#### IX. APPENDIX I

#### ANALYTICAL METHOD FOR BUTANETHIOL

The following sampling and analytical method has been validated, as Method No. S350, for 1-butanethiol [94]. It is the only NIOSH-validated method for a thiol that is included in this recommended standard. Although the method has not yet been validated at 0.5 ppm, it shows promise of being usable for determining n-alkane thiols at this concentration. This analytical method has been also considered feasible for the determination of benzenethiol in air.

## Principle of the Method

- (a) A known volume of air is drawn through a tube containing 60/80 mesh Chromosorb 104 to trap the 1-butanethiol vapor present.
- (b) The thiol is desorbed with acetone, and the solution analyzed in a gas chromatograph with a flame-photometric detector.
- (c) The area of the resulting peak is determined and compared with areas obtained from the injection of standard solutions.

## Range and Sensitivity

- (a) This method has been validated over the range of 16.8-74.2 mg/cu m at an atmospheric temperature of 22 C and atmospheric pressure of 759 mmHg, using a 1.5-liter sample. This sample size is based on the capacity of the Chromosorb 104 to collect the vapor of 1-butanethiol in air at high relative humidity.
- (b) The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- (c) The upper limit of the range of the method depends on the adsorptive capacity of the Chromosorb 104. This capacity may vary with the concentrations of 1-butanethio1 and other substances in the air.
- (d) Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Chromosorb 104) reaches 5% of the concentration in the test gas mixture. Breakthrough

occurs after sampling for 2.9 hours at an average sampling rate of 0.023 liter/minute and relative humidity of 94% and temperature of 25 C. The breakthrough test was conducted at a concentration of 74.2 mg/cu m.

## Interferences

- (a) Any compound that has the same retention time as 1-butanethiol at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- (b) When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

## Precision and Accuracy

- (a) The coefficient of variation for the total analytical and sampling method ranging from 16.8 to 74.2 mg/cu m was 0.062. This value corresponds to a 2.2 mg/cu m standard deviation at the Federal standard level.
- (b) On the average, the concentrations obtained in the laboratory validation study, at 0.5X, 1X, and 2X the Federal standard level, were 2% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias.
- (c) The coefficient of variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 35.9 mg/cu m indicate that collected samples were stable for at least 7 days.

#### Advantages and Disadvantages

- (a) The sampling device is small and portable and involves no liquids. Interferences are minimal, and most of those that do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.
- (b) One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the sorbent will hold before overloading. When the amount of 1-butanethiol found on the backup section of the sorbent tube exceeds 25% of that found on the front section, the probability of sample loss exists.

(c) The precision of the method is limited by the reproducibility of the pressure drop across the tubes. Because the pump is usually calibrated for one tube only, this drop will affect the flowrate and cause the volume to be imprecise.

## Apparatus

- (a) Personal sampling pump: Calibrated personal sampling pump, the flowrate of which can be determined within 5% at the recommended flowrate.
- (b) Chromosorb 104 tubes: Glass tubes with both ends unsealed, 8.5 cm long with a 6-mm OD and a 4-mm ID, containing two sections of 60/80 mesh Chromosorb 104 separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Chromosorb 104, and the backup section contains 75 mg of Chromosorb 104. A plug of silylated glass wool is placed at the ends of the tube. The pressure drop across the tube must be less than 10 mmHg at a flowrate of 0.025 liter/minute. (Chromosorb 104 is a polymeric solid adsorbent manufactured by the Johns-Manville Company and is commonly used as a gas chromatographic column-packing material. Its conditioning and the preparation of the adsorbing tubes are described in Procedure.)
- (c) Gas chromatograph: Gas chromatograph equipped with a flame-photometric detector with a sulfur filter. The gas chromatograph should be equipped with a valve to vent the solvent to the air before it reaches the detector.
- (d) Chromatography column: Glass tubing (4-foot x 1/4-inch OD) packed with 60/80 mesh Chromosorb 104.
- (e) Peak integrator: Electronic integrator or some other suitable method of determining peak areas.
- (f) Sample containers: 2-ml glass sample containers with glass stoppers or Teflon-lined caps.
- (g) Microliter syringes: 10  $\mu l$  and other convenient sizes for preparing standards.
  - (h) Pipets: Delivery type, 1.0 ml, and other convenient sizes.
- (i) Volumetric flasks: 10 ml and other convenient sizes for preparing standard solutions.

