

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** SULFUR DIOXIDE ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

The basic text of this document contains the draft technical standard approved by the Joint Review Committee of the NIOSH/OSHA Standards Completion Program and the supporting documentation for the substance SULFUR DIOXIDE.

The SCP draft technical standards are recommendations to the Department of Labor for its consideration in rulemaking and have no legal status until final rules have been promulgated by that agency. This draft standard is provided for your information only.

The References and Sources, Respirator Table Documentation and Use/Exposure and Control Documentation are the working documents used by the various SCP working groups during the development of the draft technical standard and serve as the technical foundation for the standard. The classification for each substance and the regulatory statements were derived following a decision logic established for the various sections of the standard.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

(a) Definitions. (1) "Permissible exposure" means exposure of employees to airborne concentrations of sulfur dioxide not in excess of 5 parts per million (ppm) (13 milligrams per cubic meter (mg/M3)) averaged over an eight-hour work shift (time weighted average), as stated in § 1910.1000, Table Z-1.

(2) "Action level" means one-half of the permissible exposure for sulfur dioxide averaged over an eight-hour work shift.

(b) Initial determination and exposure measurement. (1) Each employer who has a place of employment in which sulfur dioxide is released into the workplace air shall determine if there is any possibility that any employee may be exposed to airborne concentrations of sulfur dioxide above the permissible level. The initial determination shall be made each time there is a change in production, process, or control measures which may result in an increase in airborne concentrations of sulfur dioxide.

(2) A written record of the initial determination shall be made and shall contain at least the following information:

(i) Any information, observations, or calculations which may indicate employee exposure to sulfur dioxide;

(ii) Any measurements of sulfur dioxide taken;

(iii) Any employee complaints of symptoms which may be attributable to exposure to sulfur dioxide; and

(iv) Date of initial determination, work being performed at the time, location within work site, and employees considered.

(3) If the employer determines that any employee may be exposed to sulfur dioxide above the permissible exposure, the exposure of the employee in each work operation who is believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum eight-hour time weighted average exposure of the employee.

(4) If the exposure measurement taken pursuant to paragraph (b) (3) of this section reveals employee exposure to sulfur dioxide above the action level, the employer shall:

(i) Identify all employees who may be exposed above the permissible level; and

(ii) Measure the exposure of the employees so identified.

(5) If an employee exposure measurement reveals that an employee is exposed to sulfur dioxide above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every three months.

(6) If an employee exposure measurement reveals that an employee is exposed to sulfur dioxide above the permissible exposure, the employer shall:

(i) Measure the exposure monthly of the employee so exposed; and

(ii) Institute control measures as required by paragraph (d) of this section; and

(iii) Individually notify, in writing, within five days, every employee who is found to be exposed to sulfur dioxide above the permissible exposure. The employee shall also be notified of the results of the exposure measurements and of the corrective action being taken to reduce the exposure to below the permissible exposure.

(7) If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to sulfur dioxide below the action level, the employer may terminate measurement for the employee.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

(8) For purposes of this paragraph, employee exposure is that which would occur if the employee were not using a respirator.

(c) Methods of measurement. (1) An employee's exposure shall be obtained by any combination of long term or short term samples which represents the employee's actual exposure averaged over an eight-hour work shift (See Appendix B (IV) of this section).

(2) The method of measurement shall have an accuracy, to a confidence level of 95 percent, of not less than that given in Table 1.

Table 1

Concentration	Required Accuracy (Percent of True Value)
Above permissible exposure	± 25
At or below permissible exposure and above the action level	± 35
At or below the action level	± 50

(d) Compliance. (1) No employee shall be exposed to sulfur dioxide above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of sulfur dioxide shall be controlled to at or below the permissible exposure by engineering and work practice controls.

(i) Engineering and work practice controls shall be instituted to reduce exposures to at or below the permissible exposure, except to the extent that such controls are not feasible.

(ii) Wherever engineering and work practice controls are not sufficient to reduce exposures to at or below the permissible exposure, they shall nonetheless be used to reduce exposure to the lowest level feasible and shall be supplemented by respirators in accordance with paragraph (d)(4) of this section.

(3) Engineering controls. When local exhaust is used to control exposure, measurements which demonstrate system effectiveness, for example, air velocity or static pressure shall be made at least every three months. Measurements of system effectiveness shall also be made within five days of any change in production, process, or control which might result in an increase in airborne concentrations of sulfur dioxide.

(4) Compliance with the permissible exposure shall not be achieved by the use of respirators except:

(i) During the time period necessary to install or implement engineering or work practice controls; or

(ii) In work situations in which engineering and work practice controls are not feasible; or

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

(iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of sulfur dioxide to at or below the permissible exposure; or

(iv) For operations which require entry into tanks or closed vessels; or

(v) In emergencies.

(5) Where respirators are needed and permitted under this paragraph to reduce employee exposure, the employer shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.

TABLE 2 RESPIRATORY PROTECTION FOR SULFUR DIOXIDE

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Gas Concentration	
20 ppm or less	Any chemical cartridge respirator with a cartridge(s) providing protection against sulfur dioxide. Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against sulfur dioxide. A gas mask with a chin-style or a front- or back-mounted canister providing protection against sulfur dioxide. Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against sulfur dioxide.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

Any escape self-contained breathing apparatus.

(6) Respirators shall be approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) or by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.

