

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** ZIRCONIUM COMPOUNDS ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

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 ZIRCONIUM COMPOUNDS.

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 ZIRCONIUM COMPOUNDS

(a) Definitions. (1) "Permissible exposure" means exposure of employees to airborne concentrations of zirconium compounds (as zirconium) not in excess of 5 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 zirconium compounds averaged over an eight-hour work shift.

(b) Initial determination and exposure measurement. (1) Each employer who has a place of employment in which zirconium compounds is released into the workplace air shall determine if there is any possibility that any employee may be exposed to airborne concentrations of zirconium compounds 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 zirconium compounds.

(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 zirconium compounds;

(ii) Any measurements of zirconium compounds taken;

(iii) Any employee complaints of symptoms which may be attributable to exposure to zirconium compounds; 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 zirconium compounds 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 zirconium compounds 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 zirconium compounds 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 zirconium compounds 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 zirconium compounds 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 zirconium compounds below the action level, the employer may terminate measurement for the employee.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

(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 zirconium compounds above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of zirconium compounds 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 zirconium compounds.

(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 ZIRCONIUM COMPOUNDS

(iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of zirconium compounds 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. When an employee informs his employer that he is experiencing eye irritation from zirconium compounds while wearing a respirator allowed in Table 2, the employer shall provide and ensure that the employee use an equivalent respirator with a full facepiece, helmet or hood.

TABLE 2 RESPIRATORY PROTECTION FOR ZIRCONIUM COMPOUNDS (AS ZIRCONIUM)

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Particulate Concentration	
25 mg/M3 or less	Any dust and mist respirator, except single-use.
50 mg/M3 or less	Any dust and mist respirator, except single-use quarter mask or respirator.
	Any high efficiency particulate filter respirator.
	Any supplied-air respirator.
	Any self-contained breathing apparatus.
250 mg/M3 or less	A high efficiency particulate filter respirator with a full facepiece.
	Any supplied-air respirator with a full facepiece, helmet or hood.
	Any self-contained breathing apparatus with a full facepiece.
500 mg/M3 or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet or hood operated in continuous-flow mode.
	A powered air-purifying respirator with a high efficiency particulate filter.
Greater than 500 mg/M3 or entry and escape from unknown	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

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

concentrations	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 escape self contained breathing apparatus Any high efficiency particulate filter respirator

(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 zirconium compounds.

(2) Sources of ignition such as smoking or open flames are prohibited where zirconium compounds present a fire or explosion hazard.

(3) Zirconium hydride shall be stored so as not to come in contact with strong oxidizers. Zirconium tetrachloride shall be stored so as not to come in contact with water, moisture, and alkali metals such as sodium and potassium.

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use appropriate protective clothing and equipment necessary to prevent repeated or prolonged skin contact with zirconium oxide, zirconium oxychloride, zirconyl acetate or liquids containing these compounds, and to prevent skin contact with zirconium tetrachloride or liquids containing zirconium tetrachloride, where skin contact may occur. Face shields shall comply with § 1910.133(a)(2), (a)(4), (a)(5), and (a)(6).

(2) Employers shall ensure that employees whose clothing may have become contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride or liquids containing these compounds change into uncontaminated clothing before leaving the work premises.

(3) Employers shall ensure that clothing contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate or zirconium tetrachloride is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of the contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the employer shall inform the person performing the operation of the hazardous properties of the contaminant.

(4) Where exposure of an employee's body to zirconium tetrachloride or liquids containing zirconium tetrachloride may occur, employers shall provide facilities for quick drenching of the body within the immediate work area for emergency use.

(5) Employers shall ensure that non-impervious clothing which becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

or zirconium tetrachloride be removed promptly and not reworn until the contaminant is removed from the clothing.

(6) Employers shall provide and ensure that employees use safety goggles which comply with § 1910.133 (a)(2)-(a)(6) where there is any possibility of zirconium tetrachloride or liquids containing zirconium tetrachloride contacting the eyes.

(7) Where there is any possibility that an employee's eyes may be exposed to zirconium tetrachloride or liquids containing zirconium tetrachloride, employers shall provide an eye-wash fountain within the immediate work area for emergency use.

(g) Spills and disposal. In the event that zirconium compounds are spilled the employer shall immediately provide available ventilation and then clean up the spill.

(h) Sanitation. (1) Employers shall ensure that employees whose skin becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate or zirconium tetrachloride promptly wash or shower with soap or mild detergent and water remove any contaminant from the skin.

(2) Employers shall ensure that employees who handle zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride or liquids containing these compounds wash their hands thoroughly with soap or mild detergent and water before eating, smoking or using toilet facilities.

(i) Training and information. (1) Each employer who has a workplace in which zirconium compounds 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 zirconium compounds above the action level without regard to the use of respirators, or employees who may have skin contact with solid zirconium tetrachloride or liquids containing zirconium tetrachloride or who may have repeated or prolonged skin contact with solid zirconium oxide, zirconium oxychloride, zirconyl acetate or or liquids containing these compounds or who may have any possibility of eye contact with zirconium tetrachloride or liquids containing zirconium tetrachloride or employees who work where zirconium compounds present a fire or explosion hazard shall annually:

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

(ii) Advise affected employees as to the signs and symptoms of exposure to zirconium compounds.

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

(iv) Instruct affected employees to inform the employer if they develop any of the medical conditions listed in paragraph (j)(2) of this section; and

(v) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to zirconium compounds.

