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MINISTERIO DE TRABAJO Y ECONOMÍA SOCIAL
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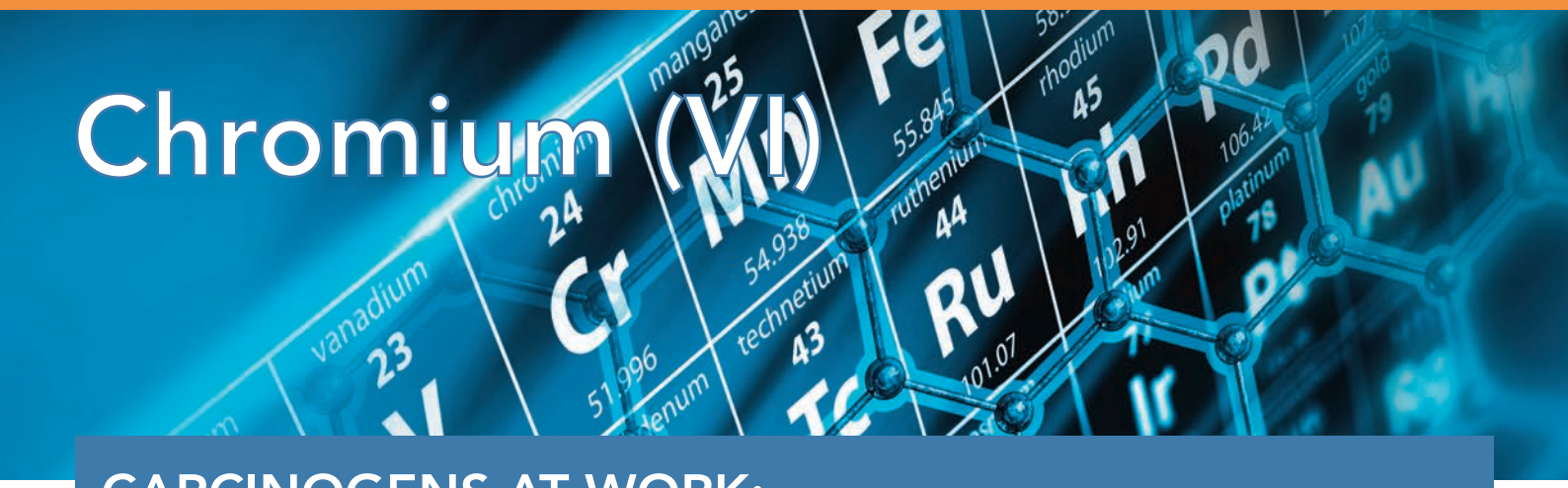
Instituto Nacional de Seguridad y Salud en el Trabajo



Chromium (VI)

CARCINOGENS AT WORK: Know to Prevent

Information about the substance and where it can be found

Elemental chromium (Cr) is a metallic element that occurs naturally in the earth's crust, as part of compounds such as the most important mineral chromite.

Moreover, chromium occurs as part of various compounds in different oxidation states. The most important are the valence states II (chromous), III (chromic) and VI (chromates). Hexavalent chromium is the second-most-stable oxidation state. Thus, Cr (VI) compounds include a large group of chemical elements with different properties, for example, acidic and oxidising properties, and with the ability to form highly coloured and insoluble salts, which makes them the most widely used in industry (*Encyclopedia OIT*, chapter 63).

Hexavalent chromium compounds, such as chromates and dichromates, exist in a wide variety of compounds, many of which are of great importance to industry. These include ammonium chromate, barium chromate, calcium chromate and dihydrate, chromium chromate, chromium (VI) chloride, chromium trioxide (chromic acid), lead chromates, molybdenum orange, potassium chromate and dichromate, sodium chromate and dichromate and zinc chromates.

Hexavalent compounds, with the exception of some small amounts in minerals, do not occur naturally in the environment, but are formed from trivalent chromium during chromium production processes. The starting point for all hexavalent compounds is chromite ore, which contains trivalent chromium oxide.

Cr (VI) compounds are mostly lemon yellow, orange and dark red. They are usually in solid form (crystalline, granular or powdered), and may be soluble or insoluble in water (*IARC*, 2012. Volume 100 C).

Examples of water-soluble Cr (VI) compounds are sodium chromate and potassium chromate, while insoluble compounds include barium chromate and lead chromate.

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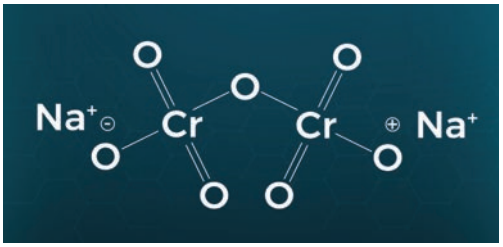
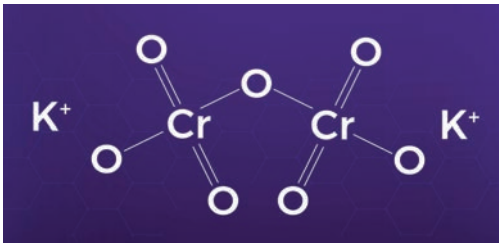
Besides the chromate producing industry, Cr (VI)-containing compounds are used in many industrial processes, including the production of ferrochrome and chromium metal alloys, the production and welding of stainless steels, metal finishing processes (chromium plating) with chromic acid, not only for decorative chromium plating, but also for hard chromium plating, with much thicker layers to obtain a highly resistant surface with a low coefficient of friction, as well as in the manufacture and use of chromium-containing chemicals.

The latter include the manufacture of inorganic paint pigments and metallic primers, such as lead chromates, molybdate oranges, zinc chromate and chromic oxide green. They can also be found in wood preservation products (sodium and potassium chromates and chromium trioxide), the manufacture of anticorrosives (strontium, calcium, zinc and barium chromates) and the manufacture of glass and coloured enamels. They are also used in mordants for dyes, catalysts and leather tanning (ammonium, sodium and potassium chromate). Other known uses of chromium chemicals include fabric printing, textiles, printing inks, fireworks, preparation of numerous chromic oxide-containing catalysts and production of light-sensitive dichromate colloids for lithography (Encyclopedia OIT, chapter 63).

