CRITERIA FOR A RECOMMENDED STANDARD

OCCUPATIONAL EXPOSURE TO

FURFURYL ALCOHOL

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
criteria for a recommended standard...

OCCUPATIONAL EXPOSURE TO

FURFURYL ALCOHOL

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

March 1979
DISCLAIMER

Mention of company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

DHEW (NIOSH) Publication No. 79-133
The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and provide for the safety of workers occupationally exposed to an ever-increasing number of potential hazards. The National Institute for Occupational Safety and Health (NIOSH) evaluates all available research data, establishes criteria, and recommends standards for occupational exposure. The Secretary of Labor will weigh these recommendations along with other considerations, such as feasibility and means of implementation, in promulgating regulatory standards.

After reviewing data and consulting with others, NIOSH formalized a system for the development of criteria on which standards can be established to protect the health and to provide for the safety of workers. The criteria and recommended standard should enable management and labor to develop better engineering controls and more healthful work environments, and simple compliance with the recommended standard should not be the final goal.

NIOSH will periodically review the recommended standards to ensure continuing protection of workers and will make successive reports as new information becomes available.

The contributions to this document on furfuryl alcohol by NIOSH staff, other Federal agencies or departments, the review consultants, the reviewers selected by the Society of Toxicology, and Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, are gratefully acknowledged.

The views expressed and conclusions reached in this document, together with the recommendations for a standard, are those of NIOSH. They are not necessarily those of the consultants, the reviewers selected by professional societies, or Federal agencies. However, all comments, whether or not incorporated, have been sent with the criteria document to the Occupational Safety and Health Administration (OSHA) for its consideration in setting the standard. The review consultants and the Federal agencies that received the document for review appear on pages vi and vii.

Anthony Robbins, M.D.
Director, National Institute for Occupational Safety and Health
SYNOPSIS

This report reviews available scientific and technical information on furfuryl alcohol and recommends a standard for the control of furfuryl alcohol hazards in the workplace. The acute hazards include eye, skin, and upper respiratory irritation from direct contact and depression of the central nervous system from inhalation or percutaneous absorption. Evidence of a chronic effect is not available. Other hazards associated with the compound include combustibility and violent reactivity when mixed with acids.

About 9,000 workers are potentially exposed to furfuryl alcohol in the United States, and about 100 million pounds are produced and used each year. Its main use is in the synthesis of furan resins, which are used in such operations as the binding of foundry core sand.

In the absence of data indicating that the existing permissible limit is not protective, the standard proposed to the US Department of Labor contains recommendations for continuation of the present Federal limit of 200 mg/cu m as a time-weighted average concentration and also for a program of medical and environmental surveillance. Based in part on information gathered from plant site visits and reviewer comments, work practices are recommended to reduce fire and explosion hazards and to minimize skin contact. Requirements for posting and labeling, a respiratory protection program, an education program for employees, and the maintenance of relevant records are also included.

Suggested research to correct deficiencies in available information includes: (1) epidemiologic studies of employees exposed to furfuryl alcohol; (2) animal studies of any chronic effects of furfuryl alcohol, including experimental studies of its possible carcinogenicity; (3) possible effects on reproduction, including whether or not furfuryl alcohol can cause terata or induce mutations; and (4) biotransformation of furfuryl alcohol, its distribution, and elimination.
The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for the development of the criteria and recommended standard for furfuryl alcohol. Terence M. Grady of this Division served as criteria manager. Equitable Environmental Health, Inc. (EEH) developed the basic information for consideration by NIOSH staff and consultants under contract CDC 210-77-0148.

The Division review of this document was provided by Keith H. Jacobson, Ph.D. (Chairman), Douglas L. Smith, Ph.D., Frank L. Mitchell, D.O., Craig R. McCormack, Pharm. D. (Division of Biomedical and Behavioral Sciences), with Seymour D. Silver, Ph.D.
REVIEW CONSULTANTS

Herbert K. Abrams, M.D.
Professor of Family and
Community Medicine
University of Arizona
College of Medicine
Tucson, Arizona 85724

Dennis I. Chamot, Ph.D.
Assistant to the Executive Secretary
Council of AFL-CIO Unions for
Professional Employees
Washington, D.C. 20006

Kingsley Kay, Ph.D.
16 Skyridge Road
Greenwich, Connecticut 06830

John W. Knauber
Director, Bureau of Occupational Health
Pennsylvania Department of
Environmental Resources
Harrisburg, Pennsylvania 17120

John E. Mutchler
Director, Health and Safety
The Quaker Oats Co.
Chemical Division
Chicago, Illinois 60654

Cedric M. Smith, M.D.
Research Institute on Alcoholism
Buffalo, New York 14203
FEDERAL AGENCIES

Department of Agriculture
  Agricultural Research Service

Department of Defense
  Office of Deputy Assistant Secretary of Defense for
    Energy, Environment, and Safety

Department of the Air Force
  Office of the Surgeon General
    Aerospace Medicine Division
    Aerospace Medical Research Laboratory
    Occupational and Environmental Health Laboratories

Department of the Army
  Army Environmental Hygiene Agency

Department of the Navy
  Navy Environmental Health Center

Department of Energy
  Division of Operational and Environmental Safety

Department of Health, Education, and Welfare
  Food and Drug Administration
  National Institutes of Health
    National Institute of Environmental Health Sciences

Environmental Protection Agency
  Office of Assistant Administrator for Research and Development
    National Environmental Research Center
    Health Effects Laboratory

National Aeronautics and Space Administration
CONTENTS

PREFACE iii

SYNOPSIS iv

REVIEW CONSULTANTS vi

FEDERAL AGENCIES vii

I. RECOMMENDATIONS FOR A FURFURYL ALCOHOL STANDARD 1

Section 1 - Environmental (Workplace Air) 2
Section 2 - Medical 2
Section 3 - Labeling and Posting 3
Section 4 - Personal Protective Equipment and Clothing 4
Section 5 - Informing Employees of Hazards from Furfuryl Alcohol 6
Section 6 - Work Practices 6
Section 7 - Sanitation Practices 9
Section 8 - Monitoring and Recordkeeping Requirements 9

II. BIOLOGIC EFFECTS OF EXPOSURE 11

Extent of Exposure 11
Historical Reports 13
Effects on Humans 14
Animal Toxicity 16
Correlation of Exposure and Effect 22
Carcinogenicity, Mutagenicity, Teratogenicity, and Effects on Reproduction 24

III. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS 28

Environmental Data 28
Sampling and Analytical Methods 29
Engineering Controls 31

IV. WORK PRACTICES 33

V. DEVELOPMENT OF STANDARD 36

Basis for Previous Standards 36
Basis for the Recommended Standard 36
CONTENTS (CONTINUED)

VI. RESEARCH NEEDS 41

VII. REFERENCES 42

VIII. APPENDIX - Sampling and Analytical Method for Furfuryl Alcohol in Air 48

IX. TABLES AND FIGURES 57
I. RECOMMENDATIONS FOR A FURFURYL ALCOHOL STANDARD

NIOSH recommends that employee exposure to furfuryl alcohol in the workplace be controlled by adherence to the following sections. The recommended standard is designed to protect the health and provide for the safety of employees for up to a 10-hour workshift, 40-hour workweek, over a working lifetime. Compliance with all sections of the recommended standard should prevent adverse effects of exposure to furfuryl alcohol on the health of employees. Methods recommended in the standard are measurable by techniques that are reproducible and available to industry and government agencies. Sufficient technology exists to permit compliance with the recommended standard. Although NIOSH considers the workplace environmental limit to be a safe level based on current information, the employer should regard it as the upper boundary of exposure, and every effort should be made to maintain the exposure at levels as low as is technically feasible. The criteria and recommended standard will be reviewed and revised as necessary.

This recommended standard for furfuryl alcohol is based on the limited information available on the effects from exposure to furfuryl alcohol. The standard is designed to safeguard workers occupationally exposed to furfuryl alcohol from absorption of the compound, possible subsequent irritation of the skin, eyes, and respiratory tract, from central nervous system (CNS) effects, and from the hazard arising from its violent, possibly explosive, reaction when in contact with acids.

These criteria and the recommended standard apply to occupational exposure of employees to hydroxymethyl furan, referred to as "furfuryl alcohol." Synonyms for furfuryl alcohol include 2-furylmethanol, 2-furylcarbinol, 2-furan methanol, furfural alcohol, and 2-(hydroxymethyl) furan. The major industrial use of furfuryl alcohol is in the production of furan resins, which are used as corrosion- and heat-resistant materials, particularly in the foundry industry.

An action level is defined as one-half the recommended time-weighted average (TWA) environmental limit. Occupational exposure to furfuryl alcohol is defined as exposure to airborne furfuryl alcohol above the action level. Exposures at lower concentrations will not require adherence to the following sections except for 2(a,e), 3(a), 4(a,c), 5, 6(a,d,e,f), 7, and 8(a).
Section 1 - Environmental (Workplace Air)

(a) Concentration

Occupational exposure to furfuryl alcohol shall be controlled so that employees are not exposed to furfuryl alcohol at a concentration greater than 200 milligrams per cubic meter (mg/cu m) of air, equivalent to 50 parts per million (ppm) parts of air by volume, determined as a TWA concentration for up to a 10-hour workshift and 40-hour workweek.

(b) Sampling and Analysis

Procedures for the collection and analysis of environmental samples shall be as provided in the appendix or by any other methods at least equivalent in precision, accuracy, and sensitivity to the methods specified.

Section 2 - Medical

Medical surveillance as described below shall be made available to all employees occupationally exposed to furfuryl alcohol. The employer shall provide information to the physician performing or responsible for the medical surveillance program such as: the requirements of the applicable standard; an estimate of the employee's potential exposure to furfuryl alcohol, including any available workplace sampling results; and a description of any protective devices or equipment the employee may be required to use.

(a) Preplacement medical examinations shall include at least: comprehensive medical and work histories with special emphasis given to the upper respiratory tract and skin; a physical examination giving special attention to the skin, eyes, and respiratory system; and a judgment of the worker's ability to use a negative or positive pressure respirator.

(b) Periodic examinations shall be made available at a frequency to be determined by the responsible physician based on such factors as the severity and frequency of exposure. These examinations should include interim medical and work histories and a physical examination as outlined in paragraph (a) of this section.

(c) Following completion of the examination, the physician shall give to the employer a written statement specifying any condition or abnormality found which would increase the risk to the employee's health by exposure to furfuryl alcohol, and any limitations that should be placed on the employee's exposure. Employees and potential employees having medical conditions such as chronic respiratory or skin disorders that could be
aggravated directly or indirectly by exposure to furfuryl alcohol shall be counseled concerning the possibly increased risk of impairment of their health as a result of working with this substance.

(d) In cases involving massive exposure to furfuryl alcohol, prompt referral and medical attention shall be provided. In the event of skin or eye contact with liquid furfuryl alcohol, skin and eyes shall be thoroughly flushed with large amounts of water. In cases of splashes, spills, or leaks, individuals who have significant skin, eye, or respiratory contact with the material shall be referred to the responsible medical authority.

(e) Pertinent medical records shall be retained for at least 30 years after the individual's last occupational exposure to furfuryl alcohol. These records shall be made available to the designated medical representative of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee.

Section 3 - Labeling and Posting

All warning signs shall be printed both in English and in the predominant language of non-English-reading workers. Workers unable to read labels and posted signs shall receive information regarding hazardous areas and shall be informed of the instructions printed on labels and signs.

(a) Labeling

The following label shall be affixed in a readily visible location on process equipment, storage tanks, containers, or other facilities used for furfuryl alcohol.

FURFURYL ALCOHOL

CAUTION!

May be absorbed through skin.
Reacts violently with strong acids.

Avoid contact with skin and eyes.
Avoid breathing vapor.
Use only with adequate ventilation.

In case of contact with skin and eyes: Immediately wash skin thoroughly or flush eyes with large amounts of water. Get medical attention.
(b) Posting

In areas where there is occupational exposure to furfuryl alcohol, signs containing health hazard warning statements appropriate for this substance shall be posted in readily visible locations. This information shall be arranged as in the example below.

FURFURYL ALCOHOL

IRRITATING TO EYES AND RESPIRATORY TRACT

Keep away from acids.
Avoid contact with skin and eyes.
Avoid breathing vapor.

Section 4 - Personal Protective Equipment and Clothing

Engineering controls and safe work practices shall be used when needed to keep concentrations of airborne furfuryl alcohol at or below the recommended exposure limit and to minimize skin and eye contact. Employers shall provide protective equipment and clothing to employees when necessary to prevent skin contact.

(a) Eye and Face Protection

Safety glasses with side shields, chemical safety goggles, or face shields with goggles, made completely of materials resistant to furfuryl alcohol, shall be provided by the employer and shall be worn during any operation in which furfuryl alcohol may enter the eyes (29 CFR 1910.133).

(b) Respiratory Protection

The use of respirators to achieve compliance with the recommended exposure limit is permitted only during the time necessary to install or test the required engineering controls, during emergencies when the concentration of airborne furfuryl alcohol may exceed the permissible environmental limit, and for nonroutine operations such as nonroutine maintenance or repair activities.

