Occupational Health Guideline for Zirconium Compounds (as Zirconium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all zirconium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Zirconium oxide

- Formula: ZrO_2
- Synonyms: Zirconia
- Appearance and odor: Colorless, odorless solid.

Zirconium oxychloride

- Formula: $ZrOCl_2\ 8H_2O$
- Synonyms: Zirconyl chloride octahydrate
- Appearance and odor: Colorless, odorless solid.

Zirconium tetrachloride

- Formula: $ZrCl_4$
- Synonyms: ZC-4
- Appearance and odor: Colorless solid with an acrid odor in moist air.

Zirconium hydride

- Formula: ZrH_2
- Synonyms: Zirconium dihydride
- Appearance and odor: Odorless, metallic powder.

Zirconyl acetate

- Formula: $H_2ZrO_2(C_2H_3O_2)_2$
- Synonyms: Diacetatozirconic acid
- Appearance: Colorless solid.
- **Summary of toxicology**

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for zirconium compounds is 5 milligrams of zirconium compounds (as zirconium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Zirconium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin.

- **Effects of overexposure**

Skin rash has been reported from exposure to zirconium-containing deodorants.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to zirconium compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to zirconium compounds at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from zirconium compounds exposure.

—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.

—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.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

• **Summary of 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/m³ as zirconium 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/m³ as zirconium 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.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Zirconium oxide**

1. Molecular weight: 123.2
2. Boiling point (760 mm Hg): 5000 C (9032 F)
3. Specific gravity (water = 1): 5.8 to 6.2
4. Vapor density (air = 1 at boiling point of zirconium oxide): Not applicable
5. Melting point: 2700 C (4892 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Zirconium oxychloride**

1. Molecular weight: 322.3
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of zirconium oxychloride): Not applicable
5. Melting point: 110 C (230 F) (approximately)
6. Vapor pressure at 20 C (68 F): 9 to 13 mm Hg vapor pressure of water
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Zirconium tetrachloride**

1. Molecular weight: 233
2. Boiling point (760 mm Hg): 331 C (628 F) (sublimes)
3. Specific gravity (water = 1): 2.8
4. Vapor density (air = 1 at boiling point of zirconium tetrachloride): Not applicable
5. Melting point: 331 C (628 F) (sublimes)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Zirconium hydride**

1. Molecular weight: 93.2
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 5.7
4. Vapor density (air = 1 at boiling point of zirconium hydride): Not applicable
5. Melting point: Decomposes above 300 C (572 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Very low
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Zirconyl acetate**

1. Molecular weight: Very high (a polymer)
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of zirconyl acetate): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **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 off 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.

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For zirconium hydride: 270 C (518 F); for others: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For zirconium hydride, sand or

inert powder; for others, not applicable

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on 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).

• **Method**

Sampling and analyses may be performed by collection of zirconium compounds on a filter, followed by treatment with nitric and perchloric acids, solution in acid, and atomic absorption spectrophotometric analysis. An analytical method for zirconium compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, and Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing 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.

• If employees' clothing may have become contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, or zirconium tetrachloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.

• Where exposure of an employee's body to zirconium tetrachloride or liquids containing zirconium tetrachloride may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate or zirconium tetrachloride should be removed promptly and not reworn until the contaminant is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of zirconium tetrachloride or liquids containing zirconium tetrachloride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to zirconium tetrachloride or liquids containing zirconium tetrachloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

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SANITATION

• Skin that becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, or zirconium tetrachloride should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.

• Employees who handle zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride, or liquids containing these compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to zirconium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from refining and casting operations, dies for metal extrusion and spout linings for continuous casting; during preparation of alloys; during manufacture of metal or alloys in nuclear power, aerospace, and chemical industries	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in manufacture of ceramics, glass, and porcelains; synthesis of pigments, dyes, and water repellants; use in tanning operations	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as abrasive and polishing materials; use as an igniter in manufacture of munitions and other items as detonators, photoflash bulbs, and lighter flints; use in manufacture of skin ointments and antiperspirants	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a gas getter in manufacture of high vacuum tubes and radio valves; use as a deoxidizer, denitrifier, and desulfurizer in iron and steel manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation from chemical synthesis	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If zirconium compounds get into the eyes, wash 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.

• **Skin Exposure**

If zirconium compounds get on the skin, wash with soap or mild detergent and water.

• **Breathing**

If a person breathes in large amounts of zirconium compounds, 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.

• **Swallowing**

When zirconium compounds have been swallowed and the person is conscious, 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 immediately.

• **Rescue**

Move the 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. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• 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.

• Waste disposal method:

Zirconium compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR ZIRCONIUM COMPOUNDS (AS ZIRCONIUM)

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
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 or quarter-mask 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 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 high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

* U.S. GOVERNMENT PRINTING OFFICE: 1981/661-362