyl chloride-toluene mixture	
Sample number	D.E.	Sample number	D.E.
1.	0.951	1.	0.953
2.	0.972	2.	0.955
3.	0.993	3.	0.966
4.	1.007	4.	0.963
5.	0.930	5.	0.954
6.	1.004	6.	0.965
7.	0.953	7.	0.992
8.	1.016	8.	0.970
9.	0.969	9.	0.954
		10.	0.947
		11.	0.953
		12.	0.954
		13.	0.973
		14.	0.955
		15.	0.972
		16.	0.960
		17.	0.969
		18.	0.975
Average	0.977	Average	0.963
Standard deviation	0.029	Standard deviation	0.011

Comparison of the determinations with the referee samples in Table B-2 shows their average recovery to be adequate; however, the standard deviation is greater than that found for referee samples. Results for two samples were outside the range of ±25% of the taken value. There was evidently no effect on the samples from transporting them as will be noted by data in Appendix A.

Table B-2. Benzyl chloride referee samples

Samples spiked with benzyl chloride from hexane solution		Samples spiked with benzyl chloride-toluene mixture	
Micrograms applied	Micrograms found	Micrograms applied	Micrograms found
66	62	66	64
66	61	66	61
66	61	66	66
66	66	66	64
66	68	66	64
66	61	66	68
66	66	66	64
66	63	66	66
66	58	66	67
66	63	66	66
66	64	66	66
66	66	66	64
66	68	66	66
66	64	66	62
66	63	66	63
66	68	66	68
66	66	66	64
		66	64
Average	64		65
Standard deviation	2.9		1.9

Table B-3 shows the results of the recovery tests from liquid phase spiking experiments with mixtures of benzyl chloride and hexane, and benzyl chloride and toluene. As shown in Tables B-4 and B-5, the average desorption efficiency for toluene recovery was 0.980 (standard deviation of 0.018 for 18 samples) with an average recovery of 100% (4.28 mg, standard deviation of 0.14).

Results for determinations of both benzyl chloride and toluene from vapor spiked samples are given in Table B-6.

Table B-3. Determination of benzyl chloride

Samples spiked with benzyl chloride from hexane solution		Samples spiked with benzyl chloride-toluene mixture	
Micrograms applied	Micrograms found	Micrograms applied	Micrograms found
66	67	66	58
66	67	66	58
66	68	66	70
66	66	66	62
66	65	66	62
66	66	66	73
66	64	66	64
66	65	66	72
66	66	66	76
66	<1*	66	59
66	63	66	65
66	66	66	69
66	43	66	69
66	66	66	70
66	63	66	74
66	62	66	78
66	59	66	77
66	68	66	68
Average	64		68
Standard deviation	5.8		6.5

*Not included in computation of average or standard deviation.

Table B-4. Desorption efficiency (D.E.) - toluene

Samples spiked with benzyl chloride-toluene mixture

Sample number	D.E.	Sample number	D.E.	Sample number	D.E.
1.	1.007	7.	0.962	13.	0.977
2.	0.992	8.	0.970	14.	0.974
3.	0.992	9.	0.952	15.	0.964
4.	0.991	10.	0.985	16.	0.975
5.	0.992	11.	0.980	17.	0.967
6.	0.960	12.	1.022	18.	0.970
	Average	0.980			
	Standard deviation	0.018			

Table B-5. Determination of toluene

Milligrams applied	Milligrams found	Milligrams applied	Milligrams found	Milligrams applied	Milligrams found
4.28	4.18	4.28	4.47	4.28	4.04
4.28	4.21	4.28	4.44	4.28	4.29
4.28	4.19	4.28	4.33	4.28	4.24
4.28	4.50	4.28	4.30	4.28	4.35
4.28	4.30	4.28	4.33	4.28	4.24
4.28	4.45	4.28	4.00	4.28	---
	Average	4.28			
	Standard deviation	0.14			

Table B-6. Analysis of charcoal tubes spiked from vapor phase

	Benzyl chloride		Toluene	
Sample	Micrograms added	Micrograms found	Milligrams added	Milligrams found
1.	66	72	4.28	4.32
2.	66	66	4.28	4.44
3.	66	65	4.28	4.35
4.	66	72	4.28	4.45
5.	66	71	4.28	4.45
6.	66	76	4.28	4.44
	Average	70		4.41
	Standard deviation	4.1		0.06
	Average recovery	106%		103%

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