When the use of a respirator is permitted, it shall be selected and used pursuant to the following requirements: The employer shall establish and enforce a respiratory protective program meeting the requirements of 29 CFR 1910.134; the employer shall ensure that no employee is exposed to furfuryl alcohol because of improper respirator selection, fit, use, or maintenance; the employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the respirator when
necessary; the respirators shall be selected in accordance with Table I-1 and shall be those approved by NIOSH or the Mine Safety and Health Administration (MSHA) as specified in 30 CFR 11; the employer shall ensure that respirators are adequately cleaned and maintained and that employees are trained and drilled at least annually in the proper use and testing for leakage of respirators assigned to them; respirators shall be easily accessible, and employees shall be informed of their location in the workplace; and protective equipment for emergency entry shall be located at clearly identified places outside the work area. Respirators specified for use in higher concentrations of furfuryl alcohol may be used in atmospheres of lower concentrations.

**TABLE I-1**

**RESPIRATOR SELECTION GUIDE FOR FURFURYL ALCOHOL**

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Respirator Type Approved under Provisions of 30 CFR 11</th>
</tr>
</thead>
</table>
| 1,000 mg/cu m or less               | (1) A chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)  
(2) A gas mask with a chin-style or a front- or back-mounted organic vapor canister  
(3) Any supplied-air respirator with a full facepiece, helmet, or hood  
(4) Any self-contained breathing apparatus with a full facepiece |
| Greater than 1,000 mg/cu m or entry and escape from area of unknown concentration | (1) Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode  
(2) A combination respirator that includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode |
| Firefighting                         | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode |
Protective clothing shall be resistant to the penetration and chemical action of furfuryl alcohol. Additional protection, including gloves, bib-type aprons, boots, and overshoes, shall be provided for, and worn by, each employee while in any operation that may cause direct contact with liquid furfuryl alcohol. Supplied-air hoods and suits resistant to penetration by furfuryl alcohol shall be worn when entering confined spaces, such as pits or storage tanks. In situations where heat stress is likely to occur, supplied-air suits, preferably cooled, are recommended. The employer shall ensure that all personal protective clothing is inspected regularly for defects and is maintained in a clean and satisfactory condition. Protective equipment suitable for emergency use shall be located at clearly identified stations outside the work area.

Section 5 - Informing Employees of Hazards from Furfuryl Alcohol

(a) All employees working with furfuryl alcohol shall be informed of the hazards, relevant signs and symptoms of exposure, appropriate emergency procedures, and proper conditions and precautions concerning safe use and handling of furfuryl alcohol.

(b) A continuing education program, conducted at least annually by qualified health and safety personnel, shall be instituted to ensure that employees whose jobs may involve exposure to furfuryl alcohol, including those engaged in maintenance and repair, have current knowledge of job hazards, proper maintenance procedures, and cleanup methods. Employees shall be informed of the general nature of the medical and environmental surveillance procedures and why it is advantageous to the workers to participate in these procedures. Each employee shall be told about the availability of the required information, which shall include, as a minimum, that prescribed in paragraph (c) of this section. Records of such training should be maintained. Employees shall also be instructed on their responsibilities for following proper work practices and sanitation procedures to help protect the health and provide for the safety of themselves and of fellow employees.

(c) Appropriate written information describing the relevant toxic, physical, and chemical properties of furfuryl alcohol and of mixtures of furfuryl alcohol that are used or otherwise handled in the workplace shall be kept on file and shall be readily available to employees.

Section 6 - Work Practices

(a) Protective equipment and clothing, as set forth in Section 4, shall be worn by employees engaged in operations where there is a likelihood of skin or eye contact with furfuryl alcohol.
(b) Engineering controls, such as process enclosure or local exhaust ventilation, shall be used as needed to keep airborne furfuryl alcohol within the recommended environmental limit.

(c) Equipment and systems used for handling and transferring furfuryl alcohol shall be enclosed to the extent feasible to prevent skin and eye contact.

(d) Containers of furfuryl alcohol shall be kept tightly closed at all times when not in use. Storage shall be in well-ventilated areas away from heat, acids, and strong oxidizers. Containers shall be periodically inspected for leakage and deterioration.

Except for catalytic amounts, acids should be avoided in processes in which furfuryl alcohol is present; otherwise an exothermic explosive reaction may result.

A fail-safe system for filling tanks and transferring furfuryl alcohol shall be installed with unique hose fittings and tanks dedicated to furfuryl alcohol use only.

Equipment and systems used for handling and transferring furfuryl alcohol shall be inspected periodically for leaks. Valves, fittings, and connections shall be checked for tightness and good working order. Needed repairs and adjustments shall be made promptly.

Before maintenance work is started, sources of furfuryl alcohol shall be eliminated from the affected area to the extent feasible. If the concentration of airborne furfuryl alcohol exceeds the recommended environmental limit, use of respiratory protective equipment shall be required during such maintenance work.

Easily accessible, well-marked emergency showers and eyewash fountains shall be provided in work areas where eye or massive skin contact with furfuryl alcohol is likely.

Contaminated clothing shall be cleaned before reuse and shall be kept in properly labeled, closed containers until it is laundered or discarded. Anyone handling or responsible for cleaning contaminated clothing shall be informed about the hazards, relevant symptoms of overexposure, appropriate emergency procedures, and proper conditions and precautions for the safe handling of furfuryl alcohol. Materials that cannot be effectively decontaminated shall be discarded.

Transportation and use of furfuryl alcohol shall comply with Federal, state, and local regulations.

(e) Emergency plans and procedures shall be developed for furfuryl alcohol work areas. The measures shall include those specified below and
any others considered appropriate for a specific operation or process. Employees shall be trained to implement the plans and procedures effectively. Prearranged plans shall be instituted for obtaining emergency medical care and for the transportation of injured workers. A sufficient number of employees shall be trained in first aid so that assistance is available immediately when necessary.

Spills and leaks of furfuryl alcohol shall be cleaned up immediately. The area of the spill shall be posted and secured. Spills and leaks of furfuryl alcohol must be washed with water or alkali solution. Washing with any acids must be avoided so that a highly exothermic explosive reaction will not result. Only authorized personnel, adequately protected and properly trained, shall be permitted to enter the area to shut off sources of furfuryl alcohol. Spilled liquids can be sorbed with vermiculite, dry sand, earth, or other appropriate material. If sufficient drainage to suitable collection basins is available, spilled liquid can be hosed away with large quantities of water. Methods of waste disposal shall comply with Federal, state, and local regulations.

(f) Cleaning, maintenance, and repair of tanks, process equipment, and lines shall be performed only by properly trained, adequately protected, and supervised personnel. Entry into confined spaces, such as tanks, pits, tank cars, barges, and process vessels, shall be controlled by a permit system. Permits shall be signed by an authorized representative of the employer and 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.

Before entry, confined spaces shall be inspected and tested for oxygen deficiency and for the presence of furfuryl alcohol and other known or suspected contaminants such as formaldehyde or phenol.

No employee shall enter any confined space that does not have an entry large enough to admit an employee wearing safety harness, lifeline, and appropriate respiratory equipment as specified in Section 4(b).

Confined spaces shall be ventilated while work is in progress to keep the concentration of airborne furfuryl alcohol at or below the recommended environmental limit, to keep the concentration of other contaminants below dangerous levels, and to prevent oxygen deficiency.

Anyone entering a confined space shall be observed from the outside by another properly trained and protected worker. An additional supplied-air or self-contained breathing apparatus with safety harness and lifeline shall be located outside the confined space for emergency use. The person entering the confined space shall maintain continuous communication with the standby worker.
Section 7 - Sanitation Practices

(a) Preparing, dispensing (including the use of vending machines), and eating food shall be prohibited in areas where furfuryl alcohol is produced, stored, processed, or otherwise used.

(b) Smoking shall be prohibited in areas where furfuryl alcohol is produced, processed, stored, or otherwise used.

(c) Employees who handle furfuryl alcohol shall be instructed to wash their hands thoroughly before eating, smoking, or using toilet facilities.

(d) Facilities such as double lockers should be provided for employees so soiled clothing can be stored separately from clean clothing.

Section 8 - Monitoring and Recordkeeping Requirements

(a) Employers shall determine by an industrial hygiene survey whether there is occupational exposure to furfuryl alcohol. Records of these surveys shall be kept; if an employer concludes that there is no occupational exposure, the records must show the basis for this conclusion. Surveys shall be repeated at least annually and within 30 days of any process change likely to result in an increased concentration of airborne furfuryl alcohol.

(b) If there is occupational exposure to furfuryl alcohol, a program of personal monitoring shall be instituted to identify and measure, or to permit calculation of, the exposure of each employee occupationally exposed to airborne furfuryl alcohol. Source and area monitoring may be a useful supplement to personal monitoring. In all personal monitoring, samples representative of the exposure to airborne furfuryl alcohol in the breathing zone of the employee shall be collected.

For each TWA concentration determination, a sufficient number of samples shall be taken to characterize employee exposures during each workshift. Variations in work and production schedules, as well as employee locations and job functions, shall be considered in decisions on sampling locations, times, and frequencies.

Each operation shall be evaluated at least once every 6 months or as otherwise indicated by a professional industrial hygienist. If an employee is found to be exposed in excess of the TWA concentration limit, controls shall be initiated, the exposure of that employee shall be evaluated at least once a week, and the employee shall be notified of the exposure and of the control measures being implemented. Such monitoring shall continue until two consecutive determinations, at least 1 week apart, indicate that employee exposure no longer exceeds the environmental limit. Semiannual monitoring may then be resumed.
(c) Environmental records shall be kept for at least 30 years after the last occupational exposure. These records shall include the dates and times of measurements; duties and location of the employees within the worksite; sampling and analytical methods used; number, duration, and results of the samples taken; TWA concentrations estimated from these samples; type of personal protective equipment used, if any; and employees' names. Each employee shall be able to obtain information on his or her exposures. Environmental records shall be available to the designated representatives of the Secretary of Labor and of the Secretary of Health, Education, and Welfare.

Pertinent medical records shall be retained for 30 years after the last occupational exposure. Copies of exposure data applicable to an employee shall be included in that employee's medical records. These medical records shall be made available to the designated medical representatives of the Secretary of Labor, of the Secretary of Health, Education, and Welfare, of the employer, and of the employee or former employee.
II. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Furfuryl alcohol is a colorless, faintly odorous liquid that darkens during storage due to auto-oxidation and intermolecular dehydrations [1]. Furfuryl alcohol also is known as 2-furylcarbinol, 2-furylethanol, 2-furanmethanol, furfural alcohol, and 2-(hydroxymethyl) furan. The structural formula for furfuryl alcohol appears below.

\[
\begin{array}{c}
\text{O} \\
\text{CH}_2 \cdot \text{OH}
\end{array}
\]

Furfuryl alcohol is a very reactive heterocyclic compound consisting of two moieties, the furan nucleus and a hydroxymethyl group. Because of the latter moiety, furfuryl alcohol undergoes reactions typical of a primary aliphatic alcohol, such as replacements, esterifications, or oxidations [2,3]. The furan ring undergoes substitution of ring hydrogens [2], or can be cleaved to yield aliphatic compounds [3].

Furfuryl alcohol has a boiling point of 170°C (338°F) and is not a highly volatile liquid at room temperature. Its vapor pressure is 1.0 mmHg at 31.8°C (89.2°F), rising to 271 mmHg at 140°C (284°F) [1,2]. The vapor pressures of furfuryl alcohol at various temperatures are presented in Figure IX-1. According to the definitions set forth in 42 CFR 1910.106, furfuryl alcohol has a IIIA combustibility rating. Its fires can be extinguished with water, foam, carbon dioxide, or dry chemicals [2]. Although sensitive to the effects of acids, it remains fairly stable in alkaline media [2,3]. Physical and chemical properties of furfuryl alcohol are presented in Table IX-1.

Furfuryl alcohol is found in processed natural foods including the oils of chicory and roasted coffee, in yellow leaf tobacco, and in heated skim milk [4-11], usually as a result of processing. In a 1932 report from Germany [5], commercially available coffee reportedly contained 0.025-0.125% furfuryl alcohol. By calculation, then, a cup containing 0.25 liter of freshly brewed coffee might contain approximately 1.9 mg of furfuryl alcohol [5]. In yellow leaf tobacco and in heated skim milk, the approximate concentrations of furfuryl alcohol are 80 μg/g and 208 mg/liter, respectively [6,11].

The high-yield industrial production of furfuryl alcohol features the hydrogenation of the aldehyde furfural, as liquid or vapor, in the presence of a suitable metallic catalyst [12], eg, a mixture of metallic nickel and magnesium oxide (60:900 parts W/W) at 90-170°C (194-338°F) and about 200
pounds per square inch (1.38 MPa) [13]. The yield of furfuryl alcohol, from either liquid or vaporized furfural, can be markedly changed by varying the catalysts, pressure, and reaction temperature and time.

Furfuryl alcohol consumption has increased for 30 of the last 40 years of its commercial availability [14]. In 1974, a single producer accounted for the estimated 51-million-pound output of furfuryl alcohol in the United States [15]. According to this producer, nearly 100 million pounds of furfuryl alcohol was used in 1976; usage is expected to increase steadily during the next 5-10 years [14]. All furfuryl alcohol is currently produced at three plants in the United States and at one facility in Belgium.

Furfuryl alcohol is used industrially as a solvent and as a chemical precursor of a host of chemical products, e.g., furfuryl halides, furfuryl cyanide, furfuryl ethers, furfuryl esters, and methyl furan. The most important product, however, is furfuryl alcohol resin (commonly called furan resin) [2], the manufacture of which consumes 90-95% of the available furfuryl alcohol [16].

