

VIII. APPENDIX I
METHOD FOR SAMPLING AND ANALYTICAL
PROCEDURES FOR DETERMINATION OF SULFURIC ACID

The following sampling and analytical method for analysis of sulfuric acid in air employs collection on a cellulose membrane filter, aqueous desorption, and volumetric titration in alcoholic solution. The analytical method is derived from Fritz and Freeland [50] and Fritz and Yamamura. [49]

General Requirements

Sulfuric acid 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) Sampling 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) Other pertinent information

Breathing-Zone Sampling

Breathing-zone samples shall be collected as near as practicable to the worker's face without interfering with his freedom of movement and shall

characterize the exposure from each job or specific operation in each production area.

(a) Sampling Equipment

A calibrated personal sampling pump with flowmeter (range up to 2 liters/minute), and an 0.8 μm nominal pore size cellulose membrane filter mounted into either 2- or 3-piece filter cassettes shall be used for sample collections.

(b) Sampling Procedure

The cassette containing the filter is connected to the personal sampling pump inlet by a piece of flexible vinyl tubing of convenient length, but not in excess of 3 feet. The filter assembly is attached to the worker's clothing so as to sample from the worker's breathing zone. A 100-liter sample is recommended to be collected at a rate of 1.5 liters/minute. If sulfuric acid concentrations greater than 5 times the standard are expected, smaller air volumes may be collected, but never less than 10 liters.

A minimum of 3 samples shall be taken for each operation (more samples if the concentrations are close to the standard) and averaged on a time-weighted basis. At least one blank filter with cassette shall be provided which has been subjected to the same handling as the samples but through which no air has been sampled. One additional blank filter with cassette shall be supplied with every 10 samples obtained.

Shipping

The cassette with samples are collected, along with the appropriate number of blanks, and shipped to the analytical laboratory in a suitable container to prevent damage in transit.

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 indication. 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 received 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 setup will be the same for all instruments. Instructions for

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

(a) Flowmeter Calibration Test Method

The calibration setup for personal sampling pumps with the sampling system of a cassette with filter is shown in Figure X-1.

(1) Procedure

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

(B) Place the cellulose membrane filter in the filter cassette.

(C) Assemble the sampling train as shown in Figure X-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 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 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 for 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 2 times, 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, and date and name of the person performing the calibration.

Analytical

(a) Principle of the Method

Sulfuric acid in the air is collected on the cellulose membrane filter and desorbed with distilled water. The pH of the sample solution is adjusted to 2.5 - 4.0 with dilute perchloric acid. After isopropyl alcohol is added bringing the alcohol concentration to approximately 80% by volume, the resulting solution is titrated with 0.005 M barium perchlorate using Thorin [o-(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid] as the indicator. The endpoint is determined as a change from yellow to pink.

(b) Range and Sensitivity

The method is sensitive to 0.1 mg sulfuric acid/cu m of air, assuming a 100-liter air sample. The upper limit is the amount of sulfuric acid retained by the filter and is at least 0.5 mg of sulfuric acid.

(c) Interferences

Soluble particulate sulfates in the air sample would give erroneously high sulfuric acid values.

Metal ion interferences can be eliminated by passing the solution through an ion exchange resin.

Concentrations of phosphate and sulfite ions greater than any sulfate ion concentration cause appreciable interference. Phosphate can be removed by precipitation with magnesium carbonate. Sulfite is corrected for by titration with standard iodine.

(d) Accuracy and Precision

At 1 mg/cu m, the accuracy is at least 10% with a relative standard deviation of 4%. At 10 mg/cu m, the accuracy and relative standard deviation can be improved to about 1%.

(e) Advantages and Disadvantages

The samples are easily collected, stable, and conveniently shipped to the laboratory for analysis.

The analysis is relatively rapid and simple.

A disadvantage is the possible error due to airborne soluble particulate sulfate salts.

(f) Apparatus

- (1) Personal sampling pump with flowmeter capable of sampling at a rate of 1 to 2 liters/minute.
- (2) 37 mm mixed cellulose ester filter, 0.8 μm nominal pore size.
- (3) Necessary glassware.
- (4) A buret of 10-ml capacity graduated in 0.05 ml subdivisions.
- (5) A daylight fluorescent lamp aids in identifying the endpoint.
- (6) Ion exchange columns may be constructed using glass burets or tubing. A column with an inside diameter of 8 mm with 7 inches of resin has a capacity of approximately 25 milliequivalents.

