

VIII. APPENDIX I

AIR SAMPLING METHOD FOR FREE SILICA

General Requirements

To evaluate the worker's exposure, environmental sampling for free silica dust requires the application of respirable dust sampling techniques such as those presented in the ACGIH Air Sampling Instruments [145] and those recommended by the AIHA-ACGIH Aerosol Technology Committee. [82] The dust is collected with a size-selective personal sampler positioned in the worker's breathing zone. Dust penetrating the precollector is collected on a low ashing polyvinyl chloride (PVC) filter and the free silica content is determined by X-ray diffraction (Appendix II) after redeposition of the dust on a silver membrane filter.

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

(b) Sampling data sheets shall include:

- (1) The date and time of sample collection.
- (2) Sampling duration.
- (3) Volumetric flowrate of sampling.
- (4) The name of the worker being sampled or the description of the sampling location.
- (5) Sampler serial number.
- (6) Name of person taking sample.

Personal Sampling

(a) Size-selective device

Personal samples shall be collected using a two-stage, 10-mm nylon cyclone size-selective sampler.

(b) Filters and filter holders

The size-selective sampler shall be connected to a 2-piece, 37-mm cassette containing as the collecting medium a 37-mm, low-ashing polyvinyl chloride (PVC) filter with a 5.0- μ m pore size. (Gelman VM -1 filters are unacceptable for use in the analytical method recommended because of the high background reading produced by the filter upon ashing.) Duplicate filters shall be subjected to identical handling, but without air being drawn through them, so that they may serve as blanks or controls.

(c) Personal sampling pumps

A portable battery operated pump, conforming to the requirements of 30 CFR-47, which is equipped with a pulsation dampener and which will draw 1.7 liters of air per minute (liters/minute) for at least 8 hours shall be used. Present technology of personal sampling pump batteries limits the sample collection time to approximately 8 hours.

(d) Sampling time

The sampling time shall be for a full work shift and the exposure calculated for up to a continuous daily 10-hour exposure. Multiple, shorter (2-4 hour) samples may be collected over a full shift and pooled for determination of an individual's average exposure to free silica during the total work shift.

Workroom (General) Air Sampling

(a) Size-selective sampling devices

When high volume respirable dust samples are required from the area of the worker's environment, a 1/2-inch metal cyclone or its equivalent shall be used to obtain samples.

(b) Filters and filter holders

The size-selective sampler is connected to the filter holder cassette containing the appropriate filter. Samples collected for chemical analysis must be collected on a 37-mm low-ashing polyvinyl chloride (PVC) filter with a 5.0- μ m pore size.

(c) Sampling pumps

Any nonpulsating flow pump with a capacity of at least 10-15 in. Hg at 9 liters/minute will be adequate if the 1/2-inch cyclone is used. For larger samplers a pump of greater capacity will be required.

(d) Sampling time

The general air samples should be collected for a period of 4 consecutive hours taken during collection of the personal samples.

Collection and Shipping of Samples

(a) The quantity of dust collected in the filter holder cassette assembly should not exceed 5 mg. The filter is kept in the cassette for shipment.

(b) Whenever an air sample or series of air samples is collected, a bulk sample of the suspected parent material of the atmospheric contaminant should be obtained and shipped back to the laboratory with the air samples.

(c) After sampling, remove the filter cassette from the sampling train. Stopper the end of the cassette. Ship the cassette to the analytical laboratory in a suitable container to prevent damage in transit.

Sampling Methods for Quantitative and Qualitative Analysis of Free Silica

There are several difficulties, especially from small sample size, in analyzing for the percent and/or form of free silica on each personal sample, so the following methods of sampling are recommended to provide an appropriate sample size for such determinations: higher volume respirable dust samples as collected with a 1/2-inch cyclone; groups of pooled personal samples; any other method shown to be equivalent in collection of a suitable size sample.