## Reagents

- (a) Acetone, reagent grade.
- (b) 1-Butanethiol, reagent grade.
- (c) n-Hexane.
- (d) Nitrogen, purified.
- (e) Hydrogen, prepurified.
- (f) Oxygen, purified.
- (g) Air, filtered, compressed.

## Procedure

- (a) Sorbent washing procedure: Prior to usage, Chromosorb 104 is washed and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch-to-batch differences in production. A quantity of Chromosorb 104 is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone equal to twice the volume of sorbent is added to the sorbent and mixed, and a vacuum is applied. The wash-mix-vacuum sequence is repeated six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120 C under 25 inches mercury vacuum for 4 hours. Immediately prior to packing, the tubes are rinsed in acetone and dried at room temperature to eliminate the problem of Chromosorb 104 adhering to the walls of the glass tubes. The Chromosorb 104 tubes are capped with plastic caps at each end.
- (b) Cleaning of equipment: All glassware used for the laboratory analysis are detergent washed, thoroughly rinsed with tapwater and distilled water, and dried.
- (c) Calibration of sampling pumps: Each personal sampling pump is calibrated with a representative Chromosorb 104 tube in the line to minimize errors associated with uncertainties in the volume sampled.

## Collection and Shipping of Samples

(a) Immediately before sampling, remove the caps from the ends of the Chromosorb 104 tube. In each sampling period, all tubes used are to be packed with Chromosorb 104 from the same manufacturer's lot.

- (b) The smaller section of Chromosorb 104 is used as a backup and should be positioned nearer the sampling pump.
- (c) The tube should be placed in a vertical position during sampling to minimize channeling through the Chromosorb 104.
- (d) Air being sampled should not be passed through any hose or tubing before entering the Chromosorb 104 tube.
- (e) A sample size of 1.5 liters is recommended. Sample at a flowrate between 0.010 and 0.025 liter/minute. Do not sample at a flowrate less than 0.010 liter/minute. Record sampling time, flowrate, and type of sampling pump used.
- (f) The temperature, pressure, and relative humidity of the atmosphere being sampled are recorded. If pressure reading is not available, record the elevation.
- (g) The Chromosorb 104 tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- (h) With each batch of 10 samples, submit one tube from the same lot of tubes used for sample collection. This tube is subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the "blank."
- (i) Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- (j) A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the Chromosorb 104 tubes. Because of postal and Department of Transportation regulations, the bulk sample should be shipped by surface mail. A minimum of 18 extra Chromosorb 104 tubes should be provided to the analyst for desorption efficiency determinations.

## Analysis of Samples

(a) Preparation of samples: Remove the plastic cap from the inlet end of the Chromosorb 104 tube. Remove the glass wool plug and transfer the first (larger) section of Chromosorb 104 to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Chromosorb 104 to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to effect complete transfer of the Chromosorb 104.

- (b) Desorption of samples: Prior to analysis, pipet 1.0 ml of acetone into each sample container. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within 1 day after the thiol is desorbed.
- (c) Gas chromatograph conditions: The following are typical operating conditions for the gas chromatograph:
  - (1) 50 ml/minute (60 psig) nitrogen carrier gas flow.
  - (2) 150 ml/minute (30 psig) hydrogen gas flow to detector.
  - (3) 20 ml/minute (20 psig) oxygen gas flow to detector.
  - (4) 30 ml/minute (20 psig) air flow to detector.
  - (5) 150 C injector manifold temperature.
  - (6) 200 C detector manifold temperature.
  - (7) 140 C column temperature.
- (A) A retention time of about 5 minutes is to be expected for 1-butanethiol under these conditions and with the use of the glass column recommended in <u>Apparatus</u>. The acetone will elute from the column before the 1-butanethiol.
- (B) Injection: The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. 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 a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle is completely After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard are made. No more than a 3% difference in area is expected. Venting of the acetone solvent for 60 seconds after injection is required at the prescribed gas chromatographic conditions. If the solvent

is not vented, the flame may be extinguished and the detector may temporarily malfunction. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Chromosorb 104.

