VII. APPENDIX I

SAMPLING FOR XYLENE

The sampling and analytical methods presented in Appendices I and II are based on those described by White et al, [95] Kupel and White, [130] and in Method No. 127 of the Physical and Chemical Analysis Branch of NIOSH. [100]

Atmospheric Sampling

Breathing zone samples representative of the individual worker's exposure shall be collected. A description of sampling location and conditions, equipment used, time and rate of sampling, and any other pertinent information shall be recorded at the time of sample collection. Enough samples shall be collected to permit calculation of a time-weighted average (TWA) exposure for every operation or location in which there is exposure to xylene.

(a) Equipment

The sampling train consists of a charcoal tube and vacuum pump.

(1) Charcoal tubes: Glass tubes, with both ends flame-sealed, 7-cm long with a 6-mm OD and a 4-mm ID, containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of polyurethane foam. The primary section contains 100 mg of charcoal, the backup section, 50 mg. A 3-mm portion of polyurethane foam is placed between the outlet end of the tube and backup section. A plug of glass wool is placed in front of the primary section. The pressure drop across the tube must be

less than 1 inch of mercury at a flowrate of 1 liter/min. Tubes with the above specifications are commercially available.

(2) Pump: A battery-operated pump, complete with clip for attachment to the worker's belt, capable of operation at 1 liter/min or less.

(b) Calibration

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 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 kept.

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 charcoal tube is shown in Figure X-1. Since the flowrate given by a pump is dependent on the pressure drop of the sampling device, in this case a charcoal tube, the pump must be calibrated while operating with a representative charcoal tube in line.

(1) The voltage of the pump battery is checked with a voltmeter to assure adequate voltage for calibration. The battery is charged if necessary.

(2) The tips of a charcoal tube are broken to produce openings of at least 2 mm in diameter.

(3) The sampling train is assembled as shown in Figure X-1.

(4) The pump is turned on and the inside of the soapbubble meter is moistened 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.

(5) The pump rotameter is adjusted to provide the desired flowrate.

(6) The water manometer is checked to insure that the pressure drop across the sampling train does not exceed 13 inches of water at 1 liter/min or 2.5 inches of water at 200 ml/min.

(7) A soapbubble is started up the buret and the time it takes the bubble to move from one calibration mark to another is measured with a stopwatch.

(8) The procedure in (7) above is repeated at least twice, the results averaged, and the flowrate calculated by dividing the volume between the preselected marks by the time required for the soapbubble to

traverse the distance. If, for the pump being calibrated, the volume of air sampled is calculated as the product of the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the quotient of the volume between the 2 preselected marks divided by the number of strokes.

(9) Data for the calibration include the volume measured, elapsed time or number of strokes, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

(c) Sampling Procedure

(1) Both ends of the charcoal tube are broken to provide openings of at least 2 mm, which is half the ID of the tube. A smaller opening causes a limiting orifice effect which reduces the flow through the tube. The smaller section of charcoal in the tube is used as a backup section and therefore is placed nearest the sampling pump. Tubing is used to connect the back of the tube to the pump, but tubing must never be put in front of the charcoal tube. The tube is supported in a vertical position in the worker's breathing zone.

(2) A maximum of 15 liters of air is sampled at a flowrate of 50-1,000 ml/min. For the determination of ceiling concentrations the sampling time is 10 minutes. For the determination of 8-hour time-weighted average concentrations 2 4-hour or 4 2-hour samples are suggested.

(3) The temperature and pressure of the atmosphere being sampled is measured and recorded.

(4) One charcoal tube is treated in the same manner as the sample tubes (break, seal, ship) with the exception that no air is drawn

through it. This tube serves as a blank.

(5) Immediately after sampling, charcoal tubes are capped with plastic caps. Under no circumstances should rubber caps be used. To minimize breakage during transport, capped tubes should be tightly packed in a shipping container. Bulk samples and charcoal tubes should be shipped separately.

VIII. APPENDIX II

ANALYTICAL METHOD FOR XYLENE

Principle of the Method

Xylene vapor trapped on charcoal from a known volume of air is desorbed with carbon disulfide. An aliquot of the desorbed sample is injected into a gas chromatograph. The area of the resulting peak is determined and compared with areas obtained from injection of standards.

Range and Sensitivity

The lower limit of detection of the analytical procedure was found to be less than 12 μg/sample.

Interferences

When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the amount of organic vapor which can be collected before breakthrough of the primary adsorbing section occurs. The capacity of the charcoal tube for xylene may also be reduced by the presence of another organic vapor in high concentration.

Any compound which has about the same retention time as one of the xylene isomers at the gas chromatographic conditions described in this method will interfere with the analysis. This type of interference can be

overcome by changing the operating conditions of the instrument, usually the column and/or the column temperature.