On the other hand, the powerful oxidising properties of chromates in acid solution allow for many industrial applications, especially with organic materials, such as the oxidation of trinitrotoluene (TNT) to produce fluoroglucinol (Encyclopedia OIT, chapter 63).

Some hexavalent chromium is present in cement as a contaminant from cement manufacture and possibly from clinker or gypsum components, and from kiln dust during firing from chromium-containing refractories. However, the hexavalent form is reduced to the trivalent form by the addition of ferrous sulphate to the cement.





Hexavalent chromium compounds include a large group of chemical elements with various properties, such as acidic and oxidising properties, and the ability to form highly coloured and insoluble salts, making them readily applicable to industry.

Table 1 Chemical Names, CAS No, and formula of some Cr (VI) compounds		
Source: IARC (2012). Arsenic, metals, fibres, and dusts. Volume 100 C. A review of human carcinogens		
CHEMICAL NAME	**CAS No[1]**	**FORMULA**
Ammonium chromate	7788-98-9	$(NH4)_2CrO_4$
Ammonium dichromate	7789-09-5	$(NH_4)_2Cr_2O_7$
Basic lead chromate	1344-38-3 (54692-53-4)	$PbO.PbCrO_4$
Calcium chromate	13765-19-0	$CaCrO_4$
Chromium (VI) chloride	14986-48-2	$CrCl_6$
Chromium trioxide	1333-82-0 (12324-05-9; 12324-08-2)	CrO_3
Chromyl chloride	14977-61-8	CrO_2Cl_2
Lead chromate	7758-97-6 (8049-64-7); 1344-37-2	$PbCrO_4$
Potassium chromate	7789-00-6	K_2CrO_7
Potassium dichromate	7778-50-9	$K_2Cr_2O_7$
Sodium chromate	7775-11-3	Na_2CrO_4
Sodium dichromate	10588-01-9 (12018-32-5)	$Na_2Cr_2O_7$
Strontium chromate	7789-06-2 (54322-60-0)	$SrCrO_4$
Zinc chromate	13530-65-9 (1308-13-0;1328-67-2; 14675-41-3)	$ZnCrO_4$
Zinc chromate hydroxides	15930-94-6 (12206-12-1; 66516-58-3)	Zn_2CrO_4 $(OH)_2$ and others
Zinc potassium chromate (hydroxides)	11103-86-9 (12527-08-1; 37809-34-0)	KZn_2 $(CrO_4)_2$ (OH) and others

Health effects

All Cr (VI) compounds are classified as Group 1 carcinogens by the IARC, meaning they are carcinogenic to humans. Moreover, most hexavalent chromium compounds are classified under the CLP Regulation as category 1B carcinogens. Exceptions are chromium trioxide and zinc chromates, including zinc potassium chromate, which are classified as category 1A carcinogens.

Cr (VI)'s main route of entry is inhalation, although exposure can also occur via the dermal route, through skin contact, and via the digestive route, in food or water, the latter being the least frequent.

1 CAS No. Chemical Abstracts Service registration number. Replaces CAS Registry numbers are given in parentheses.

The IARC (iarc.who.int) is an autonomous agency of the World Health Organization of the United Nations. It seeks to promote international collaboration in cancer research. It runs studies that are widely recognised for their quality and independence.

The health effects of exposure to chromium (VI) compounds have been extensively studied and various specialist bodies and agencies have described their toxicological profile, such that it is known that exposure to hexavalent chromium compounds can cause lung cancer, nasal sinus cancer, nephrotoxicity, hypersensitivity, skin corrosion and irritation of the respiratory and gastrointestinal tract.

The most recent studies, such as those published in 2021 by the *Dutch National Institute for Public Health and the Environment (RIVM)*, concerning the non-carcinogenic and carcinogenic health effects of exposure to Cr (VI) compounds have reached the following conclusions:

- Non-carcinogenic effects: Cr (VI) may cause perforation of the nasal septum by means of chromium ulcers, chronic lung diseases, including asthma, rhinitis, pulmonary fibrosis and COPD (chronic obstructive pulmonary disease), skin ulcers and allergic contact dermatitis in humans.
- Carcinogenic effects: Cr (VI) may cause lung cancer and sinus and paranasal cancers in humans.

Furthermore, the aforementioned studies state that it is currently not sufficiently evidence whether Cr (VI) can lead to other health effects such as:

- Non-carcinogenic effects: irreversible damage or disease due to impairment of the immune system (other than allergic contact eczema, asthma and allergic and chronic rhinitis and lung diseases) or adverse effects on fertility or prenatal development in humans.
- Carcinogenic effects: stomach cancer or cancer of the larynx in humans.

There is no current evidence from scientific studies in humans or animals that occupational exposure to Cr (VI) can cause cancers in humans other than those mentioned above.

There is also insufficient evidence from current scientific studies in humans and animals to indicate that occupational exposure to Cr (VI) can cause irreversible gastrointestinal, haematological, hepatic, renal, neurological or cardiovascular effects or adverse dental effects.

Table 2
Harmonised hazard classification of Cr (VI) compounds, with the exception of barium chromate and compounds specified elsewhere in the Appendix, according to Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures (CLP)"

Cr (VI) compounds	
Classification	
Hazard class and category code	**Hazard statement code**
Carcinogenicity. Carc.1B	H350i: May cause cancer by inhalation.
Skin sensitization. Skin Sens. 1.	H317: May cause an allergic skin reaction
Hazardous to the aquatic environment. Aquatic Acute 1.	H400: Very toxic to aquatic life.
Hazardous to the aquatic environment. Aquatic Chronic 1.	H410: Very toxic to aquatic life with long lasting effects.
Labelling. Hazard pictograms and signal words	
Danger	

Similar conclusions have been by the IARC's studies, whose monograph *"Arsenic, metals, fibres, and dusts. Volume 100 C. A review of human carcinogens"*, shows an increased risk of lung cancer among workers exposed to Cr (VI), particularly in the production of chromates, chromate pigments and electroplating. Studies also suggest a possible increased incidence of nasal and paranasal sinus among workers exposed to Cr (VI), but little evidence that Cr (VI) exposure can cause stomach or other cancers.

