XI. APPENDIX III

HYDROGEN SULFIDE MONITORS

Whenever the possibility exists that high concentrations of hydrogen sulfide may be released or created as a result of leaks, accidents, and agitation of sludge, it is essential that hydrogen sulfide monitoring devices be installed, worn, or otherwise used, and that these devices give immediate warning of concentrations likely to become hazardous to life. It is difficult to define the limiting circumstances when such devices may be required; if reasonable doubt exists, the decision should be made by an industrial hygienist. Monitoring devices may be based upon several operating principles. A variety of devices are currently available commercially. In the design or purchase of a hydrogen sulfide monitoring device the following criteria shall be considered.

Summary of Specifications

(a) Monitoring devices must sound an alarm or otherwise warn employees whenever a hydrogen sulfide concentration of 70 mg/cu m (50 ppm) is reached or exceeded. Additionally, fixed (nonportable) monitoring devices should have a different alarm to notify employees whenever there is a hydrogen sulfide concentration greater than 15 mg/cu m (10 ppm) but less than 70 mg/cu m (50 ppm). Lower limits may be voluntarily adopted.

(b) The monitoring device must have a response time of 20 seconds or less when hydrogen sulfide is at a concentration of 50 or more ppm. The

warmup time for the monitoring device should be 5 minutes or less.

(c) Sampling rate and volume are not critical, and any sampling conditions which will meet the response criteria are adequate.

(d) An operating range of up to 100 ppm of hydrogen sulfide is desirable, but other ranges may be selected to suit individual needs.

(e) The monitoring device for hydrogen sulfide should be accurate within 20% and reliable within 10%.

(f) If a monitoring device shows a systematic bias, it may still be used if the difference is small (less than 5%), if the bias predictably overestimates the hydrogen sulfide concentration, or if the device's alarm set point(s) can be recalibrated.

(g) The monitoring device's zero drift should be less than 5% of full scale in 24 hours.

(h) The set point(s) for the device's alarm(s) must be reset to the previous level(s) as soon as possible if the set point(s) has (have) been raised to silence an alarm following appropriate reaction.

(i) Fixed (nonportable) monitoring devices should activate appropriate ventilation systems at the lower set point as well as trigger an alarm. It may be desirable also to connect fixed monitoring devices to equipment to automatically shut down processes if the hydrogen sulfide concentration reaches preset levels. Automatic remote signaling (eg, by radio) is also possible. The device should have an auxiliary power supply in fixed locations.

(j) Many fixed monitoring devices and some portable ones have continuous strip-chart recording capability. This feature may be combined with an integrator circuit if the continuous monitoring device is to be

used also for indicating the ceiling environmental concentrations, but this may only complement, not replace, real-time monitoring for the peak occupational exposure limit.

(k) The device and alarm should be intrinsically safe for use in hazardous locations.

(l) Portable hydrogen sulfide monitoring devices should be durable enough for field use and be light weight, less than 20 pounds (9.08 kg), preferably less than 10 pounds (4.54 kg). They should have a battery-status indicator that can be readily seen. Batteries should be checked frequently to ascertain that they develop the required voltage.

(m) The calibration of each instrument should be checked as needed, and necessary adjustments made.

(n) Alarms that are visible as well as audible are desirable.

Discussion

Hydrogen sulfide monitors in fixed locations are appropriate in enclosed spaces and where likely sources of the gas can be identified. The detector(s) should be positioned near likely sources or equally spaced near the floor, because hydrogen sulfide is slightly heavier than air.

If outdoors, if the source cannot be predicted, or if air currents may move hydrogen sulfide away from a fixed detector, then the fixed-location system shall be supplemented or replaced with portable monitoring devices.

Where considerable distances between work stations or multiple possible sources of hydrogen sulfide exist, additional monitors may be required to ensure worker safety. Alternately, a multipoint sampling

system may be established with a single instrument, subject to the considerations in specifications (a), (b), and (c).

