

CHUBB®

**Chubb Global
Risk AdvisorsSM**
Advisory Series

New Requirements
and Methods for
Chromium Sampling
and Analysis



Due to recent significant reductions in the Threshold Limit Values (TLV) for hexavalent chromium, which was reduced to 0.2 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) as a time weighted average (TWA) as well as a new TLV-TWA for chromium III compounds of 3 $\mu\text{g}/\text{m}^3$, the sampling approach for these compounds must be changed to determine if overexposures exist under the new standard.

In 2010, the Occupational Safety and Health Administration (OSHA) reduced the permissible exposure limit (PEL) for hexavalent chromium from 100 $\mu\text{g}/\text{m}^3$ to 5 $\mu\text{g}/\text{m}^3$ as a time weighted average (TWA). This led to a significant effort by industry to identify and quantify exposures, risk and compliance. Most employers have taken samples and implemented controls so that many companies now have working environments that meet the mandated PEL of 5 $\mu\text{g}/\text{m}^3$ level. In fact, many employers have reduced exposures as low as 1/10th of the PEL [0.5 $\mu\text{g}/\text{m}^3$] to further reduce worker risk. However, this recent TLV change suggests that the protective concentration for employee exposure to hexavalent chromium should be kept below 0.2 $\mu\text{g}/\text{m}^3$ TWA and 0.5 $\mu\text{g}/\text{m}^3$ so as not to exceed the ceiling value.

Sampling for hexavalent chromium can be accomplished using the existing OSHA ID 215 method. Samples are collected on a PVC filter and need to be sent to the lab overnight for analysis. Using this method ESIS Environmental Health Laboratory (EHL) can obtain reporting limits of half the new TLV/STEL if sample volumes of 100 liters of air for a TWA sample or 40 liters of air for a short-term exposure limit (STEL) sample are obtained.

Both of these chromium TLVs are based upon the inhalable fraction of the airborne contaminant, which would require the person sampling to use an IOM sampling device to obtain the inhalable fraction or to assume that a sample collected for total dust is equivalent. OSHA continues to collect total dust samples as it monitors against its PELs, which specify samples be collected for total dust. In the case of welding samples where larger particles are unlikely to be generated, use of either the total or inhalable collection technique should yield similar results. Grinding operations are more likely to generate a variety of particle sizes, so size selective sampling should produce some variations based upon the type of sampling performed.

Until recently chromium metal and chromium III compounds shared a TLV (500 $\mu\text{g}/\text{m}^3$ TWA), and the same method was used for the collection and analysis of these compounds. However, samples were analyzed and reported as total chromium. In the future chrome metal and chromium III compounds will have to be sampled separately if results are to be compared to their TLVs. In response, to the specific TLV for chromium III compounds, Chubb Global Risk Advisor's Environmental Health Laboratory (CGRA EHL) has developed an in-house analytical method to collect and analyze chromium III compounds. The method

is based on collection using a PVC filter followed by extraction and subsequent analysis by ion chromatography and post-column derivatization in a manner similar to that which is used by OSHA ID 215. We recommend a minimum 1300 liter air volume for chromium III sampling so that we can report an air concentration that is less than 1/2 the TLV.

Processes where hexavalent chromium and chromium III compounds can coexist would be manufacturing and welding of stainless steel, plating operations and tanning operations. Chromium III compounds would also be present if any of the compounds shown as Chromium III below are being used (see Table I¹). Physical and Chemical Properties of Chromium and Compounds are also listed below (Table II²).

Both Cr (VI) and Cr (III) can be sampled on the same PVC filter, but CGRA EHL will not be able to reference the OSHA ID215 method for hexavalent chromium as required by OSHA, so we suggest in most cases that you collect side by side PVC filters and request one for chromium III and one for hexavalent chromium. If you also want to know the quantity of chromium metal you would need to collect an additional sample on an MCE filter. Please call the lab at 800-243-4903 for sampling or analytical questions, to discuss options, or for additional information or advice.

1. Toxicological Profile for Chromium. Wilbur S, Abadin H, Fay M, et al.; Atlanta (GA): Agency for Toxic Substances and Disease Registry (US); 2012 Sep.; www.ncbi.nlm.nih.gov/books/NBK158859/; accessed 2/7/2018

2. Ibid

Table 1: Chromium Compounds Commonly Used in Industry (U.S. NIOSH, 2013)

