

IX. APPENDIX I

AIR SAMPLING PRACTICES FOR PHOSGENE

General Requirements

Air concentrations shall be determined within the worker's breathing zone and shall meet the following criteria in order to evaluate conformance with the standard:

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sample data sheets shall include:

- (1) The date and time of sample collection.
- (2) Sampling duration.
- (3) Volumetric flowrate of sampling.
- (4) A description of the sampling location.
- (5) Sampling temperature and pressure.
- (6) Other pertinent information.

Breathing Zone Sampling

(a) To ensure that a sample is representative of a worker's exposure, collection shall be as near the worker's breathing zone as practical. Sampling should not hamper the typical movement patterns associated with his work.

(b) A portable, battery-operated, personal sampling pump, and a midget impinger containing 10-20 ml of a solution of 0.25% 4-(4'-nitrobenzyl)pyridine and 0.5% N-phenylbenzylamine in diethylphthalate are used to collect the sample.

(c) The sampling rate shall be 0.5-1.0 liter/minute and samples shall be taken for a time period appropriate to the estimated concentration of phosgene in the air (eg, at the recommended environmental limit, 0.1 ppm phosgene in air, a flowrate of 1 liter/minute, and a sample time of 25 minutes, 10 μ g of phosgene can be collected in 10 ml of sampling reagent.)

(d) A series of short-term samples shall be taken for each TWA. The number of TWA's shall be in compliance with Table I-2 for each operation.

The TWA may be determined as follows:

$$TWA = \frac{C_1t_1 + C_2t_2 + \dots + C_nt_n}{T}$$

where C = phosgene concentration during any period of time t
T = t₁ + t₂ + ... + t_n

Sampling times should be selected so that the calculated TWA is representative of the full 8-10 hour workshift.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the pump's indicated flow rate. The frequency of calibration should be dependent on the use, care, and handling to which the pump is subjected. In addition, the pump should be recalibrated if it has been subjected to misuse, or if it has just been repaired or received from a manufacturer. If it receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards, such as a spirometer or soapbubble meter, are recommended although other standard calibrating instruments, such as a wet-test meter, or dry-gas meter, can be used. The actual setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a midget impinger is shown in Figure XIII-1.

(a) Check the voltage of the pump battery with a voltmeter to assure adequate voltage for calibration. Charge the battery if necessary.

(b) Assemble the midget impinger with the appropriate solution.

(c) Assemble the sampling train as shown in Figure XIII-1. If a prescrubber is used to remove interferences, the sampling train should be assembled with the prescrubber in line with the midget impinger.

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

(e) Adjust the pump rotameter to provide a flowrate of 1 liter/minute.

(f) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 13 inches of water (approximately 1 inch of mercury).

(g) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes the bubble to move from one calibration mark to another. For a 1000-ml buret, a convenient calibration volume is 500 ml.

(h) Repeat the procedure in (g) above at least twice, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(i) Data for the calibration includes the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, humidity, serial number of the pump, date, and name of the person performing the calibration.

X. APPENDIX II
ANALYTICAL METHOD FOR PHOSGENE

Principle of the Method

(a) A known volume of air is drawn through a solution of 0.25% 4-(4'-nitrobenzyl)pyridine and 0.5% N-phenylbenzylamine in diethylphthalate contained in a midget impinger. Phosgene present reacts with the solution to produce a brilliant red color.

(b) The absorbance of the sample solution is determined at 475 nm using a colorimeter or spectrophotometer.

(c) Comparison of sample absorbance with a standard curve allows quantitation of phosgene present.

Range and Sensitivity

(a) The lower limit of detection is 5 μg phosgene in the sample.

(b) The upper limit of the method may be varied, according to sample requirements, by appropriate adjustment of the usual sampling parameters (ie, sample time, solution volume, and flow rate).

(c) The 95% confidence limits for 10 degrees of freedom are ± 0.007 mg at the 0.017-mg level, and ± 0.003 mg at the 0.10-mg level. The precision was determined by repeated analyses by the same technician. Rather than air sampling in the field, the precision was determined by analyzing known amounts of phosgene using the same technique as the calibration procedure.

Interference

Other acid chlorides, alkyl and aryl derivatives which are substituted by active halogen atoms and sulfate esters will produce color with this reagent. However, most of these interferents can be removed in a pre-scrubber containing 1,1,2-trichloro-1,2,2-trifluoroethane if necessary. [104] The method is not subject to interference from carbon tetrachloride, chloroform, perchloroethylene, trichloroethylene, dichlorodifluoromethane, chlorine, hydrogen chloride, or chlorine dioxide. [85,104]

Color Stability

The red color formed is stable for at least 4 hours and should be measured within 9 hours; a color density loss of 10-15% can be expected after 8 hours. A slight decrease in color density may be expected if sampling is performed during high humidity (eg, 11% decrease at 73% relative humidity). [104]

Efficiency

Sampling efficiency is 99% or better. Evaporation losses are negligible. [85,104]

Advantages of the Method

- (a) High collection efficiency.
- (b) High specificity for phosgene in most likely sample environments.
- (c) No elaborate equipment needed.