All direct-reading hydrogen sulfide monitors require electric power; some require that the detector or other parts of the device be kept at a constant temperature. These conditions are more readily met indoors than outdoors, but outdoor monitoring is still possible. If line current is used, indoors or out, there should be an auxiliary power supply, because an accident or explosion which results in the release of large quantities of hydrogen sulfide might also knock out electric power. Monitors using batteries should have battery-status indicators, and their status should be checked at least every shift to ensure that the device will continue to operate as needed. In cold climates, both batteries and electrochemical detectors may not function properly unless protected from the cold. Portable monitors may be worn under a coat for use outdoors, if the manufacturer's specifications permit, with tubing for air intake (from the lapel, usually) and exhaust. The likelihood that the tubing will absorb some of the gas is a lesser hazard than the failure of the device because of cold.

Monitoring devices should be calibrated at least once a week by exposing the detector to hydrogen sulfide gas at a known concentration. If the calibration is linear, a zero-span calibration of 0-100 ppm or higher may be desirable [171]. If the calibration is nonlinear, a zero-span calibration of 0-50 ppm or a multipoint calibration is desirable [171]. The concentration of the span gas should be checked at 6-month intervals by another method, eg, methylene-blue colorimetry or gas chromatography. A quality-control chart should be kept as a check on the stability of the

span gas. Some instruments require that the detector be conditioned and calibrated daily by exposure to an ampule of the gas; this requirement has the advantage of keeping the monitoring device calibrated and the disadvantage that the detector may not respond adequately if this step is omitted.

Many hydrogen sulfide monitors have cross-sensitivities: some compounds other than hydrogen sulfide may elicit false-positive responses. In some cases, this may be advantageous: a detector that responds to hydrocarbons in addition to hydrogen sulfide may be useful for detecting leaks in petroleum production or refining facilities; some hydrogen sulfide monitors may be calibrated with carbon monoxide and conversion tables, and if the device is sensitive to another substance which is also toxic, eg, mercaptans, it can give warning of both hazards. The cross-sensitivities of detectors are often capable of election: a hydrogen sulfide detector which is not sensitive to hydrocarbons may be selected for areas with a high background concentration of hydrocarbons.

Workers must be trained to recognize and differentiate alarms and respond appropriately. An alarm that signals the presence of hydrogen sulfide at a concentration of 50 ppm indicates a serious, perhaps worsening, situation and requires evacuation; an alarm or signal at 10 ppm does not.

XII. APPENDIX IV

MATERIAL SAFETY DATA SHEET

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

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

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of 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 conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

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 LD50 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. Typical comments might be:

> Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.
>
> Eye Contact--some pain and mild transient irritation; no corneal scarring.

"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	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA		
BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H_2O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE	

FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER	

EXTINGUISHING MEDIA	
SPECIAL FIRE FIGHTING PROCEDURES	
UNUSUAL FIRE AND EXPLOSION HAZARD	

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA

ROUTES OF EXPOSURE

INHALATION

SKIN CONTACT

SKIN ABSORPTION

EYE CONTACT

INGESTION

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

EYES

SKIN

INHALATION.

INGESTION

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STATEMENTS

OTHER HANDLING AND STORAGE REQUIREMENTS

PREPARED BY _____

ADDRESS _____

DATE _____

XIII. APPENDIX V

NIOSH INTERIM WORK PRACTICE RECOMMENDATIONS

In response to a request, the following work practice recommendations were issued by NIOSH for the gas and oil industry.