(g) Reagents

- (1) Alcohol-- isopropanol, reagent grade
- (2) Barium perchlorate, 0.005 M-- dissolve 2.0 g of barium perchlorate trihydrate in 200 ml of water and add 800 ml of isopropanol. Adjust pH to about 3.5 with perchloric acid. Standardize against the standard sulfate solution.
- (3) Thorin [o-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid]-- prepare a 0.1-2% solution in distilled water.
- (4) Standard sulfate solution-- prepare a 0.005 M solution of sulfuric acid and standardize by titration with 0.005 M sodium hydroxide

solution or dissolve 0.7393 g anhydrous sodium sulfate in distilled water and dilute to 1 liter (1 ml = 0.5 mg SO₄). The sodium is removed by passage of the standard solution through the ion exchange column.

(5) Hydrochloric acid, 4 N-- add 300 ml concentrated HCl to 600 ml of distilled water. This is needed only to regenerate the column if the ion exchange procedure is used.

(6) Perchloric acid, 1.8%-- dilute 25 ml of reagent grade perchloric acid (70-72%) to 1 liter of distilled water.

(7) Ion exchange resin-- strongly acidic cation exchange resin, 20-50 mesh, or equivalent.

(h) Procedure

(1) Cleaning of equipment-- the glassware should be chemically clean. Wash in detergent and rinse with tap water and distilled water.

(2) Ion exchange procedure (used to purify standard sulfate solution)-- when about two-thirds of the capacity of the resin has been exhausted (deterioration in sharpness of the end point), regenerate the resin by passing 30 ml of 4 N hydrochloric acid through the column. After thorough washing with distilled water, the column is ready for use. Since small volumes of sample solution are passed through the ion exchange column, care must be taken not to dilute the sample with the water that remains on the resin. One way this can be accomplished is by forcing air through

the resin with a squeeze bulb to remove most of the distilled water from the ion exchange resin. One or two ml of sample is passed through the column and is discarded after air is again forced through the resin. The remainder of the sample is then passed through the ion exchange column and an aliquot is titrated according to the general procedure in (i)(3) below.

The column is flushed with distilled water between samples to prevent contamination from the previous sample.

(i) Analysis of Samples

(1) Place the filter from the cassette in a filter holder. Desorb the sulfuric acid by passing three 5-ml portions of distilled water through the filter with suction. Dilute the filtrate to a volume of 25 ml.

(2) If air concentrations of metal ions are encountered which exceed that of the sulfate, sample should be passed through the ion exchange column by the procedure detailed in (h)(2) above.

(3) To a 10-ml aliquot, add 40 ml isopropanol. Adjust the pH, if necessary, to between 2.5 and 4.0 with perchloric acid. Add 1 to 3 drops of Thorin indicator and titrate with barium perchlorate, taking the change from yellow or yellow-orange to pink as the endpoint.

(4) Analyze the standard and reagent blank in the same manner.

(j) Standardization

The barium perchlorate solution is standardized by titrating a 5-ml aliquot with 0.005 M sulfuric acid to the endpoint using Thorin

as indicator. The molarity of the solution is calculated as follows:

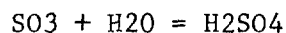
$$M[\text{barium perchlorate}] = \frac{\text{ml}[\text{sulfuric acid}] \times M[\text{sulfuric acid}]}{\text{ml}[\text{barium perchlorate}]}$$

Periodic checks of the molarity of the barium perchlorate solution should be run following this same procedure.

If anhydrous sodium sulfate is used to standardize the barium perchlorate, it must first be ion-exchanged since sodium obscures the endpoint. A 5-ml aliquot of the 0.5 mg/ml sulfate solution is ample for standardization when using a 10-ml buret.

(k) Calculations

The analytical results are calculated on the basis of the following reaction:



$$\frac{\text{mg H}_2\text{SO}_4}{\text{cu m}} = \frac{(A-B) \times C \times E \times 0.510}{D \times F \times G}$$

where

A = ml of sample titrant.

B = ml of reagent blank titrant.

C = ml of standard titrated.

D = ml of standard titrant.

E = volume in ml of sample solution.

F = ml of sample titrated.

G = cu m of air sampled.

0.510 is the product of $\frac{0.5 \text{ mg SO}_4}{1 \text{ ml standard}} \times \frac{\text{H}_2\text{SO}_4 (98.06)}{\text{SO}_4 (96.06)}$

IX. APPENDIX II
MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to sulfuric acid shall be provided in the appropriate section of the Material Safety Data Sheet or approved form. If a specific item of information is inapplicable, the initials "n.a." (not applicable) should be inserted.

(a) The product designation in the upper left-hand corner of both front and back to facilitate filing and retrieval. Print in upper case letters in as large a print as possible.

(b) 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; and the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(c) 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 or the mixture bears

to the whole mixture. This may be indicated as a range of maximum amount, ie, 10-20% by volume; 10% maximum by weight.

(3) Basis for toxicity for each hazardous material such as established OSHA standard in appropriate units and/or LD50, showing amount and mode of exposure and species, or LC50 showing concentration and species.

(d) Section III. Physical Data.

(1) 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); volatility, 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.