(C) The area of the sample peak is measured with an electronic integrator or some other suitable device for area measurement, and results are read from a standard curve prepared as discussed in the following section.

# Determination of Desorption Efficiency

- (a) The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Chromosorb 104 to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Chromosorb 104.
- (b) Chromosorb 104 equivalent to the amount in the first section of the sampling tube (150 mg) is measured into a 64-mm, 4-mm ID glass tube flame sealed at one end. This Chromosorb 104 is from the same batch as that used in obtaining the samples. The Chromosorb 104 is prewashed with acetone as previously described. The open end is capped with Parafilm. A known amount of a hexane solution of analyte containing 13.73 mg/ml is injected directly into the Chromosorb 104 with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in a 1.5-liter air sample at the selected level. It is not practical to inject the neat liquid directly onto the Chromosorb 104 because the amounts to be added would be too small to measure accurately.
- (c) Six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand at least overnight to assure complete adsorption of the 1-butanethiol onto the Chromosorb 104. These tubes are referred to as the "samples." A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Analysis of Samples.
- (d) Since the response of the flame-photometric detector is nonlinear, a series of standards is prepared to cover variations over each of the three levels (0.5X, 1X, and 2X the standard), as in <u>Calibration and Standards</u>. These are analyzed with the samples. The standards are used to confirm the calibration of the gas chromatograph.
- (e) The desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube.

(f) The desorption efficiency is dependent on the amount of l-butanethiol collected on the Chromosorb 104. Plot the desorption efficiency vs weight of thiol found. This curve is used in <u>Calculations</u> to correct for adsorption losses.

# Calibration and Standards

(a) A series of standards, varying in concentration over the range corresponding to approximately 0.1-3 times the standard for the sample under study, is prepared and analyzed under the same gas chromatograph conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml vs square root of peak area.

Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the flame-photometric detector response.

- (1) Prepare a stock standard solution containing 13.73 mg/ml l-butanethiol in acetone.
- (2) From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in acetone. Prepare at least five working standards to cover the range of 0.0055-0.165 mg/1.0 ml. This range is based on a 1.5-liter sample. Prepare a standard calibration curve by plotting concentration of 1-butanethiol in mg/1.0 ml vs square root of peak area.

#### Calculations

(a) Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/1.0 ml acetone, and the volume of sample injected is identical to the volume of the standards injected.

Corrections for the blank must be made for each sample:

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- (b) Add the weights found in the front and backup sections to determine the total weight of the sample.
- (c) Read the desorption efficiency from the curve (see <u>Determination</u> of <u>Desorption Efficiency</u>) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

For personal sampling pumps with rotameters only, the following correction should be made:

correction should be made:

Corrected volume =  $f \times f$ Corrected volume =  $f \times f$ 

where:

f = flowrate sampled

t = sampling time

P<sub>1</sub> = pressure during calibration of sampling pump (mmHg)

P<sub>2</sub> = pressure of air sampled (mmHg)

 $T_1$  = temperature during calibration of sampling

pump (K)

 $T_2$  = temperature of air sampled (K)

The concentration of 1-butanethiol in the air sampled can be expressed in  $mg/cu\ m$ .

mg/cu m = \_\_\_\_corrected mg x 1,000 (liter/cu m)
corrected air volume sampled (liters)

Another method of expressing concentration is ppm.

$$ppm = mg/cu m x \frac{24.45}{MW} \frac{760}{P} \frac{T + 273}{298}$$

where:

P = pressure (mmHg) of air sampled

T = temperature (C) of air sampled

24.45 = molar volume (liters/mole) at 25 C and 760 mmHg

MW = molecular weight (g/mole) of 1-butanethiol

760 = standard pressure (mmHg)

298 = standard temperature (K)

## Thiols Other Than Butanethiol

Attempts were made by NIOSH to extend the above method to the determination of methanethiol [140] and ethanethiol [93] in air. These failed either because retention on Chromosorb 104 was not adequate or because recovery was unsatisfactory.