(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.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

(2) Each employer who has employees exposed to airborne concentrations of zirconium compounds above the action level, without regard to the use of respirators, or employees who may have skin contact with solid zirconium tetrachloride or liquids containing zirconium tetrachloride, or who may have repeated or prolonged skin contact with solid zirconium oxide, solid zirconium oxychloride, solid zirconyl acetate or liquids containing these compounds or who may have any possibility of eye contact with zirconium tetrachloride or liquids containing zirconium tetrachloride shall obtain information as to whether such employee has a history of any of the following medical conditions:

(i) Chronic lung disease; and

(ii) Skin disease.

(3) The employer shall provide a medical examination for the employee if:

(i) The employee provides a history of any of the medical conditions listed in paragraph (j)(2) of this section; or

(ii) The employee informs the employer of the development of any of the medical conditions listed in paragraph (j)(2) of this section or any of the signs or symptoms of exposure to zirconium compounds which are listed in Appendix A which the employee suspects are caused by exposure to zirconium compounds.

(4) The employer shall provide to the examining physician the following information:

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

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

(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; and

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

(5) Where a medical examination is required by paragraph (j)(3) of this section, following such examination the employer shall obtain a written opinion from the examining physician which conforms with paragraph (j)(6) of this section.

(6)(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 zirconium compounds;

(B) Any recommended limitations upon the employee's exposure to zirconium compounds 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.

(7) No employee shall be exposed to zirconium compounds in such a way as would put the employee at increased risk of material impairment of his

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

health from such exposure. The employer shall base this decision on any information available including the physician's written opinion.

(8) The employer shall provide emergency medical treatment for any employee injured through exposure to zirconium compounds.

(9) 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.

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

(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 zirconium compounds.

(ii) This record shall include:

(A) The date of measurement;

(B) Operations involving exposure to zirconium compounds 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 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 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:

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

- (A) The name of the employee;
 - (B) Information concerning medical conditions obtained from the employee pursuant to paragraph (j)(2) of this section;
 - (C) Any employee medical complaints relative to exposure to zirconium compounds;
 - (D) A copy of information provided to the physician pursuant to paragraph (j)(4)(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.
- (iii) This record shall be maintained for the duration of and for one year 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 zirconium compounds.
- (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 zirconium compounds which is conducted pursuant to this section.
- (2) When observation of measurement of employee exposure to zirconium compounds 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 zirconium compounds that are being performed at the place of exposure; and
 - (iii) Record the results obtained.

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

APPENDIX A

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

SUBSTANCE SAFETY DATA SHEET
ZIRCONIUM COMPOUNDS

- I. SUBSTANCE IDENTIFICATION
- A. Substance: Zirconium compounds
 - B. Permissible exposure: 5 milligrams of zirconium compounds per cubic meter of air (mg/M3) averaged over an eight-hour workshift.
 - C. Appearance and odor: a) zirconium oxide: Colorless, odorless solid; b) zirconium oxychloride: Colorless, odorless solid; c) zirconium tetrachloride: Colorless solid with an acrid odor; d) zirconium hydride: Odorless, metallic powder; e) zirconyl acetate: Colorless solid
- II. HEALTH HAZARD DATA
- A. Ways in which the chemical affects your body: zirconium compounds can affect your body if you inhale them or if they come in contact with your eyes or skin.
 - B. Effects of Overexposure:
 - 1. Skin rash has been reported from exposure to zirconium containing deodorants.
 - 2. Reporting Symptoms: You should inform your employer if you develop any signs or symptoms and suspect that they are caused by exposure to zirconium compounds.
- III. EMERGENCY FIRST AID PROCEDURES
- A. Eye Exposure: If zirconium compounds get into your eyes, wash your eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
 - B. Skin Exposure: If zirconium compounds get on your skin, wash with soap or mild detergent and water.
 - C. Breathing: If you or any other person breathes in large amounts of zirconium 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. Swallowing: When zirconium compounds have been swallowed give the person large quantities of water immediately. After the water has been swallowed try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention.
 - E. 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 equipment before the need arises.
- IV. RESPIRATORS AND PROTECTIVE CLOTHING
- A. Respirators: Respirators are not the best way to control exposure to zirconium compounds. You can only be required to wear them for routine use if your employer is in the process

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

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 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 zirconium oxychloride or zirconium tetrachloride 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 repeated or prolonged skin contact with zirconium oxide, zirconium oxychloride, zirconyl acetate, or liquids containing these compounds, and to prevent skin contact with zirconium tetrachloride or liquids containing zirconium tetrachloride where skin contact may occur. Replace or repair impervious clothing that has developed leaks.
- C. Eye Protection: You must wear dust resistant safety goggles where there is any possibility of zirconium tetrachloride contacting your eyes. You must wear splash-proof safety goggles where there is any possibility of liquids containing zirconium tetrachloride contacting your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING, AND STORAGE

- A. Zirconium hydride is a combustible solid.
- B. Zirconium oxide, zirconium oxychloride, zirconium tetrachloride, zirconium hydride, or zirconyl acetate must be stored in tightly closed containers in a well ventilated area.
- C. Zirconium tetrachloride must be stored so as not to come in contact with water or moisture, and alkali metals such as sodium and potassium.
- D. Zirconium hydride must be stored so as not to come in contact with strong oxidizers.
- E. Sources of ignition such as smoking and open flames are prohibited wherever zirconium hydride is handled, used or stored in a manner that could create a potential fire or explosion hazard.
- F. If your work clothing may have become contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride or liquids containing these compounds, you must change into uncontaminated clothing before leaving the work premises.
- G. You must promptly remove any non-impervious clothing that becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, or zirconium tetrachloride and this clothing must not be reworn until the contaminant is removed from the clothing.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

