

## IX. APPENDIX I

### METHOD FOR SAMPLING ACRYLAMIDE IN AIR

The recommended sampling method presented is a modification of that described in the Dow Chemical Company analytical method PAA No. 46 [58].

Collect breathing zone samples representative of the individual employee's exposure. Collect enough samples to permit calculation of a time-weighted average (TWA) concentration for every operation or location in which there is exposure to acrylamide. At the time of sample collection, record a description of sampling location and conditions, equipment used, time and rate of sampling, and any other pertinent information.

The midget impinger recommended must be operated in a uniform and consistent way if data obtained are to have meaning in the assessment of environmental conditions. The impinger should be made of glass in all portions that may contact the collection medium or the airstream before collection is effected. It should be emphasized that the distilled water used as a collection medium must be free of contaminating substances that produce interferences (see Appendix II) when analyzed by polarography.

#### Equipment

The sampling train consists of a sampling pump and an all-glass midget impinger filled with 10 ml of distilled water. The sampling pump is protected from splash-over or water condensation by an adsorption tube loosely packed with a plug of glasswool and inserted between the exit arm

of the impinger and pump or, preferably, by a water trap inserted in the same location.

### Calibration

Since the accuracy of environmental monitoring can be no greater than the accuracy of the air volume measurement, the accurate calibration of a sampling pump is essential to the correct interpretation of the volume indicated. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. Pumps should also be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary. Regardless of use, maintenance and calibration should be performed on a regular schedule and records of these should be kept.

Ordinarily, pumps should be calibrated in the laboratory. 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 a soapbubble meter, are recommended, although other standard calibration instruments, such as a wet-test meter or dry gas meter, can be used. The actual setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. Since the flowrate given by a pump is dependent on the pressure drop of the sampling device, in this case an impinger, the pump must be

calibrated while operating with a representative filled impinger in line. The calibration system should be assembled in series following this order: soapbubble meter, water manometer, midget impinger, and pump as shown in Figure XII-1.

(a) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration and charge the battery if necessary.

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

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

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

(e) Start a soapbubble up the buret and measure with a stopwatch the time required for it to move between calibration marks.

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

(g) Record the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, the date, time, and name of the person performing the calibration.

(h) The rotometer reading should be corrected for temperature and pressure, if necessary.

### Sampling Procedure

Any air mover capable of drawing the desired flowrates through the impinger may be used, so long as flowrates do not vary more than  $\pm 5\%$  during the sampling period. The sampling pump must be capable of operating at a pressure drop of 13 inches of water while providing a flow of 1 liter/minute.

(a) For samples representative of an individual employee's exposure, place the midget impinger within the breathing zone of the exposed employee by inserting it into a holster for fastening to the employee's coat lapel or shirt collar, or hold the impinger near the face of the employee during the sampling period.

(b) Collect an air sample at a flowrate of 1 liter/minute. The flowrate of the pump must be calibrated and this calibration checked periodically to ensure that it has not changed.

(c) Transfer the contents of the impinger to a sample bottle for shipping. Wash the impinger, stem, and splash-over with 2-5 ml of distilled water, add the washing solution to the sample bottle, and record the exact amount of distilled water used. Seal the sample bottle tightly and place it upright in a carrying case. Every attempt should be made to prevent losses from spillage or evaporation.

The trapped acrylamide is analyzed as described in Appendix II. Other collection methods shown to be equivalent may be used.

## X. APPENDIX II

### ANALYTICAL METHOD FOR ACRYLAMIDE

The following analytical method for acrylamide is adapted from those described by Betso and McLean [67] and presented in the Dow Chemical Company analytical method PAA No. 46 [58].

#### Scope

This method is applicable to the determination of acrylamide monomer which may be present in the air in an industrial environment. The procedure is described for measuring potential employee exposure. Amounts of 5-200  $\mu\text{g}$  of acrylamide/10 ml of aqueous solution can be determined; larger amounts of acrylamide may be determined by appropriate dilution [58].

#### Principle of the Method

A known volume of air is drawn through a midget impinger filled with distilled water to collect the acrylamide dust and vapor. Two ml of sample are mixed with 8 ml of methanol. An aliquot of the sample is treated with ion-exchange resin and a fraction is injected into a differential pulse polarograph. The response of the resulting peak is determined and compared with responses obtained from the addition of standards. Polarographic response is based on the electrochemical reduction of the acrylamide double bond.

### Range and Sensitivity

The polarographic detection limit for acrylamide in a clean system is less than 1  $\mu\text{g}$  of acrylamide/ml of acrylamide solution [67]. Even at this low concentration, the acrylamide reduction peak is well-defined and resolved from the background.

