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## IX. APPENDIX I

#### ANALYTICAL METHOD FOR BENZYL CHLORIDE

The following analytical method is an adaption of validated No. S-115, Physical and Chemical Analysis Branch of NIOSH [74].

#### Principle of the Method

A known volume of air is drawn through a charcoal tube to trap the organic vapors present. The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide. An aliquot of the desorbed sample is injected into a gas chromatograph. The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

#### Range and Sensitivity

The original analytical method, No. S-115, was validated over the range of 2-8 mg/cu m at an atmospheric temperature and pressure of 25 C and 744 mmHg, using a 10-liter sample. The probable range of the adapted method, under the conditions of sample size (3 liters), is 1.7-50 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.05-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency (DE) is adequate. Desorption efficiency must be determined over the range used.

The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube held at least 0.39 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/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 <u>Apparatus</u>.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

#### Interferences

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

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.

It must be emphasized that any compound that 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.

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

### Precision and Accuracy

Based on validation experiments using the internal standard method, the the coefficient of variation for the total analytical and sampling method No. S-115, 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 of 5 mg/cu m as a TWA. The average values obtained using the overall sampling and analytical method were 6.3% less than the "true" value at the OSHA standard level. Precision and accuracy of the adapted method, which uses a reduced sample size of 3 liters, have not been measured.

The sampling device is small and portable and involves no liquids. Interferences are minimal, and most of those that do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick instrumental method. The method also can 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.

One disadvantage of the method is that the amount of sample that 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.

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

#### Apparatus

(a) A calibrated personal sampling pump, the flow of which can be determined accurately  $(\pm 5\%)$  at the recommended flowrate.

(b) Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm OD and a 4-mm ID, containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The adsorbing 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 adsorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flowrate of 1 liter/minute.

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

(d) Column (10-foot x 1/8-inch stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

(e) An electronic integrator or some other suitable method of determining peak areas.

(f) Glass sample containers: 2-ml, with glass stoppers or Teflonlined caps. If an automatic sample injector is used, the sample injector vials can be used.

(g) Microliter syringes:  $10-\mu 1$  and other convenient sizes for making standards.

(h) Pipets: 1.0-ml delivery type.

(i) Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

#### Reagents

(a) Eluant: carbon disulfide (chromatographic grade).

(b) Benzyl chloride (reagent grade).

(c) Internal standard: n-heptadecane (99+%) or other suitable standard.

(d) n-Heptane (reagent grade).

(e) Purified nitrogen.

(f) Prepurified hydrogen.

(g) Filtered compressed air.

#### Procedure

(a) Cleaning of Equipment

All glassware used for the laboratory analysis should be washed with detergent and thoroughly rinsed with tapwater and distilled water.

(b) 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.

(c) Collection and Shipping of Samples

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

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

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

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

(5) A maximum sample size of 3 liters is recommended. Samples should be taken at a flow of 0.20 liter/minute or less. The flowrate should be known with an accuracy of at least  $\pm 5\%$ .

(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.

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

(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.

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

(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.

(11) If samples must be stored before analysis, storage time should be minimal. Desorption efficiency has been shown to be unchanged after 7 days under unspecified conditions. Differences in storage temperature, water content, and other collected contaminants may, however, affect this time.

(d) Analysis of Samples

(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.

(2) Desorption of Samples

Prior to analysis, 1.0 ml of the eluant is pipetted into each sample container. For the internal standard method, a 0.2% solution of internal standard in carbon disulfide is used. 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.

> Extreme caution must be exercised at all times when using carbon disulfide because of its high toxicity and fire and explosion hazards. It can be ignited by hot steam pipes. All work with carbon disulfide must be performed under an exhaust hood.

(3) Gas Chromatograph Conditions

The typical operating conditions for the gas chromatograph are:

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

## (4) Injection

The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, the solvent flush injection technique should be used. The  $10-\mu 1$  syringe is first flushed with solvent several times to wet the barrel and plunger, and  $3 \mu l$  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  $\mu$ 1 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- $\mu$ 1 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  $\mu$ 1 to minimize evaporation of the sample from the tip of the needle. (The sample occupies 4.9-5.0  $\mu$ l 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,  $2-\mu 1$  injections are satisfactory.

(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 Calibration and Standards).

- (e) Determination of Desorption Efficiency
  - (1) Importance of Determination

The DE 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.

#### (2) Procedure for Determination

Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2-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  $10-\mu l$ syringe, and the container is capped. The amount injected is equivalent to 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 Analysis of Samples.

The weight of analyte found in each tube is determined from the standard curve (see <u>Calibration and Standards</u>). Desorption efficiency is determined by the following equation:

## DE = <u>average weight (mg) recovered</u> weight (mg) added

The DE is dependent on the amount of analyte collected on the charcoal. Plot the DE vs the weight of analyte found. This curve is used below in Calculation (d) to correct for adsorption losses.

#### 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 gas chromatographic conditions and during the same time as the unknown samples. Curves are established by plotting concentrations in mg/ml vs peak areas. In the case of the internal standard method, plot the concentration vs the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or the 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 of variations of the flame ionization detector's response.

#### Calculations

(a) 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 eluant, and the volume of sample injected is identical to the volume of the standards injected.

(b) Corrections for the blank must be made for each sample.

where:

mg = mg sample - mg blank

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.

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

(d) Read the DE from the curve (Procedure (e)(2)) for the amount of analyte found in the front section. Divide the total weight by this DE to obtain the corrected mg/sample.