(7) The employer shall institute a respiratory protection program in accordance with § 1910.134(b), (d), (e), and (f).

(e) Fire and safety. (1) The employer shall familiarize himself with the information contained in the Substance Technical Guidelines (Appendix B of this section) for sulfur dioxide.

(2) Sulfur dioxide shall be stored so it will not come into contact with alkali metals such as sodium or potassium.

(3) Compressed gas cylinders containing sulfur dioxide shall be stored in accordance with § 1910.101.

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use appropriate protective clothing and equipment necessary to prevent the skin from becoming frozen from contact with liquid sulfur dioxide or from contact with vessels containing liquid sulfur dioxide.

(2) Employers shall ensure that clothing which becomes wet with liquid sulfur dioxide be removed immediately and not reworn until the sulfur dioxide has evaporated.

(3) Employers shall provide and ensure that employees use splash-proof safety goggles which comply with § 1910.133 (a)(2)-(a)(6) where there is any possibility of liquid sulfur dioxide contacting the eyes.

(4) Where there is any possibility that an employee's eyes may be exposed to liquid sulfur dioxide, employers shall provide an eye-wash fountain within the immediate work area for emergency use.

(g) Spills and disposal. In the event that sulfur dioxide is inadvertently released the employer shall immediately provide available ventilation and then clean up the spill.

(h) Sanitation (Reserved).

(i) Training and information. (1) Each employer who has a workplace in which sulfur dioxide is present shall keep a copy of this regulation with Appendixes A, B and C at the workplace. This material shall be made readily available to affected employees.

(2) Each employer who has employees exposed to sulfur dioxide above the action level without regard to the use of respirators, or employees who may have skin contact with liquid sulfur dioxide or vessels containing sulfur dioxide or who may have any possibility of eye contact with liquid sulfur dioxide, or employees who work where a potentially hazardous release of sulfur dioxide may occur shall annually:

(i) Inform affected employees of the information contained in the Substance Safety Data Sheet for sulfur dioxide (Appendix A of this section);

(ii) Advise affected employees as to the signs and symptoms of exposure to sulfur dioxide.

(iii) Instruct affected employees to advise the employer of the development of signs and symptoms of overexposure to sulfur dioxide which are listed in Appendix A of the section; and

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

(iv) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to sulfur dioxide.

(j) Medical surveillance. (1) The employer shall provide medical procedures as required by this paragraph. All medical procedures shall be performed by or under the supervision of a physician at no cost to the employee.

(2) Preplacement medical examination. The employer shall make available to each employee who is exposed, or will be exposed, to airborne concentrations of sulfur dioxide above the action level, without regard to the use of respirators, or employees who may have skin contact or who may have any possibility of eye contact with liquid sulfur dioxide, a preplacement medical examination which must include the following:

(i) A medical history and physical examination with emphasis on the lungs, eyes and skin;

(ii) Forced vital capacity (FVC) and forced expiratory volume-one second (FEV (1 second)) tests;

(iii) 14" x 17" chest roentgenogram.

(3) Periodic medical examination. The employer shall make available to each employee exposed to airborne concentrations of sulfur dioxide above the action level, without regard to the use of respirators, or employees who may have skin contact or who may have any possibility of eye contact with liquid sulfur dioxide, twelve months from the date of the employee's first exposure, and every twelve months thereafter, a periodic medical examination which must include the following:

(i) A medical history and physical examination with emphasis on the lungs, eyes and skin;

(ii) Forced vital capacity (FVC) and forced expiratory volume-one second (FEV (1 second)) tests;

(iii) A 14" x 17" chest roentgenogram.

(4) Alternative medical procedures. If the examining physician chooses to use alternative medical procedures to those specified in paragraphs (j)(2) and (j)(3) of this section, the employer may accept such alternative medical procedures as meeting the requirements of this section provided that the employer:

(i) Obtains a statement from the examining physician setting forth the alternative medical procedures, the rationale for substitution, and evidence that they will be equally effective;

(ii) Informs each exposed worker of the fact that alternative medical procedures to those required in paragraphs (j)(2) and (j)(3) of this section are to be made available.

(5) Interim medical examination. The employer shall provide an interim medical examination for the employee if the employee informs the employer of any of the signs or symptoms of exposure to sulfur dioxide which are listed in Appendix A which the employee suspects are caused by exposure to sulfur dioxide.

(6) Informing the physician. The employer shall provide to the physician performing any medical examination required by this section the following information:

(i) A copy of this regulation with Appendixes A, B, and C for sulfur dioxide;

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

(ii) A description of the affected employee's duties as they relate to his exposure to sulfur dioxide;

(iii) A description of any personal protective equipment and respirators required to be used;

(iv) The results of any measurements which may indicate the affected employee's exposure;

(v) The affected employee's anticipated exposure level; and

(vi) Upon request of the physician, any available information from previous medical examinations of the affected employee.

(7) Where a medical examination is required by paragraphs (j)(2), (j)(3), or (j)(5) of this section, following such examination the employer shall obtain from the examining physician a written opinion which conforms with paragraph (j)(8) of this section.

(8) Physician's written opinion. (i) The physician's written opinion by the examining physician shall specifically state:

(A) Whether the employee has any detected medical condition which would place the employee at increased risk of material impairment of the employee's health from exposure to sulfur dioxide;

(B) Any recommended limitations upon the employee's exposure to sulfur dioxide, including limitations upon the use of personal protective equipment and respirators;

(C) That the employee has been informed by the physician of any detected medical conditions which require further medical examination or treatment.