Accordingly, until a definitive procedure can be recommended by NIOSH, a number of related methods based on the published reports previously discussed can be suggested for sampling the other thiols.

Adsorption of the higher molecular weight thiols  $(C_5-C_{1\,8})$ , cyclohexanethiol, and benzenethiol on Chromosorb 104 remains the method of choice to collect breathing zone samples by personal sampling, if feasible. The confirmation that the NIOSH-validated method for butanethiol can be extended to this group needs to be obtained in the laboratory.

Area samples can be collected by capture of the thiols in traps filled with solvents and refrigerated. Absorption of methanethiol in ethylbenzene at -78 C, with other traps to remove interfering substances [88,144], would be appropriate. Based on their physical properties (see Tables XII-1 and XII-2), the collection of the other lower molecular weight thiols (ethanethiol and propanethiol) would also be feasible in such a system. Higher molecular weight thiols (alkane thiols  $C_7$  to  $C_{12}$ ,  $C_{16}$ , and  $C_{18}$ ) may also be trapped in this system, in this case at 0 C [88].

Because of the low level recommended, benzenethiol would also require that a larger volume of air be sampled, coupled with an efficient collection system. The ethylbenzene trap at -78 C may provide it, or it may be necessary to use chemical absorption in a midget impinger.

#### X. APPENDIX II

#### FIRST AID FOR EYES CONTAMINATED WITH BENZENETHIOL

About 1884, KSF Crede at the Leipzig University Clinic and Polyclinic for Obstetrics and Gynecology and School for Midwives introduced the use of salts of silver to prevent ophthalmia neonatorum, using as a justification statements that 10.8% of 2,897 babies born before initiation instillation of an isotonic solution of 2% silver acetate into the eyes of newborn infants developed ocular infections, whereas only 0.1 to 0.2% of 1,160 infants born after adoption of routine application of silver acetate to the eyes at birth developed such infections. The use of silver salts, usually silver nitrate, for prophylaxis of ophthalmia neonatorum became common during succeeding years and indeed was required by 44 states of this country until antibiotics displaced it in the late 1940's. thereafter, silver salts have been used for topical antisepsis of burns [142]. Silver salts have, therefore, a comparatively long history of safe and beneficial application to skin and eyes.

Silver had almost as great an affinity for the sulfur atom of the sulfhydryl group as mercury and is less likely to damage the epithelium. Solutions of 0.2-0.6% concentrations have been used as eye lotions; solutions of 2% concentration are likely to induce conjunctival irritation if left in contact with the conjunctivae for 30 or more seconds. recommends a 0.5% solution of silver nitrate for instillation into the conjunctival sacs of eyes contaminated with benzenethiol before irrigation of the eyes. The solution of silver nitrate should be approximately isotonic, should be sterilized, and should be in containers that protect it from visible light. The containers should be sealed but able to be opened readily; the solution can be dispensed from the container into the conjunctival sacs of an individual. A collapsible bougie, made of an appropriate plastic, with a snippable snout should serve well. Each bougie should contain about 0.3 ml of 0.5% solution of silver nitrate, so that two drops are available for application to each eye of a worker.

When such a device is used, it is important that the tip of the snout not be allowed to touch either the cornea, the surface of the epithelium of the conjunctivae, or the skin surrounding the orbit. If the silver nitrate solution is observed to wet the skin, it should be washed off promptly. Personnel to be responsible for use of the silver nitrate solution should be trained by the responsible physician in procedures for applying solutions to the eye.

