X. APPENDIX III

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, ie, "6.8 ml/kg LD50-oral-rat," "16.4 ml/kg LD50-skin-rabbit," or "permissible exposure from 29 CFR 1910.93," 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. Flammable or reactive data could be flash point,

shock sensitivity, or other brief data indicating nature of the hazard.

(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 flash point 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 methyl alcohol. 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

XI. APPENDIX IV

COMBUSTIBLE GAS METER

Combustible gas meters are direct reading instruments and are ordinarily calibrated to read the percentage of the lower explosive limit of a flammable gas or vapor in the air being tested.

Calibration curves must be prepared using the instructions provided by the manufacturer.

The combustible gas meter can be tested by placing a sample of gas from commercially available cylinders in a rubber bellows or internal air pump which is connected to the meter. If the proper reading is not obtained, the instrument should be checked for burnt-out filaments or leaks. This should be repeated with other gases.

XII. APPENDIX V

FUTURE RESEARCH PRIORITIES FOR METHYL ALCOHOL

One of the most pressing research needs for methyl alcohol is the acquisition of updated information concerned with worker exposures and corresponding health effects, if any, in the contemporary workplace environment. The presently available information pertaining to these exposures is seriously inadequate. Most of the data deal either with overexposure to unknown high concentrations and resultant acute effects, or with longer-term exposures without evidence of adverse health effects.

Additionally, much of this information deals with outdated processes. The need to characterize contemporary airborne concentrations of methyl alcohol in industry is amplified by the possibility of stepped-up production and consumption of methyl alcohol if, for example, it were to become a major automotive fuel or fuel additive, for then the number of potentially exposed workers will correspondingly increase. Parallel studies in employees exposed at these concentrations will then need to be pursued. Particular attention should be focused upon the eyes -- specifically the retina, optic disk, and visual function -- and upon the central nervous system. Aided by such modern and sensitive techniques as electroretinography (retinal photography) with the fundus camera and direct ophthalmoscopy as well as electroencephalography to study changes in central nervous system function, the recommended research would serve both immediate and predictive purposes. In such studies, care should be taken to minimize percutaneous absorption of liquid methyl alcohol, so that any

demonstrable effects will be directly related to inhalation of a known airborne methyl alcohol concentration.

Further studies of methyl alcohol toxicity should be undertaken in primates, since their metabolic pathways and clinical signs appear to be somewhat similar to those in humans. There is evidence that the ocular and neurotoxic effects of methyl alcohol in humans are largely mediated by metabolic oxidation products, possibly formaldehyde or formate. Controlled exposures of primates in the laboratory at various concentrations of methyl alcohol vapor, including long-term, low-level intermittent exposures (8-10 hour day), accompanied by appropriate physiologic, biochemical, macro- and microscopic post-mortem examinations, could yield data on changes hitherto undetected in humans to supplement the epidemiologic studies already proposed. Appropriate caution in quantitatively extrapolating effects in other species, even primates, to humans should be applied. Studies on primates given formaldehyde or formate in doses corresponding to the experimental methyl alcohol exposures, assuming a stoichiometric conversion to these oxidation products, should be attempted. The occurrence of similar ocular and neurotoxic effects would be supportive evidence that these effects of methyl alcohol in humans are so mediated.

The sampling procedure recommended in this document, while usable, has not been tested in conjunction with the recommended analytic method. NIOSH is currently testing a modified gas chromatographic method (similar to that in this document) to be used in conjunction with the recommended sampling method.

In view of the demonstrated differences in metabolism of methyl alcohol between primates and lower animals, the utility of mutagenic,

teratogenic, or carcinogenic studies in rodents, often the species of choice for such studies, is not clear. Perhaps experimental exposures of rodents to the human metabolites of methyl alcohol would give useful information on these points.

XIII. TABLES AND FIGURE

TABLE XIII-1

PHYSICAL AND CHEMICAL PROPERTIES OF METHYL ALCOHOL

Molecular formula	CH_3OH
Formula weight	32.04
Apparent specific gravity at 20 C	0.7910
Boiling point at 760 mmHg	64.5 C
Vapor pressure at 20 C	96 mmHg
Melting point	-97.6 C
Solubility in water	Miscible
Solubility in alcohols, ketones, esters, and halogenated hydrocarbons	Miscible
Flash point, Tag open cup	16 C
Flash point, Tag closed cup	12 C
Flammable limits (% in air)	6.72-36.50
Vapor density (air=1)	1.11
Corrosivity	Noncorrosive at normal atmospheric temperatures. Exceptions: lead and aluminum
Conversion factors (760 mmHg and 25 C)	1 ppm=1.310 mg/cu m 1 mg/cu m=.763 ppm

Adapted from ANSI Z37 [2], the Manufacturing Chemists Association [3], and the Handbook of Chemistry and Physics [4]

TABLE XIII-2

US METHYL ALCOHOL CONSUMPTION, 1973

	Million Pounds	Million Gallons
Formaldehyde	2,778	420
Dimethyl terephthalate	435	66
Solvent usage	565	85
Methyl halides	435	66
Methylamines	232	35
Methyl methacrylate	265	40
Inhibitor for formaldehyde	66	10
Exports	824	124
Glycol methyl ethers	81	12
Acetic acid	240	36
Miscellaneous	1,207	181
Total	7,128	1,075