Furfuryl alcohol and furfuryl alcohol-formaldehyde resins are widely used in chemical-resistant construction materials, such as resinous cements, and in asbestos-reinforced equipment and thermosetting compounds. Furan resins, similar to those used to confer chemical resistance, have been used since the late 1950's in both the "hot-box" and "no-bake" methods of binding foundry core sand. The hot-box process, which uses furfuryl alcohol-formaldehyde-urea resin containing 25-45% furfuryl alcohol, cures from within a few seconds to 3 minutes at 177-232 C (351-450 F) to provide good corrosion resistance. The no-bake process with resin containing 50-90% furfuryl alcohol cures without heat within 3 hours and is particularly suited to the production of large foundry cores and molds [17].

Because of its combination of a high boiling point (170 C or 338 F) and excellent water solubility, as well as polarity, furfuryl alcohol is used in industry as a solvent, either alone or in combination with other solvents. For example, automatic acrylic lacquer can be removed completely from drums before their reuse with a hot solution of 40% furfuryl alcohol, 50% water, and 10% trisodium phosphate [2]. In the production of cold-molded grinding wheels, furfuryl alcohol is both a solvent and a temporary plasticizer for phenolic resin. In this process, as a solvent for the powdered phenolic resin, furfuryl alcohol promotes adhesion of the resin to the abrasive grains and becomes a part of the binder solids during curing of the wheels.

One of the principal industrial hazards in the use of furfuryl alcohol is its polymerization reaction following contact with acids. Highly exothermic, these reactions have resulted in violent explosions [18,19].
Because of its physical and chemical properties, furfuryl alcohol can be safely stored at low temperatures in unlined, airtight containers. Furfuryl alcohol is not affected for up to 6 months during storage in steel tanks, but will slowly change color and become less water soluble when stored for longer periods in the presence of air or trace amounts of acid or when heated [3]. Although not used commercially for this purpose, small amounts of an inorganic or organic base (n-butylamine or piperidine) may be added to stabilize furfuryl alcohol in storage [3].

NIOSH estimates that approximately 9,000 workers in the United States are potentially exposed to furfuryl alcohol [20]. Occupations involving potential exposure to furfuryl alcohol are listed in Table IX-2.

Historical Reports

As early as 1864, furfuryl alcohol was prepared from furfural by reduction with sodium or sodium amalgam [1,4]. Erdmann [4], in an introduction to his 1902 report on the toxicity of furfuryl alcohol in laboratory animals, described the composition and properties of coffee oil and reviewed previous chemical data on furfuryl alcohol, one of its primary ingredients.

Erdmann [4] administered furfuryl alcohol (derived from coffee oil) to 14 rabbits weighing 1.37-3.10 kg (sex, strain, and use of controls were not described) and to 1 female dog of unstated breed weighing 10.61 kg. The rabbits received furfuryl alcohol in 25 or 50% aqueous solutions, 11 by subcutaneous (sc) injection and 3 by gastric intubation, at single doses ranging from 230 to 1,330 mg/kg of body weight. The sc lethal dose was 526-600 mg/kg. Lethal amounts produced significant decreases in rectal temperature followed by what was described as respiratory paralysis within 4-24 hours. In addition to effects on body temperature and respiration, the rabbits showed a pattern of increased mucus secretion, salivation, and lacrimation. There were also increased frequency of urination and defecation, and, at higher doses, lethargy or sleepiness approaching narcosis, labored breathing, coma, and, terminally, cessation of breathing. A necropsy performed on one rabbit 12 hours after it died revealed no unusual organ changes.

The dog was given furfuryl alcohol as a 50% aqueous solution at a total dose of 520 mg/kg in two sc injections 30 minutes apart [4]. Within minutes after the second injection, sneezing and vomiting began and continued for about 20 minutes and for 2 hours, respectively. Diarrhea, bloody feces, appetite loss, lassitude, and reduction in rectal temperature persisted through the next day. Two days later, however, the dog appeared fully recovered.
Erdmann [4], in his study of three men (including himself), noted that furfuryl alcohol in small, single oral doses of 0.6-1.0 g in 5% aqueous solution consistently increased the rate of respiration.

In 1927, Okubo [21] described the results of in vivo and in vitro studies of the effects of pure furfuryl alcohol on mice, rabbits, and guinea pigs. The mice were injected sc with furfuryl alcohol in physiologic saline (0.5-1.0% solution). At 10 mg/kg, furfuryl alcohol had little or no effect, whereas at 50 mg/kg the mice showed marked respiratory depression, weakened reflexes, and disturbed gait but recovered within 4-5 hours. At 100 mg/kg, furfuryl alcohol was lethal within 3-5 hours, death being attributed to respiratory paralysis. Furfuryl alcohol injected intravenously (iv) at unspecified doses reportedly inhibited respiration and also reduced blood pressure in urethane-anesthetized rabbits.

From the in vitro study, Okubo [21] concluded that furfuryl alcohol, as a 5% solution, rapidly paralyzed both motor and sensory nerves of the frog. A 1% solution, however, paralyzed only the sensory nerves, and these effects were slowly reversible after furfuryl alcohol was replaced by Ringer's solution.

In 1932, Joachimoglu and Klissianis [5] described their studies of furfuryl alcohol in humans and in a dog. Humans were given by mouth a chamomile tea containing up to 150 mg furfuryl alcohol or up to 60 mg furfural [5]. No effects from ingestion of furfuryl alcohol at these levels were reported.

A dog was given furfuryl alcohol, 1 g/day, by stomach tube for 42 days. After a 1-month recovery period, the animal then received furfural, at 1 g/day, by stomach tube for 56 days [5]. The only effect seen was occasional salivation after administration. No changes were evident during the subsequent 1-year observation period.

Effects on Humans

Jacobson et al [22], in 1958, reported the results of experiments conducted on 13 volunteers to determine the odor threshold of furfuryl alcohol. Each volunteer sniffed geometrically increasing concentrations of furfuryl alcohol. The median detectable concentration for furfuryl alcohol was 7-8 ppm (28-32 mg/cu m). All volunteers were able to detect the furfuryl alcohol at 10 ppm (40 mg/cu m), and they described the odor as "sweet," "alcoholic," or "etherlike."

Apol [23], in 1973, reported the results of a health hazard evaluation conducted by NIOSH at a foundry. One or two workers on each shift produced cores for iron castings prepared by a two-stage, air-set cure process. The first stage involved the construction of a large core and required 10-15
minutes; the second, the cure stage, required 45 minutes. The substances used in the process included a mixture of furfuryl alcohol and paraformaldehyde, a phosphoric and sulfuric acid mixture, and sand. After these substances were mechanically mixed, they were poured into the mold. This process was usually performed at room temperature; however, in cold weather the sand was heated before mixing. The high temperature of the sand apparently caused the release of furfuryl alcohol and formaldehyde vapors.

During the coremaking and the core-curing stages, air samples were collected with charcoal tubes; all such samplings were repeated when hot sand was used [23]. The furfuryl alcohol concentration was then determined by gas chromatography. During the 15-minute core preparation, under normal temperature conditions, the concentration of furfuryl alcohol was 8.6 ppm (34.4 mg/cu m). When warm sand was used during the same cure period, the concentration of furfuryl alcohol was 10.8 ppm (43.2 mg/cu m). None of the three exposed employees reported any discomfort during those operations. However, when the hot sand was used during the 15-minute core preparation, the concentration of furfuryl alcohol was 15.8 ppm (63.4 mg/cu m) with a formaldehyde concentration of 0.33 ppm (0.41 mg/cu m). Under these conditions, the two persons present (an employee and a NIOSH representative) experienced lacrimation and wanted to leave the vicinity of the operation. These observations do not clarify whether the irritation was due to furfuryl alcohol, to formaldehyde, to other compounds conceivably present, or to the combined effects of two or more substances. Although the skin of the exposed employee also came into contact with the furfuryl alcohol, no signs of skin irritation were evident during the process, and, according to the authors, none had occurred previously.

Burton and Rivera [24], in 1972, reported results of another NIOSH health hazard evaluation study performed at a different foundry. The foundry produced large ferrous castings, an operation that involved production of no-bake resin cores and molds. In the course of the operation, three men handled a mixture of 1,000 pounds of sand, 15 pounds of base resin (containing furan resin, furfuryl alcohol, and some urea-formaldehyde resin), and 4.5 pounds of catalyst (containing toluene sulfonic acid, isopropyl alcohol, and water). These ingredients were mixed in an automatic mixer and then poured into wood molding forms.

Air samples of unspecified volume were collected for an unstated duration from the work and personnel areas by charcoal tubes and MSA personal monitor pumps [24]. The results revealed that, of the 10 exposed workers, 4 coremakers were exposed to furfuryl alcohol at 66, 32, 30, and 25 mg/cu m. One coremaker was exposed at an undetectable concentration. No furfuryl alcohol was detectable in the breathing zones of three assistant coremakers and one of two apprentices, the remaining apprentice being exposed to furfuryl alcohol at 11 mg/cu m.
The investigators [24] also reported that the 8-hour TWA exposure concentrations of furfuryl alcohol were 25 mg/cu m in the breathing zone of a coremaker and less than 20 mg/cu m in the breathing zones of an assistant coremaker and an apprentice. They pointed out that none of the workers had any of the signs and symptoms that they considered attributable to furfuryl alcohol, ie, ocular irritation, headache, nausea, or dizziness; the investigators did not cite their basis for inferring these to be the effects of furfuryl alcohol. Burton and Rivera concluded that there was no hazard from furfuryl alcohol up to 66 mg/cu m.

Mastromatteo [25], in 1965, described adverse health effects in workers exposed to furfuryl alcohol during the production of acid-resistant cements and binders for foundry sand. Two of 15 bricklayers who had skin contact with the acid-resistant cement developed dermatitis. In one incident, while 15 workers were applying an acid-resistant lining containing furfuryl alcohol to a large pickling tank during hot weather, 7 experienced respiratory irritation, including mild sore throat, severe bronchitis accompanied by intermittent coughing, and chest pain; 2 were hospitalized. Because there was also exposure to acid-resistant cement, the possible contribution of furfuryl alcohol to the skin and respiratory irritations cannot be evaluated.

An investigation reported by Sanders [26] involved four male workers exposed to furfuryl alcohol. They performed laboratory work with furfuryl alcohol and furfural from 2 months to 5 years and had skin contact in small amounts and light vapor exposure daily; however, more extensive skin contact and heavy vapor exposure also occurred, but less frequently. Medical histories and examinations of the workers revealed no significant findings.

**Animal Toxicity**

(a) Inhalation

The results of a study with commercial furfuryl alcohol, performed by Woods and Seevers [27], were reported in 1954. For this study, mice, rats, rabbits, dogs, and monkeys were exposed to furfuryl alcohol vapor for 6 hours. The animals were exposed in a 195-liter gas-tight chamber. The vapor was produced in an evolution chamber by passing air through furfuryl alcohol (50-200 g) at a constant temperature. The mixture of air and furfuryl alcohol vapor was regulated and metered before being passed through the exposure chamber. Controls were exposed to air alone. Deaths occurred only if they occurred within 48 hours after exposure.

Mice in groups of 12-24, exposed to furfuryl alcohol at 47-243 ppm (188-972 mg/cu m), had no mortality [27]. Mice exposed at 597 ppm (2,388 mg/cu m) had a 92% mortality. An LC₅₀ for mice of 397 ppm (1,588 mg/cu m)
can be approximated from the data provided. Groups of 24 rats exposed to furfuryl alcohol at 47-180 ppm (188-720 mg/cu m) showed a dose-related mortality. An LC\textsubscript{50} for rats of 85 ppm (340 mg/cu m) can be approximated from the data provided. Higher exposure levels of furfuryl alcohol, ranging from 243 to 597 ppm (972 to 2,388 mg/cu m), killed all animals.

Exposure of groups of two rabbits to furfuryl alcohol at 47-416 ppm (188-1,664 mg/cu m) produced no deaths [27]. Exposure of groups of two dogs to furfuryl alcohol at 40-349 ppm (160-1,396 mg/cu m) produced no deaths. Exposure of one monkey at 260 ppm (1,040 mg/cu m) had no harmful effects that were evident.

The effects of repeated exposures to furfuryl alcohol vapor were also studied [27]. Exposures of one male and one female dog for 6 hours/day, 5 days/week for 4 weeks, at an average concentration of 239 ppm (956 mg/cu m) had no apparent effect except a slight bronchial inflammation. Similar exposure of one monkey for 3 days had no apparent effect.

In 1952, Comstock and Oberst [28] reported on the acute and subacute inhalation toxicity of furfuryl alcohol in male Wistar rats (150-200 g) and mice (20-30 g). In the acute toxicity study, air at 2 liters/minute was passed through furfuryl alcohol and then through a 10-liter vacuum desiccator acting as the inhalation chamber. This was assumed to ensure an approximate saturated test atmosphere in the chamber that also contained a small quantity of liquid furfuryl alcohol. The concentration of the vapor, however, was calculated from the mass of compound trapped in a collection bubbler containing glacial acetic acid and from the sample volume as measured by a wet-test meter. The furfuryl alcohol of the absorbing medium was determined using a titrimetric method.

Thirty rats were divided into five groups of six rats each. Three groups were exposed for 4 hours, and the remaining two groups were exposed for 8 hours to the saturated furfuryl alcohol vapor.