(ii) The physician's written opinion shall not reveal specific medical findings or diagnoses unrelated to the employee's employment.

(iii) The employer shall provide the employee with a copy of the physician's written opinion.

(9) Results of tests. Where a preplacement or periodic medical examination is required by paragraphs (j)(2) or (j)(3) of this section, following such examination the employer shall obtain from the examining physician for inclusion in the employee's medical record:

(i) A recording of the results of the pulmonary function tests;

(ii) The 14" x 17" chest roentgenogram when required, or a medically acceptable copy;

(iii) Where alternative medical procedures have been performed in accordance with paragraph (j)(4) of this section, a recording of such alternative procedures.

(10) No employee shall be exposed to sulfur dioxide in such a way as would put the employee at increased risk of material impairment of his health from such exposure. The employer shall base this decision on any information available including the physician's written opinion.

(11) No medical procedure which would be performed pursuant to paragraphs (j)(2) or (j)(3) of this section need be performed if records of a previous such procedure performed within the past six months are acceptable to the examining physician.

(12) If an employee refuses any required medical examination, the employer shall inform the employee of the possible health consequences of such refusal and obtain a signed statement from the employee indicating that the employee understands the risk involved by refusal to be examined.

(13) The employer shall provide emergency medical treatment for any employee injured through exposure to sulfur dioxide.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

(k) Recordkeeping. (1) Exposure determination. (i) The employer shall keep an accurate record of all determinations required to be made pursuant to paragraph (b)(1) of this section.

(ii) This record shall include the written determination required in paragraph (b)(2) of this section.

(iii) This record shall be maintained until replaced by a more recent record.

(2) Exposure measurements. (i) The employer shall keep an accurate record of all measurements taken to determine employee exposure to sulfur dioxide.

(ii) This record shall include:

(A) The date of measurement;

(B) Operations involving exposure to sulfur dioxide which are being monitored;

(C) Sampling and analytical method used and evidence of their accuracy;

(D) Number, duration, and results of samples taken; and

(E) Name, social security number and exposure of the employee monitored.

(iii) This record shall be maintained until replaced by a more recent record but in no event for less than one year.

(3) Mechanical ventilation. (i) When mechanical ventilation is used as an engineering control, the employer shall maintain an accurate record of the measurements demonstrating the effectiveness of such ventilation required by paragraph (d)(3) of this section.

(ii) This record shall include:

(A) Date of measurement;

(B) Type of measurement taken;

(C) Result of measurement.

(iii) These records shall be maintained for at least one year.

(4) Employee training and information. (i) The employer shall keep an accurate record of all employee training and information required by paragraph (i) of this section.

(ii) This record shall include:

(A) Date of training;

(B) Name and social security number of employee trained;

(C) Content or scope of training provided.

(iii) This record shall be maintained until replaced by a more recent record.

(5) Medical surveillance. (i) The employer shall keep an accurate record of employee medical surveillance required by paragraph (j) of this section.

(ii) This record shall include:

(A) The name and social security number of the employee;

(B) Results of tests required by paragraph (j)(2) and (j)(3) of this section and results of any tests conducted pursuant to paragraphs (j)(4) of this section;

(C) Any employee medical complaints relative to exposure to sulfur dioxide;

(D) A copy of information provided to the physician pursuant to paragraph (j)(6)(ii), (iii), (iv), (v), and (vi) of this section.

(E) Physician's written opinion; and

(F) A signed statement of any refusal to be examined.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

(iii) This record shall be maintained for the duration of and for five years after termination of the employment of the affected employee.

(6) Access to records. (i) All records required to be maintained by this section shall be made available upon request to authorized representatives of the Assistant Secretary of Labor for Occupational Safety and Health and the Director of the National Institute for Occupational Safety and Health.

(ii) Each employee or former employee shall have access to the exposure determination and exposure measurement records required to be maintained by this section which indicate his own exposure to sulfur dioxide.

(iii) Employee medical records required to be maintained by this section shall be made available upon written request to a physician designated by the employee or former employee.

(1) Employee observation of measurement. (1) The employer shall give each employee or his representative an opportunity to observe any measurement of his exposure to sulfur dioxide which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to sulfur dioxide requires entry into an area where the use of personal protective devices, including respirators, is required, the observer shall be provided with and required to use such equipment and comply with all other applicable safety procedures.

(3) Without interfering with the measurement, observers shall be entitled to:

(i) Receive an explanation of the measurement procedure.

(ii) Visually observe all steps related to the measurement of the airborne concentration of sulfur dioxide that are being performed at the place of exposure; and

(iii) Record the results obtained.

NOTE: The information contained in the following appendix for sulfur dioxide is neither intended, by itself, to create any additional obligations not otherwise imposed, nor detract from any existing obligations. To the extent that the information supplements this regulation for sulfur dioxide, it is advisory in nature.

APPENDIX A

SUBSTANCE SAFETY DATA SHEET
FOR SULFUR DIOXIDE

I. SUBSTANCE IDENTIFICATION

A. Substance: Sulfur dioxide

B. Permissible Exposure: 5 parts of sulfur dioxide per million parts of air (ppm) (13 milligrams of sulfur dioxide per cubic meter of air, (mg/M3)) averaged over an eight-hour work shift.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

- C. Appearance and Odor: Colorless gas with a characteristic pungent odor. It can be a liquid at temperatures below -10 c (14 F).