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

(1) 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 fire fighting procedures; and unusual fire and explosion hazard information.

(f) Section V. Health Hazard Data.

(1) Toxic level for total compound or mixture, relevant symptoms of exposure, skin and eye irritation properties, principal routes

of absorption, effects of chronic (long-term) exposure, and emergency and first-aid procedures.

(g) Section VI. Reactivity Data.

(1) Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(h) Section VII. Spill or Leak Procedures.

(1) 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 holding residues, contaminated absorbents, etc.

(i) Section VIII. Special Protection Information.

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

(j) Section IX. Special Precautions.

(1) Any other general precautionary information such as personal protective equipment for exposure to the thermal decomposition products listed in Section VI, and to particulates formed by abrading a dry coating, such as by a power sanding disc.

(k) The signature of the responsible person filling out the data sheet, his address, and the date on which it is filled out.

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	LeI	UeI
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 *(Materials to avoid)*

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 *(Specify type)*

VENTILATION

LOCAL EXHAUST

SPECIAL

MECHANICAL *(General)*

OTHER

PROTECTIVE GLOVES

EYE PROTECTION

OTHER PROTECTIVE EQUIPMENT

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

OTHER PRECAUTIONS

Table X-1

STRENGTHS, PROPERTIES, AND CHARACTERISTICS
OF SULFURIC ACID AND OLEUM

I. Strengths

Sulfuric Acid

Degrees Baume'	% H ₂ SO ₄	Sp G at 60 F Compared to H ₂ O/60 F	Freezing Point	
			C	F
52	65.13	1.5591	-40.0	-40
58	74.36	1.6667	-44.0	-47
60	77.67	1.7059	- 8.0	18
66	93.19	1.8354	-32.0	-26
—	98.00	1.8438	3.0	37
—	100.00	1.8392	10.0	50

Oleums

% Free SO ₃	% Equivalent H ₂ SO ₄	Sp G at 100 F Compared to H ₂ O/60 F	Freezing Point	
			C	F
20.0	104.50	1.8820	- 9.0	15
30.0	106.75	1.9156	15.5	60
40.0	109.00	1.9473	33.0	94
65.0	114.63	1.9820	3.6	34
100.0 (Liquid SO ₃)	122.50	1.8342	17.2	63

II. Properties and Characteristics

Physical state	Liquid
Color	Clear, colorless to cloudy
Odor	Oleum has a sharp, penetrating odor
Flash point	None
Corrosivity	Highly corrosive to most metals, particularly at concentrations below 60 Be with evolution of hydrogen gas.
Reactivity	In addition to attacking many metals, the acid in its concentrated form is a strong oxidizing agent and may cause ignition on contact with organic materials and such products as nitrates, carbides, chlorates, etc. It also reacts exothermically with water.
Hygroscopicity	Yes

Derived from [3]

Table X-2

END USES OF SULFURIC ACID

Phosphatic fertilizers	Regenerated cellulose sheet film
Petroleum products	(chiefly cellophane)
aviation gasoline	Dyes
catalysts	Insecticides
sulfonates (lube oil additives)	Rubber, including synthetic
Ammonium sulfate	Hydrochloric acid
synthetic	Chromium chemicals
coke-oven	Light oil refining
Inorganic pigments	Storage batteries
Iron and steel	Tall oil
Alcohols	Chlorine drying
Rayon	Industrial water treatment
high-tenacity yarn	Medicinals
Aluminum sulfate	Textile finishing
water and sewage treatment	Copper sulfate
Nonferrous metallurgy	Fat-splitting
Industrial explosives	Sulfonated oil
Synthetic detergents	

Derived from [5]

Table X-3

OCCUPATIONS CONSIDERED TO FREQUENTLY
INCLUDE EXPOSURES TO SULFURIC ACID

aluminum sulfate makers	laboratory workers, chemical
ammonium sulfate makers	metal cleaners
battery maker, storage	paint makers
cellulose workers	paper makers
copper sulfate makers	petrochemical workers
detergent makers	petroleum refinery workers
drug makers	phenol makers
dye makers	phosphate workers
electroplaters	phosphoric acid makers
explosive makers	pigment makers
fertilizer makers	rayon workers
food processors	rubber workers
fur processors	steel workers
galvanizers	sulfuric acid workers
glue makers	textile workers
jewelers	

Derived from [6]