Acute exposure of rats to saturated furfuryl alcohol vapor, approximately 700 ppm (2,800 mg/cu m), resulted in 22% and 25% deaths after 4- and 8-hour exposures, respectively [28]. Deaths occurring within 14 days were recorded. Signs arising from these exposures included initial excitement, drowsiness, apparent sleepiness, and irritation of the eyes, which became red within 8 minutes.

In a subacute toxicity experiment, these investigators [28] exposed rats and mice in a 410-liter dynamic gassing chamber at an average concentration of 19 ppm (76 mg/cu m). The 15 rats were exposed for 6 weeks and 8 mice for 3 weeks, for 6 hours/day, 5 days/week. Additional animals (five rats and two mice) were also exposed for earlier necropsy.
Subacute exposure of the rats and mice to furfuryl alcohol vapor at a daily average concentration of 19 ppm (76 mg/cu m) resulted in no deaths except for one rat after the third exposure and one mouse after nine exposures. Signs of toxicity noted included restlessness during the initial 5-10 minutes of exposure and drowsiness that continued throughout the exposure. Both test and control animals gained weight at the same rate.

Necropsies of the animals revealed diffuse congestion of the entire respiratory tract without significant cellular changes in the case of both acute and subacute exposures [28]. All other organs of the animals remained unchanged. The authors also suggested that, because of its low vapor pressure (0.98 mmHg at 38°C or 100.4°F), furfuryl alcohol would not be expected to pose a serious occupational vapor hazard unless a prolonged exposure or a massive spill occurred in hot weather.

Jacobson et al [22], in an investigation of the toxicity of a liquid propellant mixture containing furfuryl alcohol, aniline, and hydrazine, studied the acute toxicity of furfuryl alcohol vapor in rats. Male Wistar rats, weighing 200-275 g, were exposed in groups of 10 for 4 hours to furfuryl alcohol. An LC₅₀ of 233 ppm (932 mg/cu m) was estimated from the concentration-mortality curve. Jacobson et al [29] found that all exposed rats exhibited signs of lethargy, exophthalmos, rales, and a porphyrin nasal discharge.

(b) Ocular

In a 1954 report, Woods and Seevers [27] described the ocular effects of undiluted furfuryl alcohol on a group of four rabbits. Instillation of undiluted alcohol (0.05 ml or 56 mg) slowly into one eye of each rabbit resulted in eye inflammation, viscid mucoid secretion, corneal opacity, and eyelid swelling. The eye returned to normal 40-64 days after treatment; one rabbit died of other causes after 43 days. Instillation of 0.02 ml (23 mg) furfuryl alcohol produced the same, but less severe, results as those observed with the larger dose; the eye of each rabbit returned to normal after 2-8 days.

Comstock and Oberst [28] reported that rats developed eye redness within 8 minutes after a single exposure to saturated furfuryl alcohol vapor, ie, 700 ppm (2,800 mg/cu m) for 4 or 8 hours. No evident eye irritation, however, occurred in either rats or mice during repeated exposure at 19 ppm (75 mg/cu m). These rats were exposed for 6 hours/day, 5 days/week for a total of 30 exposures; the mice were exposed for 6 hours/day, 5 days/week for 3 weeks.

(c) Dermal

Woods and Seevers [27] studied the effects of topical application of furfuryl alcohol to rabbits, guinea pigs, and mice. Undiluted furfuryl
alcohol at 400-1,100 mg/kg produced a dose-related mortality in rabbits [27]. An LD₅₀ of 657 mg/kg can be estimated from the data provided. Administration of furfuryl alcohol at 2,200 mg/kg killed all rabbits tested. An LD₅₀ of 4,920 mg/kg can be estimated from the data provided on dermal application to mice. Dermal administration of 8,500 mg/kg to three guinea pigs caused no deaths. From these results, Woods and Seevers concluded that percutaneous toxicity was much greater in rabbits than in mice or guinea pigs and that furfuryl alcohol was the least toxic to unshaved guinea pigs percutaneously.

In 1974, Chernousov [30] studied the allergenic and irritating properties of furfuryl alcohol on guinea pigs. In the study of the irritating properties, 50%, 10%, and 1% solutions in acetone were applied daily for 12 days to a 2.25-sq cm area of skin on the lateral surface of the torso. To determine the sensitizing properties of furfuryl alcohol, the investigator dissolved 150 µg in 0.2 ml of absolute Freund's adjuvant, or 40, 20, or 10 µg in acetone, and applied it topically to the hind paw pad or to the ear skin. Control animals (156 guinea pigs) received only Freund's adjuvant or acetone. Intracutaneous sensitization was tested on the 14th day. On the 21st day, the titers of humoral antihapten antibodies and the degree of leukocyte-specific agglutination (LSA) were determined. The minimum sensitizing dose of furfuryl alcohol producing humoral antibodies was 40 µg; for positive LSA response it was 20 µg. From these data, the author characterized furfuryl alcohol as a weak allergen. Chernousov believed that the antigenicity of furfuryl alcohol may be due to the unsaturated moiety of the furfuryl alcohol molecule. The irritating effects of furfuryl alcohol, which included skin dryness, hyperemia, desquamation, and necrosis, were observed in guinea pigs administered the 50% solution.

Camp [31] reported the results of topical application of furfuryl alcohol to the skin of one dog and three rats. After daily application of 11.3 g undiluted furfuryl alcohol to the hairless skin of the dog for 10 days, no toxic signs were observed other than local skin surface changes, ie, hardness or roughness. One rat that received a dermal application of 1.36 ml (1.53 g) of furfuryl alcohol died following respiratory failure, almost an hour after application. Necropsy results from that animal included congested lungs, decreased size of the heart, and darkened liver. Because of the absence of proper control data, the inadequate number of tests performed, and the uncertainty regarding the purity of the furfuryl alcohol used, these results are of questionable validity.

In a 1949 report, Prince [32] stated that furfuryl alcohol can be absorbed through the skin and could give rise to hematuria. The dermal LD₅₀ was not determined, but 11 of 12 rats died as a result of four applications of 300-1,400 mg/kg of the alcohol. The author recommended that gloves and goggles be worn when furfuryl alcohol is used in open vessels. Other precautions that were recommended included immediate washing in the event of skin contact with the furfuryl alcohol.
Sanders [26] reported that 15 ml (16.9 g) of furfuryl alcohol, when applied to the clipped skin of rabbits, was usually lethal. Dermal application of 5 ml (5.6 g) of furfuryl alcohol daily for 30 days resulted in no toxic effects in rabbits.

(d) Oral

Woods and Seevers [27] administered furfuryl alcohol as a 2 or 4% aqueous solution by gastric intubation to male Sprague-Dawley rats weighing approximately 225-275 g. With the 4% aqueous solution, the LD$_{50}$ of furfuryl alcohol was determined to be 149 mg/kg (95% confidence limits of 142-156 mg/kg). With the 2% aqueous solution, however, the oral toxicity of furfuryl alcohol was decreased as demonstrated by the LD$_{50}$ of 451 mg/kg (95% confidence limits of 444-463 mg/kg). The authors reported an oral LD$_{50}$ of 132 mg/kg for undiluted furfuryl alcohol, although no data were provided to substantiate the value. In all the tested animals, the only toxic sign reported was terminal convulsion. The investigators concluded that furfuryl alcohol was absorbed fairly completely through the gastrointestinal tract of the rats.

Boyland [33], in 1940, reported an acute oral LD$_{50}$ of 40 mg/mouse. The weight of the mouse was not given by the author, but, assuming a weight of 20 g, the LD$_{50}$ can be estimated at about 2,000 mg/kg.

Paul et al [34], in 1949, identified the major urinary metabolites excreted following administration of furfuryl alcohol and other related furan compounds. The metabolites were identified by UV absorption. Albino rats weighing 300-400 g, fasted overnight, were given by gastric intubation 20 mg of furfuryl alcohol suspended in sucrose solution. Urine was collected every 2 hours for 6 hours, combined, and then analyzed. The major urinary metabolite was identified as furoyl glycine. The proportion of the dose excreted as furoyl glycine was not stated for furfuryl alcohol, but closely related compounds were metabolized to the extent of approximately 60%.

In a 1949 abstract, Gajewski and Alsdorf [35] reported on the acute toxicity of oral administration of furfuryl alcohol to white rats. Furfuryl alcohol was administered to the rats orally as a 2% aqueous solution. The oral LD$_{50}$ for the rats was determined to be 275 mg/kg. When death occurred, it was attributed to respiratory paralysis. Rats administered unspecified amounts of the alcohol in their drinking water for 20 days lost weight and showed lack of appetite.

Prince [32] found an LD$_{50}$ of just over 0.1 ml/kg (over 0.11 g/kg) for furfuryl alcohol when it was administered by stomach tube to rats. No other observed effects were included in this report; however, necropsies revealed severe hemorrhage and edema of the lungs as well as congestion of the liver; hematuria was also present. The oral LD$_{50}$ reported by Prince agrees with the value of 132 mg/kg given by Woods and Seevers [27].
(e) Intravenous

In the previously mentioned 1949 abstract, Gajewski and Alsdorf [35] reported observing flaccid paralysis, which disappeared after about 30 minutes, in rabbits given furfuryl alcohol iv in a 10% aqueous solution; however, the paralysis became permanent with larger but unspecified doses. The LD₅₀ for the rabbits was 650 mg/kg.

Fine and Wills [36], in 1950, reported the effects of furfuryl alcohol on rabbits and cats. Pentobarbital-anesthetized cats were given a 20% solution of furfuryl alcohol in saline by vein at the rate of 100 mg furfuryl alcohol/kg every 10 minutes. The first injection of 100 mg/kg produced only a slight and temporary decrease in the blood pressure and respiration. After the total dose of furfuryl alcohol exceeded 500-600 mg/kg, each injection resulted in a severe drop in blood pressure and in a temporary apnea. After a total dose of 800-1,400 mg/kg, the animals died from respiratory paralysis. The cardiac effects of furfuryl alcohol in anesthetized rabbits, as recorded directly from the exposed heart and by the electrocardiograph (ECG), also were studied. With increasing doses of furfuryl alcohol, there was little change in the heart rate (chronotropic effect), but the intensity of contraction of both auricles and ventricles was progressively depressed (inotropic effect) as seen from the severely altered ECG characteristics. With lethal doses, the chronotropic effect was abolished as expected; however, a negative inotropic effect on the heart was evident from the ECG. This latter effect appeared to be reversed readily by perfusing the heart with fluid containing no furfuryl alcohol. Fine and Wills suggested that the cardiac changes produced by furfuryl alcohol may be due to a direct action on the myocardium.

Administration of furfuryl alcohol (100 mg/kg over 10 seconds) caused CNS depression in the rabbit, as indicated by the EEG recordings [36]. Fine and Wills pointed out that such results were similar to those produced by certain anesthetics and could be used to combat such CNS stimulants as metrazol, benzedrine, and ephedrine. They observed that furfuryl alcohol tended to affect the brain more readily than it did other organs because central respiratory depression was the usual cause of death.

(f) Subcutaneous

Woods and Seevers [27] reported the acute effects resulting from sc administration of furfuryl alcohol to rats and rabbits. LD₅₀'s were 78 mg/kg and 96 mg/kg for undiluted and for 4% aqueous furfuryl alcohol, respectively. The LD₅₀ for rabbits administered undiluted furfuryl alcohol was 796 mg/kg. Necropsy of the rats and rabbits revealed pulmonary edema and, in the rats, mottled lungs. The LD₅₀ of neat furfuryl alcohol in the rabbit was approximately one-tenth that for the rats, indicating considerable species variation in the acute toxicity of furfuryl alcohol.
In Vitro Tests of Mutagenicity

Recently, the mutagenic potential of furfuryl alcohol has been studied [37] by the Ames test [38] in which 500 µg of furfuryl alcohol was added to each plate and the number of induced revertants compared with the spontaneous ones. *Salmonella typhimurium* strains TA 198, TA 100, TA 1535, TA 1537, and TA 1538 were tested with 4-nitroquinoline-N-oxide, benzo(a)pyrene, N-methyl-N-nitroso-nitrosoguanide, 9-aminoacridine, and 2-aminofluorene, respectively, as positive controls, giving in each case strongly positive results. When furfuryl alcohol was tested with and without S-9 microsomal preparations, the number of revertants above background was not considered significant in any strain tested.

Correlation of Exposure and Effect

The results of exposure of mice [27,28], rats [22,27,28], rabbits, dogs, and monkeys [27] to furfuryl alcohol vapor have been reported. In mice, 92% mortality was observed after a 6-hour exposure to furfuryl alcohol at 2,388 mg/cu m. A similar exposure of rats at 972 mg/cu m, however, resulted in 100% mortality after 6 hours. One 6-hour exposure of a monkey at 1,040 mg/cu m resulted in only slight lacrimation. When two dogs were exposed to furfuryl alcohol vapor at 956 mg/cu m for 6 hours/day, 5 days a week, for 4 weeks, the only observed effect was slight bronchial inflammation.

No effects were observed in rats and mice at furfuryl alcohol concentrations up to 76 mg/cu m after thirty 6-hour exposures [28]. Two rabbits exposed to furfuryl alcohol vapor at 188 mg/cu m for 6 hours [27] and one monkey exposed three times at an average furfuryl alcohol concentration of 956 mg/cu m for 6 hours also showed no effects.

