Workplace Exposure Standard (WES) review

CHROMIUM (VI) COMPOUNDS
(CAS NO: 7440-47-3)

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New Zealand Government

WORKSAFE
NEW ZEALAND | MAHI HAUMARU AOTEAROA

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1.0
Introduction

This WorkSafe New Zealand (WorkSafe) review considers whether the WES for chromium (VI) compounds should be changed.

It considers the potential for exposures to chromium (VI) in New Zealand, the health effects and risks, exposure standards in other jurisdictions around the world, and the practicability of measuring chromium (VI) exposures given currently available analytical methods.

The review includes a recommendation to change the WorkSafe WES, which is currently set for chromium (VI) compounds (water soluble and water insoluble) at a **WES-TWA** of 0.05 **mg/m³**, as published in the Special Guide *Workplace Exposure Standards and Biological Exposure Indices*, 9th Edition, (WorkSafe New Zealand, 2017).

In New Zealand, chromium (VI) compounds carry notations for **sen** (sensitiser) and 6.7A (known or presumed carcinogen).

Terms that are **bold** (first occurrence only) are further defined in the Glossary.

Synonyms: Synonyms: Hexavalent chromium, chromium (VI).

2.0 Physical and chemical properties

Chromium (VI) compounds form a large group of chemicals with varying properties, including corrosion-resistance, durability and hardness.

SUBSTANCE/SYNONYMS	CAS NUMBER	FORMULA	ATOMIC/ MOLECULAR WEIGHT
Ammonium dichromate (chromic acid, diammonium salt)	7789-09-5	$(NH_4)_2Cr_2O_7$	252.06
Barium chromate	10294-40-3	$BaCrO_4$	253.33
Calcium chromate (chromic acid, calcium salt; calcium chrome yellow)	13765-19-0	$CaCrO_4$	156.09
Chromium trioxide (chromic acid; chromium anhydride)	1333-82-0	CrO_3	99.99
Lead chromate (chromic acid, lead salt; Chrome Yellow G)	7758-97-6	$PbCrO_4$	328.18
Lead chromate oxide	18454-12-1	Pb_2OCrO_4	546.37
Potassium chromate (chromic acid, dipotassium salt)	7789-00-6	K_2CrO_4	194.20
Potassium dichromate (dichromic acid, dipotassium salt)	7789-50-9	$K_2Cr_2O_7$	294.18
Silver chromate	7784-01-2	Ag_2CrO_4	331.73
Sodium chromate (chromic acid, disodium salt; Caswell No. 757)	7775-11-3	Na_2CrO_4	161.97
Sodium dichromate	10588-01-9	$Na_2Cr_2O_7$	261.97
Strontium chromate (chromic acid, strontium salt)	7789-06-2	$SrCrO_4$	203.61
Zinc chromate (chromic acid, zinc salt; CI Pigment Yellow)	13530-65-9	$ZnCrO_4$	181.97
Zinc chromate hydroxide (basic zinc chromate)	15930-94-6	$Zn_2CrO_4(OH)_2$	280.74
Zinc potassium chromate hydroxide	11103-86-9	$KZn_2(CrO_4)_2(OH)$	418.85
Basic zinc potassium chromate	37300-23-5	$\approx 4\ ZnO \times K_2O \times 4\ CrO_3 \times 3H_2O$	825

(**DFG**, 2012); (**NIOSH**, 2013); (**IPCS**, 2013)

TABLE 1: Commonly used chromium (VI) compounds

SUBSTANCE	DESCRIPTION	MELTING POINT °C	BOILING POINT °C	SOLUBILITY
Ammonium dichromate	Orange	Decomposes at 180	–	Water: 308 g/L (15°C); insoluble in alcohol; slightly soluble in ammonium hydroxide, acetone
Barium chromate		–	–	Water: 2.6 g/L (15°C); soluble in mineral acid
Calcium chromate	Yellow			Water: 22.3 g/L (20°C)
Chromium trioxide	Red	196	Decomposes	Water: 625 g/L (20°C); soluble in alcohol, ether, sulphuric and nitric acids
Lead chromate	Yellow	844	Decomposes	Water: 0.058 mg/L (20°C); soluble in acid, alkali; insoluble in acetic acid
Lead chromate oxide		–	–	Water: Insoluble; Soluble in acid, alkali
Potassium chromate	Yellow	968.3; 975		Water: 629 g/L (20°C); insoluble in alcohol
Potassium dichromate	Red	398	Decomposes at 500	Water: 49 g/L (0°C); 1020 g/L (100°C); insoluble in alcohol
Silver chromate		Decomposes	–	Soluble in ammonium hydroxide, potassium cyanide
Sodium chromate	Yellow	19.92	–	Water: 873 g/L (2°C) ; slightly soluble in alcohol; soluble in methanol
Sodium dichromate	Red		Decomposes at 400	No data; Insoluble in alcohol
Strontium chromate	Yellow	–	–	Water: 1.2 g/L (15°C); Soluble in hydrochloric, nitric, acetic acids, ammonium salts
Zinc chromate	Lemon-yellow	–	–	Water: 78-115 mg/L
Zinc chromate hydroxide				Water: 40 mg/L
Zinc potassium chromate hydroxide				Water: 600-1500 mg/L
Basic zinc potassium chromate				Water: 2500-5000 mg/L