From Blackford [5]

TABLE XIII-3

POTENTIAL OCCUPATIONAL EXPOSURES TO METHYL ALCOHOL

Acetic acid makers
Adhesive workers
Alcohol distillery workers
Alcohol lamp users
Aldehyde pumpmen
Antifreeze workers
Art glass workers
Automobile painters
Aviation fuel handlers
Bookbinders
Bronzers
Brushmakers
Denatured alcohol workers
Dimethyl sulfate makers
Drug makers
Drycleaners
Dye makers
Dyers
Ester makers
Explosives workers
Feather workers
Felt-hat makers
Flower makers, artificial
Formaldehyde makers
Foundry workers
Furniture polishers
Gilders
Glassmakers, safety
Hectograph operators
Incandescent lamp makers
Inkmakers
Japan makers
Japanners
Jet fuel workers
Lacquerers
Lacquer makers
Lasters
Leather workers
Linoleum makers
Lithographers
Metal polishers
Methyl acrylate makers
Methyl alcohol workers
Methyl amine makers
Methylation workers
Methyl bromide makers
Methyl chloride makers
Methyl methacrylate makers
Millinery workers
Motor fuel blenders
Organic chemical synthesizers
Painters
Paintmakers
Paint remover workers
Patent leather makers
Perfume makers
Photoengravers
Photographic film makers
Polish makers
Printers
Rayon makers
Resin makers
Rocket fuel handlers
Rocket fuel makers
Rubber shoe cementers
Rubber workers
Shellackers
Shellac makers
Shoe factory workers
Shoe finishers
Shoe heel coverers, wood
Shoe stitchers
Soapmakers
Straw-hat makers
Sugar refiners
Textile printers
Type cleaners
Vacuum tube makers
Varnish workers
Vulcanizers
Wood alcohol distillers
Wood stainers
Wood stain makers

From Gafafer [6]

TABLE XIII-4

ANIMAL EXPERIMENTATION RESULTS
OF METHYL ALCOHOL EXPOSURE

Species	Route of Exposure	Dose	Effect	Reference
Monkeys	Inhalation	5,000 ppm duration unknown	The monkey survived for an unstated period of time.	47
"	"	1,000 ppm duration unknown	The monkey died promptly upon exposure at this level.	47
Dogs	"	450-500 ppm 8 hr/day 7 days/week for 379 days	Blood levels of methyl alcohol were found to range from 10 to 15 mg/100 ml of blood and on occassion went as high as 52 mg/100 ml. No abnormal eye findings were reported.	41
"	Oral	2.5 to 9.0 g/kg body weight	Of the 9 treated dogs, 2 died at doses of 4 and 9 g/kg. CO2 combining capacities dropped below normal in 2 dogs, and no ophthalmoscopic changes were noted.	42

TABLE XIII-4 (CONTINUED)

ANIMAL EXPERIMENTATION RESULTS
OF METHYL ALCOHOL EXPOSURE

Species	Route of Exposure	Dose	Effect	Reference
Monkeys	Oral	1.0 to 8.0 g/kg	Acidosis developed in monkeys receiving doses ranging from 3.0 to 6.0 g/kg. The animal receiving 1.0 g/kg did not develop acidosis. Definite eye-ground change occurred to 2 of the acidotic monkeys.	42
Rats	"	4.75 g/kg	70% mortality	42
"	"	4.5 g/kg	None of the 9 tested rats developed acidosis.	42
Rabbits	"	3.5 g/kg	One animal receiving this dose died in less than 24 hours. No eye fundus changes were reported.	42
Rabbits	"	2.1 g/kg	Of the 3 animals tested at this dose, all died between 24 hours and 3 days after dosing.	42
"	Intra-cutaneous	10 mg and 35 mg	At 10 mg, there was no skin reaction, whereas at 35 mg, a 9-sq mm skin reaction occurred.	49

TABLE XIII-4 (CONTINUED)