- H. If your skin becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, or zirconium tetrachloride, you must promptly wash or shower with soap or mild detergent and water to remove any contaminant from your skin.
- I. If you handle zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride, or liquids containing these compounds, you must wash your hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- J. Fire extinguishers, quick drenching facilities, and eye flushing facilities, where provided, must be readily available and you should know where they are and how to operate them.
- K. Ask your supervisor where zirconium compounds are used 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 zirconium compounds. In addition, your employer must instruct you in the safe use of zirconium compounds emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to zirconium compounds. 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 one year 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.
- D. Your employer must give you a copy of the physician's written opinion for any physical examination required by this standard.

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

APPENDIX B

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

SUBSTANCE TECHNICAL GUIDELINES
FOR ZIRCONIUM COMPOUNDS

(This standard for zirconium compounds should not be interpreted to apply only listed below for which substance specific information has been provided.)

a. Zirconium oxide

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: zirconia
2. Formula: ZrO_2
3. Molecular weight: 123.2

B. Physical Data

1. Boiling point (760 mm Hg): 5000 C (8998 F)
2. Specific gravity (water = 1): 5.8 - 6.2
3. Vapor density (air = 1 at boiling point of zirconium oxide): Not applicable
4. Melting point: 2700 C (4892 F)
5. Vapor pressure at 20 C (68 F): Very low
6. Solubility in water, grams of zirconium oxide per 100 grams of water at 20 C (68 F): Insoluble
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Colorless, odorless solid

b. Zirconium oxychloride

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: zirconyl chloride octahydrate
2. Formula: $ZrOCl_2 \cdot 8H_2O$
3. Molecular weight: 322.3

B. Physical Data

1. Boiling point (760 mm Hg): Decomposes
2. Specific gravity (water = 1): Greater than 1
3. Vapor density (air = 1 at boiling point of zirconium oxychloride): Not applicable
4. Melting point: 110 C (230 F) approximately
5. Vapor pressure at 20 C (68 F): 9 - 13 mm Hg vapor pressure
6. Solubility in water, grams of zirconium oxychloride per 100 grams of water at 20 C (68 F): Very soluble
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Colorless, odorless solid

c. Zirconium tetrachloride

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: ZC-4
2. Formula: $ZrCl_4$
3. Molecular weight: 233

B. Physical Data

1. Boiling point (760 mm Hg): 331 C (628 F) sublimes
2. Specific gravity (water = 1): 2.8
3. Vapor density (air = 1 at boiling point of zirconium tetrachloride): Not applicable
4. Melting point: 331 C (628 F) sublimes
5. Vapor pressure at 20 C (68 F): Very low

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

6. Solubility in water, grams of zirconium tetrachloride per 100 grams of water at 20 C (68 F): Reacts
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Colorless solid with an acrid odor in moist air

d. Zirconium hydride

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: zirconium dihydrate
2. Formula: ZrH_2
3. Molecular weight: 93.2

B. Physical Data

1. Boiling point (760 mm Hg): Decomposes
2. Specific gravity (water = 1): 5.7
3. Vapor density (air = 1 at boiling point of zirconium hydride): Not applicable
4. Melting point: Decomposes above 300 C (572 F)
5. Vapor pressure at 20 C (68 F): Very low
6. Solubility in water, grams of zirconium hydride per 100 grams of water at 20 C (68 F): Very low
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Odorless, metallic powder

e. Zirconyl acetate

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Diacetatozirconic acid
2. Formula: $(H_2ZrO_2(C_2H_3O_2)_2)$
3. Molecular weight: Very high (a polymer)

B. Physical Data

1. Boiling point (760 mm Hg): Decomposes
2. Specific gravity (water = 1): Data not available
3. Vapor density (air = 1 at boiling point of zirconyl acetate): Not applicable
4. Melting point: Data not available
5. Vapor pressure at 20 C (68 F): Very low
6. Solubility in water, grams of zirconyl acetate per 100 grams of water at 20 C (68 C): Very soluble
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance: Colorless solid or water solution

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: Not applicable
2. Autoignition temperature: For zirconium hydride - 270 C (511 F); for others, not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishing media: For zirconium hydride, sand or inert powder; for others, not applicable
5. Special fire-fighting procedures: Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: zirconium hydride is a combustible solid. All ignition sources must be controlled where zirconium hydride is used, handled or

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

stored in a manner that could create a potential fire or explosion hazard.

B. Reactivity

1. Conditions contributing to instability: zirconium tetrachloride will decompose in the presence of moist air. Elevated temperatures (greater than 315 C (600 F)) cause zirconium hydride to decompose to give flammable hydrogen gas.
2. Incompatibilities: zirconium tetrachloride reacts with water or with moisture in air to form hydrochloric acid fume. Contact with alkali metals such as sodium or potassium may cause explosions. Contact of zirconium hydride with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving zirconium compounds.
4. Special precautions: zirconium tetrachloride will attack some forms of plastics, rubber and coatings.