II. HEALTH HAZARD DATA

- A. Ways in which the chemical affects your body: Sulfur dioxide can affect your body if you inhale it or if it comes in contact with your eyes or skin.
- B. Effects of Overexposure:
1. Sulfur dioxide gas is intensely irritating to the eyes and respiratory tract causing burning of the eyes and tearing, coughing and chest tightness. It may cause severe breathing difficulties. Severe exposures to sulfur dioxide may cause you to stop breathing. Liquid sulfur dioxide may cause eye burns with loss of vision and skin burns.
 2. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms and suspect that they are caused by exposure to sulfur dioxide.

III. EMERGENCY FIRST AID PROCEDURES

- A. Eye Exposure: If liquid sulfur dioxide or strong concentrations of sulfur dioxide gas gets into your eyes, wash your eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.
- B. Skin Exposure: If liquid sulfur dioxide gets on your skin, immediately flush the contaminated skin with water. If liquid sulfur dioxide penetrates through your clothing, remove the clothing immediately and flush the skin with water. If irritation or burns are present after washing, get medical attention.
- C. Breathing: If you or any other person breathes in large amounts of sulfur dioxide move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
- D. Rescue: Move affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty yourself. Understand your emergency rescue procedures and know the locations of the emergency rescue equipment before the need arises.

IV. RESPIRATORS AND PROTECTIVE CLOTHING

- A. Respirators: Respirators are not the best way to control exposure to sulfur dioxide. You can only be required to wear them for routine use if your employer is in the process of installing controls or control measures prove inadequate. You may be required to wear respirators for non-routine activities or in emergencies. If respirators are worn, they must have a Mining Enforcement and Safety Administration (MESA) or National Institute for Occupational Safety and

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

Health (NIOSH) approval label. (Older respirators may have a Bureau of Mines approval label.) For effective protection, respirators must fit your face and head snugly. Respirators should not be loosened or removed in work situations where their use is required. If you can smell sulfur dioxide while wearing a respirator, the respirator is not working correctly; go immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.

- B. Protective Clothing: You must wear appropriate protective clothing and equipment to prevent the skin from becoming frozen from contact with liquid sulfur dioxide or from contact with vessels containing liquid sulfur dioxide. Replace or repair impervious clothing that has developed leaks.
- C. Eye Protection: You must wear splash-proof safety goggles where there is any possibility of liquid sulfur dioxide contacting your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

- A. Sulfur dioxide must be stored so as not to come in contact with alkali metals such as sodium or potassium.
- B. You must immediately remove any clothing that becomes wet with liquid sulfur dioxide and this clothing must not be reworn until the sulfur dioxide has evaporated from the clothing.
- C. Eye flushing facilities, where provided, must be readily available and you should know where they are and how to operate them.
- D. Ask your supervisor where sulfur dioxide is used or inadvertently released in your work area and for any additional safety and health rules.

VI. ACCESS TO INFORMATION

- A. Each year your employer is required to inform you of the information contained in this Substance Safety Data Sheet for sulfur dioxide. In addition, your employer must instruct you in the safe use of sulfur dioxide, emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to sulfur dioxide. You or your representative have the right to observe employee exposure measurements and to record the results obtained. If your employer determines that you are being overexposed, he is required to inform you of the exposure and the actions which are being taken to reduce your exposure.
- C. Your employer is required to keep records of your exposure and medical examinations. Your employer is required to keep exposure data for at least one year and to keep medical data during your employment, and for a period of five years following your termination of employment. Your employer is required to make the exposure data available to you upon your request. Your employer is also required to release your medical records to your physician upon your written request.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

- D. Your employer must give you a copy of the physicians written opinion for any physical examination required by this standard.

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APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
FOR SULFUR DIOXIDE

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: None
2. Formula: SO_2
3. Molecular weight: 64.1

B. Physical Data

1. Boiling point (760 mm Hg): -10°C (14°F)
2. Specific gravity (water = 2): 1.46 (liquid)
3. Vapor density (air = 1 at boiling point of sulfur dioxide): 2.26
4. Melting point: -75.5°C (-104°F)
5. Vapor pressure at 20°C (68°F): Greater than 1 atmosphere
6. Solubility in water, grams of sulfur dioxide per 100 grams of water (68°F): 10
7. Evaporation rate (butyl acetate = 1): Much greater than 1
8. Appearance and odor: Colorless liquid or gas with a characteristic pungent odor. It can be a liquid at temperatures below -10°C (14°F).

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Not combustible
2. Compressed gas cylinders containing sulfur dioxide shall be stored in accordance with 1910.101.

B. Reactivity

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
2. Incompatibilities: Contact with some powdered metals and with alkali metals such as sodium or potassium may cause fires and explosions.
3. Hazardous decomposition products: None.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

4. Special precautions: Liquid sulfur dioxide will attack some forms of plastics, rubber and coatings.

III. SPILL AND LEAK PROCEDURES

- A. If sulfur dioxide is spilled or leaked, the following steps should be taken:
 1. Ventilate area of spill or leak to disperse gas.
 2. If in gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair leak or allow cylinder to empty.
 3. If in liquid form, allow to vaporize.
- B. Persons not wearing protective equipment should be restricted from areas of spills or leaks until cleanup has been completed.