A minimum total sample of 500 μg of dust or a minimum free silica dust sample of 25 μg is needed for accurate analysis of the collected dust.

Calibration of Sampling Trains

Since the accuracy of an analysis is no greater than the accuracy of the volume of air which is measured, accurate calibration of a sampling pump is essential for correct interpretation of the pump's indicated volume. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should 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.

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 on 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 calibrating instruments such as a wet-test or a dry-gas meter can be used. The actual setup will be the same for these instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is used, equivalent procedures should be followed.

The calibration setup for a personal sampling pump with a filter cassette is shown in Figure XI-1. The procedure is described below.

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

(b) Place the PVC filter in the filter cassette.

(c) Assemble the sampling train as shown in Figure XI-1.

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

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

(f) Check the water manometer to insure that the pressure drop across the sampling train does not exceed 13 inches of water (1 in. of Hg).

(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 include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, pump number, date of the calibration, and name of the operator.

IX. APPENDIX II
ANALYTICAL METHOD FOR DETERMINATION OF
FREE SILICA IN ATMOSPHERIC DUST

The following method for determination of the polymorphs and/or free silica content in airborne dusts employs X-ray diffraction as recommended in the NIOSH Manual of Analytical Methods. [146] This method is based upon the work of Bumsted, [135] Leroux and Powers, [130] Talvitie and Brewer, [147] Bradley, [148] the Handbook of X-rays, [149] and Leroux et al. [150]

(a) Principle of the Method

(1) Atmospheric dust samples are collected on low-ashing PVC membrane filters.

(2) The filters are ashed and the residues along with an internal calibration standard are redistributed onto silver-membrane filters.

(3) Each sample is scanned by X-ray diffraction to determine the polymorphs of free silica that may be present.

(4) If present, the mass of each polymorph is determined by measuring the ratio of the diffraction peak intensities of the free silica polymorph and the internal standard, and comparing this ratio to a calibration curve.

(b) Range and Sensitivity

(1) The analytical range extends from 5 $\mu\text{g}/\text{sq cm}$ to 200 $\mu\text{g}/\text{sq cm}$ for each free silica polymorph; the total atmospheric dust loading on the filter must not exceed 1 $\text{mg}/\text{sq cm}$.

(2) The sensitivity is 5 μg for each free silica polymorph.

(3) A minimum total dust sample of 500 μg or a minimum free silica dust sample of 25 μg is needed for accurate analysis of collected dusts.

(c) Interferences

(1) Several minerals have diffraction peaks that correspond in position to the major peak for quartz; these include micas (biotite, muskovite, potash, feldspars [microcline], plagioclase), sillimanite, graphite, iron carbide, and zirconium silicate. The presence of these interferences is usually encountered in specific, recognizable situations and can be seen in the X-ray diffraction pattern. Analytical measurements can be carried out at a secondary quartz peak with a commensurate decrease in sensitivity.

(2) Comparable interference may occur from other free silica polymorphs such as cristobalite and tridymite. This can be determined by X-ray diffraction analysis. If interference occurs, secondary peaks must be used.

(3) Diffraction peak interference may also occur for the fluorite (CaF_2) internal calibration standard. Compensation must be made for increased peak intensity from the interfering minerals, or an alternate standard must be employed.

(4) In certain cases, some elements (iron and iron compounds) present in the sample may give rise to appreciable X-ray fluorescence leading to high background intensity. This situation may be circumvented by using a diffracted beam monochromator or by utilizing an alternate X-ray tube target material.

(d) Precision and Accuracy

(1) Leroux et al [150] stated that dust deposits may be analyzed with a precision of better than $\pm 3\%$.

(2) Bumsted [135] reported 21 replicate measurements of quartz in 2 mg of coal dust as having an average of 0.63% (12.6 μg), a range of 0.51-0.91% (10.2-18.2 μg) and a standard deviation of 0.114 ($\pm 1.4 \mu\text{g}$); he reported an accuracy of $\pm 30\%$ ($\pm 3.8 \mu\text{g}$) of the quartz present in these samples. No information is available regarding the accuracy for cristobalite or tridymite.