Where the exposure can take place

It is estimated that around 900,000 workers in the EU are potentially exposed to Cr (VI). Studies of workers in the chromate, chromate pigment and chromate electroplating industries employed prior to the 1980s show higher rates of lung cancer mortality (*The facts Chromium VI*. Roadmap on carcinogens).

Exposure to Cr (VI) occurs through inhalation of dust, mist or fumes, as well as dermal contact with Cr (VI)-containing products. Depending on the industry, simultaneous occupational exposure to different hexavalent compounds may occur and, in some industries, may even be further complicated by exposure to trivalent and hexavalent compounds. The most important involve sodium, potassium, calcium and ammonium chromates and dichromates during chromate production, chromium trioxide in chromium plating operations, insoluble zinc and lead chromates in pigment production and spray painting, water-soluble alkali chromates in steel smelting and welding, and other chromates in cement production and use (*IARC*, 2012. Volume 100 C).

The *Royal Decree 1299/2006, of 10 November, approving the table of occupational diseases in the Social Security system and setting out criteria for reporting and recording them, includes in its Appendix I. Table of occupational diseases (codification)*, the following activities in which workers may be exposed to Cr (VI) and its compounds, giving rise to the diseases covered therein: malignant neoplasm of the nasal cavity, bronchus and lung due to preparing, using and handling hexavalent chromium compounds, especially chromates, alkali dichromates and chromic acid, and especially in the following activities:

Regulatory references

The *Royal Decree 1154/2020*, amending Royal Decree 665/1997 of 12 May 1997 on the protection of workers from the risks related to exposure to carcinogens at work, which transposes *Directive 2017/2398* into Spanish law, included in its **Appendix III** on occupational exposure limit values, chromium (VI) compounds as carcinogens, taken to mean substances or mixtures meeting the criteria for classification as car cinogenic or mutagenic in germ cells of category 1A or 1B established in Appendix I from *Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures.*

- Manufacture of catalysts, tanning chemicals, and wood treatment products containing chromium compounds.
- Manufacture and use of pigments, dyes and paints based on chromium compounds.
- Sawing and machining of wood treated with chromium compounds.
- Spray application of chromium-containing paints and varnishes.
- Skin tanning.
- Preparation of photo etched plates by bichromate colloids.
- Manufacture of matches.
- Electroplating and surface treatment of metals with chromium.
- Pickling and cleaning of metals and glass (sulphochromic acid or chromic acid).
- Manufacture of alkaline chromates.
- Lithographs.
- Manufacture of stainless steels.
- Work involving welding and flame cutting of stainless steels.
- Manufacture of cement and its derivatives.
- Processing of waste containing chromium.

Exposure assessment

Royal Decree 665/1997 on the protection of workers from the risks related to exposure to carcinogens at work incorporated, by Royal Decree 1154/2020 amending it, the binding occupational exposure limit values for Cr (VI) compounds, expressed as chromium, which are listed in Table 4.

Tabla 3
Estimated number of workers exposed to Cr (VI) by application group. Source: NIOSH 2013. Occupational Exposure to Hexavalent Chromium. Criteria for a Recommended Standard

Application group	Number of exposed workers
Welding (stainless steel and carbon steel)	269.379
Painting	82.253
Electroplating	66.859
Steel mills	39.720
Iron and steel foundries	30.222
Textile dyeing	25.341
Woodworking	14.780
Printing	6.600
Glass producers	5.384
Construction, other(2)	4.069
Chemical distributors	3.572
Paint and coatings producers	2.569
Solid waste incineration	2.391
Non-ferrous metallurgical uses	2.164
Chromium catalyst users	949
Plastic colorant producers and users	492
Chromium catalyst producers	313
Chromate production	150
Plating mixture producers	118
Printing ink producers	112
Chromium dye producers	104
Refractory brick producers	90
Ferrochromium producers	63
Chromate pigment producers	52
Chromated copper arsenate producers	27
Chromium sulfate producers	11
TOTAL	558.431

[2] Does not include welding, painting, and woodworking; does include government construction.

Table 4 Occupational exposure limit values. RD 665/ 1997				
Name of agent	**EC No.[3]**	**CAS No.[4]**	**8 hour-OEL[5]**	**Transitional measures**
Chromium (VI) compounds which are carcinogenic within the meaning of article 2.1 of this Royal Decree (expressed in chromium)	-	-	0,005 mg/m^3 [6]	Limit value: 0.010 mg/m^3 until 17 January 2025. Limit value: 0.025 mg/m^3 for welding or plasma-jet cutting or similar processes generating smoke until 17 January 2025.

This Royal Decree transposes into Spanish law Directive (EU) 2017/2398 of the European Parliament and of the Council of 12 December 2017 amending Directive 2004/37/EC on the protection of workers from the risks related to exposure to carcinogens or mutagens at work, which provides that certain hexavalent chromium compounds meet the criteria to be classified as carcinogens (category 1A or 1B) under Regulation (EC) No 1272/2008 of the European Parliament and of the Council and are therefore carcinogens within the meaning of Directive 2004/37/EC. Thus, this Directive provided that, on the basis of the available information, including scientific and technical data, it is possible to determine a limit value for hexavalent chromium compounds which are carcinogenic and that it is therefore appropriate to establish a limit value for these Cr (VI) compounds.

Accordingly, Royal Decree 665/1997 sets a limit value of 0.005 mg/m3 for Cr (VI). This limit value may not be appropriate and, in some sectors, may be difficult to achieve in the short term. Therefore, a transitional period is established during which a limit value of 0.010 mg/m3 applies (Table 4). In the specific situation where the work activity involves welding or plasma-jet cutting or other similar work that generates smoke, a limit value of 0.025 mg/m3 must apply during the transient period, after which the usual limit of 0.005 mg/m3 must apply. For its part, the document "Occupational Exposure Limits for Chemical Agents in Spain", drawn up by the INSST, updated in 2021, the Cr (VI) compounds, such as Cr, in the list of chemical agents, establishing an OEL according to the Directive and adding the notes detailed in tables 5 and 6 on the following page, as well as the BLV, shown in table 7.