IV. MONITORING AND MEASUREMENT PROCEDURES

- A. EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the eight-hour exposure may be determined from a single eight-hour sample or two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR part 84, portable direct-reading instruments, dosimeters, or gas and vapor adsorption tubes with subsequent chemical analysis. The method of measurement must determine the concentration of sulfur dioxide to plus or minus 35%.
- B. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring and measurements under this section should be essentially the same as described under paragraph IV. A. Laboratories performing chemical analyses should be accredited in Industrial Hygiene Chemistry by the American Industrial Hygiene Association. The method of measurement must determine the concentration of sulfur dioxide to plus or minus 25%.
- C. METHODS: Methods meeting these accuracy requirements are available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161 under the title "NIOSH Analytical Methods for Set V" (Order number XXXXXXXXXX).
- D. QUALIFIED PERSONS: Since many of the duties relating to employee protection are dependent on the results of monitoring and measuring procedures, employers should assure that the evaluation of employee exposures is performed by a competent industrial hygienist or other technically qualified person.

V. MISCELLANEOUS PRECAUTIONS

- A. Store in tightly closed containers in a well ventilated area.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

- B. Employers should advise employees of all plant areas and operations where their exposure to sulfur dioxide could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to sulfur dioxide is likely to occur are: In the vicinity of furnaces burning coal or oil; in the vicinity of sulfur burners or the roasting of sulfide ores; during its production and its use as a solvent in petroleum refining; as a bleach; in the purification of foods; as a dechlorinating agent; as a mild acidifying agent; as an intermediate in the manufacture of sulfone resins, chlorine dioxide sulfites and hydrosulfite; in the metallurgy of certain metals such as magnesium and cobalt; and in paper pulp manufacture.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

Sulfur dioxide gas is a severe irritant of the eyes, mucous membranes, and skin. Its irritant properties are due to the rapidity with which it forms sulfurous acid on contact with moist membranes. In combination with certain particulate matter and/or oxidants, the effects may be markedly increased. Approximately 90 percent of all sulfur dioxide inhaled is absorbed in the upper respiratory passages, where most effects occur; however, high concentrations may produce respiratory paralysis, and is a cause of pulmonary edema. Exposure to concentrations of 10 to 50 ppm for 5 to 15 minutes causes irritation of the eyes, nose, and throat, rhinorrhea, choking, cough, and, in some instances, reflex bronchoconstriction with increased pulmonary resistance. Some 10 to 20 percent of the healthy young adult population are estimated to be hypersusceptible to the effects of sulfur dioxide, while the phenomenon of adaptation to irritating concentrations is a recognized occurrence in experienced workers. Workers repeatedly exposed to 10 ppm experienced upper respiratory irritation and some nosebleeds, but the symptoms did not occur at 5 ppm; in another study, initial cough and irritation did occur at 5 ppm and 13 ppm, but subsided after 5 minutes of exposure. In a human experimental study with the subjects breathing through the mouth, brief exposure to 13 ppm caused a 73 percent increase in pulmonary flow resistance; 5 ppm resulted in a 40 percent increase; 1 ppm produced no effects. Exposure of the eyes to liquid sulfur dioxide from pressurized containers causes corneal burns and opacification resulting in a loss of

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

vision. The liquid on the skin produces skin burns from the freezing effect of rapid evaporation.

III. SIGNS AND SYMPTOMS

Irritation of eyes, nose, throat, rhinorrhea; choking, cough; reflex bronchoconstriction; eye and skin burns.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Immediately flush eyes with water and wash skin with soap or mild detergent and water. Give artificial resuscitation and administer oxygen if indicated. Consideration should be given to hospitalization and observation for the possible delayed onset of pulmonary edema.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of sulfur dioxide are caused by its irritant properties. It can cause reflex bronchoconstriction with increased pulmonary resistance. It is important that the physician become familiar with plant operating conditions in which exposure to sulfur dioxide occurs. Those with skin disease may not tolerate the wearing of protective clothing and those with chronic respiratory disease may not tolerate the wearing of negative pressure respirators.

B. PREPLACEMENT

The following medical procedures must be made available to each employee who is exposed to sulfur dioxide:

1. A complete history and physical examination -- The purpose is to detect preexisting conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.
2. 14" x 17" chest roentgenogram -- Sulfur dioxide causes human lung damage. Surveillance of the lungs is indicated.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

3. FVC and FEV (1 sec) -- Sulfur dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

C. PERIODIC EXAMINATIONS

The above medical examinations are to be repeated on an annual basis.