(e) Advantages and Disadvantages

(1) The X-ray diffraction method offers sensitivity equivalent to or greater than other methods (infrared or colorimetric), is nondestructive to the sample and is rapidly performed.

(2) The X-ray diffraction method is limited to a sample size of a few milligrams. Application of the method requires a rather high degree of technical skill and expensive equipment.

(f) Apparatus

(1) X-ray diffraction equipment, including copper and/or molybdenum target X-ray tubes. (Gelman VM-1 filters are unacceptable for use with X-ray diffraction because of the high background reading produced by the filter upon ashing.)

(2) Low temperature radiofrequency asher or muffle furnace.

(3) Ultrasonic bath.

(4) Filtration apparatus.

(5) 25-mm diameter silver membrane filters having a 0.45 μm pore size.

(6) Aluminum weighing pans.

- (7) Porcelain crucibles with covers.
- (8) 100-ml Pyrex beakers.
- (9) Glass microscope slides.
- (10) Nonserrated, nonmagnetic forceps.
- (11) Metal spatula.

(g) Reagents

(1) Quartz, cristobalite, and tridymite powders and other free silica polymorphs as needed: Acid washed and wet-sieved through 10 μm sieves.

- (2) Fluorite (CaF_2): 400 mesh powder, analytical grade.
- (3) Wetting agent.
- (4) Petroleum jelly.

(h) Procedure—Cleaning of Equipment

It is important that all equipment be kept as free of contaminant dust as possible.

(1) The spatula, forceps, etc may be satisfactorily cleaned by using ethyl alcohol and disposable nonlinting tissues.

(2) The aluminum weighing pans are cleaned by rinsing them twice with distilled water and twice with ethyl alcohol, and allowing them to dry in a dust-free environment.

(i) Analysis of samples

(1) Either of the following described methods may be used to ash the sample:

(A) With forceps and spatula, place the filter sample in an aluminum weighing pan and situate within the sample compartment of the low-temperature asher so that the sample exposure to the radiofrequency-excited oxygen plasma is optimized. The sample is ashed for

1 hour at 100 watts RF power and at an oxygen flow rate of 75 cc/min, using the techniques recommended in the instrument manual.

(B) Using forceps and spatula, put the filter sample in a porcelain crucible, cover loosely and place in muffle furnace. Maintain for 2 hours at 600 C (800 C if graphite is present in the sample).

(2) Carefully scrape the ash residue into a 100-ml beaker. Rinse the weighing pan (or crucible) several times with about 5 ml of water and pour the rinse water into the beaker. Add 1 ml of the fluorite standard solution, a few drops of wetting agent, and distilled water to bring volume up to 50 ml.

(3) Ultrasonically agitate the beaker and its contents for 30 minutes at maximum setting.

(4) Filter solution, under suction, through a 25-mm diameter, 0.45- μ m pore size silver-membrane filter. Thoroughly wash down the filter holder with distilled water to ensure that all dust particles have been transferred to the filter.

(5) Remove the filter with forceps, place in a Petri dish, and dry at 105 C for 15 minutes.

(6) The silver filter is then attached to a glass microscope slide with petroleum jelly and inserted into the X-ray diffractometer. A portion of the filter should be inserted beneath the clamping surface of the diffractometer.

(7) The diffractometer is then scanned over the 2 Theta-range corresponding to $d = 4.5$ to 2.8 Angstroms (for a copper tube, 2 Theta = 18-32 degrees and for a molybdenum tube, 2 Theta = 9-15 degrees). The

presence of crystalline forms of silica are determined by the occurrence of diffraction peaks as follows:

<u>Mineral</u>	<u>d (Most Intense)</u>	<u>d (Second Most Intense)</u>
Quartz	3.34 Angstroms	4.26 Angstroms
Cristobalite	4.05 "	2.49 "
Tridymite	4.07 "	3.80 "
Fluorite Standard	3.15 "	----

The presence of interfering compounds can be determined by the presence and identification of other X-ray diffraction peaks.