Workplace exposure to furfuryl alcohol also may occur via dermal contact. Furfuryl alcohol is readily absorbed through the skin of animals [27,30-32]. Death occurred in rabbits after dermal application of 700 mg of furfuryl alcohol [27] and in rats after four applications of 300-1,400 mg/kg each [32]. For the rats, 92% mortality was reported, as was hematuria in an unspecified number of animals [32]. A rabbit receiving 5.6 g of furfuryl alcohol/day for 30 days showed no visible effects [26]; this was also the case when 11.3 g/day of furfuryl alcohol was applied to the hairless skin of a dog for 10 days [31]. Dermal application to guinea pigs of furfuryl alcohol at 8,500 mg/kg body weight and 3,200 mg/kg and 400 mg/kg in mice and rabbits, respectively, did not have any apparent effects [27]. However, 50%, 10%, and 1% solutions of furfuryl alcohol in acetone applied daily to guinea pig skin for 12 days resulted in skin dryness, hyperemia, and desquamation [30]. Since these local skin effects were not observed in other studies in which animals received furfuryl alcohol cutaneously, it is likely that the observed surface changes were caused by
the acetone carrier rather than by furfuryl alcohol, an inference consistent with the excellent lipid solvent characteristics of acetone. With the 50% solution, necrosis also was observed. Sensitization tests were performed on guinea pigs by topical administration, to the ear skin or hind paw, of furfuryl alcohol in acetone or in Freund's adjuvant [30]. After 14 days, titers of humoral antihaptens and the degree of LSA were determined. The minimum sensitizing amount of furfuryl alcohol that produced humoral antibodies was 40 μg. In humans, dermatitis has been reported in two workers handling acid-resistant cement, which probably contained, among other possible irritants, liquid furfuryl alcohol [25]; but it is not clear which component was responsible.

Studies have shown that furfuryl alcohol has caused eye irritation in animals [27,28]. Furfuryl alcohol vapor at 2,800 mg/cu m caused eye redness in rats after 8 minutes of exposure [28]. When instilled directly into the eye of a rabbit, 56 or 23 mg furfuryl alcohol produced severe eye irritation and corneal opacity, which were reversible after 40–64 days or 2–8 days, respectively [27].

The only report of ocular effects from furfuryl alcohol vapor in humans was lacrimation in one worker and one visitor performing a survey of possible health hazards. The exposure, measured at 63.4 mg/cu m furfuryl alcohol and 0.4 mg/cu m formaldehyde, lasted about 15 minutes. As was previously discussed, it is not clear whether this eye irritation was due to either component, both components, or to unknown airborne materials.

Although the primary routes of workplace exposure to furfuryl alcohol are by inhalation or by skin or eye contact, some ingestion also may occur. The oral toxicity of furfuryl alcohol has been studied in rats and dogs. In rats, the oral LD₅₀ is between 132 and 451 mg/kg [27,35]. A dog of unspecified weight was administered furfuryl alcohol at 1 g/day for 42 days with no apparent effects [5]. Similarly, humans, after ingesting 40–150 mg (0.57–2.14 mg/kg) of furfuryl alcohol, showed no effects [5].

Fine and Wills [36] stated that furfuryl alcohol had a direct, depressive action on the heart. A total of 600–800 mg/kg, when administered by vein to cats, caused a severe blood pressure drop and temporary apnea, and 800–1,400 mg/kg resulted in death by respiratory paralysis. (A dose of 600 mg/kg in a 70-kg man breathing 10 cu m/workday would be equivalent to 4,200 mg/cu m, so it does seem likely that the effects observed by Fine and Wills would be relevant to the question considered in Chapter V of the appropriateness of a permissible limit of 200 mg/cu m.)

Furfuryl alcohol has been found to be acutely toxic by most routes of administration relevant to an occupational health standard. The data indicate that, in most cases, death occurred as a result of CNS depression and subsequent respiratory paralysis. Furfuryl alcohol is readily absorbed
by all routes, as exemplified by the similar LD$_{50}$'s by oral and sc routes of administration in rats. For example, the oral LD$_{50}$'s of 110 mg/kg [32] and 132 mg/kg [27] were less than twice the sc LD$_{50}$ of 78 mg/kg [27]. Similarly, when 4% furfuryl alcohol was used, the oral LD$_{50}$ of 149 mg/kg for rats was close to the sc LD$_{50}$ of 96 mg/kg [27]. Similar evidence is found by comparing the LD$_{50}$ values in rabbits by iv, sc, and oral routes of administration, reported to be 650 mg/kg [35], greater than 500-526 mg/kg [4], and less than 1,000 mg/kg [4], respectively.

The metabolic pathway and excretion pattern of furfuryl alcohol were studied by Paul et al [34], who found that in rats, 65-70% of orally administered furfuryl alcohol was excreted as furoyl glycine. No information on human biotransformation of furfuryl alcohol has been found.

The effects of furfuryl alcohol on humans and animals are summarized in Tables II-1, II-2, and II-3.

Carcinogenicity, Mutagenicity, Teratogenicity, and Effects on Reproduction

No reports were found on whether there are carcinogenic or teratogenic effects from furfuryl alcohol. There was one report [37] that indicated that furfuryl alcohol was not mutagenic in tests with Salmonella in vitro.


<table>
<thead>
<tr>
<th>Number of Subjects</th>
<th>Exposure</th>
<th>Duration</th>
<th>Observations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>32 mg/cu m</td>
<td>A few seconds</td>
<td>Odor threshold</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>63.4 mg/cu m with 0.4 mg/cu m formaldehyde</td>
<td>15 min</td>
<td>Lacrimation</td>
<td>23</td>
</tr>
<tr>
<td>10</td>
<td>Up to 66 mg/cu m with 0.24-0.91 mg/cu m formaldehyde</td>
<td>(Probably a few seconds)</td>
<td>Eye irritation</td>
<td>24</td>
</tr>
</tbody>
</table>

TABLE II-1
EFFECTS OF FURFURYL ALCOHOL VAPOR ON HUMANS
<table>
<thead>
<tr>
<th>Species</th>
<th>Exposure</th>
<th>Observations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mouse</td>
<td>6.9 g/kg</td>
<td>Killed 89% within 48 hr</td>
<td>27</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.2 g/kg</td>
<td>No apparent effect</td>
<td>27</td>
</tr>
<tr>
<td>Rat</td>
<td>0.3-1.4 g/kg</td>
<td>Hematuria; killed 92%</td>
<td>32</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.53 g</td>
<td>Respiratory failure, lung congestion</td>
<td>31</td>
</tr>
<tr>
<td>Guinea pig</td>
<td>8.5 g/kg</td>
<td>No apparent effect</td>
<td>27</td>
</tr>
<tr>
<td>Rabbit</td>
<td>16.9 g</td>
<td>Death</td>
<td>26</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.7 g/kg</td>
<td>Killed 58% within 48 hr</td>
<td>27</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.4 g/kg</td>
<td>No apparent effect</td>
<td>27</td>
</tr>
<tr>
<td>Guinea Pig</td>
<td>50%, 10%, 1%</td>
<td>Skin dryness, hyperemia, desquamation accompanied by necrosis with 50% solution</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>solutions</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Daily/12 d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rabbit</td>
<td>5.6 g</td>
<td>No apparent effect</td>
<td>26</td>
</tr>
<tr>
<td>Dog</td>
<td>11.3 g</td>
<td>&quot;</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Daily/10 d</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
III. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

Environmental Data

In an extensive study, reported in 1963, of pyrolysis of furfuryl alcohol and furfuryl alcohol-filler resins [39], the off-gases produced between 150 and 850 °C (302 and 1,562 °F) were both qualitatively and quantitatively analyzed at 50 °C (122 °F) intervals. No trace of furfuryl alcohol could be found by gas chromatography or mass spectrometry.

In a NIOSH survey [24] of health hazards in a foundry using no-bake resins in the production of cores and molds, area and personal samples were taken for formaldehyde, furfuryl alcohol, isopropyl alcohol, and free silica. The base resin contained furan, furfuryl alcohol, and some urea-formaldehyde resins. Furfuryl alcohol samples, collected on charcoal tubes, showed that the coremakers were exposed at a TWA level of 6.25 ppm (25 mg/cu m), whereas the other workers were exposed at below the 5-ppm (20 mg/cu m) level. In the 10 samples collected, furfuryl alcohol concentrations up to 16.5 ppm (66 mg/cu m) were found.

A similar foundry survey [23], reported in 1973, also involved the use of no-bake resin systems composed of paraformaldehyde and furfuryl alcohol and catalyzed by phosphoric and sulfuric acids. Breathing zone and area samples were collected during the coremaking operation and during the coremaking-curing operation. The concentration of furfuryl alcohol rose to 8.6 ppm (34.4 mg/cu m) during the core preparation cycle (15 minutes) and remained at 2.2 ppm (8.8 mg/cu m) during the full core production cycle (1 hour). During the core preparation cycle (15 minutes), if the sand used was warm, the furfuryl alcohol concentration rose to 10.8 ppm (43.2 mg/cu m); when the sand was hot, it rose to 15.8 ppm (63.2 mg/cu m). Formaldehyde concentrations of 0.33 ppm (0.4 mg/cu m) were also found from the samples collected during the latter process.

A series of 24 air samples was taken during 4 months in 1976 at a plant producing furfuryl alcohol [40]. Only one sample had 0.2 ppm (0.8 mg/cu m) furfuryl alcohol; the rest showed less than 0.1 ppm (0.4 mg/cu m). On February 15, 1978, four air samples were collected in another furfuryl alcohol plant. The average furfuryl alcohol concentration was 0.3 ppm (range 0.2-0.4 ppm).

In 1976, Virtamo and Tossavainen [41] reported the results of a study carried out at 10 iron and steel foundries in Finland that used furan resins as binding agents for sand, mainly in coremaking. These furan binders were copolymers of furfuryl alcohol (containing 50-95% furfuryl alcohol) with either urea-formaldehyde or phenol-formaldehyde resins. The urea-furan resins were used in iron founding, and the phenol-furan resins
were used in steel founding. The unhardened resin produced gases that included furfuryl alcohol, formaldehyde, and possibly small amounts of phenol. The exothermic hardening reaction increased the evaporation rates of these compounds, and, therefore, the concentrations of their airborne compounds. The concentrations of these airborne gases were measured in the coremaking areas. From a total of 36 furfuryl alcohol and 43 formaldehyde samples examined, the arithmetic means of the concentrations of the airborne gases were 4.3 ppm (17.2 mg/cu m) for furfuryl alcohol (range 0.15-40 ppm; 0.6-160 mg/cu m) and 2.7 ppm (3.32 mg/cu m) for formaldehyde (range 0.15-20 ppm; 0.19-24.6 mg/cu m). As a result, 22% of the furfuryl alcohol determinations and 38% of the formaldehyde determinations exceeded their established permissible limits in Finland (5 ppm or 20 mg/cu m for furfuryl alcohol and 2 ppm or 2.46 mg/cu m for formaldehyde).

Sampling and Analytical Methods

(a) Sampling

Furfuryl alcohol may be readily absorbed in water [42-45], glacial acetic acid [46], aqueous sodium hydroxide [47], or acetone [48]. Sampling can be performed by drawing contaminated air through a collecting device at a measured flowrate that is low enough to ensure complete absorption of the contaminant, ie, the slower the sampling rate, the higher the absorption efficiency should be in any specific system.

Furfuryl alcohol can be sampled in at least three kinds of absorbers that use liquid collection media. Simple gas washing bottles, such as midget impingers, may be used, but, since the degree and duration of contact between the sampled air and the liquid are not maximized, it may be necessary to use two or more of these absorbers in series in order to achieve maximum collection efficiency. Simple gas washing bottles have the advantage of being simply constructed and easy to clean, and they require only a small volume of liquid. The spiral or helical absorber can also be used for organic vapor collection. Although it is larger and contains more liquid than a gas washing bottle, its chief advantage is a higher collection efficiency because of the longer contact path between the sampled air and the collection liquid. Fritted bubblers provide high collection efficiency because of the extensive gas-liquid contact and the low flowrate used (0.5-1.0 liters/minute), but do not have the advantage of small size and volume and ease of cleaning.

Collection of furfuryl alcohol vapor in liquid allows a wide variety of analytical techniques such as oxidation by bromine, polarography, or UV spectrophotometry. However, the use of a liquid impinger for collection of breathing zone samples is at least inconvenient. Successful use of collectors containing liquids requires careful handling of glassware during collection and shipment of samples to avoid breakage and spillage.
Another method of collecting nonreactive vapors such as furfuryl alcohol is by the use of solid adsorbents such as silica gel or activated charcoal. Because of its polar nature, silica gel attracts polar substances, such as water. Alcohols are easily collected on silica gel but may be displaced if samples are collected under humid conditions. The volume of air sampled may have to be limited under these conditions in order to minimize loss. The nonpolarity of activated charcoal enables it to adsorb most organic vapors and gases in preference to atmospheric moisture, permitting long sampling times. The reliability of charcoal sampling depends on the efficiency of desorption of furfuryl alcohol from the charcoal. Greinke [49] tested a number of solvents and found that acetone gave the best recovery of furfuryl alcohol from charcoal, about 85%; with carbon disulfide, only about 50% was recovered. Pyridine has recently been found to permit desorption of furfuryl alcohol from charcoal with desorption efficiencies approaching 100% [46]. Porapak Q has been studied recently [50] as an adsorbent for furfuryl alcohol vapor. This medium is not composed of highly polar molecules and thus does not strongly adsorb highly polar molecules such as water or formaldehyde. When acetone is used, furfuryl alcohol can be desorbed from Porapak Q with recoveries greater than 91% and with a coefficient of variation of 0.033 [50]. Acetone will also desorb impurities that are sometimes present in the Porapak Q, so the sorbent may need to be washed in acetone and dried prior to sampling [50].

