

Occupational Health Guideline for Soluble Chromic and Chromous Salts (as Chromium)*

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 soluble chromic and chromous salts. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Chromic sulfate hydrate

- Formula: $\text{Cr}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (approximately)
- Synonyms: None
- Appearance and odor: Violet or green, odorless solid.

Chromic potassium sulfate

- Formula: $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
- Synonyms: Potassium chrome alum; potassium chromium (III) sulfate
- Appearance and odor: Red-violet, odorless solid.

Chromous chloride

- Formula: CrCl_2
- Synonyms: None
- Appearance and odor: Colorless to gray, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble chromic or chromous salts is 0.5 milligrams of soluble chromic or

chromous salts (as chromium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: They are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to $0.001 \text{ mg}/\text{m}^3$ and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to $0.025 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of $0.05 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Soluble chromic or chromous salts can affect the body if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

Exposure to certain soluble chromic or chromous salts have been reported to cause an allergic skin rash.

• 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 soluble chromic or chromous salts.

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.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to soluble chromic and chromous salts 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 soluble chromic and chromous salts exposure.

—Skin disease: Chromic salts may cause an allergic dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

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

• Summary of toxicology

The soluble chromic and chromous salts have no established toxicity. Since exposures are often mixed, consideration should be given to the possible exposure to hexavalent chromium, which is a more toxic form. The compound hexaaquachromium trichloride has been found to react with protein *in vitro*, indicating that it is not biologically inert. Of 35 rats implanted with chromic acetate in the thigh muscle, 1 developed sarcoma; this was considered to be evidence of weak carcinogenicity of this soluble trivalent compound. When taken by mouth, the trivalent compounds do not give rise to local or systemic effects and are poorly absorbed; no specific effects are known to result from inhalation. Animals ingesting chromic salts showed one-ninth as much chromium in the tissues as did animals ingesting equal amounts of chromates. Dermatitis from some chromic salts has been reported. Some investigators believe that all persons sensitized to hexavalent chromium are also sensitive to the trivalent form, although this has not been firmly established.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data—Chromic sulfate hydrate

1. Molecular weight: 680 (approximately)
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of chromic sulfate hydrate): Not applicable
5. Melting point: 90 C (194 F) Loses water, residue does not melt
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 84–120
8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Chromic potassium sulfate

1. Molecular weight: 499.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.83

4. Vapor density (air = 1 at boiling point of chromic potassium sulfate): Not applicable

5. Melting point: 89 C (192 F) Loses water, then melts at 400 C (752 F)

6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)

7. Solubility in water, g/100 g water at 20 C (68 F): 19.6

8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Chromous chloride

1. Molecular weight: 122.9
2. Boiling point (760 mm Hg): 1300 C (2372 F)
3. Specific gravity (water = 1): 2.93
4. Vapor density (air = 1 at boiling point of chromous chloride): Not applicable
5. Melting point: 820 C (1508 F)
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
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: None
2. Incompatibilities: Water (chromyl chloride)
3. Hazardous decomposition products: None
4. Special precautions: None

• Flammability

1. Most soluble chromic or chromous salts are not combustible. However, chromyl chloride reacts vigorously with water, forming chromic acid, chromic chloride, hydrochloric acid, and chlorine. Also, chromyl chloride causes ignition of ammonia, ethyl alcohol, turpentine, and other combustible materials.

• Warning properties

Grant states that "chromium compounds . . . are known to cause dermatitis, ulcers of the skin and mucous membranes, and perforation of the nasal septum." Chromium chloride is an example of the chromium compounds which Grant states produces these effects. Not all chromic and chromous salts produce eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

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).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of soluble chromic or chro-

mous salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of soluble chromic or chromous salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for soluble chromic and chromous salts is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

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 liquids or solids containing soluble chromic or chromous salts.

• Clothing contaminated with soluble chromic or chromous salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chromic or chromous salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic or chromous salts, the person performing the operation should be informed of soluble chromic or chromous salts's hazardous properties.

• Non-impervious clothing which becomes contaminated with soluble chromic or chromous salts should be removed promptly and not reworn until the soluble chromic or chromous salts are 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 liquids or solids containing soluble chromic or chromous salts contacting the eyes.

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

SANITATION

• Skin that becomes contaminated with soluble chromic or chromous salts should be promptly washed or showered to remove any soluble chromic or chromous salts.

• Employees who handle liquids or solids containing soluble chromic or chromous salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble chromic or chromous salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in textile treatment in dyeing, printing, moth-proofing, and water-proofing; use in tanning of leather in gloves, garments, and shoe uppers	Local exhaust ventilation; personal protective equipment
Use in manufacture of pigments for green varnishes, inks, paints, and glazes	Local exhaust ventilation; personal protective equipment
Use for metal treatment and polishing	Local exhaust ventilation; personal protective equipment
Use in photographic fixing baths for hardening of emulsions; use as catalysts and in manufacture of catalysts	Local exhaust ventilation; personal protective equipment
Use in chemical synthesis; use as corrosion inhibitors	Local exhaust ventilation; personal protective equipment

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 liquids or solids containing soluble chromic or chromous salts 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 these chemicals.

• Skin Exposure

If liquids or solids containing soluble chromic or chromous salts get on the skin, promptly flush the contaminated skin with water. If liquids or solids containing soluble chromic or chromous salts penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of soluble chromic or chromous salts, 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 liquids or solids containing soluble chromic or chromous salts 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 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 soluble chromic or chromous salts 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 soluble chromic or chromous salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Soluble chromic or chromous salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

RESPIRATORY PROTECTION FOR SOLUBLE CHROMIC AND CHROMOUS SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m ³
Particulate Concentration	
2.5 mg/m ³ or less	Any dust and mist respirator, except single-use.**
5 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume respirator or high efficiency particulate respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m ³ 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.
250 mg/m ³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m ³ 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.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