- (d) Minimal technical expertise required for sampling and analysis.
- (e) Relative ease of personal sampling.

Disadvantages of the Method

- (a) Potential spillage of liquid sampling solution.
- (b) Potential breakage of glass sampling equipment.
- (c) Sample color instability on standing.
- (d) Color density decreased by high relative humidity.

Apparatus

- (a) Sampling
 - (1) Portable, battery-operated, personal sampling pump.
 - (2) Midget impinger.
 - (3) Flexible plastic tubing as appropriate.
- (b) Analysis
 - (1) Glassware as required for reagent measurement.
 - (2) Colorimetric spectrophotometer capable of absorbance measurements at 475 nm.
 - (3) Spectrophotometer cells (cuvettes).
- (c) Calibration
 - (1) Pressurized cylinder of phosgene gas.
 - (2) Pressure regulator.
 - (3) Flow meter.
 - (4) Appurtenant equipment for gas dilution methods or a midget impinger.
 - (5) Gas drying tubes.

Reagents

All reagents are ACS Reagent Grade.

(a) 4-(4'-nitrobenzyl) pyridine/N-phenyl benzylamine absorbing solution: Dissolve 0.25 g 4-(4'-nitrobenzyl)pyridine and 0.5 g N-phenylbenzylamine (may also be called N-benzylaniline) in 100 ml diethylphthalate. Store in an amber bottle.

(b) Gas purifying reagent: Approximately 50% anhydrous sodium iodide and 50% sodium thiosulfate, by weight.

(c) Diethylphthalate.

Standards

Method A: Use commercially available compressed phosgene gas (99.0%) to bubble known amounts of the gas through a midget bubbler containing the absorbing solution. Measure with a spectrophotometer (475 nm) the color developed to establish a standard curve. It has been recommended [141] that the phosgene be passed through a drying tube filled with a mixture of anhydrous sodium iodide/sodium thiosulfate prior to bubbling.

Method B: Pass the compressed phosgene gas through a tube containing anhydrous sodium iodide/sodium thiosulfate and into a glass bubbler containing diethylphthalate solution with excess normal alcoholic sodium hydroxide solution. Analyze for chloride by any of the standard titrametric methods. [142,143] Use demineralized water for this analysis. Dilute aliquots of phosgene-containing diethylphthalate with additional diethylphthalate to prepare a series of samples of known concentration (based on chloride analyses). To each sample add an equal volume of

double-strength absorbing solution (0.5% 4-(4'-nitrobenzyl) pyridine and 1.0% N-phenylbenzylamine in diethylphthalate). Mix and measure the absorbance (475 nm) after 5 minutes.

Analysis

Transfer an aliquot of the phosgene-containing absorbing solution to a spectrophotometer cuvette and measure the absorbance at 475 nm against a blank of the pure reagent. Determine the phosgene concentration from a calibration curve suitable for the specific volume of reagent used and the volume of air sampled.

Standard Curve Preparation

Using linear graph paper, plot absorbance readings on the ordinate (vertical axis) and phosgene concentration on the abscissa (horizontal axis). Standard phosgene concentrations are prepared by Method A or Method B above.

XI. APPENDIX III

PHOSGENE MONITORS

Whenever phosgene may be released or created as a result of leaks, accidents, etc, in quantities sufficient to produce exposures above the recommended ceiling concentration limit, it is essential that phosgene monitoring devices be installed, and that these devices give immediate warning of concentrations likely to be hazardous to life or health. It is difficult to define the limiting circumstances when such devices may be required, but if reasonable doubt exists, the decision should be made by a professional industrial hygienist. Monitoring devices may be based upon several operating principles, and at least one is currently (1976) commercially available. No matter what device is used, certain criteria common to phosgene monitors should be considered before purchasing any instrument.

Summary of Specifications

(a) The monitoring device must sound an alarm or otherwise warn employees whenever a phosgene concentration of 0.2 ppm is reached or exceeded.

(b) The monitoring device must have a response time of 90 seconds or less when exposed to phosgene at a concentration of 0.2 ppm.

(c) Zero drift should be less than 1% of full scale reading in 24 hours. That portion of the signal manifested as background noise should be less than plus or minus 1% of full scale reading.