(8) The intensity of the most intense diffraction peak for quartz, cristobalite, and tridymite, or other free silica polymorphs is determined by measuring peak height or peak area from the diffraction scan or by scaler (fixed time or fixed count) measurement at peak position. All measurements must be corrected for background. Comparable measurements are made for the fluorite standard at $d = 3.15$ Angstroms. If diffraction peaks from other compounds interfere with the most intense peak for quartz, cristobalite, tridymite, or other free silica polymorphs, the second most intense peak for these free silicas must be employed.

(9) The free silica to calcite intensity ratios are determined, and the mass of quartz, cristobalite, tridymite, and/or other polymorphs of free silica is determined from the appropriate calibration curve.

(j) Calibration and Standard

(1) Standards

(A) A standard solution of fluorite is prepared by adding 20 mg of fluorite to 100 ml of distilled water containing a few drops of wetting agent and then agitating.

(B) Known amounts of quartz, cristobalite, tridymite, and/or other polymorphs of free silica are weighed to the nearest 0.1 mg and are added to 100 ml distilled water containing a few drops of wetting agent to provide five standard solutions of each mineral covering a concentration range of 0.01 - 0.3 mg/ml.

(2) Standard curve

(A) One ml of the standard fluorite solution and one of the free silica solutions are added to 50 ml distilled water and are analyzed according to steps (i) (4) through (i) (8). Similar data are collected for each of the free silica solutions.

(B) Standard curves are prepared for quartz, cristobalite, tridymite, or other forms of free silica in which the intensity ratio of the free silica standard to fluorite is plotted against free silica mass in micrograms. This plot should give a nearly straight line that passes through the origin.

(k) Calculations

The concentration of free silica in air can be expressed as micrograms of free silica per cubic meter of air sampled ($\mu\text{g}/\text{cu m}$).

$$\mu\text{g SiO}_2/\text{cu m} = \frac{\mu\text{g Q} + \mu\text{g C} + \mu\text{g T} + \mu\text{g P}}{V_s}$$

where:

$\mu\text{g SiO}_2/\text{cu m}$ = total micrograms of free silica per
cubic meter of air sampled.

$\mu\text{g Q}$, $\mu\text{g C}$, $\mu\text{g T}$, $\mu\text{g P}$ = quantity of free silica
as determined from the
appropriate calibration curve.

V_s = volume of air sampled in cubic meters.

Q,C,T,P = quartz, cristobalite, tridymite, polymorph
of free silica.

X. APPENDIX III
MATERIAL SAFETY DATA SHEET

The following items of information applicable to any product or material containing free silica shall be provided in the appropriate section of the Material Safety Data Sheet or other approved form. If a specific item of information is not applicable (eg, flash point) the initials "na" should be inserted.

(a) Section I. Source and Nomenclature.

(1) The name, address, and telephone number of the manufacturer or supplier of the product.

(2) The trade name and synonyms for a mixture of chemicals, a basic structural material, or for a process material; the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(b) Section II. Hazardous Ingredients.

(1) Chemical or widely recognized common name of all hazardous ingredients.

(2) 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, eg 10-20% by volume; 10% maximum by weight.

(3) Basis for toxicity for each hazardous material such as an established standard in appropriate units.

(c) Section III. Physical Data.

Physical properties of the total product including boiling point and melting point in degrees Fahrenheit; vapor pressure in millimeters of

mercury; vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatile, indicate if by weight or volume, at 70 degrees Fahrenheit; evaporation rate for liquids (indicate whether butyl acetate or ether = 1); and appearance and odor.

(d) Section IV. Fire and Explosion Hazard Data.