### Interferences

Differential pulse polarography is reasonably specific and relatively free from interferences. In addition, the ion-exchange resin treatment removes most common interferences, such as acrylic acid, acrylonitrile, and sodium and potassium ions. However, any compounds which are reducible in the same potential region (-2.0 v) will interfere. Substituted acrylamides and acrylate esters are reducible in the same potential region and, if present, will interfere.

### Apparatus

- (a) Glass-fiber filter disc, or equivalent.
- (b) Magnetic stirrer and bar.
- (c) Differential pulse polarographic analyzer (Princeton Applied Research (PARC) Model 174 equipped with PARC droptimer or equivalent).
- (d) Two dimensional (x-y) recorder, or equivalent.
- (e) Polarographic cell, 10-ml, equipped with a dropping mercury working electrode, a platinum-wire counterelectrode, and a saturated calomel reference electrode connected to the cell via a tetra-n-butylammonium chloride bridge. The cell should be equipped for deaeration with solvent-saturated, oxygen-free nitrogen.

(f) A gas scrubbing tower filled with a methanol-water solution (80:20 V/V) for nitrogen scrubbing.

(g) Eppendorf pipet, 100- $\mu$ l, or equivalent.

(h) Watch glass.

(i) Beakers, 10- and 20-ml.

(j) Volumetric flasks, 100- and 250-ml.

### Reagents

(a) Methanol, ACS reagent grade.

(b) Methanol-water solution (80:20 V/V).

(c) Nitrogen, oxygen-free (prepurified).

(d) Mixed ion-exchange resin, Bio-Rad Analytical Grade Mixed Bed Resin Ag 501-X8 or equivalent.

(e) Tetra-n-butylammonium chloride, 1.0 M, polarographic grade.

(f) Tetra-n-butylammonium hydroxide, 1.0 M, polarographic grade.

(g) Acrylamide, purified.

(h) Acrylamide standard solution. Accurately weigh about 0.02 g of acrylamide, transfer it to a 100-ml volumetric flask, and dilute to volume with 80:20 methanol-water solution. The solution will contain approximately 200  $\mu$ g of acrylamide/ml.

### Preparation of Mixed Ion-Exchange Resin

Preextract and partially dry a 1-2 week supply as follows: fill a 16-oz bottle about half full of resin. Add about 200 ml of methanol and shake the tightly closed bottle for 8-24 hours. Decant the solvent through a suction filter and wash the resin twice (by decantation from the bottle)

using the methanol-water solution (80:20). Transfer the resin to the filter and wash twice more with the 80:20 solution. Air dry until the resin will fall off a tilted spatula. This washing procedure will give a resin which has an equal mixture of hydrogen and hydroxide ions.

#### Analytical Procedure

(a) Measure the volume of each sample to the nearest 0.1 ml. Record the volume as "V."

(b) Add methanol: four times the volume measured in (a).

(c) Place 15 ml of the solution in (b) into a 20-ml beaker and add 1 g of prepared resin and a miniature magnetic stirring bar. Cover the beaker with a watch glass, place on a magnetic stirrer, and stir for 20 minutes.

(d) Prepare a reagent blank as in (c) using 15 ml of methanol-water solution in place of the sample solution.

(e) Transfer 10 ml of the resin-treated extract of the reagent blank to the polarographic cell and add 0.5 ml of 1.0 M tetra-n-butylammonium hydroxide.

(f) Insert the electrodes into the cell and deaerate for 5 minutes by purging with nitrogen.

(g) Record the differential pulse polarogram from -1.6 to -2.4 v against the saturated calomel electrode and a full-scale current range of 2  $\mu$ amp, a pulse height of 50 mv, and a drop time of 0.5 seconds.

(h) Repeat (e-g) employing 10 ml of the resin-treated sample.



(i) To the sample, add 0.1 ml of acrylamide standard solution (20  $\mu$ g) with a 100- $\mu$ l Eppendorf pipet to each of the samples and repeat (f) and (g). Record micrograms of acrylamide added.

(j) Measure the peak height of the sample at about -2.0 v, correcting for any blank reading, both before (value "A") and after (value "B") adding acrylamide (i).