(d) The monitoring device must be accurate to within plus or minus 10% of the reading for the range of 0.05-0.4 ppm phosgene.

(e) Precision and repeatability must be plus or minus 5% of full scale reading.

(f) It is desirable that the instrument respond only to phosgene, but devices which respond to other gases not normally present in the atmosphere may be acceptable. Whenever there is a possibility that gases or vapors, such as hydrogen chloride, chlorine, benzoyl chloride, acetyl chloride, and oxalyl chloride, may be present, it would be desirable to determine in advance the response of the instrument to such gases or vapors.

(g) An operating range of 0-0.4 ppm phosgene is recommended, but other ranges may be selected to suit individual needs.

(h) The device should be capable of 168 hours of continuous, unattended operation.

(i) The device and alarm should be intrinsically safe for use in locations where explosion hazards may occur.

Discussion

The principal requirements for such monitors in addition to responding to phosgene gas are that they be sufficiently rugged to withstand pressure, vibration, normal extremes of temperature, etc, and not be susceptible to plugging or interferences due to contaminants likely to be encountered in most workplaces. They should be so constructed that it is possible to routinely and quickly check the zero setting of the instrument and the response to phosgene at 0.2 ppm. It is permissible to

perform such checks by electrical means, but at least once each month instruments should be checked with a known concentration of 0.2 ppm phosgene in air.

Pressurized cylinders containing phosgene in nitrogen are commercially available. According to the National Bureau of Standards, [144] phosgene concentrations in cylinders are stable up to at least 3 months if the nitrogen originally put in the cylinder was very dry. In order to avoid the problems of degradation of the phosgene in the cylinder, it is recommended that phosgene at concentrations of 50-100 ppm in nitrogen be obtained and then diluted to the selected check concentration, ie, 0.2 ppm, as needed. This new concentration should be verified by the analytical procedure in Appendix II. Permeation tubes can also be used for generation of phosgene at known concentrations, but this requires a temperature-controlled manifold. A single calibration point at 0.2 ppm can be checked to determine whether the instrument has maintained its calibration. If the reading differs by more than 0.02 ppm from the previous calibration, then several other calibration points over the useful range of the instrument should be checked and a new calibration established. If the monitor is off by more than 0.02 ppm, the other variables should be checked, eg, flow rate, electronics, detection media.

In large plants, where there are considerable distances between work stations, additional monitors may be required to ensure worker safety. Alternately, a multipoint sampling system bringing sampled air to a single instrument may be satisfactory.

XII. APPENDIX IV
MATERIAL SAFETY DATA SHEET

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

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

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of this section. 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 this section shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

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

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

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

(c) Section III. Physical Data

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

(d) Section IV. Fire and Explosion Data

This section should contain complete fire and explosion data for the product, including flash point 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, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD 50, 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.

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

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

(f) Section VI. Reactivity Data

The comments in this section 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 workers 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

This section 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 joint NIOSH and US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," "Suitable for dusts not more toxic than lead," 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 this section. 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 workers potentially exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.	
ADDRESS		
TRADE NAME		
SYNONYMS		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H ₂ O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H ₂ O, % BY WT.
% VOLATILES BY VOL.		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE	
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER
EXTINGUISHING MEDIA			
SPECIAL FIRE FIGHTING PROCEDURES			
UNUSUAL FIRE AND EXPLOSION HAZARD			

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA
ROUTES OF EXPOSURE
INHALATION

SKIN CONTACT

SKIN ABSORPTION

EYE CONTACT

INGESTION

EFFECTS OF OVEREXPOSURE
ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES
EYES:

SKIN:

INHALATION:

INGESTION:

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

OTHER HANDLING AND
STORAGE REQUIREMENTS

PREPARED BY: _____

ADDRESS: _____

DATE: _____

XIII. TABLES AND FIGURE

TABLE XIII-1

CHEMICAL AND PHYSICAL PROPERTIES OF PHOSGENE

Synonyms	Carbonyl chloride, carbon oxychloride, chloroformyl chloride, CG
Chemical formula	COCl ₂
Formula weight	98.9
Boiling point (1 atm)	7.5 C
Freezing point (1 atm)	-127.8 C
Density, liquid, 0 C	1.4187 g/ml
Density, gas, 20 C	4.39 g/liter
Specific gravity, gas, 20 C (air = 1)	3.4
Specific gravity, liquid, 19 C/4 C	1.392
Expansion ratio, liquid to gas, boiling point to 21 C	1-343
Solubility	Slightly soluble in water, hydrolyzes to hydrochloric acid and carbon dioxide. Soluble in carbon tetrachloride, chloroform, acetic acid, benzene, toluene
Color	Colorless
Odor	Sweet in low concentrations; sharp, pungent in higher concentrations
<u>Flammability</u>	<u>Nonflammable</u>
From references 1,2,10,11,12	