Fire and explosion hazard data about a single chemical or a mixture of chemicals, including flash point, in degrees Fahrenheit; flammable limits in percentage by volume in air; suitable extinguishing media or agents; special firefighting procedures; and unusual fire and explosion hazard information.

(e) Section V. Health Hazard Data.

Toxic level for total compound or mixture. Effects of exposure, and emergency and first-aid procedures.

(f) Section VI. Reactivity Data.

Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(g) Section VII. Spill or Leak Procedures.

Detailed procedures to be followed with emphasis on precautions to be taken in cleaning up and safe disposal of materials leaked or spilled. This includes proper labeling and disposal of containers with residues, contaminated absorbants, etc.

(h) Section VIII. Special Protection Information.

Requirements for personal protective equipment, such as respirators, eye protection, protective clothing, and ventilation, such as local exhaust (at site of product formulation, use or application), general, or other special types.

(i) Section IX. Special Precautions.

Any other precautionary information.

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing,
Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME		EMERGENCY TELEPHONE NO.
ADDRESS (Number, Street, City, State, and ZIP Code)		
CHEMICAL NAME AND SYNONYMS		TRADE NAME AND SYNONYMS
CHEMICAL FAMILY	FORMULA	

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					
HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES				%	TLV (Units)

SECTION III - PHYSICAL DATA

BOILING POINT (°F.)	SPECIFIC GRAVITY (H ₂ O=1)
VAPOR PRESSURE (mm Hg.)	PERCENT, VOLATILE BY VOLUME (%)
VAPOR DENSITY (AIR=1)	EVAPORATION RATE (_____ =1)
SOLUBILITY IN WATER	
APPEARANCE AND ODOR	

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	FLAMMABLE LIMITS	Lel	Uel
EXTINGUISHING MEDIA			
SPECIAL FIRE FIGHTING PROCEDURES			
UNUSUAL FIRE AND EXPLOSION HAZARDS			

SECTION V - HEALTH HAZARD DATA
THRESHOLD LIMIT VALUE
EFFECTS OF OVEREXPOSURE
EMERGENCY AND FIRST AID PROCEDURES

SECTION VI - REACTIVITY DATA			
STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE		
INCOMPATIBILITY <i>(Materials to avoid)</i>			
HAZARDOUS DECOMPOSITION PRODUCTS			
HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR		

SECTION VII - SPILL OR LEAK PROCEDURES	
STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED	
WASTE DISPOSAL METHOD	

SECTION VIII - SPECIAL PROTECTION INFORMATION		
RESPIRATORY PROTECTION <i>(Specify type)</i>		
VENTILATION	LOCAL EXHAUST	SPECIAL
	MECHANICAL <i>(General)</i>	OTHER
PROTECTIVE GLOVES	EYE PROTECTION	
OTHER PROTECTIVE EQUIPMENT		

SECTION IX - SPECIAL PRECAUTIONS	
PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING	
OTHER PRECAUTIONS	

XI. TABLE AND FIGURE

TABLE XI-1

PERMISSIBLE CONCENTRATIONS OF DUST CONTAINING FREE SILICA
FOR THE PARTICULAR INDUSTRIES IN THE LOCALITIES INDICATED*

Industry	Percentage Silica in the Dust	Permissible Maximum Safe Dust Concentration Million Particles/cu ft
South Africa gold mines**	80	4.5
Ontario gold mines**	About 35 (in the rock)	8.5
Australia sandstone**	90 (in the rock)	6
Barre granite***	31 to 38	10-20
Pennsylvania anthracite coal	35	5-10
Broken Hill, Australia**	10 to 17	14

*National Silicosis Conference, Bulletin No. 13, Division of Labor
Standards, United States Department of Labor.