III. SPILL AND DISPOSAL PROCEDURES

- A. If zirconium compounds are spilled, the following steps should be taken:
1. Ventilate area of spill.
 2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing zirconium oxide, zirconium oxychloride, zirconium tetrachloride, zirconium hydride, or zirconyl acetate should be absorbed in vermiculite, dry sand, earth or a similar material.
- B. Persons not wearing protective equipment should be restricted from areas of spills until cleanup has been completed.
- C. Waste disposal methods: zirconium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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 collection of the particulates using a high efficiency membrane filter with subsequent chemical analysis of the sample. Detector tubes certified by NIOSH under 42 CFR part 84 or other direct-reading devices calibrated to measure zirconium oxide, zirconium oxychloride, zirconium tetrachloride, zirconium hydride, or zirconyl acetate may be used. The method of measurement must determine the concentration of zirconium oxide, zirconium oxychloride,

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

zirconium tetrachloride, zirconium hydride, or zirconyl acetate to plus or minus 35% of the true value.

B. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring and measurements under this section should be essentially the same as described above. 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 zirconium oxide, zirconium oxychloride, zirconium tetrachloride, zirconium hydride, or zirconyl acetate to plus or minus 25% of the true value.

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 M" (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 zirconium compounds in tightly closed containers in a cool, well ventilated area.

B. Employers should advise employees of all areas and operations where their exposure to zirconium compounds could occur.

VI. COMMON OPERATIONS

Common operations in which high exposures to zirconium compounds may occur are:

a) Zirconium oxide: During its use in ceramics stains; as a catalyst and as a bonding agent in rubber and plastics formulation, as a refractory.

b) Zirconium oxychloride: During its use in preparing pigments; in waterproofing textiles; in tanning leather; in making other zirconium compounds.

c) Zirconium tetrachloride: During its use as an intermediate in the preparation of zirconium metal and its alloys.

d) Zirconium hydride: During its use in the manufacture of military flares, tracer bullets, and incendiary compositions; as a foaming agent for aluminum; for depositing metallic zirconium by flame spraying.

e) Zirconyl acetate: During its use in the waterproofing of textiles; as a catalyst for silicone resins in textiles and leather; as a hardening agent for gelatin; and in the manufacture of zirconia fibers.

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

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

Zirconium compounds are of generally low toxicity, although granulomata have been produced by repeated topical applications of zirconium salts to human skin. In rats, the oral LD50 of several zirconium compounds ranged from 2.5 to 10 g/kg. Repeated inhalation of zirconium tetrachloride mist by dogs for 2 months at 6 mg of zirconium/M3 caused slight decreases in hemoglobin and in erythrocyte counts, with some increases in mortality over that of controls; these effects may have been due to the liberation of hydrogen chloride. However, animals exposed to zirconium dioxide dust for 1 month at 75 mg of zirconium/M3 showed no detectable effects. Rats exposed to high concentrations of zirconium silicate dust for 7 months developed radiographic shadows in the lungs; these were attributed solely to the deposition of the radiopaque particles, since histologic examination showed no cellular reaction. A study of 22 workers exposed to fumes from a zirconium reduction process for 1 to 5 years revealed no abnormalities referable to the exposure. There are no well documented cases of toxic effects from industrial exposure. Granulomata of the human axillary skin have occurred from use of deodorants containing zirconium, although the metal is not regarded as a skin sensitizer in other types of exposure.

III. SIGNS AND SYMPTOMS

Possible granulomas of skin; by analogy to effects caused in animals, x-ray evidence of retention in lungs. Zirconium tetrachloride may be irritating to the skin and mucous membranes due to the formation of hydrochloric acid.

IV. SPECIAL TESTS

None in common usage.

-V. TREATMENT

Remove from exposure. Flush eyes and skin with water.
If swallowed and the person is conscious, induce vomiting.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

A. GENERAL

Granulomas of the skin have been reported in persons using deodorant containing zirconium. It is important that the physician become familiar with plant operating conditions in which exposure to zirconium compounds occur. 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

Routine medical histories and physical examinations are not required. However, the employer must screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from zirconium compounds exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. Chronic respiratory disease -- Zirconium compounds (silicate) have been reported to cause radiographic changes in animals due to pulmonary retention. Zirconium hexachloride may be irritating to the mucous membranes of the respiratory tract.
2. Skin disease -- Zirconium may cause granulomas of the skin. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

C. PERIODIC EXAMINATIONS

Routine periodic examinations are not required. However, if the employer becomes aware of an employee with the above listed conditions, he must refer such employee for further medical examination.

VII. REFERENCES

1. American Conference of Governmental Industrial Hygienists: "Zirconium Compounds (as Zr)," Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, pp. 285-286.
2. Hygienic Guide Series: "Zirconium," American Industrial Hygiene Association Journal, 19:446-447, 1958.
3. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1188-1194.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

4. Browning, Ethel: Toxicity of Industrial Metals (2d ed.), Butterworths, London, 1969, pp. 356-360.
5. Reed, C.E.: "A Study of the Effects on the Lung of Industrial Exposure to Zirconium Dusts," AMA Archives of Industrial Health, 13:578-580, 1956.
6. Shelley, W.B. And H.J. Hurley: "The Allergic Origin of Zirconium Deodorant Granulomas," British Journal of Dermatology, 70:75-101, 1958.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