Chemical Name	Synonyms	CAS Number	Chemical Formula	Chemical Structure
Chromium(0)	Chrome, Chrom (Ger)	7440-47-3	Cr	Metallic element
Chromium(III)	Acetic acid, chromium salt; Chromic acetate, hydrate	2503-82-5	$\text{Cr}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$	
Chromium(III) nitrate nonahydrate	Nitric acid, chromium(III) salt, nonahydrate; Chromium nitrate, nonahydrate	7789-02-8	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	
Chromium(III) chloride	Chromium trichloride; Chromic Chloride	10025-73-7	CrCl_3	
Chromium(III) chloride, hexahydrate	Hexaaquachromium(III) chloride	10060-12-5	$\text{Cr}(\text{Cl})_3 \cdot 6\text{H}_2\text{O}$	
Chromite, chromium(III)	Chromite ore; Chromite homogeneous mineral; Chromite (mineral)	1308-31-2	FeCr_2O_4	
Chromium(III) oxide	Chromium sesquioxide; Dichromium trioxide; Chromic oxide	1308-38-9	Cr_2O_3	
Chromium(III) phosphate	Chromium orthophosphate; Phosphoric acid, chromium(III) salt; Amaudon's Green	7789-04-0	CrPO_4	
Chromium(III) Sulfate	Sulfuric acid, chromium (III) salt; Chromatin B	10101-53-8	$\text{Cr}_2(\text{SO}_4)_3$	
Sodium chromite, chromium(III)	None	12314-42-0	NaCrO_2	NaO-Cr=O
Chromium hydroxide sulfate, chromium(III)	Chromium hydroxide sulfate $[\text{Cr}(\text{OH})(\text{SO}_4)]$; Basic chromium sulfate	12336-95-7	CrOHSO_4	$(\text{CrOH})^{2+} \text{O}^- \text{S}(\text{O})_2 \text{O}^-$
Chromium(III) picolinate	CrPic; Chromium 2-pyridine-carboxylate; Chromium tris(picinato); Picolinic acid, chromium(III)salt	14639-25-9	$\text{Cr}_{18}\text{H}_{12}\text{CrN}_3\text{O}_6$	
Ammonium dichromate, chromium(VI)	Chromic acid, diammonium salt	7789-09-5	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	

Table 1: Chromium Compounds Commonly Used in Industry (U.S. NIOSH, 2013)
(continued)

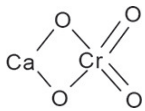
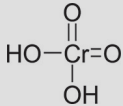
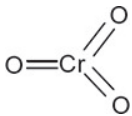
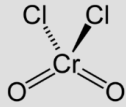
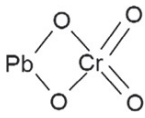
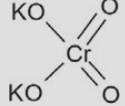
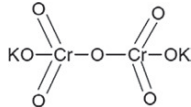
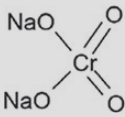
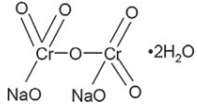
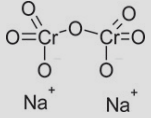
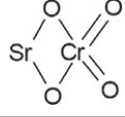
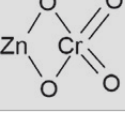
Chemical Name	Synonyms	CAS Number	Chemical Formula	Chemical Structure
Calcium chromate, chromium(VI)	Chromic acid, calcium salt; Calcium chrome yellow	13765-19-0	CaCrO ₄	
Chromic acid, chromium(VI)	Chromic(VI) acid; Acid chromique	7738-94-5	H ₂ CrO ₄	
Chromium(VI) trioxide	Chromic acid, chromium anhydride	1333-82-0	CrO ₃	
Chromyl chloride	Chromium dioxychloride; Chromium oxychloride	14977-61-8	CrO ₂ Cl ₂	
Lead chromate, chromium(VI)	Chromic acid, lead salt	7758-97-6	PbCrO ₄	
Potassium chromate, chromium(VI)	Chromic acid, dipotassium salt	7789-00-6	K ₂ CrO ₄	
Potassium dichromate, chromium(VI)	Chromic acid, dipotassium salt	7778-50-9	K ₂ Cr ₂ O ₇	
Sodium chromate, chromium(VI)	Chromic acid, disodium salt; Caswell No. 75	7775-11-3	Na ₂ CrO ₄	
Sodium dichromate, dihydrate, chromium(VI)	Chromic acid, disodium salt, Dihydrate	7789-12-0	Na ₂ Cr ₂ O ₇ • 2H ₂ O	
Sodium dichromate, chromium(VI)	Chromic acid, sodium salt (1:2)	10588-01-9	Na ₂ Cr ₂ O ₇	
Strontium chromate, chromium(VI)	Chromic acid, strontium salt	7789-06-2	SrCrO ₄	
Zinc chromate, chromium(VI)	Chromic acid, zinc salt	13530-65-9	ZnCrO ₄	

Table 2 Physical and Chemical Properties of Chromium and Compounds (U.S. NIOSH, 2013)