(DFG, 2012); (NIOSH, 2013); (IPCS, 2013)

TABLE 2: Chemical and physical properties

SUBSTANCE	HSNO CLASSIFICATION
Ammonium dichromate	5.1.1B, 6.1B (I), 6.1C (O), 6.1D (D), 6.5A, 6.5B, 6.6A, 6.7A, 6.8A, 6.9A (O), 8.2C, 8.3A, 9.1A (C), 9.1C (F), 9.2B, 9.3B
Chromium trioxide	5.1.1B, 6.1B (I), 6.1B (D), 6.1C (O), 6.5A, 6.5B, 6.6A, 6.7A, 6.8A, 6.9A (O), 8.1A, 8.2B, 8.3A, 9.1A (F), 9.1A (C), 9.2B, 9.3B
Potassium chromate	6.3A, 6.4A, 6.5B, 6.6A, 6.7A, 9.1A (F), 9.1 A (C), 9.1A (A)
Strontium chromate	6.1D (O), 6.7A, 9.1A (F), 9.1 A (C), 9.1A (A)
Sodium chromate	6.1B (I), 6.3A, 6.5B, 6.6A, 6.7A, 6.8A, 8.3A, 9.1A (F), 9.1A (C), 9.1A (A), 9.3A
Sodium dichromate	5.1.1B, 6.1A (I), 6.5A, 6.5B, 6.6A, 6.7A, 6.8A, 8.2C, 8.3A, 9.1A (F), 9.1A (C), 9.2B, 9.3B
Zinc potassium chromate hydroxide	6.1D (O), 6.5B, 6.7A, 9.1A (F)

(All) = overall classification for that endpoint (O) = oral exposure route (D) = dermal exposure route
(I) = inhalation exposure route (A) = algae (C) = crustacean (F) = fish

TABLE 3: Hazard classifications of some commonly used chromium (VI) compounds (EPA, 2017).

3.0
Exposures

Chromium (VI) exposure can occur in various industries, including electroplating, welding and painting, and due to its presence in cement.

Chromium is a relatively common element, occurring naturally in rocks, soil, plants, animals and volcanic dust and gases. The most stable valence states are chromium (0), trivalent chromium (chromium (III)) and hexavalent chromium (chromium (VI)) (IPCS, 2013). Chromium is chiefly found as the trivalent form in nature, with chromium (VI) generally produced by industrial processes (IPCS, 2013; SCOEL, 2004).

The 2013 NIOSH review noted that:

> "Chromium (VI) compounds include a large group of chemicals with varying chemical properties, uses, and workplace exposures. Their properties include corrosion-resistance, durability, and hardness. Workers may be exposed to airborne chromium (VI) when these compounds are manufactured from other forms of chromium (eg the production of chromates from chromite ore); when products containing chromium (VI) are used to manufacture other products (eg chromate-containing paints, electroplating); or when products containing other forms of chromium are used in processes that result in the formation of chromium (VI) as a by-product (eg welding). In the marketplace, the most prevalent materials that contain chromium are chromite ore, chromium chemicals, ferroalloys, and metal. Sodium dichromate is the most common chromium chemical from which other chromium (VI) compounds may be produced. Chromium (VI) compounds commonly manufactured include sodium dichromate, sodium chromate, potassium dichromate, potassium chromate, ammonium dichromate, and chromium (VI) oxide. Other manufactured materials containing chromium (VI) include various paint and primer pigments, graphic arts supplies, fungicides, and corrosion inhibitors." (NIOSH, 2013).

In the United States, the industries in which the largest numbers of workers are exposed to high concentrations of airborne chromium (VI) compounds include electroplating, welding and painting. Dermal exposure to chromium (VI) can also occur, most notably in the construction industry where chromium (VI) is present in cement.

The number of persons exposed or potentially exposed to chromium (VI) compounds in New Zealand is unknown. Statistics New Zealand 2016 data (Statistics New Zealand, 2017) indicate that 76,880 New Zealand workers were working in the areas of:

- building construction
- basic organic chemical manufacturing
- basic inorganic chemical manufacturing
- paint and coatings manufacturing
- metal coating and finishing
- heavy and civil engineering construction
- automotive body, paint and interior repair.