REFERENCES AND SOURCES
ZIRCONIUM COMPOUNDS

1910.1000

(f)

Personal Protective Equipment, and, (h) Sanitation

Eye: Sax, "Dangerous Properties of Industrial Materials;" Stauden, "Kirk-Othmer Encyclopedia of Chemical Technology"

Skin: Sax, "Dangerous Properties of Industrial Materials;" Harrison et al., "The Acute, Chronic and Topical Toxicity of Zirconium Carbonates, J. of Phar. and Exptl. Thera., 102, p. 179-84, 1926; Browning, "Toxicity of Industrial Metals;" "Zirconium," AIHA Hygienic Guide Series; Deichmann and Gerarde, "Toxicology of Drugs and Chemicals;" Plummer, "Handbook of Industrial Toxicology;" "Encyclopedia of Occupational Safety and Health," International Labour Office; Williams, R. M. G. B. Skipworth, "Zirconium Granulomas of the Glabrous Skin Following Treatment of Rhus Dermatitis," Archives of Dermatology, vol. 80, pp. 63-66/273-276, 1959; Zhilova, N. A. and A. A. Kasparov, "Toxicological Studies of Niobium and Zirconium Chlorides," Hygiene and Sanitation, vol. 31, EPA and National Science Foundation, Wash., D. C., p. 32, 1966; Stauden, "Kirk-Othmer Encyclopedia of Chemical Technology"

Ingestion: Cochran et al., "Acute Toxicity of Zirconium, Strontium, Lanthanum, Cesium, Tantalum and Yttrium," AMA Arch. Ind. Hy. and Occ. Med., June, 1950, p. 537-50; Browning, "Toxicity of Industrial Metals;" "Zirconium," AIHA Hygienic Guide Series; Christensen, "NIOSH Toxic Substances List;" Patty, "Industrial Hygiene and Toxicology;" "Encyclopedia of Occupational Health and Safety," International Labour Office

COMMENTS

Eye - Classification: See below

Output statement numbers: See below

Exceptions: None

A search of the literature failed to reveal specific data concerning the effects of direct eye contact with zirconium compounds. Some sources such as Sax, simply state that most of the zirconium compounds in common use are insoluble and are considered to be inert.

For four of the specific zirconium compounds we are concerned with in this standard, the lack of data necessitates a classification. For two of them, zirconium oxychloride and zirconyl acetate, this is without assurance that they are indeed inert, since they are both soluble in water.

Of zirconium tetrachloride, Stauden reports that it reacts violently and irreversibly with water to form zirconium oxychloride and HCl. Since the reaction is violent, liberates heat, and produces hydrochloric acid, it is concluded that classifications of 1 and 5 are warranted for this compound. Consequently, statements 9, 11, and 13 are specified for this compound. (Particles of zirconium tetrachloride in the eye can be expected to produce localized areas of high acid concentration.)

Skin - Classification: 2 and 6

Output statement numbers: See below

Exceptions: See below

Sax reports that "most zirconium compounds in common use are insoluble and considered inert" and thus their "inherent toxicity is low." According to the abstract of Harrison et al., "no signs of

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

untoward systemic effects became evident when was applied . . . t shaved skins of guinea pigs." They elaborate, "during this test, quantities of the ointment as high as 8 g/kg (1.68 g of zirconium oxide per kg) were massaged into the skin until absorbed." They noted that "there was no evidence of sensitization when 0.5 g per the ointment were applied 12 times to the same area of the shaved of albino guinea pigs at weekly intervals."

Sax also reports that "sodium zirconium lactate has been held responsible for skin granulomas." The Hygienic Guide states "app of ointments containing zirconium compounds to the skin of animal humans is reported to produce no irritation, sensitization, or absorption, although more recent work suggests some reaction from sodium zirconium lactate."

Browning contains a description of an experimental program with human volunteers and deodorant sticks containing sodium zirconium lactate. She notes that investigations "have shown that the eruption might appear after one application only or after several months of use. Generally it disappears spontaneously but slowly, persisting months or years." Of 30 volunteers using a stick containing 5% of zirconium, "only one developed a typical granuloma in the test area granulomatous." When the concentration of the sodium zirconium lactate was increased to 10%, one again developed a true granuloma and 3 an inflammatory reaction. Two of these two cases "showed a granulomatous response to intracutaneous injection of a dilute aqueous solution (in one case a concentration of 1 in 10,000) of sodium zirconium lactate. These subjects were also "found to have the same response to other zirconium salts, indicating that they had a specific hypersensitivity to zirconium, which manifested itself as a granuloma." Also noted is that the researchers "explain the occurrence of the granuloma reaction after a single application by assuming the patient has possibly been sensitized previously by an inhalant allergen."

Plunkett lists dermatitis as a symptom of contact with zirconium salts. ILO suggests that carbonated hydrous zirconia and hydrous zirconia may also cause granulomatous conditions of the skin. According to Williams, "the mode of action is thought to be an allergic sensitization to the zirconium ion rather than to a specific salt of zirconium or impurity." An abstract of Zhilova's work reports that "experimental studies of . . . zirconium tetrachloride revealed a moderate degree of toxicity" Penetration was investigated in doses of 100 mg/kg for prolonged periods" and was found to result in "a mild toxic effect on mice and rats, expressed mainly by development of disorders of the liver. The marked local effect . . . on mucous membranes and skin of rabbits apparently was due to formation of hydrochloric acid by hydrolysis."