TABLE X-4

DISTRIBUTION OF AIRBORNE SULFURIC ACID CONCENTRATIONS

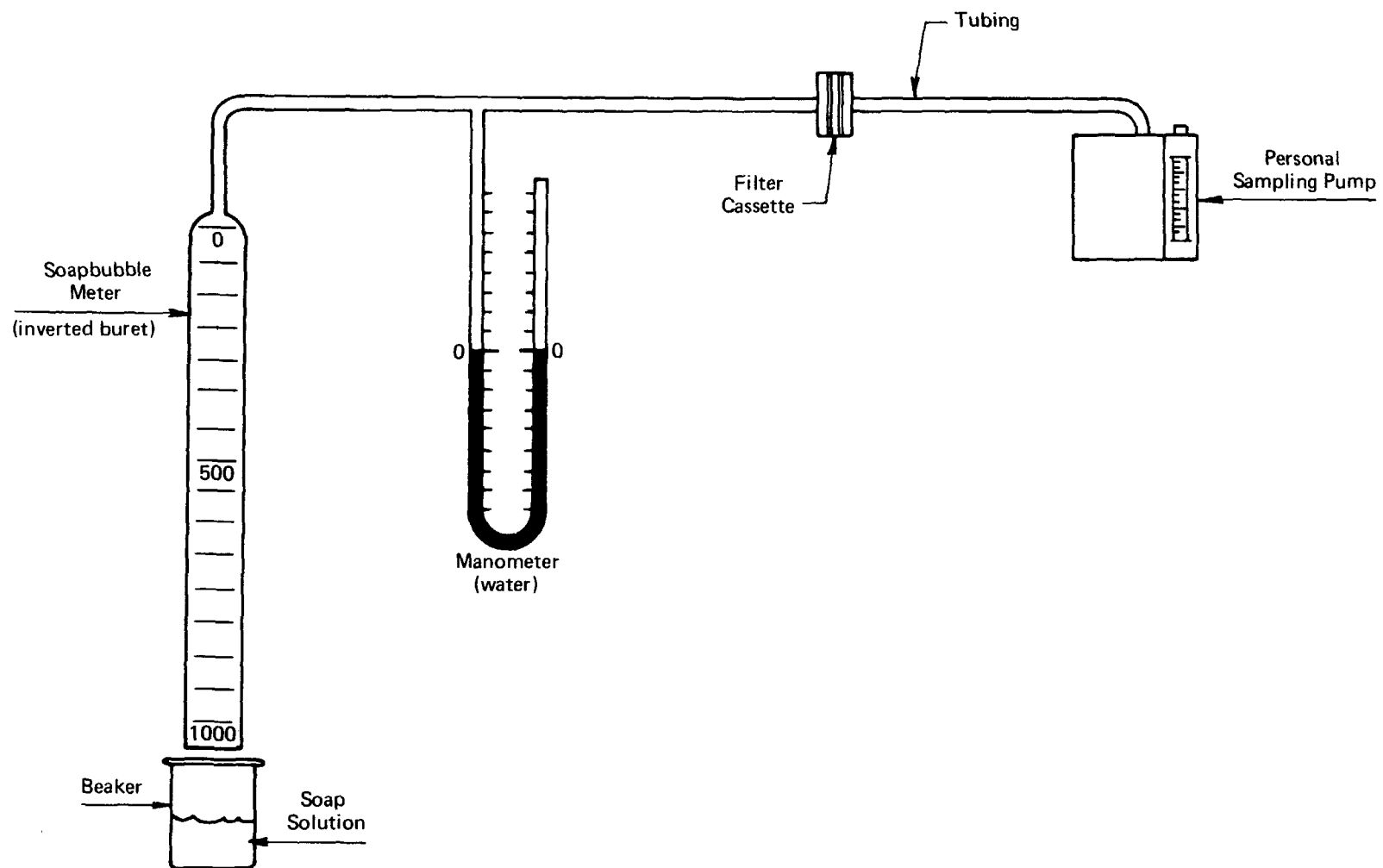
Dept.	Number of times sulfuric acid concentration observed ($\mu\text{g}/\text{cu m}$)									Total No. of Observations
	0-499	500-999	1000-1499	1500-1999	2000-2999	3000-3999	4000-4999	5000-9999	10000 and over	
A	41 (248)*	5 (676)	2 (1205)	- -	- -	- -	- -	- -	- -	48 (333)
B	19 (277)	10 (746)	4 (1292)	8 (1729)	1 (2626)	- -	- -	- -	- -	42 (795)
C	15 (360)	21 (718)	13 (1187)	4 (1753)	7 (2412)	4 (3427)	4 (4441)	11 (6704)	6 (14433)	85 (2960)
D	10 (183)	10 (791)	10 (1228)	1 (1751)	1 (2462)	3 (3560)	1 (4291)	2 (5618)	- -	38 (1380)
E	3 (221)	6 (755)	1 (1395)	1 (1551)	- -	1 (3517)	- -	- -	- -	12 (971)
Total No. of Observations	88	52	30	14	9	8	5	13	6	225

*Mean concentrations for each cell are shown in parentheses.

Derived from [29]

FIGURE X-1

CALIBRATION SETUP FOR PERSONAL SAMPLING
PUMP WITH FILTER CASSETTE AND FILTER



74-128 H₂SO₄