4.0 Health effects of hexavalent chromium

IN THIS SECTION:

The health effects of hexavalent chromium have been investigated.

4.1 Non-cancer

Humans

Effects in humans exposed occupationally to airborne chromium (VI) compounds may include respiratory tract and eye irritation, which may lead to nasal septum ulceration and perforation, and increased incidence of respiratory tract cancer. Exposure to chromium (VI) compounds may also induce asthma (IPCS, 2013).

Occupational exposure by dermal contact to chromium (VI) compounds can result in deeply penetrating ulcers on the skin. Chromium (VI) is a frequent cause of allergic contact dermatitis, which can be a serious and long-term disability (IPCS, 2013).

Accidental or intentional ingestion of high doses of chromium (VI) compounds by humans has resulted in severe respiratory, cardiovascular, gastrointestinal, haematological, hepatic, renal and neurological effects (IPCS, 2013).

The 2004 ACGIH® review noted that the occupational health literature contained evidence that chromium (VI) compounds may cause irritant and allergic contact dermatitis, skin ulcers, and nasal irritation from rhinitis to perforation of the nasal septum. Soluble chromium (VI) compound exposure has been associated with dermatitis in lithographers (McCord et al, 1930; Levin et al, 1959), diesel repair shop workers (Winston and Walsh, 1951), and leather workers (Morris, 1955), while soluble chromates have been linked to 'cement dermatitis" (Engebrigtsen, 1952). Various studies cited indicated that nasal irritation had been observed at concentrations as low as 0.06 mg/m^3. (References cited in ACGIH®, 2004). (ACGIH®, 2004).

The 2004 ACGIH® review also noted that chromium (VI) compounds were associated with kidney damage in workers exposed through damaged skin (Major, 1922; Hunter and Roberts, 1933). (References cited in ACGIH®, 2004).

Animals

Oral exposure of animals to very high doses of chromium (VI) compounds has resulted in gastrointestinal, hepatic, renal, immunological, haematological, neurological, developmental and reproductive effects. Dermal exposure of animals to chromium (VI) compounds has resulted in skin ulcers and allergic response (IPCS, 2013).

Among the effects of oral exposure of rats and mice to drinking-water containing chromium (VI) for 13 weeks or 2 years, were transient anaemia, lesions in the oral cavity and intestines, inflammation in the liver, lymph nodes and pancreas and tumours in the oral cavity in rats and in the small intestine in mice (IPCS, 2013).

4.2 Cancer

Humans

The meta-analyses carried out by Cole and Rodu (2005) and Steenland et al. (1996) clearly show a significantly increased risk of lung cancer in workers exposed to chromium (VI) in chromate (pigment) production and in chrome-plating plants. It is not clear whether exposure to chromium (VI) also contributes to an increase in lung cancer risk where welding is involved. (References cited in DFG, 2012).

In addition, there is evidence of a possibly increased risk of cancer in the region of the nasal epithelium and the nasal sinuses after exposure to chromium (VI) compounds (DFG, 2012).

The 2013 NIOSH review on chromium (VI) compounds based its quantitative risk assessment on several studies and meta-analyses, including that on the Baltimore cohort (the Gibb et al, 2000 study) because it had the greater number of lung cancer deaths, better smoking histories, and a more comprehensive retrospective exposure archive (NIOSH, 2013):

> "Gibb et al. [2000b] conducted a retrospective analysis of lung cancer mortality in a cohort of Maryland chromate production workers first studied by Hayes et al. [1979]. The cohort studied by Hayes et al. [1979] consisted of 2,101 male salaried and hourly workers (restricted to 1,803 hourly workers) employed for at least 90 days between January 1, 1945, and December 31, 1974, who had worked in new and/or old production sites. Gibb et al. [2000b] identified a study cohort of 2,357 male workers first employed between 1950 and 1974. Workers who started employment before August 1, 1950, were excluded because a new plant was completed on that date and extensive exposure information began to be collected. Workers starting after that date, but with short-term employment (ie < 90 days) were included in the study group to increase the size of the low exposure group. The Hayes et al. [1979] study identified deaths through July 1977. Gibb et al. [2000b] extended the follow-up period until the end of 1992, and included a detailed retrospective assessment of Cr(VI) exposure and information about most workers' smoking habits. The mean length of employment was 3.3 years for white workers (n = 1,205), 3.7 years for non-white workers (n = 848), 0.6 years for workers of unknown race (n = 304), and 3.1 years for the total cohort (n = 2,357). The mean follow-up time ranged from 26 years to 32 years; there were 70,736 person-years of observation. The mean cumulative exposures to Cr(VI) were 0.18 mg/m^3-years for non-white employees (n = 848) and 0.13 mg/m3-years for white employees (n = 1,205). The mean exposure concentration was 43 µg/m^3 [Park and Stayner 2006; NIOSH 2005b]."
>
> "Lung cancer mortality ratios increased with increasing cumulative exposure (ie mg CrO_3/m^3-years) – from 0.96 in the lowest quartile to 1.57 (95% CI 1.07–2.20; 5-year exposure lag) and 2.24 (95% CI 1.60–3.03; 5-year exposure lag) in the two highest quartiles. The number of expected lung cancer deaths was based on age-, race-, and calendar year-specific rates for Maryland. Proportional hazard models that controlled for the effects of smoking predicted increasing lung cancer risk with increasing Cr(VI) cumulative exposure (relative risks: 1.83 for second exposure quartile, 2.48 for third exposure quartile, and 3.32 for fourth exposure quartile, compared with first quartile of cumulative exposure; confidence intervals not reported; 5-year exposure lag) [Gibb et al. 2000b]." (References cited in (NIOSH, 2013)).