[3] The EC number is the official EU number of the substance as defined in section 1.1.1.2 of Part 1 of appendix VI to Regulation (EC) No 1272/2008.
[4] CAS No. Chemical Abstracts Service registration number.
[5] Measured or calculated in relation to a time-weighted average with an eight-hour reference period.
[6] mg/m^3 = milligrams per cubic metre of air at 20°C and 101.3 KPa (760 mm mercury pressure).

Table 5 Occupational Exposure Limit (OEL)						
EC No.	CAS No.	Chemical agent (year of inclusion or update)	Limit values		Notes	Hazard statement (H)
			8 hours-OEL	Short-term		
-	-	Cr (VI) compounds, such as Cr (2021)	0,01 mg/m³ [7]	-	C1, BLV, Sen, r, v[8]	

Source: Document "Límites de Exposición Profesional para Agentes Químicos en España 2022

Table 6 Occupational exposure limit with entry into force in the coming years						
EC No.	CAS No.	Chemical agent	8 hours-OEL	Short-term	Notes	Date of entry into force
-	-	Cr (VI) compounds, such as Cr	0,005 mg/m³	-	C1, BLV, Sen, r, v[8]	2025

Source: Document "Límites de Exposición Profesional para Agentes Químicos en España 2022"

Table 7 Biological Limit Values							
EC No.	CAS No.	Chemical agent	Biological indicator (BI)	Limit values (BLV)	Sampling moment	Notes	Hazard statement (H)
-	-	Chromium (VI), water soluble fume (2008)	Total Chromium in Urine	10 µg/l	Beginning and end of the working day[9]		350i-317-400-410
			Total Chromium in Urine	25 µg/l	End of the working week[10]		

Source: Document "Límites de Exposición Profesional para Agentes Químicos en España 2022"

[7] A limit value of 0.025 mg/m³ is set for welding or plasma-jet cutting or similar processes generating smoke until 17 January 2025.

[8] C1: Carcinogens or suspected human carcinogens. Check for each specific agent its classification according to Regulation (EC) No 1272/2008.
BLV: Chemical agent that has a specific Biological Limit Value in this document.
Sen: Sensitising. See Chapter 6 of the Document "Límites de Exposición Profesional para Agentes Químicos en España 2022".
r: This substance has restrictions on manufacture, placing on the market or use as specified in "Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals" (REACH) of 18 December 2006 (OJEU L 369 of 30 December 2006). Restrictions on a substance may apply to all uses or only to specific uses. Appendix XVII of the REACH Regulation contains the list of all restricted substances and specifies the uses that have been restricted.
v: Carcinogenic agent with binding limit value listed in appendix III of RD 665/1997 and subsequent amendments.

[9] The value refers to the difference between the results of the samples taken at the end and at the beginning of the working day.

[10] After four to five consecutive days of work with exposure, as soon as possible after the end of the last working day since biological indicators are eliminated with half-lives longer than five hours. These indicators accumulate in the body during the working week; therefore, the timing of sampling is critical regarding previous exposures.

To make the quantitative assessment of exposure to hexavalent chromium, and to verify compliance with the occupational exposure limit values, the analytical methods used to determine environmental contaminants must meet the general requirements of the measurement procedures of the standard *UNE-EN 482:2021 Workplace exposure - Procedures for the determination of the concentration of chemical agents - Basic performance requirements*.

Therefore, the assessment of exposure to chemical agents requires sampling and analytical methods to determine the concentration of pollutants in the air in the working environment and/or the concentration of a pollutant or one of its metabolites or effect indicators in specific physiological fluids.

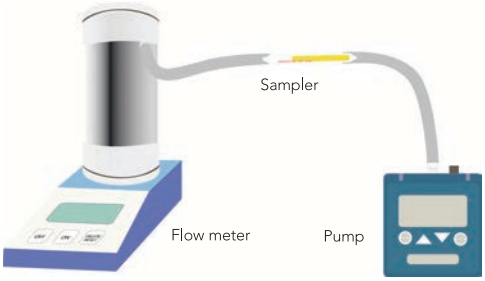
Because these are activities involving exposure to carcinogenic or mutagenic agents, which are included in appendix I of the *Royal Decree 39/1997 of 17th January, by virtue of which the Regulations for Prevention Services are approved* and, according to article 11 of the same Regulation, the assessment may in not in any circumstances be made personally by the employer. Regardless of whether it is made with own resources or the employer uses one or several External Prevention Services (EPS), given the importance and possible complexity of the assessment process, it is advisable that the Prevention Technician who makes it has a specialisation in Industrial Hygiene.

For Cr (VI), the method has been validated by the National Institute for Safety and Health at Work (INSST): *MTA/MA-063/A23 Determination of hexavalent chromium in air (inhalable fraction). Filter collection method. Ion chromatography*. This method describes the procedure for determining the concentration of Cr (VI) in workplace air by collection on a filter impregnated with a sodium hydroxide solution and analysis by ion chromatography with an ultraviolet-visible (UV-visible) detector. The sample is obtained by passing, with the aid of a personal sampling pump, a volume of air through a quartz fibre filter impregnated with a 1 M NaOH solution and incorporated into a sampler of the inhalable fraction. Cr (VI) compounds, which are present in the air in the workplace, are retained in the filter. In document *"CR-03/2006. Samplers for the inhalable fraction of particulate matter"* information about the types of inhalable fraction samplers to be used can be found in the INSST.

It must be noted that solid-state hexavalent chromium compounds are generally not very reactive and their interaction with the collection filter is practically negligible, regardless of the nature of the filter. However, in the case of hexavalent chromium compounds which are in the environment in

Representativeness of the samples

Whenever a quantitative assessment of inhalation exposure to a hazardous chemical agent, a sampling strategy must be adopted to ensure the representativeness of the data obtained. The standard **UNE-EN 689:2019+AC:2019 "Workplace exposure - Measurement of exposure by inhalation to chemical agents Strategy for testing compliance with occupational exposure limit values "** proposes a possible strategy for comparing daily exposure with the occupational exposure limit values.