(e) The concentration of analyte in the air sampled can be expressed mg/cu m, which is numerically equal to g/liter of air.

mg/cu m = <u>corrected mg x 1,000 (liter/cu m</u>) air volume sampled (liter)

(f) Another method of expressing concentration is in ppm:

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

where:

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

#### X. APPENDIX II

#### MATERIAL SAFETY DATA SHEET

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

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

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

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

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

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

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg; "100 ppm LCso-rat," "25 mg/kg LDso-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity, or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

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

(d) Section IV. Fire and Explosion Data

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

(e) Section V. Health Hazard Information

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

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

Skin Contact--single short contact, some irritation likely; prolonged or repeated contact, possibly strong irritation.

Eye Contact--some pain, transient irritation; corneal scarring if prolonged contact.

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

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

(f) Section VI. Reactivity Data

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

(g) Section VII. Spill or Leak Procedures

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

(h) Section VIII. Special Protection Information

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

(i) Section IX. Special Precautions

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

(j) Signature and Filing

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

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

]	

# MATERIAL SAFETY DATA SHEET

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ADDRESS				
TRADE NAME			· · · · · · · · · · · · · · · · · · ·	
SYNONYMS				
II HAZARD	OUS INGREDIER	ITS		
MATERIAL OR COMPONENT		*	HAZARO DATA	
III PH	YSICAL DATA			
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SPECIFIC GRAVITY (H20=1)	VAPOR PI	VAPOR PRESSURE		
VAPOR DENSITY (AIR=1)	SOLUBIL	SOLUBILITY IN H20, % BY WT		
% VOLATILES BY VOL	EVAPORA	EVAPORATION RATE (BUTYL ACETATE - 1)		
APPEARANCE AND ODOR				

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VI REACTIVITY DATA
CONDITIONS CONTRIBUTING TO INSTABILITY
INCOMPATIBILITY
HAZARDOUS DECOMPORTION PRODUCTS
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION
VII SPILL OR LEAK PROCEDURES
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED
NEUTRALIZING CHEMICALS
WASTE DISPOSAL METHOD
VIII SPECIAL PROTECTION INFORMATION
VENTILATION REQUIREMENTS
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT
RESPIRATORY (SPECIFY IN DETAIL)
EYE
GLOVES
OTHER CLOTHING AND EQUIPMENT

	IX SPECIAL PRECAUTIONS
PRECAUTIONARY STATEMENTS	
OTHER HANDLING AND STORAGE REQUIREMENTS	
REPARED BY	

ADDRESS

DATE

# XI. TABLES AND FIGURE

# TABLE XI-1

CHEMICAL AND PHYSICAL PROPERTIES OF BENZYL CHLORIDE

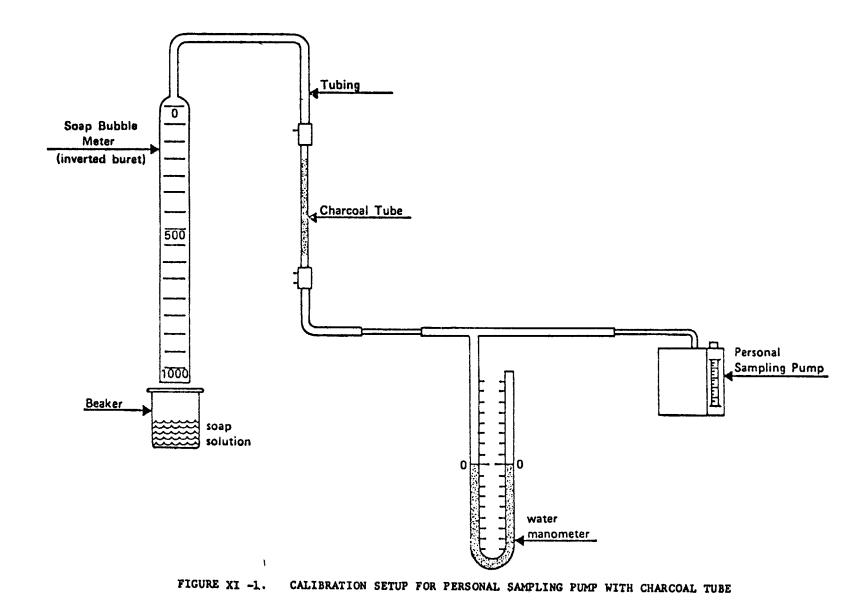
Molecular formula Molecular weight Physical state Color Boiling point (760 mm) Freezing point Flammable limits (lower limit) Flashpoint (closed cup) anhydrous (open cup) anhydrous	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl 126.58 Liquid at normal temperatures Colorless to slightly yellow 179.4 C (355 F) -39.2 C (-38.6 F) 1.1% by vol in air 67 C (153 F) 74 C (165 F)
Autoignition temperature	585 C (1085 F)
Vapor Pressure 22 C	1 mmHg
60.8 C	10 mmHg
114.2 C	100 mmHg
Specific gravity 25/25 C	1.0986
20/20 C	1.100
Refractive index nl5D	1.541
Solubility in water at 20 C (68 F)	49.3 mg/100 m1
Miscibility	Decomposes in hot water; miscible in all proportions with alcohol, chloroform, ether

Adapted from references 2,4,5,9,13,88,99

# TABLE XI-2

# OCCUPATIONS WITH POTENTIAL EXPOSURE TO BENZYL CHLORIDE

Adapted from references 5,13,100





#### DEPARTMENT OF

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## HEALTH, EDUCATION, AND WELFARE

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