Deichmann and Gerarde state "a dermatologic disorder called zirconium deodorant granuloma is the result of an acquired hypersensitivity to the zirconium content in deodorants (antiperspirants). The granulomas are clinically similar and histologically indistinguishable from those of other sarcoid granulomas, such as sarcoidosis and beryllium granulomas. In a sensitized individual, a zirconium deodorant granuloma can be produced locally by intradermal injection

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

of 1:10,000 to 1:1,000,000 dilutions of any water-soluble zirconium salt." An incident is described involving a 15-year-old boy who applied a poison oak medication containing zirconium oxide "for a total of 6 days to skin areas affected by poison ivy. Approximately 6 months later, many 2 - 6 mm, firm, shiny, erythematous, nontender papules appeared over the previously treated area. Many of the granulomatous lesions were still present 18 months later."

Stauden reports that zirconium hydride behaves quite similar to zirconium metal. He adds, however, that "zirconium hydride powder differs from zirconium metal powder in presenting little if any explosion hazard, and it can be handled quite safely." Of zirconium tetrachloride, he notes that it reacts violently and irreversibly with water to form zirconium oxychloride and HCl.

Zirconium oxide has a melting point of 4892 degrees F and is insoluble in water. Zirconium oxychloride melts at approximately 230 degrees F and is very soluble in water. Zirconium tetrachloride sublimes at 628 degrees F and, as reported upon above, reacts with water. Zirconium hydride is a metallic powder which is insoluble in water and decomposes above 572 degrees F. Zirconyl acetate is very soluble in water and is normally a colorless solid.

Deichmann and Gerarde's comments illustrate that Zr oxide can sensitize an individual and produce granulomas. Of interest is that these authors report that granulomas can be produced by any "water-soluble zirconium salt," yet utilize Zr oxide as an example, a substance which numerous sources record as practically insoluble in water. Being very soluble in water, the oxychloride and acetate must also be considered very capable of similar skin effects. Based on the above, these three substances are assigned classifications 2 and 6.

Zirconium tetrachloride, because of its reactivity, can be expected to have a corrosive effect on the skin in the presence of moisture. This deduction is supported by the comments of Zhilova. Consequently, it is concluded that classifications of 2 and 6 are warranted if statement 2 is utilized to prevent contact where it "may occur" and statement 8b is specified.

Zirconium hydride appears to be a completely inert compound and is unlikely to cause skin effects. This substance is therefore assigned a classification of zero.

With the exceptions noted for Zr tetrachloride, the set of statements specified includes 2, 5b, 7a, 17g, 17i, and 20a.

Ingestion - Classification: 0

Output statement numbers: None

Exceptions: None

On the basis of the experiments with 5 representative zirconium compounds, Cochran et al. conclude that "this metal may be classified among those considered relatively non-toxic." Their data on the toxicity of the five zirconium compounds given orally ranged from 2500 mg/kg as a compound (853 mg/kg metal) for zirconyl nitrate to 10,000 mg/kg as a compound (2290 mg/kg metal) for sodium zirconium sulfate. They add that "animals acutely poisoned by zirconium compounds show progressive depression and decreased activity until death." They also comment that death occurs from within a few hours to a few days.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

following administration, but rarely after five days.

Christensen lists an oral mouse LD50 of 655 mg/kg and an oral rat LD50 of 1688 mg/kg for zirconium tetrachloride. For zirconium oxide, an oral rat LD50 of 3500 mg/kg is given while a similar rat LD50 for zirconium acetate is given as 4100 mg/kg.

According to Patty, "the toxicity of Zr salts is very low by the oral route; the LD50 dose of the nitrate, chloride, sulfate, and oxide of Zr, and sodium zirconyl sulfate for rats ranged from 2.5 to 10 g/kg."

A zirconium carbonate compound "incorporated in a standard diet at a level of 4 per cent and fed to rats for 17 weeks was without adverse effect on all criteria examined Tracer studies of the oral absorption of zirconium tetrachloride, with the stable chlorine as carrier, show less than 0.001% of the dose passed from the gastrointestinal tract to the blood stream."

Browning notes that "there were no deaths among rats from oral administration of doses equivalent to 2, 4, 8, or 10 mg/kg of Zr oxide. There were also no chronic or cumulative effects from feeding rats a diet including up to 20 per cent by weight of a moist paste containing 20.9 per cent of Zr oxide, or in kittens continuously ingesting food containing as much as 5% of the compound."

The AIHA concludes that "administration of zirconium or its compounds orally or by inhalation in animals, produces no significant chronic or acute effects No occupational case of systemic poisoning has been reported."

The ILO reports in general that "it has been stated many times that zirconium compounds are physiologically inert. While this is not an accurate statement, there is no doubt that the tolerance of most organisms to zirconium is large as compared to their tolerance for heavy metals Zirconium is found in all animal tissues. The daily intake in the USA is about 4 mg, and there is some evidence, although no proof, that zirconium may be an essential trace element."