Drops to be instilled into a conjunctival sac usually are placed into the lower cul-de-sac, formed by downward traction on the skin below the

lower lid just over the lower rim of the orbit. If the affected person is recumbent, or if the head is tilted back when the person sits or stands, the lids of the eye may be simply spread apart with the first and second fingers of a hand while two drops of the silver nitrate solution are allowed to fall directly on the cornea of the eye. The eye should be irrigated with normal saline solution or water after the silver nitrate has been given a few seconds to react with benzenethiol.

#### XI. APPENDIX III

#### MATERIAL SAFETY DATA SHEET

The following items of information that 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 that 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 that 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 and another component because of its flammability; 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) that 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  $LC_{50}$ -rat," "25 mg/kg  $LD_{50}$ -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 by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 F (21.1 C); 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 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  $LD_{5\,0}$  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, some irritation likely; prolonged or repeated contact, possibly strong irritation.

Eye Contact--some pain, transient irritation; corneal scarring if prolonged contact.

"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 that 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 Mine Safety and Health Administration 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.

## (i) 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.

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SYNONYMS				
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MATERIAL OR COMPON	ENT		%	HAZARD DATA
				·····
<u> </u>	PHYSICAL D	ATA		
BOILING POINT, 760 MM HG	DOILING POINT, 760 MM HG MELTING POINT			
SPECIFIC GRAVITY (H <sub>2</sub> O=1)		VAPOR PR	ESSURE	
SOLUBILITY IN H2O, % BY WT				Y WT
% VOLATILES BY VOL		EVAPORA	TION RATE IBL	ITYL ACETATE:1)
APPEARANCE AND ODOR				

IV FIRE AND EXPLOSION DATA					
FLASH POINT (TEST METHOD)			AUTOIGNITION TEMPERATURE	ž	
FLAMMABLE LIMITS	IN AIR, % BY VOL.	LOWER		UPPER	
EXTINGUISHING MEDIA					
SPECIAL FIRE FIGHTING PROCEDURES					
UNUSUAL FIRE AND EXPLOSION HAZARD					
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SKIN					
INHALATION:					
INGESTION					
NOTES TO PHYSICIAN	ı				
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VI REACTIVITY DATA
CONDITIONS CONTRIBUTING TO INSTABILITY
INCOMPATIBILITY
HAZARDOUS DECOMPORITION 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		

TABLE XII-1 PHYSICAL AND CHEMICAL PROPERTIES OF ALKANE THIOLS, CYCLOHEXANETHIOL, AND BENZENETHIOL

Thiol	Molecular Formula	Molecular Weight	Refractive Index $n_D^{20}$	Density or Specific Gravity	Melting Point (C)		g Point (mmHg)		por ssure ) (C)	Flash Point (F)*	Conversion Factors** (mg/cu m for 1 ppm)
Methanethiol	сн, ѕн	48.11	-	0.8665,	-123	6.2	-	2,259	37.8	<0	1.97
Ethanethiol	C2H5SH	62.13	1.4310	0.8391,	-144.4	35	760	442	20	<0	2.54
1-Propanethiol	C3H7SH	76.17	1.4380	0.8411,	-113.3	67-68	760	155	25	<0	3.12
l-Butanethiol	с,н,ян	90.19	1.4440	0.8337,	-115.67	98.46	760	98.2	37.8	55	3.69
l-Pentanethiol	C <sub>5</sub> H <sub>11</sub> SH	104.22	1.4469	0.8421,	-75.7	126.638 19.505	760 10	13.8	25	80	4.69
l-Hexanethiol	C <sub>6</sub> H <sub>15</sub> SH	118.24	1.4496	0.8424,	-81	151	760	-	-	-	4.84
l-Heptanethiol	C,H1sSH	132.27	1.4521	0.84274	-43	177	760	-	-	-	5.41
1-Octanethiol	CaH <sub>17</sub> SH	146.30	1.4540	0.843340	-49.2	199.1	760	3.0	100	175	5.98
l-Nonanethiol	C <sub>9</sub> H <sub>1,9</sub> SH	160.32	~	-	-	-	-	-	-	-	6.56
1-Decamethiol	C, H, SH	174.35	1.4569	0.8443,	-26	240.6	760	-	-	-	7.13
l-Undecanethiol	С <sub>11</sub> Н <sub>23</sub> SH	188.37	-	-	-	-	-	-	-	-	7.69
l-Dodecanethiol	C <sub>12</sub> H <sub>25</sub> SH	202.41	1.4589	0.845020	-	142.5	15	2.5	25	190	8.28
l-Hexadecanethiol	C, 6 H, 3 5 SH	258.52	-	-	18-20	123-128	0.5	0.1	-	275	10.57
1-Octadecanethiol	C , 8 H 3 7 SH	286.57	1.4645	0.8475,	24-26 28	188	1-2	-	-	-	11.72
Cyclohexanethiol	С <sub>6</sub> Н <sub>11</sub> SH	116.23	1.4921	0.9782,	-	158 1	760 12	10	-	120	4.75
Benzenethiol	C <sub>6</sub> H <sub>5</sub> SH	110.18	1.5893	1.0766,	-14.8	168.7 46.4	760 10	1.0	18.6	-	4.51