The 2004 ACGIH® review noted that epidemiological studies on workers exposed to chromium (VI) compounds, mainly water-insoluble compounds were associated with an increase in lung cancer. Studies in animal models supported the evidence that water-insoluble chromium (VI) compounds (eg chromic and zinc chromates) were carcinogenic (Laskin et al, 1969). ACGIH® cited IARC designating all chromates as Group 1, Human Carcinogens (IARC, 1990), and cited IPCS, **ATSDR**, **HSE** and IARC concluding that 'insoluble' chromates are recognised human carcinogens (IPCS, 1988; ATSDR, 1989; HSE, 1989; IARC, 1990). (References cited in ACGIH®, 2004).

The 2004 SCOEL review summarised:

> "The health effects associated with occupational exposure to hexavalent chromium compounds are carcinogenicity (specifically lung cancer), sensitisation, renal toxicity and irritancy, and corrosivity of the skin, respiratory and gastrointestinal tract. Clearly, the most serious of these outcomes in health terms is lung cancer and, given the magnitude of occupational cancer risks shown in some of the earlier epidemiological studies, and given that hexavalent chromium compounds are comprehensively genotoxic, it follows that lung cancer is the critical effect upon which to base any occupational exposure limit. Ideally, it would be preferable to develop lung cancer risk estimates for individual hexavalent chromium compounds (or a few groups of compounds). Unfortunately, the quantity and quality of the epidemiological data are not sufficient to rank, with any confidence, the carcinogenic potencies of the various hexavalent chromium compounds encountered in industry. The available animal carcinogenicity investigations do not provide this missing information. Notwithstanding the dearth of appropriate human studies, the available human and experimental animal data indicate that poorly soluble hexavalent chromium compounds have a lower carcinogenic potency than soluble compounds. Such an effect might be explained be the relatively lower delivery of bioavailably-active chromium ions to the intracellular target in the respiratory epithelium." (SCOEL, 2004)

The 2004 review concluded that:

> "The preferred risk assessment is thus based on a summary of ten published studies (Steenland et al, 1996) and it has been estimated that about 5-28 excess lung cancers will occur in a cohort of 1000 male workers, followed-up from age 20 to age 85 and occupationally exposed to 50 μg/m^3 [50 μg/m^3] of hexavalent chromium until retirement at age 65. The corresponding number of excess lung cancers has been estimated to be 2-14 for an exposure level of 25 μg/m^3, 1-6 for an exposure level of 10 μg/m^3, 0.5-3 for an exposure of 5 μg/m^3 and 0.1-0.6 for and exposure level of 1 μg/m^3." (Reference cited in (SCOEL, 2004)).

The 2004 review concluded that:

> "The available evidence, albeit incomplete, strongly suggests that poorly soluble hexavalent compounds carry a lesser lung cancer risk although the size of such a reduction cannot be quantified. Thus, in establishing occupational exposure limits a pragmatic approach may be appropriate. As an example, an exposure limit of 50 μg/m^3 of hexavalent chromium may well provide adequate protection for workers exposed to poorly soluble hexavalent chromium compounds but, on the basis of the risk assessments ... consideration could be given to setting exposure limits at 25 μg/m^3 or 10 μg/m^3 for other hexavalent chromium compounds." (SCOEL, 2004).

Animals

Chromium (VI) has also been shown to be genotoxic in in vivo and in vitro tests (IPCS, 2013).