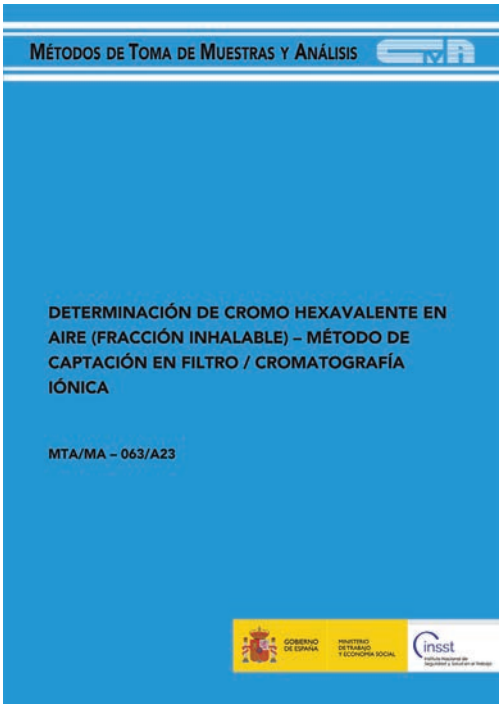


the form of liquid aerosols (fog, mists, etc.), especially chromic acid mists, Cr (VI) reacts with the filter and leads to lower analytical recoveries.

In these situations, it is necessary to assess the analytical recovery and sample stability for different types of filters to validate the suitability of these filters for use in the sampling of liquid Cr (VI) aerosols (*CR-10/2016*, INSST).

In this regard, in the document *CR-10/2016 CR-10/2016 Determination of hexavalent chromium in air. Criteria and recommendations for selecting the sampling filter for chromium (VI) determinations in chromic acid mists*, prepared by INSST, contains a study on assessing the influence of the sampling filter and considerations and recommendations for the determination of Cr (VI) in chromic acid mists.

On the other hand, to determine compliance with the biological limit values, the following method accepted by the National Institute for Safety and Health at Work (INSST) is available: *MTA/MB-018/A94 Determination of chromium in urine. Graphite chamber method. Atomic absorption spectrometry*. This method specifies the procedure to be followed and the equipment required to determine chromium (CAS No 7440-47-3) in urine by atomic absorption spectroscopy in the concentration range 1 to 20 g/l urine (19.2 to 384 nmol/l), applicable to monitoring occupational populations potentially exposed to chromium and chromium compounds.



Controlling exposure

Measures to prevent exposure to carcinogens or mutagens must be implemented in order of priority according to their effectiveness. Articles 4, 5 and 6 of Royal Decree 665/1997 set out the employer's obligations in this respect.

The first option should always be the replacement of the agent, and when this cannot be done, the possibility of working in a closed system should be considered. Where it is also not possible to work in a closed system, all necessary measures should be taken to reduce exposure to as low a level as technically feasible. Finally, where the above measures are not sufficient, personal protective equipment (PPE) must be used.

Prioritisation of preventive measures for carcinogens:

1. Substitution
2. Closed system
3. Reduction of exposure to as low a level as is technically possible.
4. Personal protective equipment

1. Substitution

The priority measure, and mandatory whenever feasible, when working with carcinogens or mutagens, is always substitution with another non-hazardous or less hazardous agent or process. This is provided in art. 4 of RD 665/1997.

Furthermore, art. 10 of RD 665/1997 provides that the employer must provide the labour and health authorities, when requested by them, with adequate information about the criteria and results of the process of substitution of the carcinogenic or mutagenic agents referred to in the aforementioned art. 4.

This measure is the most difficult to implement, especially when a production process is already in place, and many variables must be taken into account, but it must be planned and implemented whenever feasible, even if it is more costly, and it is necessary to keep up to date with technological advances in each sector.

Substitution may be based on changing an agent to a less hazardous agent or changing procedures. In any case, the new risks that may be introduced by substitution must always be assessed.

There are a number of useful tools to assist in this process. Some experiences with the replacement of Cr (VI) can be found on the SUBSPORTplus (Substitution Support Portal).

Furthermore, due to its carcinogenic properties, hexavalent chromium is a substance of very high concern (SVHC) according to Regulation (EU) No 1907/2006 (REACH Regulation). Since the end of 2017, there has been an authorisation requirement for Cr (VI) under REACH in the European Union (EU), that is, an application must be submitted to the European Chemicals Agency (ECHA) for use, import and placing on the EU market. Therefore, the sectors concerned are working on ways to replace Cr (VI) in surface treatments, for example, in the health sector. In a study conducted by the BAuA (*Federal Institute for Occupational Safety and Health, Germany*) in 2022, three case studies of companies using trivalent chromium as an alternative to hexavalent chromium were collected. In this case, it is even possible for companies to avoid another substance of concern, nickel, in the surface treatment of sanitary installations (*SUBSPORT Substitution Support Portal, 2022*).

It is also possible to replace Cr (VI) used in decorative chromium plating processes with trivalent chromium, provided that the material's requested characteristics do not require the use of hexavalent chromium. Another option would be to use a different type of finish that also offers corrosion resistance and reduction of the friction coefficient, for example, zinc and aluminium la-

Resources for substitution

More practical experiences of risk substitution or elimination can be found in the following links:

– Solutions, examples of substitution and good practice for carcinogens, from the Roadmap on carcinogens.

https://roadmaponcarcinogens.eu/solutions/good-practices/

- SUBSPORT Substitution Support Portal

https://www.subsportplus.eu/

- The OECD Substitution and Alternatives Assessment Toolbox - SAAT Toolbox

http://www.oecdsaatoolbox.org/

- INRS Substitution Assistance Cards.

http://www.inrs.fr/actualites/nouvelles-far-fas.html

BASEQUIM. Ficha 011: Soldadura manual TIG de aceros inoxidables y de alta aleación con cromo o níquel: exposición a humos metálicos.

BASEQUIM. Ficha 023. Tratamientos de superficies. Cromado electrolítico ma nual: Exposición a cromo hexavalente

minar coating, electrolytic zinc plating together with organic coating, etc. In 2006, a pilot project to replace Cr (VI) in chromium anti-corrosion coatings on military aircraft with cerium oxides was presented with promising results (*SUBSPORT Substitution Support Portal*, 2022).

2. Closed system

Art. 5.2 of RD 665/1997 states that if it is not technically feasible to replace the carcinogen or mutagen, the employer shall ensure that the carcinogen or mutagen are produced and used in a closed system. It is therefore the first technological option for preventing and reducing exposure, to be designed preferably at negative pressure. This measure consists of preventing the dispersion of the agent in the air breathed by the worker by placing the process within a closed system with evacuation of the pre-treated air to a safe environment to prevent the agents from harming the environment or public health.