Sampling by absorption of furfuryl alcohol on Porapak Q is the preferred method. This method has the advantage of minimal interference from airborne moisture and polar organic vapors such as formaldehyde. In addition, desorption of furfuryl alcohol from Porapak Q is efficient and reproducible without the disadvantages of using pyridine, the odor of which is highly objectionable.

(b) Analysis

Furfuryl alcohol collected in liquid media can be analyzed by UV spectrophotometry, polarography, or oxidation by bromine. Aqueous scrubber samples have been analyzed for furfuryl alcohol by measuring the absorbance at 217 nm [44]. The limit of detection for this method was below 0.8 mg/cu m for a 25-liter air sample collected in 20 ml of water at 1-3 liters/minute. However, other substances, such as phenol, formaldehyde, and furfural, which also absorb in the region of 217 nm and are usually present in the air with furfuryl alcohol, will interfere. In a 1971 report, Pfaffli [45] described an analytical method by which furfuryl alcohol could be determined without interference from phenol, formaldehyde, or furfural. The analysis was based on the opening of the furan ring in the presence of dilute acid. By adding methanol, polymerization was prevented and reaction of the open ring with hydrazine was permitted, yielding a cyclic hydrazone that absorbed strongly at 242 nm. With a 50-liter sample collected in 20 ml of water, the detection limit of this method of furfuryl alcohol analysis was estimated to be 0.4 mg/cu m.
Microgram quantities of furfuryl alcohol can also be determined polarographically after being collected in a fritted sampler containing water [42]. Air was sampled at 1 liter/minute for 3-6 minutes. The analysis was based on the oxidation of furfuryl alcohol to furoic acid by hexavalent chromium, the unconsumed quantity of which was determined polarographically. Up to 3 mg of furfural in the sample solution does not interfere with the analytical procedure.

An analytical method applicable to furfuryl alcohol, but not to furfural, is bromination to saturate the furan ring [51]. Potassium iodide was added to the brominated sample to permit subsequent titration of the liberated iodine. According to the authors, the overall error of this method is ±1%, provided that the total furfural present in the sample does not exceed 20%. This method has been used to measure furfuryl alcohol in air after sampling at less than 1.5 liters/minute through a fritted bubbler containing glacial acetic acid [22,28].

Gas chromatography has become a prevalent method of detection and analysis of organic materials. This technique has been used in the occupational environment [52] in conjunction with sampling the breathing zone on a solid sorbent followed by carbon disulfide desorption. Pyridine, however, when used as a desorption solvent, has given excellent desorption efficiencies. This method has been used to evaluate worker exposure in furfuryl alcohol production facilities [46]. For a 10-liter sample, the lower detection limit of the method was 0.8 mg/cu m, but the authors calculated that by sampling 100 liters of air, this limit would be 0.08 mg/cu m.

Gas chromatography has also been tested with an adsorbent normally used as a column packing for gas chromatographs. In this method [50], furfuryl alcohol was collected in a glass tube containing Porapak Q and desorbed with acetone. Sampling 6 liters of air at 0.01-0.05 liters/minute, furfuryl alcohol concentrations of 120-470 mg/cu m can be detected. The relative standard deviation of the combined sampling and analytical method is 0.072. The sampling device has the advantages of being small, of containing no liquids, and of allowing efficient, reproducible desorption of furfuryl alcohol. This analytical method is selected as the method of choice because it is sensitive, rapid, subject to few interferences, and, in conjunction with the compatible sampling method selected, avoids the possibly hazardous use of carbon disulfide or highly objectionable pyridine. This method [50] has been validated by NIOSH. Details of the method are described in the appendix.

Engineering Controls

In processes for the production, storage, and use of furfuryl alcohol, the application of chemical engineering principles, together with care in
selecting process equipment, particularly pumps and valves, are necessary to ensure that furfuryl alcohol is not released to the occupational or community environments [53]. The use of instrumentation and remote controls is recommended for monitoring processes, for allowing rapid and safe intervention into routine operations, and for emergencies that might develop from failures of the process or equipment. The use of closed systems to prevent release of materials from a process is generally recommended, but to maintain the integrity of such a system, an engineering control program, including frequent inspections, preventive maintenance, and prompt repair of leaks, is essential.

When closed systems are not practical or leaks develop, the probability of exposure to furfuryl alcohol in the occupational environment is increased. The likelihood of exposure also increases during operations that require handling, transferring, or sampling of raw materials of furfuryl alcohol products or wastes. Exposure may also occur during required maintenance or repair of equipment by entry into tanks, vessels, or other confined spaces or when an emergency or a nonroutine situation develops. Therefore, when furfuryl alcohol is handled in an open system, a ventilation system, such as a hood, glove box, or local exhaust system, may be necessary. In addition, a ventilation system is desirable as a standby if a closed system should fail. The principles set forth in *Industrial Ventilation—A Manual of Recommended Practice* [54] and *Fundamentals Governing the Design and Operation of Local Exhaust Systems*, ANSI Z9.1-1971 [55], should be applied to control atmospheric concentrations and prevent the release of raw materials, furfuryl alcohol products, or wastes during those operations when exposure is possible.

To ensure effective operation of ventilation systems, routine inspection should include face velocity measurements of the collecting hood, examination of the air mover and collection or dispersion system, and measurements of atmospheric concentrations of furfuryl alcohol in the work environment. Any changes in the work operation, process, or equipment that may affect the ventilation system must be promptly evaluated to ensure that control measures provide adequate protection for employees. All facilities require frequent inspection and preventive maintenance to ensure that leaks are readily detected and repaired to avoid exposure of employees. Exhaust gases that may contain furfuryl alcohol or hazardous raw materials or wastes should be prevented from being released into the occupational and community environments.

32
IV. WORK PRACTICES

Undiluted furfuryl alcohol has a flashpoint of 75 °C (167 F) [56]. It is therefore classified as a combustible liquid of Class IIIA by the rules in 29 CFR 1910.106. The lower and upper flammable limits in air at 72.5-122 °C (162.5-251.6 F) are 1.8% (18,000 ppm) and 16.3% (163,000 ppm), respectively [2]. Furfuryl alcohol can therefore be handled safely at temperatures below its flashpoint. Nevertheless, as good practice, all ignition sources should be controlled in areas where furfuryl alcohol is processed, stored, manufactured, or otherwise used. In the event of a fire, foam, dry chemical, or carbon dioxide extinguishers or water should be used [57]. Firefighting personnel should be advised that the flames of burning alcohols are difficult to see in daylight and that extra care must be taken in fighting these fires [58].

The principal safety problem associated with furfuryl alcohol is its violent polymerization reaction when in contact with acids. Improper use or negligent handling and storage of furfuryl alcohol can result in explosive reactions [18,19,59]. Furfuryl alcohol should be stored in tightly closed containers in cool, well-ventilated areas away from all acids or heat sources. Containers should bear labels that contain information on the sensitivity of furfuryl alcohol to acids. In storage areas, signs conveying this caution should be posted in readily visible locations.

Where furfuryl alcohol is stored in tanks, the tanks should be diked to contain the tanks' volume, reducing the probability of runoff to areas where acids may be used or stored.

Protective clothing and safety glasses with side shields or chemical safety goggles should be worn by employees to reduce the possibility of skin absorption of, or eye irritation by, furfuryl alcohol, since animal data [26-28,31] indicate these to be hazards associated with exposure to furfuryl alcohol. The degree of protection required depends on the severity of the potential exposure. Eye protection should be used in any situation where liquid furfuryl alcohol may enter the eye. For jobs where there is the possibility of the body being soaked, face shields and full-body suits that are rubberized or otherwise resistant must be used. Under routine working conditions, however, regular long-sleeved work clothing should suffice for skin protection against small amounts of furfuryl alcohol. When exposure is limited to the handling of contaminated equipment or small amounts of furfuryl alcohol, rubberized gloves should afford adequate protection. Protective clothing and equipment should be decontaminated before reuse, and any apparel or equipment showing signs of deterioration should be discarded or repaired.
Compliance with the recommended exposure limit should protect workers against adverse effects from inhaled furfuryl alcohol. When respiratory devices are permitted, they must meet the specifications of Table I-1. A respiratory protection program in accordance with 29 CFR 1910.134 must be followed to ensure that respirators are routinely inspected and properly cleaned, maintained, and stored.

As a good practice, the employer should provide locker and changing facilities as well as showers, and should encourage workers to shower before they leave the workplace. Good personal hygiene can help avoid accidental eye or skin contact with furfuryl alcohol. Workers should wash thoroughly before eating, smoking, or drinking to prevent ingestion of furfuryl alcohol and to limit its inhalation.

The plant should establish contingency plans to meet any emergency that can reasonably be anticipated. Stations equipped with first-aid supplies, approved respiratory protective devices, protective garments, or other special equipment should be maintained at easily accessible locations. Eyewash fountains and emergency showers must be available and clearly marked in furfuryl alcohol work areas. In the event of eye contact with furfuryl alcohol, the affected area should be flushed with a copious flow of water followed by appropriate medical attention.

Standard procedures should be formulated for maintenance and repair of engineering control systems; these procedures should not depend on the use of respiratory protection. There are several essential elements in these maintenance procedures. Tanks, pumps, valves, or lines must be drained and thoroughly flushed with water or steam prior to repair activities, especially welding, grinding, or other operations that might offer an ignition source for flammable vapor or combustible liquid. All personnel entering confined spaces must be supplied with whole body protection, such as overalls or impermeable clothing, and suitable respiratory protection in accordance with Table I-1. Workers should wear this respiratory protective equipment unless prior measurements indicate that the air concentration of furfuryl alcohol is at or below the recommended TWA concentration limit and that there is an acceptable oxygen concentration (about 20%). A second properly protected worker must be on standby outside the confined space, and effective communication must be maintained between all involved persons. A safety harness and lifeline should be used.

Spilled furfuryl alcohol must be cleaned up immediately by properly trained, adequately protected personnel. Liquid can be sorbed with vermiculite, sand, or other suitable mineral aggregate and removed from the work area for disposal. If sufficient drainage to a suitable collection basin is available, spilled liquid may be hosed away with large quantities of water. When feasible, the area of the spill should be ventilated to remove any aerosol or vapor. Methods of disposal must comply with Federal, state, and local regulations.
Employee education on the safe handling of furfuryl alcohol and its hazards is essential. It is particularly important that employees be informed of the danger arising from contact of furfuryl alcohol with acids. This information and instructions informing employees of proper handling methods, cleanup procedures, personal protective equipment, and emergency procedures should be presented as part of a continuing education program as well as in written form. The NIOSH publication An Identification System for Occupationally Hazardous Materials [60] should be consulted in the design of written material describing the relevant physical, chemical, and toxicologic properties of furfuryl alcohol or of mixtures or formulations containing the compound.
V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1960, the American Conference of Governmental Industrial Hygienists (ACGIH) proposed a threshold limit value (TLV) of 50 ppm (200 mg/cu m) for furfuryl alcohol [61] expressed as a TWA concentration limit for an 8-hour day. In 1971, a tentative change to reduce the TLV to 5 ppm (20 mg/cu m) was proposed [62], and this value was adopted in 1974 [63]. The ACGIH did not give a reason for recommending a reduction of the TLV to 5 ppm from 50 ppm. No new evidence was presented [64]. It is reasonable to infer from comparing the documentations [62,63] that the change was made in order to reduce the likelihood of eye irritation.

In 1976, the ACGIH [65] also recommended a short-term exposure limit (STEL) of 40 mg/cu m for furfuryl alcohol. The STEL was defined by the ACGIH as an absolute ceiling not to be exceeded at any time during a 15-minute excursion period. It was proposed that no more than four excursions be permitted each day, with at least 60 minutes between excursions.

In 1976, the International Labour Office in Geneva [66] reported an established limit for furfuryl alcohol of 50 ppm (200 mg/cu m) in Australia, the Federal Republic of Germany, Rumania, and Yugoslavia, but 5 ppm (20 mg/cu m) in Belgium, Finland, and Sweden.

The current Federal limit is 50 ppm (200 mg/cu m) expressed as a TWA concentration for an 8-hour day [66]. This limit was based on the 1968 ACGIH recommendation.

Basis for the Recommended Standard

(a) Permissible Exposure Limit

Furfuryl alcohol has been shown to be readily absorbed by inhalation, ingestion, or percutaneous application. The available toxicity information on furfuryl alcohol is largely on acute toxicity. Whether furfuryl alcohol can cause chronic toxicity is not clear from presently developed information. It may be that chronic injury does not occur, conceivably because of rapid detoxification or excretion. Incomplete information suggests this may be so, but investigations of furfuryl alcohol have been too limited to allow confidence on this point.

In rats, CNS depression leading to respiratory paralysis and death has been observed at furfuryl alcohol concentrations as low as 188 mg/cu m for
6 hours [27]. Identical exposure of mice and rabbits resulted in no
effects. A monkey exposed to furfuryl alcohol vapor for 6 hours at 1,040
mg/cu m had only very slight lacrimation, but when exposed to 956 mg/cu m
for 6 hours/day for 3 days, it showed no effects whatsoever.