VII. REFERENCES

1. American Conference of Governmental Industrial Hygienists: "Sulfur Dioxide," Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, pp. 238-239.
2. Hygienic Guide Series: "Sulfur Dioxide," American Industrial Hygiene Association Quarterly, 16:332-333, 1955.
3. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 892-895.
4. Occupational Exposure to Sulfur Dioxide, Federal Register, 40:54520-54534, November 24, 1975.
5. National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: Criteria for a Recommended Standard...Occupational Exposure to Sulfur Dioxide, U.S. Government Printing Office, Washington, D.C., 1974.
6. Whittenberger, J.L. and R.N. Frank: "Human Exposures to Sulfur Dioxide," Archives of Environmental Health, 7:244-245, 1963.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

REFERENCES AND SOURCES
SULFUR DIOXIDE

1910.1000

- (f) Personal Protective Equipment, and, (h) Sanitation
Eye: API, "API Toxicological Reviews;" Grant, "Toxicology of the
Eye;" Hunter, "The Diseases of Occupations"
Skin: API, "API Toxicological Reviews;" MCA, "Chemical Safety
Data Sheets;" Deichmann and Gerarde, "Toxicology of
Drugs and Chemicals;" International Labour Office, "Encyclo-
pedia of Occupational Health and Safety"

Ingestion: None

COMMENTS

Eye - Classification: 1

Output statement numbers: 9, 13

Exceptions: None

According to the API, "liquid sulfur dioxide can produce serious eye and skin burns resulting from sudden freezing of the tissues. Severe corneal damage can occur as a result of freezing rather than from any direct chemical action." Grant, however, takes exception to this by stating, "severe injuries of human eyes by sulfur dioxide have been produced only by the liquefied form. Formerly this circumstance, and the fact that liquid sulfur dioxide was commonly used as refrigerant, led to the belief that injury was attributable to freezing of the eye, but an investigation in experimental animals and comparison of the clinical characteristics of freezing and of sulfur dioxide burns have established conclusively that the ocular damage is attributable to chemical toxic effect and not to freezing."

Hunter reports, "accidental spraying of liquefied sulfur dioxide into the eyes of men working on refrigeration machines may cause permanent reduction of visual activity from its effect on the cornea. At first there is only minor discomfort even with serious injury, and this is followed by considerable swelling of the eyelids with opacity of the corneal epithelium. After several days this epithelium is shed, revealing infiltration of the stroma together with interstitial vascularization. The complications are corneal scarring, conjunctival overgrowth of the cornea and symblepharon. It has been shown experimentally in rabbits that sulphur dioxide readily penetrates the corneal epithelium and acts, principally as sulphurous acid, by denaturing corneal proteins and inactivating corneal catalase."

Grant adds, "typically, in severe burns of the eyes from a spray of liquid sulfur dioxide the patient may experience little discomfort at the time of exposure, and may be aware of the seriousness of his injury only in the course of several hours or days. The vision is immediately blurred, but may become progressively poorer. Discomfort is slight even with serious injury, owing to the fact that sulfur dioxide damages the corneal nerves and renders the anterior segment anesthetic." Grant further states that "in treatment of burns of the eye

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

by liquid sulfur dioxide, no specific antidote or therapy has been discovered."

The substance clearly warrants a classification of 1.

Skin - Classification: Low boiling liquid

Output statement numbers: Special statements

Exceptions: None

According to the API, "liquid sulfur dioxide can produce serious eye and skin burns resulting from sudden freezing of the tissues."

The MCA agrees with the API and adds that "local chronic effects have not been a problem with sulfur dioxide."

Deichmann and Gerarde state that "liquid sulfur dioxide is corrosive."

The ILO notes that "sulphur dioxide causes skin irritation and desquamation. Skin disorders are aggravated by perspiration, and this may be attributed to the conversion of sulfur dioxide to sulphurous acid under the effect of sweat."

Sulfur dioxide has a boiling point of 14 degrees F. It is 10% soluble in water and is not combustible.

Since this compound has a low boiling point and only slowly reacts with water to form sulfuric acid, it is concluded that treatment as a low-boiling liquid is most appropriate.

Ingestion - Classification: 0

Output statement numbers: None

Exceptions: None

The low boiling point of this compound precludes the possibility that ingestion of sulfur dioxide per se, in the context of this standard, would present a hazard in the industrial environment.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

Manufacturing Chemists' Association, Chemical Safety Data Sheet SD-52 (MCA)

National Fire Protection Association, "Fire Protection Guide on Hazardous Materials," 5th edition, 1975 (NFPA)

"Matheson Gas Data Book," 5th edition, p. 513 (Math)

Ansul Co., "Sulfur Dioxide" and Material Safety Data Sheet (Ansul)

Sources of data items used:

- | | | | |
|-----|----|----|---|
| I. | A. | 1. | Synonyms: None |
| | | 2. | Formula: MCA |
| | | 3. | Molecular weight: Math |
| | B. | 1. | Boiling point: MCA, Ansul |
| | | 2. | Specific gravity: Math, Ansul |
| | | 3. | Vapor density: MCA |
| | | 4. | Melting point: Math |
| | | 5. | Vapor pressure: Math |
| | | 6. | Solubility in water: Math, Ansul |
| | | 7. | Evaporation rate: ADL |
| | | 8. | Appearance and odor: MCA, NFPA-49 |
| II. | A. | 1. | Not combustible |
| | B. | 1. | Conditions contributing to instability: ADL |
| | | 2. | Incompatibilities: NFPA-491M |
| | | 3. | Hazardous decomposition products: None |

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

4. Special precautions: ADL
- III. A. Steps if released or spilled: MCA, Ansul
C. Waste disposal method: MCA, Math
- V. Miscellaneous precautions: MCA

USE/EXPOSURE AND CONTROL DOCUMENT

References used in the preparation of this document include:

- American Petroleum Institute, API Toxicological Review, "Sulfur Dioxide," 1963 (API)
- Anderson, A., "Possible Long Term Effects of Exposure to Sulphur Dioxide," Brit. J. Industrial Med., 7, 82 - 6, 1950 (Anderson)
- Baskin, A. D. - editor, "Handling Guide for Potentially Hazardous Commodities," Railway Systems and Management Assoc., Chicago, 1972 (Baskin)
- Hunter, D., "The Diseases of Occupations," 4th edition, Little, Brown, 1969 (Hunter)
- International Labour Office, "Encyclopedia of Occupational Health and Safety," Geneva, 1972 (ILO)
- Jacobs, M. B., "The Analytical Toxicology of Industrial Inorganic Poisons," Interscience, 1967 (Jacobs)
- Kirk, R. and Othmer, D., "Encyclopedia of Chemical Technology," Interscience Publishers, 2nd edition, vol. 19, 1969 (K-O)
- Semrau, K. T., "Control of Sulfur Oxide Emissions from Primary Copper, Lead and Zinc Smelters - A Critical Review," J. Air Pollution Control Assoc., 21(4), 185 - 94, 1971 (Semrau)
- Spector, W. S., "Handbook of Toxicology," Saunders, 1956 - 1959 (Spector)
- "Sulfur Dioxide," American Industrial Hygiene Assoc., Hygiene Guide Series, Dec. 1955 (Guide)
- "Sulfur Dioxide," The Ansul Co., "Sulfur Dioxide" (Ansul SO2)
- "Sulfur Dioxide," The Ansul Co., Material Safety Data Sheet (Ansul MSDS)
- "Sulfur Dioxide," Hazard Process Index, Hazard Entry No. 177, NIOSH-HSM-99-73-62 (HPI)
- "Sulfur Dioxide," Manufacturing Chemists' Assoc., Chemical Safety Data Sheet SD-52, 1953 (MCA)
- "Sulfur Dioxide," Mass Dept. Labor and Industries, Div. Occup. Hyg., Chemical Data Sheet No. 23, July 1972 (Mass #23)
- "Sulfur Dioxide," Commonwealth of Pennsylvania, Dept. Environ. Resources, Occup. Health, Hygienic Information Guide No. 17, July, 1971 (Penna #17)
- Utiddjian, M. D., "Recommendations for a Sulfur Dioxide Standard," J. Occup. Med., 16(6), 406 - 11, 1974 (Utiddjian)

References for Specific Use/Exposure

1. Jacobs, HPI, Ansul SO2, K-O
2. HPI, Guide, Anderson, API, Ansul SO2
3. HPI, API, K-O, Guide, Ansul SO2
4. HPI, Guide, Jacobs, K-O, Ansul SO2
5. Jacobs, HPI, API, Semrau
6. Ansul SO2, K-O, HPI, MCA, Baskin
7. K-O, HPI, API, Guide
- 8. K-O, Hunter, Jacobs, Guide, Ansul SO2
9. Spector, Jacobs, Hunter, Guide
10. Ansul SO2, Guide
10. Ansul SO2, Guide
11. K-O, Ansul SO2

References for Specific Control Methods

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

MCA, Mass #23, Penna #17, Guide, ILO, Ansul MSDS, API and Utidjian were the references used in all the Specific Control Methods.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Sulfur dioxide

D. O. L. STANDARD: 5 ppm

WARNING PROPERTIES:

Odor Threshold: The Documentation of TLV's reports that "Henderson and Haggard gave the odor threshold as 3 to 5 ppm."

Eye Irritation Level: Patty states that "20 ppm is the least amount irritating to the eyes." For the purposes of this standard, half - facepiece respirators are permitted up to 20 ppm.

Other Information: Patty states that "sulfur dioxide is an irritant gas: 6 to 12 ppm causes immediate irritation to nose and throat. Three tenths to 1 ppm can be detected by the average individual, probably by taste rather than by odor, and 3 ppm has an easily noticeable odor."

Evaluation of Warning Properties: Through odor and taste, sulfur dioxide can be detected at or below the permissible exposure limit. Through nose and throat irritation, sulfur dioxide can be detected within three times of the permissible exposure limit. For the purposes of this standard, therefore, sulfur dioxide is treated as a material with good warning properties. Gas sorbent respiratory equipment is permitted.

IDLH: 100 ppm

Basis for IDLH Value: This IDLH is based upon the report in the AIHA Hygienic Guides that "50 to 100 ppm is considered the maximum concentration for 1/2 to 1 hour exposure." Concerning the atmospheric concentration immediately hazardous to life, the Hygienic Guides state that "400 - 500 ppm (is) considered dangerous for even short periods of exposure. Exposure to unendurable concentrations is not necessarily hazardous if escape is made within a few minutes."

Other Toxicological Information: The Documentation of TLV's states that "the chief effect of sulfur dioxide is irritation of the mucous membranes. According to Flury and Zernik most animals survive exposures of one to five hours at 400 ppm, but deaths resulted from 600 to 800 ppm in some species. The concentrations dangerous to humans are given as 150 to 190 ppm by one source, while another estimates that 65 to 245 ppm can be tolerated for one-half to one hour. For several hours' exposure, concentrations of 8 to 12, and 25 to 40 ppm are suggested.