ANIMAL EXPERIMENTATION RESULTS
OF METHYL ALCOHOL EXPOSURE

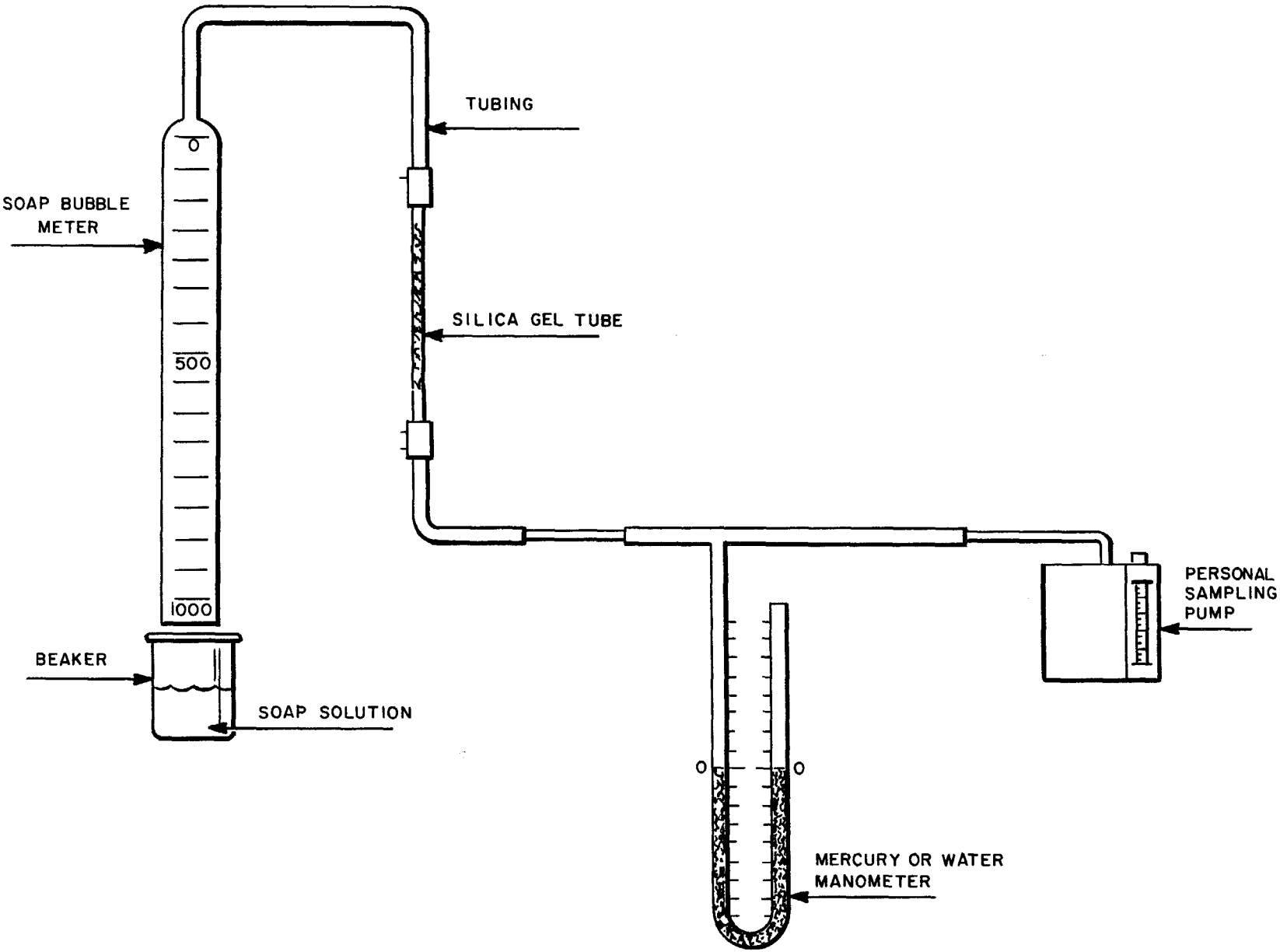
Species	Route of Exposure	Dose	Effect	Reference
Monkeys	i.p. inj	0.5 g/kg of 14 C-methyl alcohol with an equimolar amount of ethyl alcohol	The ethyl alcohol reduced the oxidation of methyl alcohol 90%.	52
"	"	1.0 g/kg 14 C-methyl alcohol and 6.0 g/kg 14C-methyl alcohol	The methyl alcohol was oxidized at a rate of 37 mg/kg/hour between the first and fourth hour. The CO2 formation was linear at the high dose; the oxidation rate was 47 mg/kg/hour which is a significant difference.	52
Rats	"	1.0/kg 14C-methyl alcohol	The oxidation rate of the methyl alcohol was 24 mg/kg/hr for the first 28 hours. At the end of 36 hours 77% of the methyl alcohol had been oxidized to 14C-labled CO2 and 24% was excreted unchanged in approximately equal amounts by the pulmonary and combined urinary and fecal routes.	51

TABLE XIII-4 (CONTINUED)

ANIMAL EXPERIMENTATION RESULTS
OF METHYL ALCOHOL EXPOSURE

Species	Route of Exposure	Dose	Effect	Reference
Monkeys	i.p. inj	2-4 g/kg	Consitent development of acidosis. At 4 g/kg methyl alcohol the following occurred: blood bicarbonate (p CO2 and total CO2) decreased, blood pH decreased, blood pH decreased over 7 1/2 to 21 hours, glucose increased moderately. There was a marked formate increase, also increases of lactate, alpha-hydroxybutyrate, beta-hydroxybutyrate, alpha-ketobutyrate, acetoacetate, p-hydroxyphenylacetate and p-hydroxyphenyllactate.	53

FIGURE XIII-1 CALIBRATION SET UP FOR PERSONAL SAMPLING WITH SILICA GEL TUBE



☆USGPO: 1976 — 657-696/5535 Region 5-11

DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

HEW Publication No. (NIOSH) 76–148