The NIOSH 2013 review on chromium (VI) compounds concluded that the body of animal studies supported the classification of chromium (VI) compounds as occupational carcinogens (NIOSH, 2013):

> "The few chronic inhalation studies available demonstrate the carcinogenic effects of Cr(VI) compounds in mice and rats [Adachi et al. 1986, 1987; Glaser et al. 1986]. Animal studies conducted using other respiratory routes of administration have also produced positive results with some Cr(VI) compounds. Zinc chromate and calcium chromate produced a statistically significant ($P < 0.05$) number of bronchial carcinomas when administered via an intrabronchial pellet implantation system [Levy et al. 1986]. Cr(VI) compounds with a range of solubilities were tested using this system. Although soluble Cr(VI) compounds did produce tumors, these results were not statistically significant. Some lead chromate compounds produced squamous carcinomas, which although not statistically significant may be biologically significant because of the historical absence of this cancer in control rats".
>
> "Steinhoff et al. [1986] administered the same total dose of sodium dichromate either once per week or five times per week to rats via intratracheal instillation. No increased incidence of lung tumors was observed in animals dosed five times weekly. However, in animals dosed once per week, a statistically significant ($P < 0.01$) tumor incidence was reported in the 1.25 mg/kg exposure group. This study demonstrates a dose-rate effect within the constraints of the experimental design. It suggests that limiting exposure to high Cr(VI) levels may be important in reducing carcinogenicity. However, quantitative extrapolation of these animal data to the human exposure scenario is difficult".
>
> "Animal studies conducted using nonrespiratory routes of administration have also produced positive results with some Cr(VI) compounds [Hueper 1961; Furst 1976]. These studies provide another data set for hazard identification".
>
> "**IARC** [2012] concluded "there is sufficient evidence in experimental animals for the carcinogenicity of chromium (VI) compounds".
>
> "Molecular toxicology studies provide support for classifying Cr(VI) compounds as occupational carcinogens. They demonstrate the cy-totoxic and genotoxic effects associated with carcinogenesis of Cr(VI) compounds." (References cited in NIOSH, 2013).

4.3 Absorption, Distribution, Metabolism and Excretion

The ICPS provide the following summary:

> "The toxicokinetics of a given chromium compound depends on the valence state of the chromium atom and the nature of its ligands. Absorption of chromium(VI) compounds is higher than that of chromium(III) compounds via all exposure routes. This is because the chromate anion can enter cells through cell membrane anion channels, whereas absorption of chromium(III) compounds is via passive diffusion and phagocytosis. Absorption of inhaled chromium compounds takes place in the lung via transfer across cell membranes and in the gastrointestinal tract from particles cleared from the lungs. Absorption after oral exposure in humans is approximately 2–8% for chromium(VI) as potassium chromate or dichromate. Absorption after oral exposure to chromium(VI) is lowered by reduction to chromium(III) in the acidic conditions of the stomach".

> "Once in the blood, chromium compounds are distributed to all organs of the body. Particles containing chromium can be retained in the lung for years after occupational exposure. Chromium(VI) is unstable in the body and is reduced to chromium(V), chromium(IV) and ultimately to chromium(III) by many substances, including ascorbate and glutathione. It is believed that the toxicity of chromium(VI) compounds results from damage to cellular components during this process (eg generation of free radicals). There is also the potential for interaction with deoxyribonucleic acid (DNA), causing structural DNA damage".
>
> "Absorbed chromium is excreted primarily in urine, with the half-time for excretion of chromium orally administered as potassium dichromate estimated to be approximately 40 hours in humans. Hair and nails are minor pathways of excretion." (IPCS, 2013)

4.4 DFG MAK evaluation and rationale

The 2012 **MAK** (Maximale Arbeitsplatz-Konzentration, translated as maximum workplace concentration) review summarised the toxicological and epidemiological database:

> "Chromium(VI) compounds cause lung cancer in humans. In several epidemiological studies of workers at chromate production plants and chrome-plating plants, chromium(VI) compounds were shown to cause an increased relative risk of mortality from lung cancer. Animal studies confirm the carcinogenic effects of chromium(VI) compounds".
>
> "In a small study with workers from factories producing lead chromate pigment, an increased risk of lung cancer was found in one subgroup for workers with lead poisoning. The subcutaneous and intramuscular administration of poorly soluble lead chromate led in rats to a significant increase in the incidence of rhabdomyosarcomas and fibrosarcomas at the site of injection. Furthermore, after intramuscular injection of lead chromate in rats, in addition to local tumours renal carcinomas were also induced".
>
> "Chromium(VI) compounds were found to be genotoxic in numerous studies with bacteria and mammalian cells. In mice, intraperitoneal injection produces micronuclei in the bone marrow and dominant lethal mutations in the germ cells".
>
> "Chromium(VI) compounds can be absorbed by inhalation, ingestion or through the skin. Under physiological conditions, they are available in the form of a mixture of chromate and hydrogen chromate ions. These anionic compounds are easily transported into the cells via non-specific anion channels".
>
> "The reduction of chromium(VI) to chromium(III) takes place via chromium(V) and chromium(IV), during which process radical oxygen species and sulfur compounds are produced".
>
> "So-called chromium ulcers occur in humans after repeated inhalation. These are found particularly in the nasal septum, and may progress to cause septal perforation. Repeated ingestion of chromium doses of about 0.57 mg/kg body weight and [per] day results in oral ulcers, diarrhoea, stomach pains, digestive disorders, vomiting, leukocytosis and an increased number of immature neutrophilic granulocytes".