Precision and Accuracy

In a collaborative test, [101] the total relative error in the range of 60-200 ppm (260-870 mg/cu m) was 9.5%. At approximately 5 ppm (20 mg/cu m) this error was 13%.

Advantages and Disadvantages of the Method

The sampling device is small, portable, and involves no liquids. Interferences are minimal and most can be eliminated by altering the chromatographic conditions. The analysis is accomplished using a rapid instrumental method, which can also be used for the simultaneous analysis of 2 or more solvents present in the same sample by changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 20% of that found on the front section, the possibility of sample loss exists.

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

Apparatus

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

(b) Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh acid washed DMCS Chromosorb W solid support. Other columns which achieve the desired separation may be used.

(c) A mechanical or electronic integrator or a recorder and some method for determining peak area.

(d) Small glass-stoppered test tubes or equivalent.

(e) Syringes: 10-μl, and convenient sizes for preparation of standards.

Reagents

(a) Carbon disulfide, chromatographic quality.

(b) Xylene, preferably having an isomer distribution close to that of the sample.

(c) Bureau of Mines Grade A helium.

(d) Prepurified hydrogen.

(e) Filtered compressed air.

Analysis of Samples

All glassware used for the laboratory analysis should be washed in detergent followed by tap and distilled water rinses.

(a) Preparation: Each charcoal tube, including the blank from field samples, is scored with a file and broken open in front of the first section of charcoal. The glass wool is removed and discarded. The

charcoal in the first (larger) section is transferred to a small stoppered test tube. The foam separating section is removed and discarded, and the second section of charcoal is transferred to another test tube. The 2 charcoal sections are then analyzed separately.

(b) Desorption: Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each test tube to desorb the xylene from the charcoal. Desorption is complete in 30 minutes if the sample is stirred occasionally.

EXTREME CAUTION MUST BE EXERCISED AT ALL TIMES WHEN USING CARBON DISULFIDE BECAUSE OF ITS HIGH TOXICITY AND FIRE AND EXPLOSION HAZARDS. IT CAN BE IGNITED BY HOT STEAM PIPES. ALL WORK WITH CARBON DISULFIDE MUST BE PERFORMED UNDER AN EXHAUST HOOD.

(c) Typical gas chromatographic operating conditions:

(1) 40 cc/min (70 psig) helium carrier gas flow.

(2) 65 cc/min (24 psig) hydrogen gas flow to detector.

(3) 500 cc/min (50 psig) airflow to detector.

(4) 200 C injector temperature.

(5) 200 C manifold temperature (detector).

(6) 110 C isothermal oven or column temperature.

(d) Injection: The first step in the analysis is the injection of the sample into the gas chromatograph. The solvent flush injection technique is employed. This eliminates difficulties arising from blowback or distillation within the syringe needle, thus increasing the accuracy and reproducibility of the injected sample volume. The 10.0-μl syringe is first flushed with solvent several times to wet the barrel and plunger, then 3.0 μl of solvent are drawn into the syringe. Next, the needle is removed from the solvent and the plunger is pulled back about 0.2 μl to

separate the solvent flush from the sample with an air pocket to be used as a marker. The needle is then immersed in the sample and a 5.0-μl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection in the gas chromatograph, the plunger is pulled back a short distance to minimize sample evaporation from the needle tip. Duplicate injections should be made of each sample and of the standard. No more than a 3% difference should result in the peak areas that are recorded.

(e) Measurement of area: The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement and preliminary sample results are read from a standard curve prepared as outlined below. The integration of the signals from all three xylene isomers is recommended.

Determination of Desorption Efficiency

The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus it is necessary to determine at least once the percentage of xylene that is removed in the desorption process. This procedure should be repeated for each new batch of charcoal used. The Physical and Chemical Analysis Branch of NIOSH has found desorption efficiencies for xylene varying from 92-99% between batches.

Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5-cm, 4-mm ID glass tube, flame-sealed at one end. This charcoal must be from the same batch as that

used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm or equivalent. A known amount of xylene is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm or equivalent. A known amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal limit of 100 ppm, or about 4.3 mg.

At least 5 tubes are prepared in this manner and allowed to stand overnight or longer to assure complete adsorption of the xylene onto the charcoal. These 5 tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no xylene is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described for unknown air samples.

Two or 3 standards are prepared by injecting the same volume of xylene into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or:

$$\text{desorption efficiency} = \frac{\text{area sample} - \text{area blank}}{\text{area standard}}$$

Calibration and Standards

It is convenient to express the concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the xylene is used to convert

milligrams into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area.