Closed, airtight systems not only eliminate exposure, but also prevent exposure to process intermediates. However, an adequate programme of preventative and, where possible, predictive maintenance of these systems should be ensured to minimise potential failures that could give rise to a risk of exposure.

INSST offers on its website access to the Chemical Agents Control Sheets (FCAQ in Spanish), developed by the Health and Safety Executive (HSE) of its COSHH Essentials model. The COSHH Essentials provide basic good work practice recommendations for different operations to control exposure to hazardous chemicals in the workplaces. The 300 series: containment (closed systems), is particularly helpful in this case.

An illustrative example can be found in surface treatments by manual electrolytic chromium plating, where the worker may be exposed to the chemical agents present in the vats (chromium, strong acids, etc.) during chromium plating. In these operations, risk reduction and control measures also include total enclosure and automation of the process, along with isolation of the process from the rest of the activity, so that the number of people exposed is kept to a minimum. Moreover, local exhaust ventilation will be used in the chrome vats. It would also be advisable to have local exhaust ventilation in the areas where the removed frames are moved with the chrome-plated parts of the tank for cleaning the chrome-plated surface (*Basequim. Sheet 023*, INSST).

3. Reduction of exposure to as low a level as is technically possible

Art. 5.3 of RD 665/1997 provides that, when closed system is not technically feasible, the employer shall ensure that workers' level of exposure is reduced to as low a level as is technically possible.

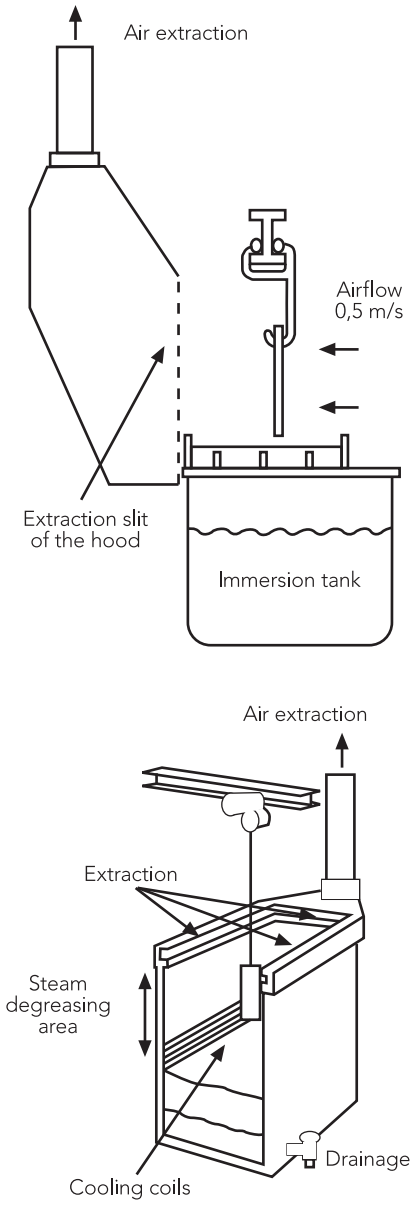
The aim is to implement technical and organisational measures so that exposure is reduced as much as technically feasible. This obligation implies that it is not sufficient to achieve exposure levels below the established occupational exposure limit, but rather that it is necessary to go beyond it by applying all available measures.

Furthermore, art. 5.5 of Royal Decree 665/1997 states that whenever a carcinogenic or mutagenic agent is used, the employer shall apply all the necessary measures set out in the aforementioned article. In general, these requirements are along the same lines as what should already be applied to conform to Royal Decree 374/2001, on the protection of the health and safety of workers against risks related to chemical agents at work, adding the express mention of installing devices that detect and alert in the event of situations that could generate abnormally high exposures, such as a failure in a local exhaust ventilation.

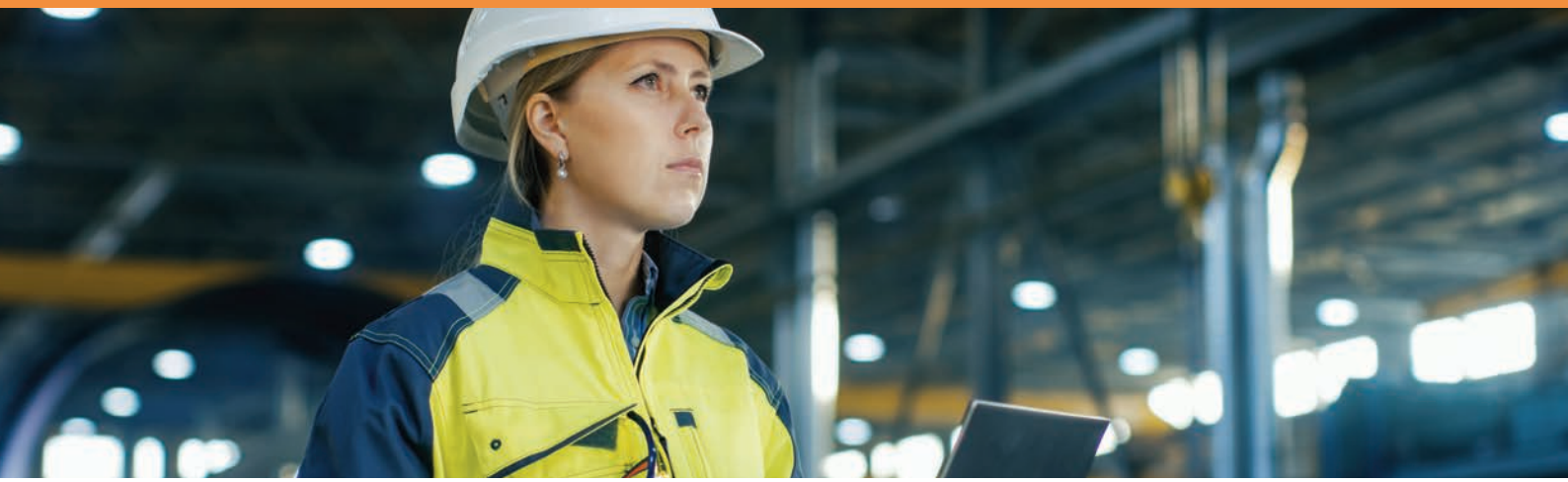
Measures to minimise exposure as much as technically feasible include limiting the quantities of the carcinogen or mutagen in the workplace and designing work processes and technical measures to prevent or minimise the formation of carcinogens or mutagens.