HYDROGEN SULFIDE IN THE GAS AND OIL INDUSTRY: INTERIM WORK PRACTICE RECOMMENDATIONS

National Institute for Occupational Safety and Health
Division of Criteria Documentation & Standards Development
Office of Extramural Coordination & Special Projects
August 1976

Introduction

Hydrogen sulfide is found in solution in some crude oil. The gas begins to "pass off" as it reaches the surface with the process being greatly accelerated by heat, especially during refining. It is generally believed that excessive exposure can occur at many points in the oil drilling and refining operations. Some of the area/activities in which there might be a potential exposure to hydrogen sulfide are as follows:

1. Drilling operations: Recycled drilling mud, water portion from the sour crude wells, blow outs (infrequent).
2. Tank gauging (the opening of the tank hatch to measure the liquid level in the tank can result in the release of build-up hydrogen sulfide). Includes run-down tanks, storage tanks at pipeline stations, crude oil storage tanks in refineries, storage tanks for intermediate and finished products.
3. Field maintenance of wells (replacement of packing, pulling of pumping rods, etc.).
4. Entry into closed spaces including trenches, pits, process vessels, and tanks.
5. Leaks in pumps or lines (consideration of corrosion and embrittlement). Equipment maintenance.
6. Stripping of hydrogen sulfide and carbon dioxide from crude oil at the oil field and at the refinery.
7. Sulfur recovery during desulferization [sic] of sour crude; and from contaminated molten sulfur.

8. Injection of sour gas back into formation to stimulate oil production.
9. Asphalt storage and associated operations.
10. Acid cleansing of wells and process units.

Because of the extremely serious nature of the rapidly developing effects which may result from exposure to hydrogen sulfide at high concentrations in the oil and gas industry, we recommend that special attention be given to the development and implementation of certain work practices. Work practices related to controlling hydrogen sulfide exposures have been prepared by a number of organizations including the American Petroleum Institute (API), Society of Petroleum Engineers of the American Institute of Mining, Metallurgical and Petroleum Engineers (SPE of AIME), the National Safety Council, and may also be found in several state rules and regulations. If complied with, existing recommendations could provide worker protection, but it appears that they have not been fully implemented. Engineering controls, maintenance of equipment and implementation of work practice procedures are all important in preventing serious "accidents" reulting from exposure to hydrogen sulfide.

Work Practices and Recommendations

General work practices are well covered in the materials referred to above and need not be repeated. However, because of the type of serious accidents and deaths among workers in the gas and oil industry as well as community residents, special emphasis shall be placed on several types of work which have been involved in these accidents. They include entrance into confined spaces, tank gauging, line repair, and the use or lack of use of respirator equipment when working in areas of potentially high hydrogen sulfide concentrations (suspect areas). Automatic monitoring equipment is available in both stationary and portable styles. NIOSH recommends that continuous monitoring, with an automatic audible signal, be required in certain areas where sudden overexposure to hydrogen sulfide is possible.

1. Confined Spaces
   (a) Entry into confined spaces such as tanks, pits, process vessels, and trenches shall be controlled by a permit system. Permits signed by an authorized employer representitive [sic] shall certify that preparation of the confined space, precautionary measures, and personal protective equipment are adequate, and that precautions have been taken to ensure that prescribed procedures will be followed. Entry procedures should be maintained in written form and readily available for review by affected employees.
   (b) Confined spaces which have contained hydrogen sulfide shall be inspected and tested for oxygen

deficiency, hydrogen sulfide, and other contaminants and shall be thoroughly ventilated, cleaned, neutralized or washed, and then retested for hydrogen sulfide and oxygen prior to and during entry.

(c) Possible buildup of hydrogen sulfide into the confined space while work is in progress shall be prevented by positive means. (Example: Forced air ventilation of closed spaces during repair of leaks or equipment maintenance; securing intake valves or disconnecting intake lines.)

(d) Individuals entering confined spaces where they may possibly be exposed to hydrogen sulfide shall wear either a combination type-C supplied-air respirator operated in the continuous-flow mode (positive pressure) or pressure-demand mode (positive pressure) and an auxiliary self-contained breathing air supply, or a self-contained breathing apparatus operated in the pressure-demand mode (positive pressure) equipped with a full facepiece. Each individual shall also wear a suitable harness with lifelines tended by another employee outside the space who shall also be equipped with the necessary protective equipment, including a self-contained breathing apparatus which operates in the pressure-demand mode (positive pressure) and has a full facepiece. Communications (visual, voice, signal line, telephone, radio or other suitable means) shall be maintained by the standby person with the employee inside the enclosed space.