<sup>\*</sup>Temperature determined for all substances except propanethiol by open cup method \*\*ppm = mg/cu m x  $\frac{24.45}{MW}$  at 760 mmHg and 25 C

Adapted from references 83,143

TABLE XII-2
SOLUBILITY OF ALKANE THIOLS, CYCLOHEXANETHIOL, AND BENZENETHIOL

	Solvents								
Thiol	Water	Alcohol	Ether	Other					
Methanethiol	Soluble	Soluble	Soluble	-					
Ethanethiol	"	H.	n	Soluble in dilute alkali, acetone					
l-Propanethiol	"	11	н	Soluble in acetone and benzene					
1-Butanethiol	н	11	II.	-					
-Pentanethiol	Insoluble	н	11	-					
1-Hexanethiol	rt	Very soluble	Very soluble	-					
1-Octanethiol	-	u	-	-					
1-Nonanethiol	-	-	-	-					
1-Decamethiol	Insoluble	Soluble	Soluble	-					
l-Undecamethiol	-	-	-	-					
Dodecanethiol	Insoluble	Soluble	Soluble	-					
1-Hexadecanethiol	11	Slightly soluble	u	-					
l-Octadecanethiol	18	11	u .	-					
Cyclohexanethiol	11	Soluble	11	Soluble in acetone, benzene, chloroform					
Benzenethiol	11	п	и	Soluble in benzene					

Adapted from references 83,143

# TABLE XII-3 SYNONYMS FOR 16 THIOLS

Thiol Nomenclature	Synonyms
Methanethiol	Mercaptomethane, methylmercaptan, methylsulfhydrate, thiomethylalcohol
Ethanethiol	Ethylmercaptan, ethylsulfhydrate, ethylthioalcohol, mercaptoethane, thioethanol, thioethylalcohol
1-Propanethio1	3-Mercaptopropane, propane-1-thio1, n-propylmercaptan
l-Butanethiol	l-Butylmercaptan, n-butylthioalcohol, l-mercaptobutane, thiolbutylalcohol
1-Pentanethiol	Amylhydrosulfide, amylmercaptan, amylsulfhydrate, amylthioalcohol, pentylmercaptan
1-Hexanethio1	n-Hexylmercaptan, n-hexylthiol
1-Heptanethiol	n-Heptylmercaptan
1-Octanethio1	l-Mercaptooctane, n-octylmercaptan, octylthiol
1-Nonanethiol	n-Nonylmercaptan, nonylthiol
l-Decamethiol	Decylmercaptan, 1-mercaptodecane
1-Undecanethiol	~
l-Dodecanethiol	Dodecylmercaptan, laurylmercaptan
1-Hexadecanethio1	Cetylmercaptan, hexadecylmercaptan
1-Octadecanethiol	l-Mercaptooctadecane, octadecylmercaptan, stearylmercaptan
Cyclohexanethiol	Cyclohexylmercaptan, cyclohexylthiol
Benzenethiol	Phenylmercaptan, thiophenol

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