Moreover, these measures include limiting as far as possible the number of workers exposed or likely to be exposed, evacuating carcinogens or mutagens at source, by local exhaust ventilation or, where this is not technically feasible, by general ventilation, under conditions which do not pose a risk to public health and the environment, and using the most appropriate measuring methods, in particular for immediate detection of abnormal exposures due to unforeseen events or accidents, and applying the most appropriate procedures and working methods.

100 series: General ventilation, 200 series: Technical Control and the 400 series: Especial, from the Chemical Agents Control Sheets (FCAQ in Spanish), contains relevant practical information that can assist in the implementation of these measures.



Examples of technical control measures by local exhaust ventilation in pickling baths (above) and in vapour degreasing tanks (below).



For example, there is a risk of exposure to metal fumes in manual TIG welding of stainless and high alloy steels containing chromium or nickel. In the course of these tasks, workers may be exposed to metallic fumes from both the base metal and the filler rods, if used, and to gases from environmental reactions. Risk reduction and control measures in this case involve the application of local exhaust ventilation (Basequim. Sheet 011, INSST).

Thus, depending on the circumstances, the following equipment may be appropriate:

- For work in relatively fixed positions and with small workpieces: a small welding booth.
- For work in relatively fixed positions and with medium to large workpieces: a centralised ventilation unit with the necessary inlets, each consisting of an articulated duct and a capture-type extraction hood. Capture hoods are hoods that do not enclose the source and are not located in the natural path of the pollutant.
- For other work: mobile equipment consisting of a trolley on wheels, containing the fan and filters, the duct and the capture-type extraction hood.

Besides the aforementioned equipment, a number of other measures may be applied to reduce exposure to as low a level as possible, such as (*Basequim. Sheet 011*, INSST):

- General ventilation: The general ventilation of the enclosure where the welding stations are located must provide sufficient airflow to dilute residual contamination to negligible levels, with a complete sweep, and to ensure rapid compensation with clean outside air of the air extracted by the extraction equipment, to prevent excessive depression of the local air from causing malfunctioning of the extraction equipment.
- Maintenance measures for the engineering control system: the local exhaust ventilation equipment shall be maintained according to the manufacturer's instructions.
- Monitoring measures for the engineering control system: visual inspection of the ventilation equipment should be conducted before each use to look for external signs of damage, such as broken ducts, deformed hoods, etc. It is advisable to periodically (at least every six months) check the performance of the equipment by measuring key parameters and comparing the data with the design values.
- Demarcation, signage and access restriction: areas where stainless steel welding work is done must be demarcated and marked with signs warning of the danger it poses for health to breathe welding fumes, due

to the possible presence of chromium and nickel compounds. Only personnel who are required to operate in them shall be allowed access to them. The measures described here as examples must be adapted to the specific conditions at each workplace.

In other cases, such as in surface treatments by manual electrolytic chromium plating, exposure can be reduced to as low a level as technically feasible by acting on some bath parameters such as chromium concentration, temperature and plating times, surface tension, etc., in such a way that the generation of hexavalent chromium mists during the chromium plating process is reduced (*Basequim. Sheet 023*, INSST).

Also, the use of defoamers to limit mist formation or the use of injection nozzles when mixing chemicals to avoid agitation of the bath are practices that can contribute to the reduction of exposure.

A recent example of good practice in reducing exposure to hexavalent chromium compounds is URSA Chemie GmbH, the winner of the 2020 *"German Hazardous Substance Protection Award in 2020"*, for its technical solutions for the safe handling of carcinogenic substances. URSA Chemie GmbH, Montabaur, developed a system with which chromic acid canisters can be opened, emptied and cleaned without contact (*Roadmap on Carcinogens. Good practices*).

4. Personal protective equipment (PPE)

As a general rule in prevention, PPE should be used as a last resort, only when all priority prevention measures have been implemented and are not sufficient.

The results of the risk assessment will be the basis for determining the need for personal protective equipment and for the selection of the most appropriate equipment. In addition, when selecting equipment, the anatomy of the workers who will be using it must be taken into account and, in the case of respiratory protective equipment based on facial adjustment, it is highly recommended that a fit test be carried out on each person.

The products' Safety Data Sheets (SDS) and the International Chemical Safety Cards (ICSC), the latter of which can be consulted on the INSST website, also provide relevant information regarding, among other issues, the individual protection measures to be adopted depending on each Cr (VI) compound.

Regulatory references

In selecting, using and maintaining personal protective equipment, the prescriptions set out in *Royal Decree 773/1997, of May 30, on the minimum health and safety requirements for the use by workers of personal protective equipment*, must be observed.

More information can be found in the Technical Guide for the use of personal protective equipment by workers, drawn up by the INSST to clarify the technical aspects set out in the Royal Decree.

For detailed information about different types of PPE, please consult the Equipment Selection and Use Sheets that appear in the different links of the Personal Protective Equipment section of the INSST website, included in the corresponding sections of Appendix 4 of the Technical Guide.

Colour code	Type of filter	Application
	B	Inorganic vapours and gases
	P	Particulate matter

Table 8 Personal Protective Equipment covered by the ICSC for some Chromium (VI) compounds		
Compound	**Identification**	**Personal Protection**
Sodium chromate	CAS: 7775-11-3 UN No: 3288	Full protective suit including self-contained breathing apparatus.
Potassium chromate	CAS: 7789-00-6 UN No: 3288	Chemical protective suit, including self-contained breathing apparatus.
Zinc chromate	CAS: 13530-65-9 UN No: 3288	Respirator with particulate filter adapted to the concentration of the substance in air.