Calculations

The weight in mg, corresponding to the total peak area, is read from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

Corrections for the blank from the field sampling are made for each sample by subtracting the amounts of xylene found on the front and back sections of the blank from the amounts found in the respective sections of the sample:

Corrected amount = amount on sample - amount on blank

The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total amount of xylene in the sample. This total amount is divided by the desorption efficiency to obtain the adjusted total amount of xylene in the sample.

The volume of air sampled is converted to standard conditions of 25 C and 760 mm Hg:

$$\text{Adjusted total amount} = \frac{\text{total amount}}{\text{desorption efficiency}}$$

The concentration of xylene in the air sampled, expressed in mg/cu m (which is numerically equal to μg/liter of air) is given by the quotient of the adjusted amount in μg divided by the volume of air sampled in liters:

$$\text{concentration } (\mu g/\text{liter}) = \frac{\text{adjusted amount } (\mu g)}{\text{volume (liters)}}$$

Another method of expressing concentration is ppm:

$$\text{concentration (ppm)} = \text{concentration } (\mu g) \times \frac{24.45}{106} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

24.45 = molar volume (liter/mole) at 25 C and 760 Torr

106 = molecular weight of xylene (g/mole)

760 = standard pressure

P = pressure (Torr) of air sampled

T = temperature (degrees C) of air sampled

298 = standard temperature (degrees K)

or

$$\text{concentration (ppm)} = \text{concentration } (\mu g) \times \frac{0.588\ (T + 273)}{P}$$

IX. APPENDIX III

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material containing xylene shall be provided in the appropriate section of the Material Safety Data Sheet or other approved form. If a specific item of information is inapplicable (eg, flash point), the initials "na" (not applicable) 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; and 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 per hundred parts of water by weight; specific gravity (water = 1); percent volatile (indicate if by weight or volume) at 70 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 percent 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 containing residues, contaminated absorbents, etc.

(h) Section VIII. Special Protection Information.

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

(i) Section IX. Special Precautions.

Any other general precautionary information.

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved
OMB No. 44-R1387

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_2O=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			

(Continued on reverse side)

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

GPO 934-110

X. TABLES AND FIGURE

TABLE X-1

PHYSICAL PROPERTIES OF XYLENE ISOMERS

	o-xylene	m-xylene	p-xylene
Specific gravity (25/4 C)	0.8758	0.8598	0.8567
Vapor density (air = 1)	3.7	3.7	3.7
Freezing point	-25.2 C	-47.9 C	+13.3 C
Boiling point	144.4 C	139.1 C	138.4 C
Density of saturated vapor-air mixture at 760 mm and 25 C (air = 1)	1.02	1.03	1.03
Flammable limits (% in air)	1.1-6.4	1.1-6.4	1.1-6.6
Vapor pressure (mm Hg) at 25 C	5.2	8.3	8.6
Flash point (closed cup)	17.2 C	25.0 C	25.0 C
Conversion factors (760 mm and 25 C)	1 ppm = 4.35 mg/cu m 1 mg/cu m = 0.230 ppm		

from ANSI Z37.10-1971 [1]

TABLE X--2

HUMAN SENSORY THRESHOLDS FOR MIXED XYLENES

Measured Concentration (ppm)	106	233	454
Number:			
Volunteers	6	7	6
Detecting Odor	6	7	6
Olfactory Fatigue	3	3	3
Throat Irritation	1	0	1
Eye Irritation	0	1	4
With Tears	0	1	1
Reporting Dizziness	0	1	1
Tasting "Something"	0	1	0
With Effects 10 min after Exposure	0	0	0

from Carpenter et al [19]

TABLE X-3

URINARY EXCRETION OF METHYLHIPPURIC ACID AFTER XYLENE EXPOSURE

Sampling (hours)		0-3			4-8			0-8		
		m-xylene		p-xylene	m-xylene		p-xylene	m-xylene		p-xylene
ppm		100	200	100	100	200	100	100	200	100
Uncorrected	Mean	1.75	3.59	2.11	3.14	5.79	1.42	1.86	4.56	1.45
(mg/ml)	SD	0.85	0.65	1.27	1.50	0.91	0.10	0.48	0.49	0.10
Corrected	Mean	1.78	3.19	2.26	2.63	5.58	3.09	2.39	5.32	2.50
(mg/ml)	SD	0.61	0.46	0.96	0.75	1.33	0.82	0.33	0.24	0.69
Rate	Mean	1.69	3.89	1.56	2.16	4.49	2.11	1.78	4.10	1.75
(mg/min)	SD	0.29	0.89	0.23	0.19	1.15	0.77	0.34	0.84	0.21

from Ogata et al [112]

TABLE X-4

SCREENING LEVELS OF METHYLHIPPURIC ACID IN URINE OF WORKERS EXPOSED TO m-XYLENE OR p-XYLENE

	Exposure period (hours)		
	7 (mg/min)	0-3 (mg/ml)	4-8
m-xylene	1.10	0.56	1.13
p-xylene	1.33	0.34	1.45

from Ogata et al [112]