2. Suspect Areas

In such job activities which could be expected to potentially expose the worker to high levels of hydrogen sulfide (not defined in section 1 above), the work practices specified (in Sections 1(a), (b), (c), and (d)) shall be modified to provide adequate monitoring, ventilation, and personal protection. Examples of those job activities are: tank gauging, maintenance operations, and line repair.

3. Monitoring

Because of olfactory nerve fatigue (concentrations of hydrogen sulfide at 100 ppm or more can kill the sense of smell) a worker can enter an area where high concentrations of hydrogen sulfide are present without knowing it. Some means for constant monitoring with an automatic audible warning device shall be used in places where a sudden release of hydrogen sulfide might not be expected and would not be recognized without such continuous monitoring.

4. Training and Education

The effectiveness of any work practice program depends on type and availability of training and education services and materials which are available to employees. It is recommended

that employee training be provided prior to initial assignment into a potential hydrogen sulfide exposure work area and that refresher training be conducted at regular intervals to keep all employees alerted to the potential danger which exists. This should include training in first aid and emergency procedures and since the worker will probably be responsible for his own protective gear, he should be instructed in proper inspection, maintenance, and emergency repair of his respiratory equipment [144].

XIV. TABLES AND FIGURE

TABLE XIV-1

PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN SULFIDE

Molecular formula	H_2S
Formula weight	34.08
Specific gravity compared to air	1.192
Melting point	-82.9 C
Boiling point	-61.8 C
Solubility in water, 20 C	2.9 volumes gas/volume H_2O
Autoignition temperature	250 C
Explosive range in air	4.5-45.5%
Color	Colorless
Odor threshold	0.02 ppm
Olfactory fatigue level	100 ppm
Vapor pressure, 25 C	19.6 atm
Conversion factors	1 mg/cu m = 0.717 ppm 1 ppm = 1.394 mg/cu m

Adapted from references 1 and 2

TABLE XIV-2

OCCUPATIONS WITH POTENTIAL EXPOSURE TO HYDROGEN SULFIDE

Animal fat and oil processors	Lead removers
Animal manure removers	Lithographers
Artificial-flavor makers	Lithopone makers
Asphalt storage workers	Livestock farmers
Barium carbonate makers	Manhole and trench workers
Barium salt makers	Metallurgists
Blast furnace workers	Miners
Brewery workers	Natural gas production and processing workers
Bromide-brine workers	Painters using polysulfide caulking compounds
Cable splicers	Papermakers
Caisson workers	Petroleum production and refinery workers
Carbon disulfide makers	Phosphate purifiers
Cellophane makers	Photoengravers
Chemical laboratory workers, teachers, students	Pipeline maintenance workers
Cistern cleaners	Pyrite burners
Citrus root fumigators	Rayon makers
Coal gasification workers	Refrigerant makers
Coke oven workers	Rubber and plastics processors
Copper-ore sulfidizers	Septic tank cleaners
Depilatory makers	Sewage treatment plant workers
Dyemakers	Sewer workers
Excavators	Sheepdippers
Felt makers	Silk makers
Fermentation process workers	Slaughterhouse workers
Fertilizer makers	Smelting workers
Fishing and fish-processing workers	Soapmakers
Fur dressers	Sugar beet and cane processors
Geothermal-power drilling and production workers	Sulfur spa workers
Gluemakers	Sulfur products processors
Gold-ore workers	Synthetic-fiber makers
Heavy-metal precipitators	Tank gagers
Heavy-water manufacturers	Tannery workers
Hydrochloric acid purifiers	Textiles printers
Hydrogen sulfide production and sales workers	Thiophene makers
Landfill workers	Tunnel workers
Lead ore sulfidizers	Well diggers and cleaners
	Wool pullers