Chemical Name	MW	Physical State	Color	MP	BP	Density at 20°C	Solubility	
							In Water at 20°C	In Organic Solvent
Chromium(o)	52.0	Solid	Steel-gray	1900°C	2642°C	7.14	Insoluble	Insoluble
Chromium(III) Acetate, monohydrate	229.1	Solid	Gray-green, blue-green	—	—	—	Soluble	45.4 g/L in methanol (15°C) 2 g/L in acetone (15°C)
Chromium(III) nitrate, nonahydrate	400.2	Solid	Purple or violet	60°C	100°C decomposes	—	Soluble	Soluble in ethanol and acetone
Chromium(III) chloride	158.4	Solid	Purple or violet	1150°C	1300°C decomposes	2.87	Sparingly soluble	Insoluble in cold water, acetone, ether, and methanol
Chromium(III) chloride, hexahydrate	266.5	Solid	Violet	83°C	—	1.76	585 g/L	Soluble in ethanol
Chromite, chromium(III)	223.84	Solid	Brown-black	—	—	4.97	Insoluble	—
Chromium(III) oxide	152.0	Solid	Green	2435°C	3000°C	5.22	Insoluble	Insoluble in ether
Chromium(III) phosphate	147.0	Solid	Gray-brown to black	>1800°C	—	2.94	Insoluble	Insoluble in alcohol, acetone
Chromium(III) Sulfate	392.2	Solid	Violet, red, peach	—	—	3.01	Insoluble	Soluble in alcohols
Sodium chromite, chromium(III)	106.98	—	—	—	—	—	—	—
Chromium hydroxide sulfate, chromium(III)	165.1	Solid	Green powder	>900°C	—	1.25	2000 g/L	—

Table 2: Physical and Chemical Properties of Chromium and Compounds (U.S. NIOSH, 2013)
(continued)

Chemical Name	MW	Physical State	Color	MP	BP	Density at 20°C	Solubility	
							In Water at 20°C	In Organic Solvent
Chromium(III) picolinate	418.3	Crystal	Ruby red	—	—	—	1 ppm	>6 g/L in DMSO
Chromium(VI) oxide	84.0	Solid	Brown-black	300°C decomposes		—	Insoluble	—
Ammonium dichromate, chromium(VI)	252.1	Solid	Orange	180°C decomposes		2.15	2670 g/L	Soluble in alcohols; Insoluble in acetone
Calcium chromate, chromium(VI)	156.1	Solid	Yellow	—	—	2.89	22.3 g/L	—
Chromic acid, chromium(VI)	118.0	Solid	Dark red-purple	196°C decomposes		1.67-2.82	1000 g/L	Soluble in alcohol; mineral acids
Chromium(VI) trioxide	100.0	Solid	Red	197°C decomposes		2.70	Soluble	Soluble in acetic acid, acetone
Chromyl chloride	154.9	Liquid	Opaque, dark, blood-red liquid at room temp.	-96.5°C	117°C	1.91	Reacts vigorously	Reacts vigorously with water; fumes on contact with water vapor, to form Cr(VI) trioxide, hydrochloric acid, Cr(III) chloride and Cl ₂ . Soluble in dichloromethane, carbon tetrachloride, carbon disulfide

Table 2 continues on page 7

Table 2: Physical and Chemical Properties of Chromium and Compounds (U.S. NIOSH, 2013)
(continued)

							Solubility	
Chemical Name	MW	Physical State	Color	MP	BP	Density at 20°C	In Water at 20°C	In Organic Solvent
Lead chromate, chromium(VI)	323.2	Solid	Yellow	844°C decomposes		6.12	Insoluble	Insoluble in acetic acid and ammonia; soluble in dilute nitric
Potassium chromate, chromium(VI)	194.2	Solid	Yellow	975°C	—	2.73	629 g/L	Insoluble in alcohol
Potassium dichromate, chromium(VI)	294.2	Solid	Red	389° C	De-composes at 500°	2.68	49 g/L	Insoluble in ethanol, acetone
Sodium chromate, chromium(VI)	162.0	Solid	Yellow	792° C	—	2.71-2.74	873 g/L	Soluble in methanol
Sodium dichromate, dihydrate, chromium(VI)	298.0	Solid	Red	357° C	De-composes at 400°	2.52	2300 g/L	Insoluble in ethanol
Sodium dichromate, chromium(VI)	261.97	Crystal	Orange-red	357° C	De-composes at 400°	2.35	1870 g/L	Soluble in methanol
Strontium chromate, chromium(VI)	203.6	Solid	Yellow	—	—	3.90	Insoluble	Insoluble in acetone
Zinc chromate, chromium(VI)	182.0	Solid	Lemon-yellow	3.40	—	—	Insoluble	Insoluble in acetone
Solubility in Water (U.S. OSHA, 2006)								
Insoluble	<0.01 g/L							
Sparingly soluble	0.01 g/L - 500 g/L							
Soluble	>500 g/L							

Tables 1 and 2 are from Toxicological Profile for Chromium. Wilbur S, Abadin H, Fay M, et al.; Atlanta (GA): Agency for Toxic Substances and Disease Registry (US); 2012 Sep.; www.ncbi.nlm.nih.gov/books/NBK158859/; accessed 2/7/2018