TABLE X-5

XYLENE EXPOSURE LIMITS

Country	mg/cu m	ppm
Bulgaria	100	23*
Czechoslovakia	200	46
(Single Exposure)	1,000	230
Finland	870	200
Germany (Federal Republic)	870	200
Hungary	50	12*
Japan	670	150
Poland	100	23*
Rumania	200	46*
United States	870	200
Florida	870*	200
Hawaii	870*	200
Massachusetts	435*	100
Mississippi	870*	200
Pennsylvania	870*	200
(30-minutes)	1,300*	300
South Carolina	870*	200
USSR	50	12*
Yugoslavia	400	100

*Equivalent values calculated by NIOSH from reference 36

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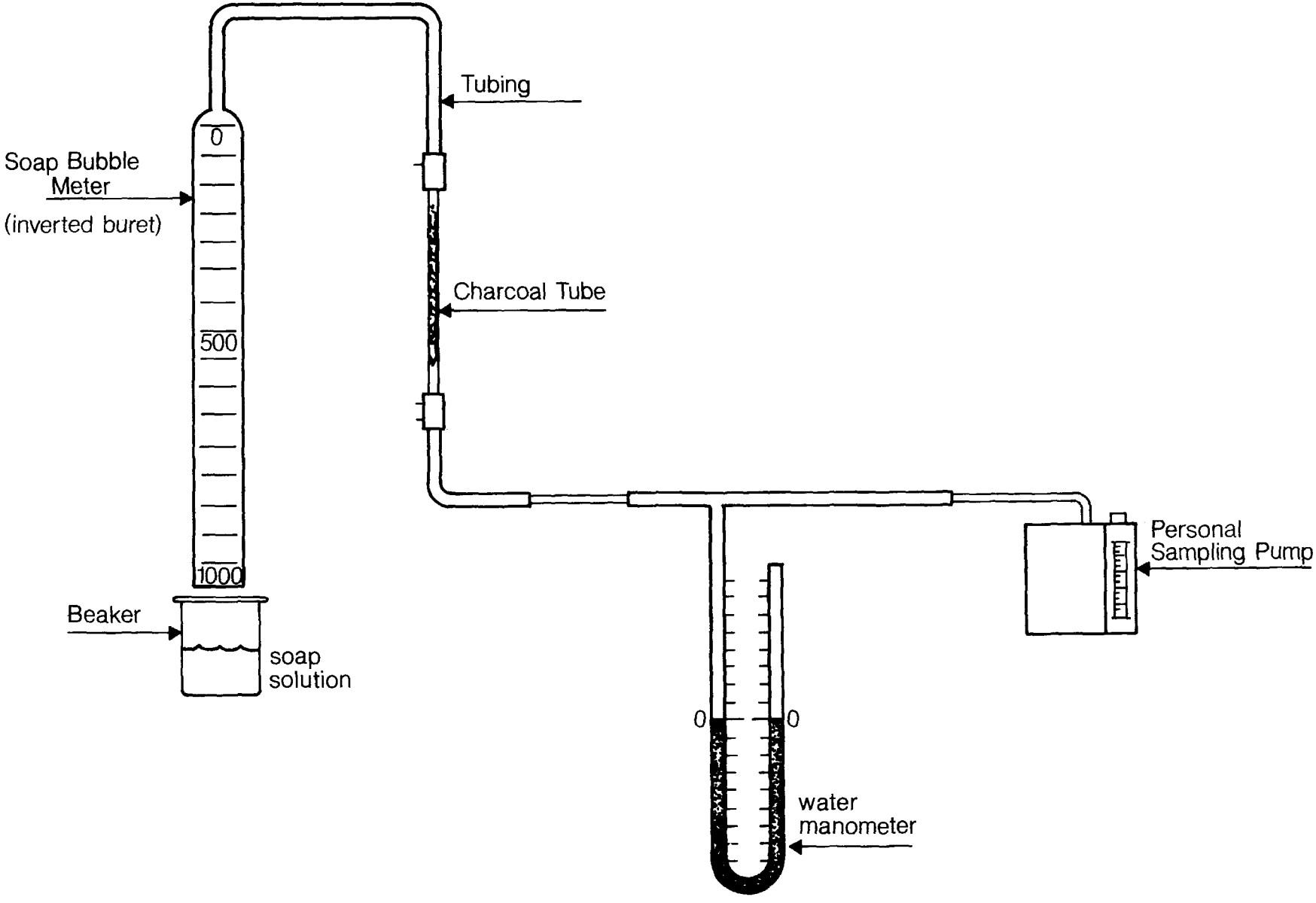
FIGURE X-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH CHARCOAL TUBE



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