Adapted from references 3-6

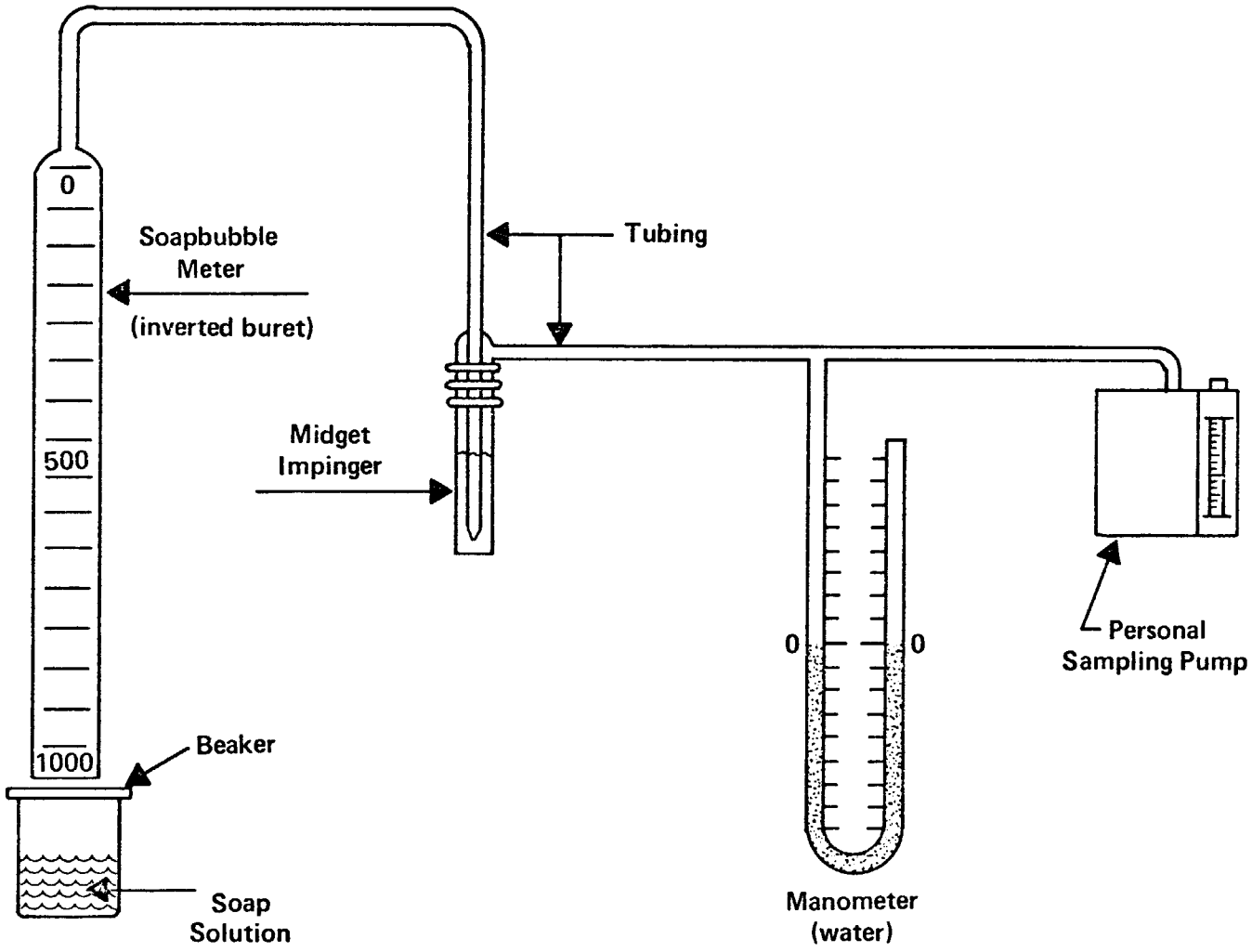

Figure XIV-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH MIDGET IMPINGER

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