> "Chromates are irritating to corrosive on the human skin. Chrome ulcers are formed on the skin of workers exposed to high concentrations of sodium chromate, potassium dichromate or ammonium dichromate. Chromates are highly irritating to the conjunctiva".
>
> "In humans and in animal studies, chromium(VI) compounds, with the exception of lead and barium chromate, can induce skin sensitization".
>
> "Chromium(VI) compounds are embryotoxic and foetotoxic, and have toxic effects on postnatal development." (DFG, 2012).

The MAK review concluded that:

- All chromium(VI) compounds must be considered as carcinogenic in humans; and classified in Carcinogen Category 1.
- Chromium(VI) compounds must be regarded as genotoxic, and classified in Category 2 for Germ Cell Mutagens.
- Chromium(VI) compounds, with the exception of barium chromate, lead chromate and similarly poorly soluble zinc chromates, should be designated with 'Sh', but not with 'Sa'; (not barium and lead chromates) ['Sh' designation indicates substances with the potential to cause skin sensitisation; 'Sa' designation indicates substances with the potential to cause airway sensitisation].
- Soluble chromium(VI) compounds pose a danger of dermal penetration with exposure to more highly concentrated solutions, and should be designated with an 'H' (not barium, lead, strontium and zinc chromates) – 'H' designation indicates substances where dermal absorption can contribute significantly to the toxicity profile.
- As chromium(VI) compounds are classified in Carcinogen Category 1, they are not assigned to a Pregnancy Risk Group. (DFG, 2012)

No MAK value, occupational exposure limit (**OEL**) or Peak Limitation values were recommended due to the Carcinogen Category 1 classification. A BAR (Biologischer Arbeitsstoff-Referenzwert – biological reference value) of 0.6 µg/L urine was recommended.

5.0 Exposure standards and guidance values in use around the world

IN THIS SECTION:

Table 5 below shows the chromium (VI) exposure standards from around the world.

This information is published by the Institute for Occupational Safety and Health of the German Social Accident Insurance (Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung, 2017).

JURISDICTION OR ADVISORY BODY	8-HOUR LIMIT VALUE (mg/m^3)	SHORT-TERM LIMIT VALUE (mg/m^3)
Australia	0.05	
Austria	0.05[1]	0.2[1]
Belgium	0.05	
Canada – Ontario	0.05	
Denmark	0.005	0.01
Finland	0.05	
Hungary		0.05
Ireland	0.05[2]	
Japan	0.05	
New Zealand	0.05	
Singapore	0.05[2] 0.01[3]	
South Korea	0.05[2] 0.01[3]	
Spain	0.01[2] 0.05[3]	
Sweden	0.005[4]	0.015[5]
Switzerland	0.005[1]	
The Netherlands	0.025	0.05
USA – NIOSH	0.001[6]	
USA – OSHA	0.005	
UK	0.05	
ACGIH®	0.05[2] 0.01[3]	

TABLE 4: Exposure standards for chromium (VI) from around the world

It is noted that the only organisations who provide information on how and why they set occupational exposures standards on chromium (VI) compounds are NIOSH, DFG, ACGIH® and SCOEL.

[1] Inhalable aerosol.
[2] Water soluble.
[3] Water insoluble.
[4] Total aerosol.
[5] 15 minute average value.
[6] 10 hour TWA.

5.1 New Zealand

WorkSafe's WES for chromium (VI) compounds (water soluble and water insoluble) of 0.05 mg/m³ has been unchanged since adoption in 1994.

The toxicological database reviewed above indicates that occupational exposures to chromium (VI) compounds are associated with:

- increased risks of lung cancer
- non-malignant respiratory effects, including irritated, ulcerated, or perforated nasal septa and other potential adverse health effects
- dermal effects including skin irritation, skin ulcers, skin sensitisation, and allergic contact dermatitis.

The latest reviews by NIOSH (2013) and DFG (2012) concluded that the available scientific evidence supports the inclusion of all chromium (VI) compounds in the WES-TWA to reduce workers' risk of lung cancer associated with occupational exposure.

NIOSH and DFG concluded that the increased risk of lung cancer was the most significant adverse effect of occupational exposure to chromium (VI) compounds; the putative mechanism was predominantly genotoxic; and hence without a threshold.