TABLE XIII-2

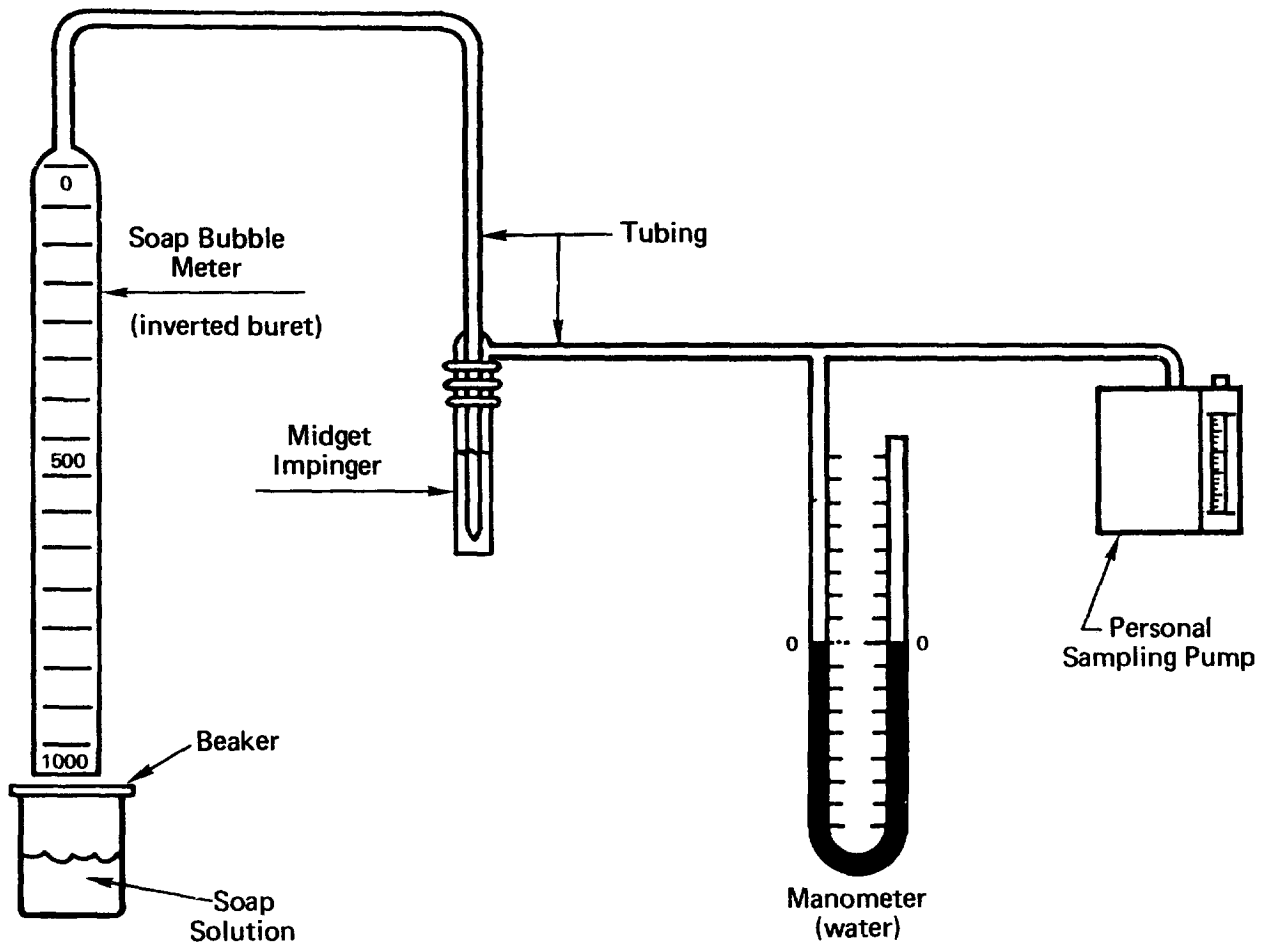
OCCUPATIONS WITH POTENTIAL EXPOSURE TO PHOSGENE

Chlorinated compound makers	Isocyanate makers
Dyemakers	Organic chemical synthesizers
Firemen	Phosgene workers
Glass makers	Resin makers
Herbicide makers	Welders or brazers (near chlorinated
Insecticide makers	solvent vapors)

Adapted from Gafafer [15]

FIGURE XIII-1

**CALIBRATION SETUP FOR PERSONAL SAMPLING
PUMP WITH MIDGET IMPINGER**



DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

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