The available exposure data do not indicate the furfuryl alcohol
concentration below which there will be no adverse effects in workers. In
humans, the only effects reported to be associated with exposure to
furfuryl alcohol have been slight lacrimation [23], bronchitis, and mild
sore throat [25]. In the case of lacrimation [23], it is not clear whether
it was caused by formaldehyde, by furfuryl alcohol, or by the combined
action of the two. The exposure concentrations associated with the
respiratory irritation [25] are not known. Since the current Federal limit
(200 mg/cu m for 8 hours) is about one-fifth the concentration that
reportedly caused no effects in monkeys [27], this limit may be adequate to
protect workers from adverse effects from furfuryl alcohol vapor. Thus, in
the absence of other information either showing that 200 mg/cu m offers
inadequate protection or showing that some other limit is more appropriate,
it is recommended that the existing limit (200 mg/cu m) be continued.
Research to develop a better basis for a permissible exposure limit should
be conducted.

As with the present Federal limit, this limit of 200 mg/cu m is
proposed as a TWA concentration. So long as the workweek is limited to 40
hours, the total dose inhaled from exposure for four 10-hour days at that
concentration will not be greater than that from five 8-hour days, hence
the proposal that the limit be expressed as a TWA concentration for up to a
10-hour workshift.

Many workers handle small amounts of furfuryl alcohol or work in
situations in which, regardless of the amount used, there is only
negligible contact with the substance. Under these conditions, it should
not be necessary to comply with many of the provisions of this recommended
standard that has been prepared primarily to protect workers' health under
more hazardous conditions. Concern for workers' health requires that
protective measures and emergency procedures be instituted below the
enforceable limit to ensure that exposures stay below that limit. For
these reasons, the action level has been defined as one-half the
recommended TWA environmental limit, thereby delineating those work
situations that do not require the expenditure of health resources for
environmental and medical monitoring and for associated recordkeeping.
This level has been chosen on the basis of professional judgment rather
than on quantitative data that delineate nonhazardous areas from areas in
which a hazard may exist. However, because of nonrespiratory hazards, such
as those resulting from eye contact or skin absorption, appropriate work
practices and protective measures to prevent skin and eye contact should be
required regardless of the concentration of airborne furfuryl alcohol.
(b) Sampling and Analysis

The technology is currently available to sample and to analyze furfuryl alcohol at the recommended environmental concentration limits. As discussed in Chapter III and presented in greater detail in the appendix, the use of a tube containing Porapak Q to collect furfuryl alcohol from an air sample is recommended. Elution of the Porapak Q with acetone and analysis by gas chromatography allows the determination of furfuryl alcohol over the range of 117-469 mg/cu m using a 6-liter air sample [50]. Other techniques, such as collection in a charcoal tube followed by desorption with pyridine and gas chromatographic analysis [46] or collection with a bubbler and analysis by colorimetric, spectrophotometric, or physical-chemical methods, have also been described and may be useful.

(c) Medical Surveillance

The available information reviewed in Chapter II (Correlation of Exposure and Effect) on the toxicity of furfuryl alcohol, though limited, suggests acute upper respiratory irritation and CNS depression as possible effects. In addition, dermal penetration has been demonstrated in animals in tests indicative of similar action in humans; it seems from this and from its lipid solvent characteristics (based on its miscibility with such common lipid solvents as ethyl ether mentioned in Table IX-1) that furfuryl alcohol should also be capable of causing dermatitis. This is supported by evidence [30] that furfuryl alcohol can cause skin sensitization in tests with guinea pigs.

Inasmuch as furfuryl alcohol is not very toxic acutely and apparently is not toxic chronically to a significant degree, no requirement for frequent periodic physical examinations is proposed. Nevertheless, preplacement examinations should be required to establish a baseline with which data from subsequent examinations can be compared. Specific tests of furfuryl alcohol toxicity are not indicated by available information, so history and physical examination of structures that might be affected (eyes, upper respiratory tract, and skin) should suffice. The responsible physician should determine the frequency of periodic examinations after considering such points as the employees' exposures, work histories, and other stresses believed by the physician to be relevant.

(d) Personal Protective Equipment and Clothing

Where there is a likelihood of skin contact with liquid furfuryl alcohol, gloves and other appropriate skin protection such as personal full-body work clothing are recommended. To minimize the risk of eye contact with liquid furfuryl alcohol, employees should wear eye protection such as safety glasses with side shields or chemical safety goggles. To prevent absorption of potentially harmful amounts of furfuryl alcohol by inhalation, respiratory protective measures may also be needed. Proper
engineering controls should be the primary means of reducing the atmospheric concentration of furfuryl alcohol in the work environment. Respirators should be used only during emergencies and nonroutine repair and maintenance activities when airborne furfuryl alcohol concentrations may not be reduced by appropriate engineering controls or administrative measures to concentrations at or below its TWA limit.

(e) Informing Employees of Hazards

At the beginning of employment, all employees should be informed of the hazards from exposure to furfuryl alcohol because of possible eye, respiratory, and skin irritations. Brochures and pamphlets may be effective as aids in informing employees of hazards. In addition, warning signs should be posted in areas of potential exposure, such as sampling points and loading and unloading facilities, and near material-handling equipment, process lines, and pumps.

A continuing education program is an important part of a preventive hygiene program for employees potentially exposed to furfuryl alcohol. A continuing education program, which includes training in the use of protective equipment, emergency procedures, and first aid, should be available to the employees. Trained persons should periodically apprise employees of possible sources of exposure to furfuryl alcohol, the potential adverse health effects associated with such exposure, the engineering controls and work practices in use to limit exposure and those being planned, and those environmental and medical monitoring procedures in use to check control procedures and to evaluate the health status of employees. Personnel potentially exposed to furfuryl alcohol or wastes associated with manufacturing, material handling, or use must be warned of the adverse effects of accidental exposure and must be informed of the signs and symptoms that may occur.

Employees should also be instructed as to their responsibilities, complementing those of their employers, in preventing effects of furfuryl alcohol on their health and in providing for their safety and that of their fellow workers. These responsibilities of employees apply primarily in the areas of sanitation and work practices, but attention should be given in all relevant areas so that employees faithfully adhere to safe procedures.

(f) Work Practices

Since adverse effects from exposure to furfuryl alcohol are possible by skin [25-27,30,32] and eye [27,28] contact and inhalation, proper work practices must be followed to prevent exposures by these routes [22,25-28,32].

Processes should be operated to minimize leaks of hazardous substances and to prevent spills during material handling, transfer, storage, and
sampling. For operations that may increase the concentration of airborne furfuryl alcohol in the work environment, adequate ventilation must be used at all times. Anyone entering the area of an accidental leak or spill must be protectively clothed to prevent accidental contacts with the skin or eyes and must wear suitable respiratory protective devices if needed.

Furfuryl alcohol will undergo violent, sometimes explosive, polymerization reactions when in contact with acids [18,19,59]. Thus, barriers or distance should separate the two substances in storage areas and, to the extent allowed by the operation, during use. If it is not known whether a specific acid or acid solution will react in an unsafe manner, the supplier or controlled tests should give needed information.

Furfuryl alcohol has a flashpoint of 75 C (167 F), so it is classified by 29 CFR 1910.106 as a combustible liquid of Class IIIA. Although at temperatures below its flashpoint furfuryl alcohol can be handled with little danger of fire, flammable vapor may be evolved at higher temperatures. Thus, smoking, open flames, or other ignition sources should be prohibited in any area where furfuryl alcohol is found.

(g) Monitoring and Recordkeeping Requirements

To characterize employee exposures, employers must conduct personal sampling and analysis for furfuryl alcohol. Estimates of the exposure of each employee should be made, whether or not each employee's exposure is measured. Thus, sampling strategy that allows reasonable estimates of all exposures should be employed.

Records of such monitoring should include sampling and analytical methods, times and locations of samples, whether protective devices (especially respiratory protective devices) were in use, and the exposure concentrations found or estimated. In the case of estimated concentrations, information on which the estimates were based must be included. These environmental records should be kept for 30 years, and copies of exposure data should be included with medical records to allow correlation of employees' health status with their working environment. Medical records should be kept for 30 years, since the Toxic Substances Control Act of 1976 requires that "Records of...adverse reactions to the health of employees shall be retained for thirty years from the date such reactions were first reported to or known by the person maintaining such records..." Because medical examinations will often provide the first recognized evidence of an adverse reaction, whether at the time of the examination or retrospectively, it appears consonant with this Act to require that medical records on furfuryl alcohol workers be maintained for 30 years.
VI. RESEARCH NEEDS

Proper assessment of the toxicity of furfuryl alcohol and evaluation of its potential hazard to the working population require human epidemiologic and animal studies. Research is needed to assess the effects of long-term workplace exposure to furfuryl alcohol.

Epidemiologic studies should be performed and should consider morbidity and mortality in exposed workers with attention to possible pulmonary, skin, eye, and CNS effects. In addition, there should be investigations of possible chronic effects of furfuryl alcohol in experimental animals, the compound preferably being administered by dermal contact as well as by inhalation of vapor. These experiments should be designed and conducted so that they also give definitive information on carcinogenic potential. Additional experiments should be performed to investigate whether furfuryl alcohol can cause germinal mutations, terata, or other effects on reproduction.

There is some evidence that furfuryl alcohol is at least partially metabolized in rats to furoyl glycine, which is excreted in the urine [34]. Further research is needed on biotransformation of furfuryl alcohol and on its distribution and elimination.
VII. REFERENCES


2. QO Furfuryl Alcohol, Bulletin 205-B. Chicago, The Quaker Oats Co, Chemicals Division, 1971, 25 pp


4. Erdmann E: [Coffee oil and physiological action of the furfuryl alcohol which it contains.] Arch Exp Pathol Pharmakol 48:233-61, 1902 (Ger)


18. Tobie WC: Explosive reaction of furfuryl alcohol with formic acid. Chem Eng News 18:72, 1940


30. Chernousov AD: [The allergenic properties of furanic compounds.] Gig Sanit 39:28-32, 1974 (Rus)


38. Ames BN, McCann J, Yamasaki E: Methods for detecting carcinogens and mutagens with the Salmonella mammalian microsome mutagenicity test. Mutat Res 31:347-64, 1975


42. Kemka R, Domsky A: [Determination of furfuryl alcohol and furfural jointly in the atmosphere.] Prac Lek 17:353-56, 1965 (Cze)


44. Furfuryl Alcohol, in Analytical Guide. American Industrial Hygiene Association, 2 pp (undated)


46. Furfuryl Alcohol in Air by Charcoal Tube, Bulletin M-103. Chicago, The Quaker Oats Co, 1977, 4 pp

47. [The presence of furfuryl alcohol and phenol in foundries.] Fonderia (Milan) 25:78-80, 1976 (Ita)


Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, vol 4, 1978, pp S365-1 to S365-9


54. Industrial Ventilation--A Manual of Recommended Practice. Lansing, MI, American Conference of Governmental Industrial Hygienists, Committee on Industrial Ventilation, 1976, pp 1-1 to 14-8


62. Threshold Limit Values of Airborne Contaminants, Adopted by ACGIH for 1971. Cincinnati, American Conference of Governmental Industrial Hygienists, 1971, pp 16-17,32-33

63. TLVs— Threshold Limit Values for Chemical Substances in Workroom Air, Adopted by ACGIH for 1974. Cincinnati, American Conference of Governmental Industrial Hygienists, 1974, pp 20-21

64. Documentation of the Threshold Limit Values for Substances in Workroom air, ed 3. Cincinnati, American Conference of Governmental Industrial Hygienists, 1976, pp 121,323


68. Treon JF: Alcohols, in Patty FA (ed.): Industrial Hygiene and Toxicology, ed 2 rev; Toxicology (Fassett DW, Irish DD, eds.). New York, Interscience Publishers, 1963, vol 2, pp 1489-91


VIII. APPENDIX

SAMPLING AND ANALYTICAL METHOD FOR FURFURYL ALCOHOL IN AIR

This method is NIOSH Method No. S-365 [50].

Principle of the Method

A known volume of air is drawn through a glass tube containing Porapak Q to adsorb furfuryl alcohol vapor. Furfuryl alcohol is desorbed from the Porapak Q with acetone, and the sample is analyzed by gas chromatography.

Range and Sensitivity

This method was validated over the range of 117-469 mg/cu m at an atmospheric temperature of 22 C (71.6 F) and atmospheric pressure of 765 mmHg, using a 6-liter sample. This sample size is based on the capacity of the Porapak Q to collect vapors of furfuryl alcohol in air at high relative humidity. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

The upper limit of the range of the method depends on the adsorptive capacity of the Porapak Q. This capacity may vary with the concentrations of furfuryl alcohol and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Porapak Q) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 7 hours at an average sampling rate of 0.044 liter/minute and relative humidity of greater than 80% and temperature of 19 C (66.2 F). The breakthrough test was conducted at 418 mg/cu m.

Interferences

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.

Any compound that has the same retention time as furfuryl alcohol at the operating conditions described in this method will interfere. Retention-time data on a single column should not be considered proof of chemical identity.
Precision and Accuracy

The coefficient of variation for the total analytical and sampling method in the range of 117-469 mg/cu m was 0.072. This value corresponds to a 34 mg/cu m standard deviation at the limit of 200 mg/cu m.