5.2 ACGIH®

The 2004 ACGIH® review recommended that chromium (VI) compounds be grouped into two **TLVs®** as described in Table 5:

GROUP	INCLUDES	TLV-TWA	REASON FOR TLV-TWA	HUMAN CARCINOGEN NOTATION
Water-soluble hexavalent chromium (VI) compounds	Chromic acid, chromic acid anhydride, mono- and di-chromates of sodium, potassium, ammonium, lithium, caesium, and rubidium.	0.05 mg/m³ (as Cr)	To minimise the potential for respiratory tract irritation and cancer, dermatitis, and possible kidney damage.	A1, Confirmed Human Carcinogen notation
Insoluble chromium (VI) compounds	Zinc chromate, calcium chromate, lead chromate, barium chromate, strontium chromate, and sintered chromium trioxide.	0.01 mg/m³ (as Cr)	To minimise the potential for respiratory tract irritation and cancer, and dermal irritation.	A1, Confirmed Human Carcinogen notation

TABLE 5: Grouping of chromium compounds (ACGIH®, 2004)

ACGIH® concluded that there were insufficient data to recommend **Skin** or **SEN** notations, or a **TLV-STEL** (ACGIH®, 2004).

5.3 NIOSH

NIOSH recommended that airborne exposure to all chromium (VI) compounds be limited to a concentration of 0.2 µg/m³ Cr(VI) (0.0002 mg/m³) for an 8-hour TWA exposure, during a 40-hour workweek. The recommended exposure limit (**REL**) is intended to reduce workers' risk of lung cancer associated with occupational exposure to chromium (VI) compounds over a 45-year working lifetime.

The NIOSH risk assessment estimates an excess lifetime risk of lung cancer death of approximately 1 per 1,000 workers at the **REL** of 0.2 µgCr(VI)/m³. The REL for chromium (VI) compounds is expected to also reduce the non-malignant respiratory effects, including irritated, ulcerated, or perforated nasal septa and other potential adverse health effects. The available scientific evidence supports the inclusion of all chromium (VI) compounds into this recommendation (NIOSH, 2013).

NIOSH also recommended that dermal exposure to chromium (VI) compounds be prevented in the workplace to reduce adverse dermal effects including skin irritation, skin ulcers, skin sensitization, and allergic contact dermatitis (NIOSH, 2013).

5.4 DFG

No MAK Value OEL or Peak Limitation were recommended due to the Carcinogen Category 1 classification. A BAR (biological reference value) of 0.6 mg/L urine was recommended (DFG, 2012).

All chromium (VI) compounds should be classified in Carcinogen Category 1; Germ Cell Mutagen Category 2; 'Sh' (with some exceptions); and, 'H' (with some exceptions) (DFG, 2012).

Carcinogen designations are given when evidence indicates that the substance does, or may cause cancer:

- Category 1 indicates substances that cause cancer in humans and can be assumed to contribute to cancer risk.
- 'Germ Cell Mutagen' designations are given when evidence indicates that the substance does, or may cause germ cell mutations, and
- Category 2 indicates that increases in the mutant frequency has been observed in the progeny of exposed animals.
- 'Sh' designation indicates substances with potential to cause skin sensitisation.
- 'H' designation indicates substances where dermal absorption can contribute significantly to the toxicity profile, when observance of the MAK value may be insufficient (DFG, 2016).

5.5 SCOEL

The 2004 SCOEL review did not make a specific limit recommendation, but noted the following excess risk of lung cancer (SCOEL, 2004):

EXCESS LUNG CANCER CASES PER 1000 MALE WORKERS	EXPOSURE (WORKING LIFETIME) TO A RANGE OF CHROMIUM (VI) COMPOUNDS
5-28	50 µg/m³
2-14	25 µg/m³
1-6	10 µg/m³
0.5-3	5 µg/m³
0.1-0.6	1 µg/m³

TABLE 6: SCOEL risk of lung cancer

6.0 Analytical methods for the assessment of hexavalent chromium

A common practice in New Zealand to measure airborne chromium (VI) is using a modification of NIOSH Method 7600 (NIOSH, 1994).

Using this method, an 8 to 400 litre air sample is collected onto a PVC membrane filter using a sampling train set at a flow rate of 1 to 4 litres of air per minute. Following exposure of the filter for an appropriate period of time, the filter is extracted using alkaline solution, and after addition of a developing reagent, analysis is undertaken using visible spectrophotometry at 540 nm. The detection limit of this method has been quoted as 0.01 µg per sample for chromium (VI).

This would allow a minimum concentration of 0.000025 mg of chromium (VI) per m^3 of air to be quantified over a collection period of 400 minutes. The sampling time and/or flow rate can be adjusted within the guidelines of the method.

7.0
Discussion and recommendation

WorkSafe considers its current WES-TWA of 0.05 mg/m^3 for chromium (VI) compounds (water soluble and water insoluble) to be inadequate to protect workers exposed to chromium (VI), based on the information presented above.