**Based upon engineering practice.

***Based upon clinical studies.

From Reference 33

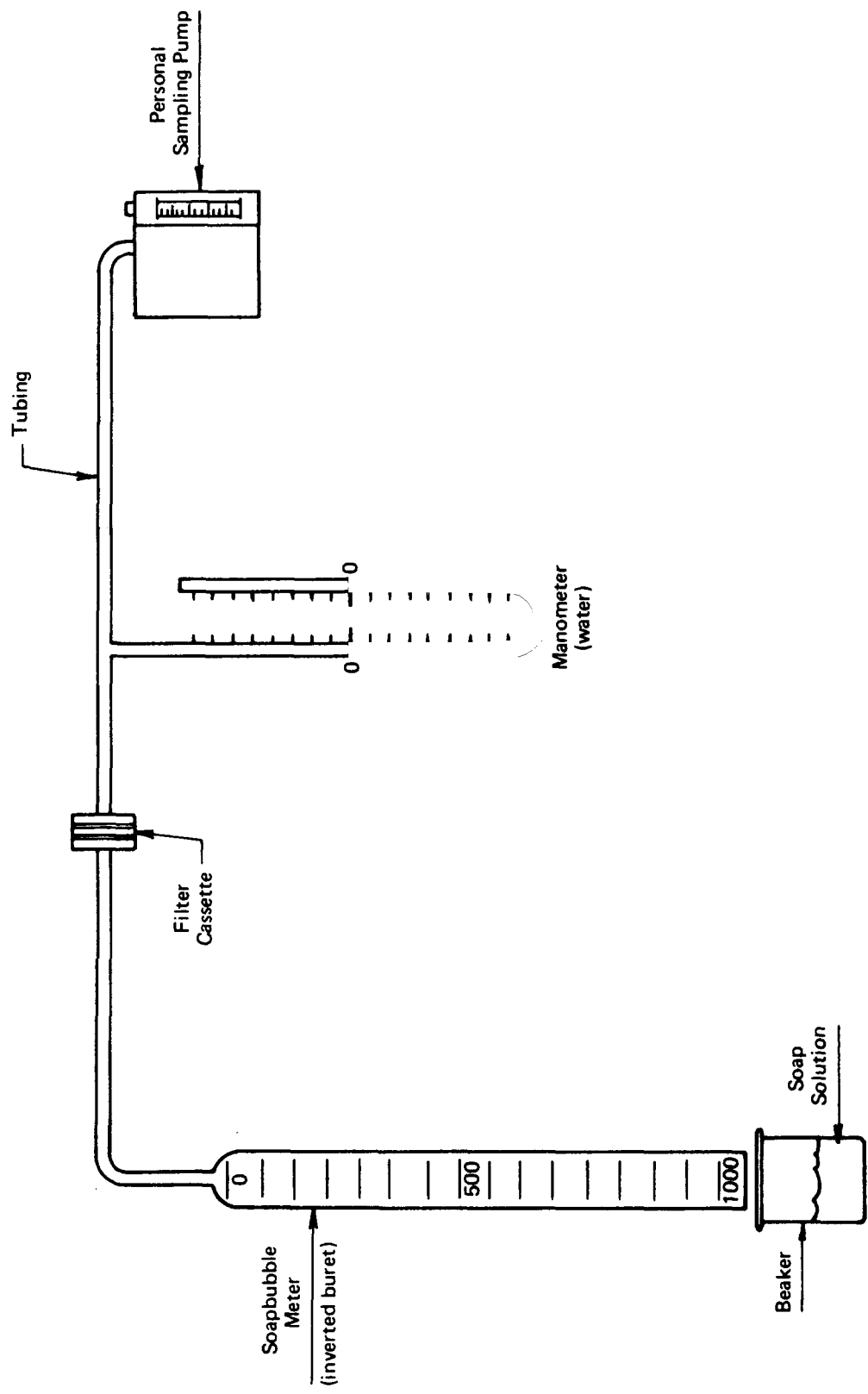


FIGURE XI - 1. CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH FILTER CASSETTE