### Calculations

$$\text{Let } F = \frac{\text{micrograms of acrylamide added}}{B-A}$$

The total micrograms of acrylamide in the sample of air are calculated by the following equation:

$$\begin{aligned} \text{micrograms of acrylamide in the sample} &= 5 \times \frac{(A) \times (F) \times (V)}{10} \\ &= 0.5 \times (A) \times (F) \times (V) \end{aligned}$$

The concentration of acrylamide in the air sampled can be expressed in mg/cu m:

$$\text{mg/cu m} = \frac{\text{total micrograms of acrylamide in sample}}{\text{total volume of air sampled in liters}}$$

XI. APPENDIX III  
MATERIAL SAFETY DATA SHEET

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

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

(a) Section I. Product Identification

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

competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

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

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

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

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

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

(c) Section III. Physical Data

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

(d) Section IV. Fire and Explosion Data

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

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LC50 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. Comments pertinent to acrylamide might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation, erythema, and skin peeling.

Eye Contact--some pain and mild transient irritation; conjunctival injury.

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

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

(f) Section VI. Reactivity Data

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

(g) Section VII. Spill or Leak Procedures

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

(h) Section VIII. Special Protection Information

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

(i) Section IX. Special Precautions

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

(j) Signature and Filing

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

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous 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 control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

--


## MATERIAL SAFETY DATA SHEET

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



<b>IV FIRE AND EXPLOSION DATA</b>				
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				
<b>V HEALTH HAZARD INFORMATION</b>				
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				

<b>VI REACTIVITY DATA</b>	
CONDITIONS CONTRIBUTING TO INSTABILITY	
INCOMPATIBILITY	
HAZARDOUS DECOMPOSITION PRODUCTS	
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION	
<b>VII SPILL OR LEAK PROCEDURES</b>	
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	
NEUTRALIZING CHEMICALS	
WASTE DISPOSAL METHOD	
<b>VIII SPECIAL PROTECTION INFORMATION</b>	
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 \_\_\_\_\_

XII. TABLES AND FIGURE

TABLE XII-1

PHYSICAL AND CHEMICAL PROPERTIES OF ACRYLAMIDE

---

Molecular formula	CH <sub>2</sub> =CHCONH <sub>2</sub>
Formula weight	71.08
Melting point	84.5 ± 0.3 C
Vapor pressure	0.007 mmHg at 25 C 0.033 mmHg at 40 C 0.07 mmHg at 50 C
Appearance	White crystalline solid
Boiling point	87 C at 2 mmHg 103 C at 5 mmHg 125 C at 25 mmHg
Heat of polymerization	19.8 kcal/mole
Density	1.122 g/ml at 30 C
Solubility in g/100 ml of solvent at 30 C:	
acetone	63.1
benzene	0.346
chloroform	2.66
ethanol	86.2
ethyl acetate	12.6
n-heptane	0.0068
methanol	155
water	215.5

---

Adapted from Kirk-Othmer Encyclopedia of Chemical Technology [1]

TABLE XII-2

OCCUPATIONS WITH POTENTIAL EXPOSURE TO ACRYLAMIDE

---

Acrylamide manufacturing workers  
Adhesive tape-making workers  
Chemical grouting workers  
Electrophoretic gel-making workers  
Flocculator workers  
Papermaking workers  
Soil stabilization workers  
Surface coating workers  
Synthetic fiber-making workers  
Textile workers  
Well drillers

---

Adapted from Chemistry of Acrylamide [3]

TABLE XII-3

## SAMPLING DATA FROM AN ACRYLAMIDE MANUFACTURING PLANT

Job Description	Date	Airborne Exposure to Acrylamide*	
		Personal Monitoring Data	Stationary Site Data
Supervisor, preparation and mixing of solution	4/29/75	0.5	0.2
	4/30/75	0.7	0.2
	"	0.6	0.2
	5/2/75	0.6	0.2
	"	0.5	0.2
	5/5/75	0.8	0.2
	5/6/75	0.2	0.1
	5/7/75	1.5	0.2
Bagging	1/6/75	0.5	0.1
	1/7/75	3.6	0.1
	1/10/75	0.5	0.2
	1/14/75	0.6	0.1
	1/15/75	0.7	0.1
	1/16/75	2.0	0.1
	1/17/75	1.3	0.2
	2/7/75	0.3	0.1
	2/10/75	0.3	0.1
	2/11/75	2.3	0.3
	2/12/75	0.5	0.1
	2/14/75	0.3	0.2
	4/29/75	1.8	0.2
	5/28/75	0.8	0.2
General, solid only	9/5/74	0.5	0.1
	5/8/75	0.7	0.2
	5/12/75	0.4	0.2
	5/13/75	0.3	0.1
	5/15/75	0.5	0.2
	5/16/75	1.8	0.2
General, solutions only	5/8/75	0.7	0.2
	5/13/75	0.5	0.1
	5/15/75	0.2	0.2
	5/16/75	0.1	0.2

TABLE XII-3 (CONTINUED)

## SAMPLING DATA FROM AN ACRYLAMIDE MANUFACTURING PLANT

Job Description	Date	Airborne Exposure to Acrylamide*	
		Personal Monitoring Data	Stationary Site Data
General, solutions and solid	5/7/75	0.4	0.2
	5/9/75	0.6	0.3
	"	0.8	0.3
	5/14/75	0.3	0.1
	"	1.0	0.1

\*All concentrations are given in mg/cu m for 8-hr exposures.