Based upon the above information, it is concluded that ingestion of these zirconium compounds, in the context of this standard, would not present a hazard in the industrial environment, especially since statements 5b and 20a are specified under the skin section for other reasons.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

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

NL Industries, Inc., Material Safety Data Sheet (NL)

Gmelin's Handbuch der Anorganischen Chemie, vol. 42 (Gmelin)

Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd ed., vol. 22, - 651 (Kirk-Othmer)

Lange's Handbook of Chemistry, 11th ed. (Lange)

Sources of data items used:

- I. A.1. Synonyms: K-O, NFPA-49
- 2. Formula: Gmelin
- 3. Molecular weight: Lange
- B.1. Boiling point: Gmelin
- 2. Specific gravity: Gmelin
- 3. Vapor density: Not applicable
- 4. Melting point: Gmelin

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

5. Vapor pressure: K-O, Gmelin
6. Solubility in water: Gmelin, NL
7. Evaporation rate: Not applicable
8. Appearance and odor: K-O, NL, Gmelin, NFPA-49
- II. A. 1. Flash point: Not applicable
2. Autoignition temperature: Gmelin
3. Flammable limits: Not applicable
4. Extinguishing media: K-O
5. Special fire fighting procedures: NFPA-49, K-O
6. Unusual fire and explosion hazards: K-O, NL, Gmelin
- B. 1. Conditions contributing to instability: K-O
2. Incompatibilities: NL, NFPA-491M, Gmelin
3. Hazardous decomposition products: NFPA-49
4. Special precautions: ADL
- III. A. Steps if released or spilled: NL, ADL
- C. Waste disposal method: NL
- V. Miscellaneous precautions: NL, ADL
- VI. Common operations: K-O

USE/EXPOSURE AND CONTROL DOCUMENT

The references used in the preparation of this document include:

- Brown, J. R., Mastromatteo, E. and Horwood, J., "Zirconium Lactate and Barium Zirconate Acute Toxicity and Inhalation Effects in Experimental Animals," American Industrial Hygiene Association Journal, March - April:131 - 132, 1963 (Brown)
- Browning, E., "Toxicity of Industrial Metals," Butterworths, London, 1961 (Browning)
- Fairhall, L. T., "Industrial Toxicology," 2nd edition, Williams and Wilkins, Baltimore, 1957 (Fairhall)
- International Labour Organization, "Encyclopedia of Occupational Health and Safety," Geneva, 1972 (ILO)
- Kirk, R. and Othmer, D., "Encyclopedia of Chemical Technology," Interscience Publishers, Division of John Wiley, 2nd edition, 1972 (K-O)
- "Merck Index of Chemicals and Drugs," Merck and Co., Inc., Rahway, N. J., 8th edition, 1968 (Merck)
- Middleton, J. M., "Zircon - Its Application in the Foundry," Industrial Minerals, January:29 - 31, 1969 (Middleton)
- Moilliet, J. L., "Water Proofing and Water Repellency," Elsevier, New York, 1963 (Moilliet)
- Patty, F. A., "Industrial Hygiene and Toxicology," Vol. II, Interscience Publishers, 1962 (Patty)
- Reed, C. E., "A Study of the Effects on the Lung of Industrial Exposure to Zirconium Dusts," Arch. Ind. Health, 13:578 - 580, 1956 (Reed)
- Roberts, W. C., "The Ferroalloy Industry Hazards of the Alloys and Semi-metallics - Part II," Journal of Occupational Medicine, 7:71 - 77, 1965 (Roberts)
- Tubich, G. E., Davis, I. H. and Bloomfield, B. D., "Occupational Health - Studies of the Shell-Molding Process," A. M. A. Archives of Industrial Health, 21:424 - 444, 1960 (Tubich)
- "Zirconium," American Conference of Government Industrial Hygienists, Hygienic Guide Series, October 1958 (Hygienic Guides)
- References for Specific Use/Exposure

1. Reed, ILO

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

2. Middleton, Tubich
3. Roberts, Browning
4. Fairhall, Merck, ILO
5. Patty, ILO
6. ADL estimate
7. Merck
8. Fairhall, ILO
9. Brown, Moilliet
10. Merck, Brown
11. K-O, Merck
12. Browning, Merck
13. Merck, Browning
14. Browning
15. Fairhall
16. Merck

References for Specific Control Methods

1. Hygienic Guides, ILO
2. Tubich, Patty

Hygienic Guides and ILO were the references used in numbers 3 - 16.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Zirconium compounds

D. O. L. STANDARD: 5 mg/M3

IDLH: 500 mg/M3

Basis for IDLH Value: The available toxicological information indicates that zirconium compounds possess a low order of toxicity. The chosen IDLH (500 mg/M3) has been based on the report in the NIOSH Toxic Substances List that a 30-minute exposure to 500 mg/M3 zirconium nitrate is the lowest concentration of this substance which has been shown to be lethal to rats. The reference to which the NIOSH Toxic Substances List refers is the National Technical Information Service, Springfield, Va. (formerly U. S. Clearinghouse for Scientific and Technical Information) AEC-TR-6710, 47, 67. Since there is no indication that zirconium compounds present an unusual eye irritation problem, full face respirators are not called for unless the employee experiences eye irritation while wearing respirators with quarter or half-mask facepieces.

Other Toxicological Information

The AIHA Hygienic Guides state that the severity of the health hazards of zirconium is "low, for both acute and chronic exposures. Administration of zirconium or its compounds, orally or by inhalation in animals, produces no significant chronic or acute effects. . . . No occupational case of systemic poisoning has been reported."