On the average, the concentrations obtained in the laboratory validation study at 100, 200, and 400 mg/cu m were 1.6% 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 evident bias. 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 224.2 mg/cu m indicate that collected samples are stable for at least 7 days.

Advantages and Disadvantages

The sampling device is small and portable and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick instrumental method.

One disadvantage of the method is that the amount of sample that can be taken is limited by the mass of furfuryl alcohol that the tube will hold before overloading. When the amount of furfuryl alcohol found on the backup section of the Porapak Q tube exceeds 25% of that found on the front section, the probability 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 flowrate and cause the measured volume to be imprecise because the pump is usually calibrated for one tube only.

Apparatus

(a) Personal sampling pump: A calibrated personal sampling pump, the flowrate of which can be determined within 5% at the recommended flowrate.

(b) Porapak Q tubes: Glass tube with both ends unsealed, 8.5-cm long with a 6-mm OD and a 4-mm ID, containing two sections of 50/80 mesh Porapak Q separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Porapak Q, and the backup section contains 75 mg. A plug of silylated glass wool is placed at each end of the tube. The pressure drop across the tube must be less than 10 mmHg at a flowrate of
0.05 liter/minute. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Porapak Q adhering to the walls of the glass tubes. The Porapak Q tubes are capped with plastic caps at each end.

Sorbent washing procedure: Prior to usage, Porapak Q is washed with acetone and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch-to-batch differences in production. A quantity of Porapak Q is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone, of a volume equal to twice that of Porapak Q, is added to the sorbent and mixed, and the pressure is reduced. Repeat the operation of wash-mix-vacuum six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120°C (248°F) under slight vacuum (635 mmHg) for 4 hours.

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

(d) Column (.94 m long x 3-mm OD stainless steel) packed with 50/80 mesh Porapak Q.

(e) An electronic integrator or some other suitable method of determining peak areas.

(f) Sample containers: 2-ml glass sample containers with glass stoppers or Polyseal caps (or equivalent).

(g) Microliter syringes: 10-μl 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.

(j) Stopwatch.

Reagents

(a) Acetone, reagent grade.

(b) Furfuryl alcohol, Baker grade (or equivalent). Furfuryl alcohol is a clear viscous liquid. If furfuryl alcohol is received from the manufacturer as a dark-colored liquid, it should be distilled before use. The boiling point of furfuryl alcohol is 170°C (338°F).

(c) Benzene, chromatographic quality.

(d) Nitrogen, purified.
(e) Hydrogen, prepurified.

(f) Filtered compressed air.

Procedure

(a) Cleaning of Equipment

All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tapwater and distilled water, and dried.

(b) Calibration of Sampling Pumps

Each personal sampling pump must be calibrated with a representative Porapak Q tube in the line to minimize errors associated with uncertainties in the volume sampled. Figure IX-2 shows a typical setup for calibrating sampling pumps with a soapbubble meter.

(c) Collection and Shipment of Samples

(1) Immediately before sampling, the caps from the ends of the Porapak Q tube should be removed. All tubes must be packed with Porapak Q from the same manufacturer’s lot.

(2) The smaller section of Porapak Q is used as a backup and should be positioned nearer the sampling pump.

(3) The tube should be placed in a vertical direction during sampling to minimize channeling through the Porapak Q.

(4) Air being sampled should not be passed through any hose or tubing before entering the Porapak Q tube.

(5) A sample size of 6 liters is recommended. A flowrate between 0.01 and 0.05 liter/minute is used for sampling; a flowrate less than 0.010 liter/minute should not be used. The sampling time, flowrate, and type of sampling pump used should be recorded.

(6) The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, the elevation should be recorded.

(7) The Porapak Q tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

(8) With each batch of 10 samples, 1 tube from the same lot of tubes used for sample collection should be submitted. This tube must be
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. A minimum of 18 extra Porapak Q tubes should be provided for desorption efficiency determinations.

(9) Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

(10) A sample of the bulk material should be submitted to the laboratory in a glass container with a Polyseal cap. This sample should not be transported in the same container as the Porapak Q tubes.

(d) Analysis of Samples

(1) Preparation of Samples

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

(2) 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. Complete analysis within 1 day after the furfuryl alcohol is desorbed.

(3) Gas Chromatographic Conditions

The typical operating conditions for the gas chromatograph are:

- 50 ml/minute (60 psig) nitrogen carrier gas flow.
- 65 ml/minute (24 psig) hydrogen gas flow to detector.
- 500 ml/minute (50 psig) airflow to detector.
- 225 C injector manifold temperature.
- 225 C detector manifold temperature.
- 200 C column temperature.

A retention time of approximately 11 minutes is to be expected for furfuryl alcohol under these conditions and using the column recommended in Apparatus (d). The acetone will elute from the column before the furfuryl alcohol.
(4) Injection

The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback 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 will be completely injected. 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. It should be observed that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Porapak Q.

(5) The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

(e) Determination of Desorption Efficiency

(i) The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Porapak Q 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 Porapak Q.

(2) Porapak Q, 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 Porapak Q must be from the same batch as that used in obtaining the samples. The open end is capped with Parafilm. A known amount of a benzene solution of furfuryl alcohol containing 300 mg/ml is injected directly into the Porapak Q with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in a 6-liter air sample at the selected level. It is not practical to inject the neat liquid directly onto the Porapak Q because the amounts to be added would be too small to measure accurately.

Six tubes at each of three levels, equivalent to 100, 200, and 400 mg/cu m, are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the furfuryl alcohol onto the
Porapak Q. 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.

Two or three standards are prepared by injecting the same volume of furfuryl alcohol into 1.0 ml of acetone with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

\[
DE = \frac{\text{average weight recovered (mg)}}{\text{weight added (mg)}}
\]

The desorption efficiency is dependent on the amount of furfuryl alcohol collected on the Porapak Q. Plot the desorption efficiency vs weight of furfuryl alcohol found. This curve is used in Calculations (d) to correct for adsorption losses.

In any handling of benzene, stringent precautions must be exerted to limit occupational exposure and to prevent discharges to community air and water. The standard promulgated by the Occupational Safety and Health Administration (29 CFR 1910.1028) should be adhered to in any handling of benzene. It would be desirable if a solvent less toxic than benzene were used in the preparation of samples for the determination of the desorption efficiency of furfuryl alcohol from Porapak Q, but the necessary experimental work has not been performed. For guidance of those who prefer to use a solvent other than benzene, such a solvent should meet the following criteria: (1) it should be a good solvent for furfuryl alcohol, so that concentrated solutions of furfuryl alcohol can be prepared, (2) it should not dissolve the Porapak Q, and (3) it should be less strongly adsorbed by Porapak Q than is furfuryl alcohol. It seems likely that cyclohexane would meet these requirements, but necessary tests to prove its utility have not yet been conducted.

**Calibration and Standards**

A series of standards, varying in concentration over the range corresponding to about 0.1-3 times the permissible exposure limit 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/1.0 ml vs 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-ionization detector response.

(a) Prepare a stock standard solution containing 120 mg/ml of furfuryl alcohol in acetone.

(b) 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 0.12-3.6 mg/1.0 ml. This range is based on a 6-liter sample.

(c) Prepare a standard calibration curve by plotting concentration of furfuryl alcohol in mg/1.0 ml vs 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.

(b) Corrections for the blank must be made for each sample.

\[ \text{mg} = \text{mg sample} - \text{mg blank} \]

where:

\( \text{mg sample} = \text{mg found in front section of sample tube} \)
\( \text{mg blank} = \text{mg found in front section of blank tube} \)

A similar procedure is followed for the backup sections.

(c) Add the weights found in the front and backup sections to determine the total weight of the sample.

(d) Read the desorption efficiency from the curve (see Procedure (e)(2)) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

\[ \text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}} \]

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

\[ \text{corrected volume} = f \times t \left( \frac{P_1}{P_2} \times \frac{T_2}{T_1} \right) \]
where:

\( f \) = flowrate sampled
\( t \) = sampling time
\( P_1 \) = pressure during calibration of sampling pump (mmHg)
\( P_2 \) = pressure of air sampled (mmHg)
\( T_1 \) = temperature during calibration of sampling pump (K)
\( T_2 \) = temperature of air sampled (K)

(f) The concentration of furfuryl alcohol in the air sampled can be expressed in mg/cu m.

\[
\text{mg/cu m} = \frac{\text{corrected mg} \times 1,000 \ (\text{liters/cu m})}{\text{corrected air volume sampled (liters)}}
\]

(g) Another method of expressing concentration is in ppm.

\[
\text{ppm} = \frac{\text{mg/cu m} \times 24.45 \times 760 \times T + 273}{98.10 \ P \ 298}
\]

where:

\( P \) = pressure (mmHg) of air sampled
\( T \) = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mmHg
760 = standard pressure (mmHg)
298 = standard temperature (K)
<table>
<thead>
<tr>
<th>Properties</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>[Image]</td>
</tr>
<tr>
<td>Formula weight</td>
<td>98.10</td>
</tr>
<tr>
<td>Physical state</td>
<td>Colorless syrupy liquid</td>
</tr>
<tr>
<td>Melting point (stable form)</td>
<td>-14.63 C</td>
</tr>
<tr>
<td>Freezing point</td>
<td>-20 C</td>
</tr>
<tr>
<td>Boiling point, at 760 mmHg</td>
<td>170 C</td>
</tr>
<tr>
<td>Flashpoint:</td>
<td></td>
</tr>
<tr>
<td>Open cup</td>
<td>75 C</td>
</tr>
<tr>
<td>Closed cup</td>
<td>65 C</td>
</tr>
<tr>
<td>Ignition temperature in air</td>
<td>391</td>
</tr>
<tr>
<td>Flammability limits (in dry air at 72.5-122 C):</td>
<td></td>
</tr>
<tr>
<td>Lower limit</td>
<td>1.8% (by vol)</td>
</tr>
<tr>
<td>Upper limit</td>
<td>16.3% (by vol)</td>
</tr>
<tr>
<td>Density (g/ml at 20 C)</td>
<td>1.1296</td>
</tr>
<tr>
<td>Vapor density (air = 1)</td>
<td>3.38</td>
</tr>
<tr>
<td>Percent in saturated air (at 31.8 C)</td>
<td>0.13</td>
</tr>
<tr>
<td>Density of saturated air (air = 1)</td>
<td>1.003</td>
</tr>
<tr>
<td>Viscosity (centipoise at 25 C)</td>
<td>4.62</td>
</tr>
<tr>
<td>Refractive index:</td>
<td></td>
</tr>
<tr>
<td>At 20 C</td>
<td>1.4868</td>
</tr>
<tr>
<td>At 25 C</td>
<td>1.484</td>
</tr>
<tr>
<td>Surface tension (dynes/cm) at 25 C</td>
<td>38.2</td>
</tr>
<tr>
<td>Specific heat of liquid (cal/g/C):</td>
<td></td>
</tr>
<tr>
<td>At 0 C</td>
<td>0.472</td>
</tr>
<tr>
<td>At 25 C</td>
<td>0.502</td>
</tr>
<tr>
<td>Solubility:</td>
<td></td>
</tr>
<tr>
<td>In water</td>
<td>Miscible</td>
</tr>
<tr>
<td>In ethyl ether</td>
<td>&quot;</td>
</tr>
<tr>
<td>In ethanol</td>
<td>&quot;</td>
</tr>
<tr>
<td>In chloroform</td>
<td>&quot;</td>
</tr>
<tr>
<td>In benzene</td>
<td>&quot;</td>
</tr>
<tr>
<td>In petroleum hydrocarbons and most oils</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Conversion factors (760 mmHg at 25 C)</td>
<td>1 mg/cu m = 0.25 ppm</td>
</tr>
<tr>
<td></td>
<td>1 ppm = 4.01 mg/cu m</td>
</tr>
<tr>
<td>Occupation</td>
<td>Occupation</td>
</tr>
<tr>
<td>---------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Asbestos-reinforced equipment manufacturing workers</td>
<td>Grinding-wheel makers</td>
</tr>
<tr>
<td>Carbon and graphite binders production workers</td>
<td>Laboratory workers using furfuryl alcohol</td>
</tr>
<tr>
<td>Cellulose ester production workers</td>
<td>Oil-drilling workers</td>
</tr>
<tr>
<td>Chemical distributors of furfuryl alcohol</td>
<td>Paint-remover makers</td>
</tr>
<tr>
<td>Coumarone resin production workers</td>
<td>Paper and pulp industry workers</td>
</tr>
<tr>
<td>Foundry core binders manufacturing workers</td>
<td>Phenol-furfuryl alcohol production workers</td>
</tr>
<tr>
<td>Furan resin manufacturing workers</td>
<td>Thermoplastic cement, mortar, and grout manufacturing workers</td>
</tr>
<tr>
<td>Furfuryl alcohol manufacturing workers</td>
<td>Thermosetting resin workers</td>
</tr>
<tr>
<td>Furfuryl alcohol-formaldehyde workers</td>
<td>Tetrahydrofurfuryl alcohol production workers</td>
</tr>
<tr>
<td>Furfuryl alcohol-formaldehyde-urea production workers</td>
<td>Workers using furfuryl alcohol as a solvent to remove automotive acrylic lacquer</td>
</tr>
</tbody>
</table>

Adapted from references 68,70-72
FIGURE IX.1
VAPOR PRESSURE OF FURFURYL ALCOHOL

Adapted from reference 2
FIGURE IX-2

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH PORAPAK Q TUBE