In general, workers exposed to Cr (VI) must wear dust masks, preferably with an efficiency of more than 99% to retain 0.5 µm particles, in all cases where concentrations exceed the levels set out in regulations and self-contained breathing apparatus must be provided for tasks that are considered hazardous. The employer must ensure that dust deposits and other surface contaminants have been removed by washing or vacuuming before commencing any such work. It is also necessary to provide personnel with protective clothing. The use of hand and eye protection is recommended, and inspection, repair and replacement of personal protective equipment (PPE) must be ensured (*Encyclopedia OIT*, chapter 63).

For example, in manual TIG welding of stainless and high-alloy chromium or nickel steels with exposure to metallic fumes, the use of closed welding shields with filtered air supply is highly recommended because of their greater convenience and the difficulty of making other protective equipment compatible with overhead welding helmets, which are always preferable to hand-held welding helmets.

In any case, if environmentally dependent respiratory protective equipment is used, it should be of high efficiency against solid particles (FFP3 self-filtering mask or half mask with removable filters P3) and compatible with the welding head shield. (*Basequim. Sheet 011*, INSST).

Hygiene measures

Hygiene measures are of particular importance in preventing exposure to carcinogens such as Cr (VI) compounds. These measures have several objectives:

- Prevent the agent from penetrating through the skin in case of accidental contact.
- Avoid the extent and duration of exposure by contact with soiled protective clothing or equipment.
- Avoid secondary exposure of others who may come into contact with soiled clothing or surfaces.

Article 6 of Royal Decree 665/1997 sets out the personal hygiene and personal protection measures to be taken by the company, including the following:

- Prohibit eating, drinking and smoking in risk areas.
- Provide protective or other appropriate clothing.
- Have separate places for storing work clothes and street clothes.
- Have a designated place to store PPE and ensure it is cleaned and checked for proper functioning.
- Provide appropriate and adequate toilets and washrooms.

The same article states that workers identified as exposed must be allowed time for personal cleanliness, with a maximum of 10 minutes before lunch and a further 10 minutes before leaving work.

The employer must also be responsible for washing and decontaminating work clothes, and it is forbidden for workers to take work clothes home for this purpose. If the clothes are sent to a specialist company for cleaning, it should be labelled such that the personnel of the company can identify the risk.

Regulatory references

Royal Decree 1154/2020, amending Royal Decree 665/1997 on the protection of workers from the risks related to exposure to carcinogens at work, specifies that the time devoted to personal hygiene of workers identified as exposed, before lunch and before leaving work, may not accumulate or be used for other purposes.

Health surveillance

Carcinogens or mutagens are generally characterised by long-term effects or diseases with long latency periods. Thus, Royal Decree 665/1997 creates a right for workers who have been exposed to these agents to the extension of health surveillance beyond the end of the exposure or of the employment relationship.

In order for the health surveillance programme to be adjusted to the risks arising from the presence of chemical agents in the workplace, the employer must provide information about these risks and safety data sheets to the basic health unit (BHU). In the absence of specific guidelines and action protocols, this BHU, based on the risk assessment and the effects of Cr (VI) compounds, will draw up a protocol and document the method and criteria used for the aforementioned health surveillance (INSST, 2018).

There is currently no specific worker health surveillance protocol for Cr (VI) compounds.

Regulatory references on health surveillance

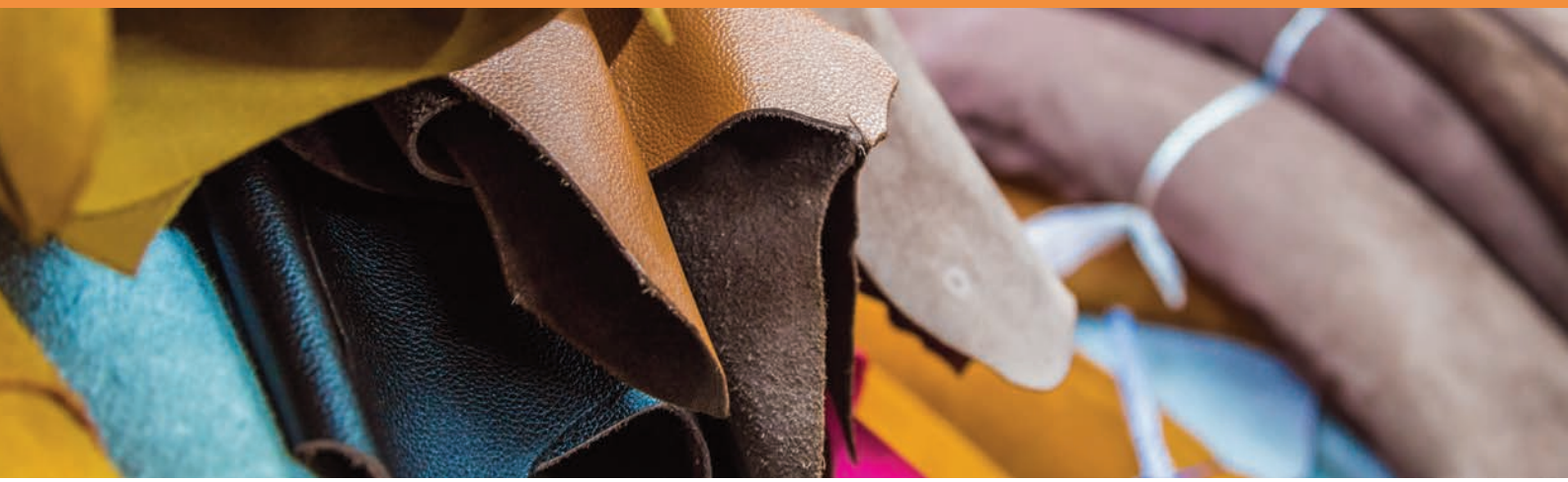
Health surveillance must be performed (Royal Decree 665/1997, art. 8):

- Before the beginning of the exposure.
- At regular intervals, as often as medical knowledge dictates.
- When it is necessary because a disorder has been detected in one of the company s workers with similar exposure, which may be due to exposure to carcinogenic or mutagenic agents.

Other preventive measures

In work with risk due to exposure to Cr (VI) compounds another series of preventive measures set out in Royal Decree 665/1997 must be complied with, such as the following:

- Measures to be taken in the event of accidental and non-regular exposures (article 7).
- Obligations with regard to documentation (article 9).
- Information to the competent authority (article 10).
- Consultation, information and training of workers (articles 11 and 12).



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