It is proposed that WorkSafe lower the WES-TWA for inhalable chromium (VI) to 0.0002 mg/m^3.

The proposed inhalable WES-TWA value is based on the available toxicological and epidemiological database, and risk assessments particularly that by NIOSH 2013 indicating that 0.0002 mg /m^3 of Cr(VI) posed an excess lifetime risk of lung cancer death of approximately 1 per 1,000 workers. This WES-TWA value is expected to limit the probability for increased risks of lung cancer in chromium (VI)-exposed workers, and should also be protective for non-malignant respiratory and dermal effects.

It is further proposed that WorkSafe:

- retain the current 'sen' notation for chromium VI compounds with some exceptions (barium chromate, lead chromate and poorly soluble zinc chromates) and
- introduce a 'skin' notation for soluble chromium VI compounds.

Appendices

IN THIS SECTION:

Appendix 1: Glossary

TERM	MEANING
ACGIH®	The American Conference of Governmental Industrial Hygienists (ACGIH®) is a 501(c)(3) charitable organisation, established in 1938, that advances occupational and environmental health. Examples of this include their annual edition of the *TLVs® and BEIs® book* and *Guide to Occupational Exposure Values*.
ASTDR	Agency for Toxic Substances and Disease Registry is part of the United States Department of Health and Human Services and is responsible for specific functions concerning the effect on public health of hazardous substances in the environment. These functions include public health assessments of waste sites, health consultations concerning specific hazardous substances, health surveillance and registries, response to emergency releases of hazardous substances, applied research in support of public health assessments, information development and dissemination, and education and training concerning hazardous substances.
DFG	Deutsche Forschungsgemeinschaft (German Research Foundation), the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Federal Republic of Germany. The science-based MAK values are recommended to the German Minister of Labour and Social Affairs for possible adoption under the German Hazardous Substances Ordinance.
HSE	United Kingdom Health and Safety Executive.
HSNO	Hazardous Substances and New Organisms Act, New Zealand.
IPCS	International Programme on Chemical Safety – a World Health Organisation Programme.
MAK	Maximale Arbeitsplatz-Konzentration (trans. maximum workplace concentration). A German term.
mg	Milligram or one thousandth of a gram.
mg/m3	Milligrams of substance per cubic metre of air.
NIOSH	The National Institute for Occupational Safety and Health (NIOSH) is the United States federal agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness. NIOSH is part of the Centers for Disease Control and Prevention (CDC) within the U.S. Department of Health and Human Services.
OEL	Occupational Exposure Limit.
REL	Recommended Exposure Limit – an OEL that has been recommended by NIOSH to the Occupational Safety and Health Administration (OSHA) for adoption as a permissible exposure limit.
SCOEL	The Scientific Committee on Occupational Exposure Limits is a committee of the European Commission, established in 1995 to advise on occupational health limits for chemicals in the workplace within the framework of Directive 98/24/EC, the chemical agents directive, and Directive 90/394/EEC, the carcinogens at work directive.
sen	A substance that can 'sensitise' the skin or respiratory system, inducing a state of hypersensitivity to it, so that on subsequent exposures, an allergic reaction can occur (which would not develop in non-sensitised individuals). It is uncommon to become sensitised to a compound after just a single reaction to it. A New Zealand term.
SEN	A notation indicating the subject substance is a sensitiser. DSEN and RSEN are used in place of SEN when specific evidence of sensitisation by the dermal or respiratory route, respectively, is confirmed by human or animal data. An ACGIH® term.
Skin	A notation indicating the potential for significant contribution to the overall exposure, by the cutaneous route, including mucous membranes and the eyes, by contact with vapours, liquids and solids. An ACGIH® term.
TLV®	Threshold Limit Value (see TLV-C, TLV-STEL and TLV-TWA below). An ACGIH® term.
TLV-STEL	TLV-Short-Term Exposure Limit; a 15 minute TWA exposure that should not be exceeded at any time during a work day, even if the 8-hour TWA is within the TLV-TWA. An ACGIH® term.
TLV-TWA	TLV – Time-Weighted Average; the TWA concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed to, day after day, for a working lifetime without adverse effect. An ACGIH® term.

TERM	MEANING
WES	Workplace Exposure Standard – WESs are values that refer to the airborne concentration of substances, at which it is believed that nearly all workers can be repeatedly exposed to, day after day, without coming to harm. The values are normally calculated on work schedules of five shifts of eight hours duration over a 40 hour week. A New Zealand term.
WES-TWA	The average airborne concentration of a substance calculated over an eight-hour working day. A New Zealand term.
µg	Microgram, or millionth of a gram.

Appendix 2: References

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Notes

Disclaimer

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