"Henderson and Haggard gave the odor threshold as 3 to 5 ppm, the least concentration causing throat irritation 8 to 12 ppm, the maximum concentration for prolonged exposure 10 ppm, while 20 ppm is the least concentration causing coughing or eye irritation. Concentrations of 400 - 500 ppm are dangerous for even short exposure . . .

"Greenwald, in a review of the effects of sulfur dioxide on man and animals, criticized the TLV of 10 ppm which was in effect at that time. He stated that few healthy adults find concentrations up to 5 ppm objectionable, but that a level of 10 ppm is apt to be irritating. The Michigan Division of Occupational Health reported that a concentration of 10 ppm of sulfur dioxide caused definite discomfort in exposed workers, while the Occupational Health Section

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

of Oregon reported upper respiratory irritation and some nosebleeds in workers exposed at 10 ppm. The symptoms disappeared at 5 ppm.

"The TLV of 5 ppm should prevent respiratory tract irritation in most workers and cause only minimal effects in those workers who are sensitive to irritant gases."

Spector states that "exposure to 500 ppm for 1 hour is dangerous, but 200 ppm is intolerable and will drive a man out."

LFL: Sulfur dioxide is not combustible.

VAPOR PRESSURE AT 20 C: Sulfur dioxide is a gas at 20 C.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

USE/EXPOSURE AND CONTROL DOCUMENT
SULFUR DIOXIDE

Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1. Inhalation of gas and skin contact with liquid or gas during use in paper pulp manufacture. Widely used in sulfite, Kraft, and semi-chemical mills for fortification of sulfite liquors, acid flash bleaching, and neutralization of peroxides. Used in preparation of sodium sulfite, magnesium and ammonium bisulfites, chlorine dioxide, zinc and sodium hydrosulfite bleaches.	A,B	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice
2. Inhalation of gas and skin contact with liquid or gas during use in oil refineries: selective solvent extraction of lubricating oils; solvent dewaxing of paraffin distillate or feedstock; treatment of low molecular weight stocks; oil sulfonation	A,B	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice
3. Inhalation of gas and skin contact with liquid during use in the food industry: wine preparation (for control of acidity and color, as a selective antiseptic - allowing unrestricted growth of added yeasts, as anti-oxidant); modification and separation of starches; bleach and preservative for dried fruits and vegetables; grain milling; beet sugar production; malting processes; cherry brining; manufacture of industrial and food	A,B	Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

proteins as extractant,
precipitant, bleach, and
preservative (soybean protein,
casein, gelatin, and glue)

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| 4. | Inhalation of gas and skin contact with liquid or gas during use for synthesis: sulfuric acid (used in fertilizers, chemicals, petroleum refining, paints and pigments, metallurgy, explosives, textile finishing); sulfites and bisulfites (disinfectants, oil refining, chemical analysis, bleaching, food preservation); sulfur trioxide (sulfonation); thionyl and sulfuryl chlorides (synthesis, solvents, catalysts, pharmaceuticals); chlorine dioxide and sodium bisulfate (bleaching, water treatment, odor control); other chemicals used for tanning, photography, mordants, ore treatment, metal cleaning, antiseptics, rubber manufacture; used as catalyst, acidifying and neutralizing agent, preparation of sulfone resins; used as oxidizing, reducing, and purifying agent | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice |
| 5. | Inhalation of gas and skin contact with gas during evolution of SO ₂ as a by-product of ore refining (iron, copper, zinc, and lead ores) and industrial fuel burning. The SO ₂ is often converted to sulfuric acid or elemental sulfur. | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice |
| 6. | Inhalation of gas and skin contact with gas or liquid during manufacture, distribution, | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective |

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

and maintenance of
equipment

equipment (respiratory
protective devices, face
shield, goggles, gloves);
good personal hygiene
practice

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|-----|---|-----|--|
| 7. | Inhalation of gas and skin contact with gas during use as a commercial refrigerant (in mechanical refrigerators) | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice |
| 8. | Inhalation of gas and skin contact with gas or liquid during use as bleach (for wood pulp, straw, wool); also used as antichlor to remove traces of chlorine and other oxidizing bleaches (used following peroxide bleaching of wood); used in sugar refining, processing of fruits and grains, apple slice treatment | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice |
| 9. | Inhalation of gas and skin contact with gas or liquid during use as fumigant (for ships; anti-plague - killing rats) | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice |
| 10. | Inhalation of gas and skin contact with gas or liquid during use in mining and metallurgy: production (melting and casting) of magnesium and cobalt; extraction, enrichment, and recovery of copper and lead; ores containing uranium, selenium, and tellurium | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice |

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SULFUR DIOXIDE

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| 11. Inhalation of gas and skin contact with gas or liquid during miscellaneous uses: leather tanning (preparation of chrome liquor); chrome waste treatment; manufacture of special glass (neutralization); photography; water treatment; cleaning of filter beds and wells; textile processing (antichlor); ore flotation | A,B | Process enclosure and/or local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, face shield, goggles, gloves); good personal hygiene practice |
|--|-----|--|

- A -- Inhalation
- B -- Skin and eye contact resulting in localized irritation
- C -- Ingestion
- D -- Skin contact resulting in absorption and subsequent systemic poisoning

----- JES2 JOB STATISTICS -----

1,356 CARDS READ

0 SYSOUT PRINT RECORDS

0 SYSOUT PUNCH RECORDS

0.00 MINUTES EXECUTION TIME

[illegible]