Adapted from Brinkley (written communication, June 1976)

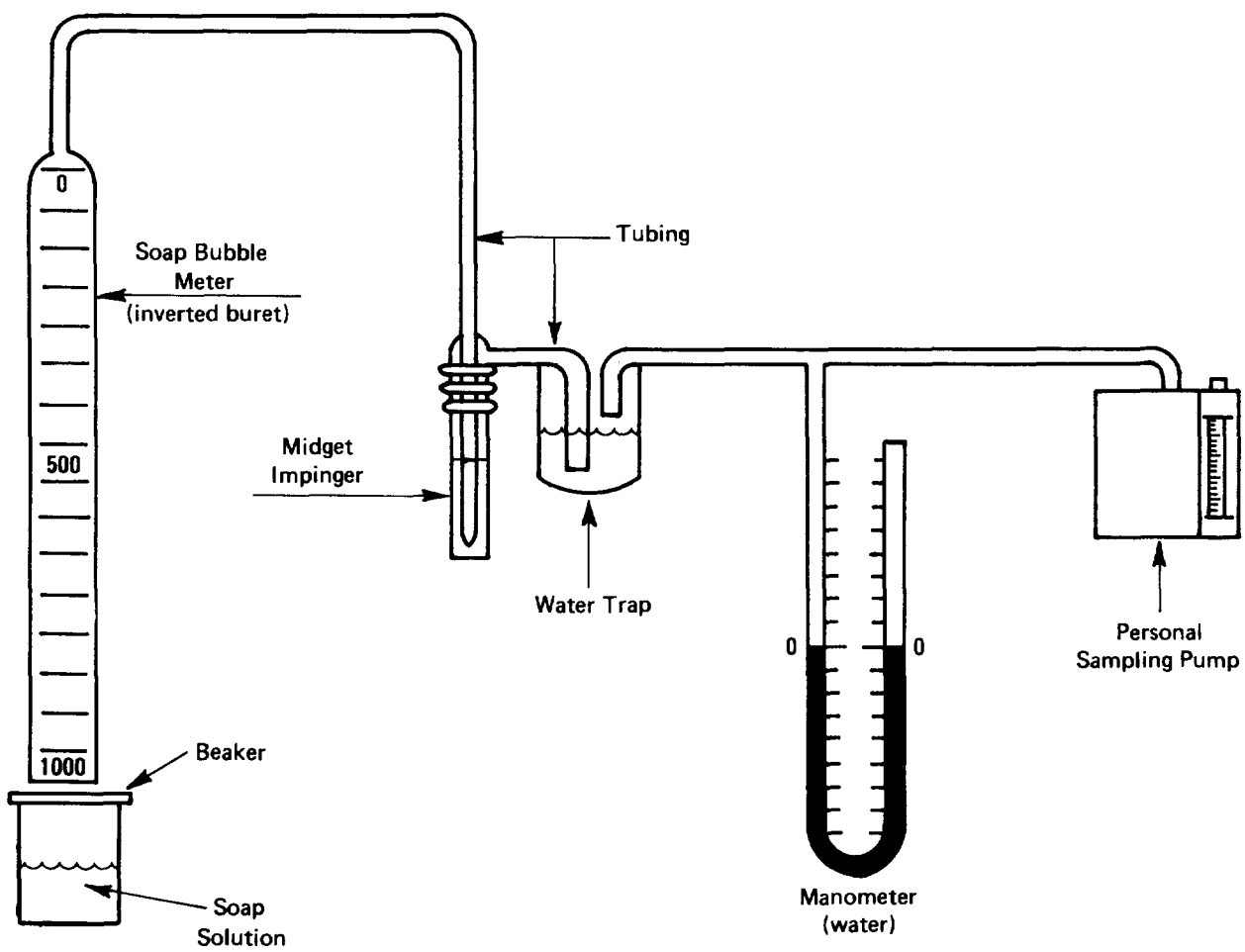


FIGURE XII-1 CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH MIDGET IMPINGER



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

---

OFFICIAL BUSINESS  
PENALTY FOR PRIVATE USE. \$300



POSTAGE AND FEES PAID  
U.S. DEPARTMENT OF H.E.W.  
HEW 399