The ILO states that "it has been stated many times that zirconium compounds are physiologically inert. While this is not an accurate statement, there is no doubt that the tolerance of most organisms to zirconium is large as compared to their tolerance for most heavy metals." According to the ILO, the effects of inhaling zirconium compounds have not been investigated as extensively as the effects produced by other routes of administration. "Exposure of experimental animals to zirconium compounds showed that zirconium lactate and barium zirconate both produce severe, persistent, chronic interstitial pneumonitis at atmospheric zirconium concentrations of about 5 mg/M3. Much higher atmospheric sodium zirconium lactate

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

concentrations of 0.049 mg/cm³ for shorter exposures have been found to produce peribronchial abscesses (sic), peribronchiolar granulomas and lobular pneumonia." These exposures were chronic exposures.

Patty notes that the "toxicity of ZrO₂ dust by inhalation is of a very low order; neither 75 mg of Zr/cu meter inhaled by laboratory animals daily for 1 month or 11 mg of Zr/cu meter for 2 months produced any significant alterations in growth rate, mortality, hematological values, biochemical constituents, or in morphological structure. On the other hand, inhalation of ZrCl₄ mist at a level of 6 mg of Zr/cu meter was perceptibly toxic in 2 months, as shown by slight decreases in hemoglobin and erythrocyte count of dogs, and some increase in mortality over that of controls."

The Documentation of TLV's states that "a value of 5 mg Zr/M³ is, therefore, recommended (for zirconium compounds as Zr) as the TLV to protect against a slightly toxic metal."

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

USE/EXPOSURE AND CONTROL DOCUMENT
ZIRCONIUM COMPOUNDS

	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of dust and fume during refining of zirconium (including zirconium chloride, zirconium oxide, and zirconium metal)	A	Process enclosure; local exhaust ventilation; general dilution ventilation
2.	Inhalation of dust during preparation and handling of zircon and zirconia molds for metal casting (including sand preparation, shell molding and curing and shake out in shell molding; dyes for metal extrusion; and spout linings for continuous casting)	A	Process enclosure; local exhaust ventilation; general dilution ventilation
3.	Inhalation of dust and fume during preparation of alloys containing zirconium (including alloys of nickel, iron, copper, magnesium lead, niobium, and tantalum)	A	Process enclosure; local exhaust ventilation; general dilution ventilation
4.	Inhalation of dust and fume during manufacture of items containing zirconium metal or alloy for nuclear power, aerospace, and chemical industries (including shielding, structures, and piping for nuclear reactors; non-corrosive reaction vessels, pumps, and piping for chemical synthesis; rayon spinnerets; metal cutting tools; thermocouple jackets for open-hearth furnaces)	A	Process enclosure; local exhaust ventilation; general dilution ventilation
5.	Inhalation of dust (zircon and zirconia) during manufacture of refractories	A	Process enclosure; local exhaust ventilation; general dilution ventilation

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

for glass, aluminum, and
brass processing

lation

- | | | | |
|-----|---|---|--|
| 6. | Inhalation of dust during production and handling of zircon sand | A | Process enclosure; local exhaust ventilation; general dilution ventilation |
| 7. | Inhalation of dust during synthesis and handling of zirconium compounds (including zirconium carbonate, tetrachloride, hydride, hydroxide, oxide, sulfate and zirconyl acetate and chloride) | A | Process enclosure; local exhaust ventilation; general dilution ventilation |
| 8. | Inhalation of dust (primarily oxide, also hydroxide and silicate) during manufacture of ceramics, glass, and porcelains (including high-duty porcelain bodies, high-temperature dielectrics, enamels and special pottery glazes, lenses and television tubes) | A | Process enclosure; local exhaust ventilation; general dilution ventilation |
| 9. | Inhalation of dust during synthesis and handling of pigments, dyes, and water repellants (including zirconyl acetate and chloride) | A | Process enclosure; local exhaust ventilation; general dilution ventilation |
| 10. | Inhalation of dust (sulfate) during leather tanning operations (including white leather) | A | Process enclosure; local exhaust ventilation; general dilution ventilation |
| 11. | Inhalation of dust during preparation and handling of abrasives and polishing materials (silicate) | A | Process enclosure; local exhaust ventilation; general dilution ventilation |
| 12. | Inhalation of dust during use as an igniter in manufacture of munitions and other items (including | A | Process enclosure; local exhaust ventilation; general dilution ventilation |

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ZIRCONIUM COMPOUNDS

detonators, photoflash
bulbs, lighter flints,
lamp filaments, and
flares)

- | | | | |
|-----|---|---|---|
| 13. | Inhalation of dust
(zirconium carbonate,
zirconyl chloride, and
zirconium oxide)
during manufacture of
skin ointments and
antiperspirants | A | Process enclosure; local
exhaust ventilation;
general dilution venti-
lation |
| 14. | Inhalation of dust during
use as a gas getter in
manufacture of high
vacuum tubes and radio
valves | A | Process enclosure; local
exhaust ventilation;
general dilution venti-
lation |
| 15. | Inhalation of dust during
use as a deoxidizer,
denitrifier, and desul-
furizer in iron and steel
manufacture | A | Process enclosure; local
exhaust ventilation;
general dilution venti-
lation |
| 16. | Inhalation of dust
(hydride, sulfate, and
zirconyl acetate) in
chemical synthesis | A | Process enclosure; local
exhaust ventilation;
general dilution venti-
lation |

- 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 -----

1,577 CARDS READ

0 SYSOUT PRINT RECORDS

0 SYSOUT PUNCH RECORDS

0.00 MINUTES EXECUTION TIME

[illegible]