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Solid and liquid state speciation of chromium of relevance for health

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Abstract

The chemical form (chemical speciation) of chromium (Cr) is important for human health. Hexavalent Cr (Cr^{VI}), present as oxyanions in water, is of great concern even at trace levels. Here, we briefly describe and discuss common and additional liquid state (often standardized) and solid state Cr speciation methods for typical samples of health concerns. This review covers common standardized, extraction-based liquid state methods and various solid state Cr speciation methods. Liquid state methods include chromatography, colorimetric methods, mass spectrometry, and electrochemical methods, with widely varying detection limit ranges to accommodate all sample needs. The most sensitive liquid state method can detect trace amounts of Cr^{VI} in the nanograms per litre range. Colorimetric methods can be used both for the liquid and solid state and are the simplest methods without the need for a laboratory or equipment. Other solid state methods include vibrational spectroscopy, electrochemical methods, and various laboratory- or synchrotron-based methods: X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and X-ray diffraction. No method is perfect on its own, and we therefore recommend best practices, the investigation of potential interfering agents, and validating the method with another method. However, the largest threat to accurate Cr speciation-based hazard assessments is the dynamic change of Cr speciation in a potential exposure scenario or during sample preparation for the analytical method. To avoid wrong conclusions, we recommend considering the Cr chemistry, the sample chemistry, and the method-specific interferences and detection limits.

Key words: Cr(VI), hexavalent chromium, toxicity, characterization, analytical

1. Introduction

Chromium (Cr) is a technologically and nutritionally important element; however, depending on its chemical form (speciation), it can range from toxic to useful.[1] It is hard to find other elements that can be found both on most countries' chemical hazards lists and in nutritional supplements. Because the chemical speciation of Cr is so important to identify, analytical chemists and materials scientists have developed numerous methods to determine it in aqueous solutions, various materials, consumer products, and environmental sources such as nanoparticles from fly ash or welding fume.[2,3]

However, many relevant samples are difficult to analyze, and the Cr speciation can change dynamically during storage, transport, and sample preparation. This has resulted in many chemical and legal debates on how to develop best practices and how to interpret analytical results that might not necessarily reflect the state of the sample under its relevant exposure condition. Exposure is here defined in the way that is common within regulatory toxicology: an organism, environment, or human body (or part of it) is exposed to the material/chemical in question, which potentially could cause harm. In the case of hexavalent Cr (Cr^{VI}), the route of exposure is most often skin exposure, inhalation, or ingestion. From a chemical perspective, an exposure scenario is a dynamically changing environment (e.g., rapidly changing pH and protein concentration), which impacts the speciation of Cr. Except in a few cases, the final chemical form of Cr in the human body is always trivalent Cr (Cr^{III}). However, this does not mean that exposure to Cr^{VI}, even if short-lived, is harmless. Human health effects of Cr^{VI} exposure are well-documented and include various cancer types, reproductive health, and skin allergy.[1,4,5] Most importantly, Cr^{VI} also increases the risk of actual uptake (bioavailability).[5] For example, there was a significantly decreased amount of detected Cr in the urine of cement workers when they were exposed to Cr^{III} compared with Cr^{VI} in cement through dermal exposure.[6]

The dynamic nature of Cr speciation makes it difficult to use traditional analytical chemistry methods to determine the Cr speciation in a sample. For example, extraction methods might change the Cr speciation that existed in the solid state as part of a solid sample.[7,8] Another reason for the need for continued analytical developments in this field is the increasing regulatory pressure around the world during the past decades to analyze trace amounts of Cr^{VI} in complex samples. This mini-review gives an overview of solid state and liquid state Cr speciation methods, their common pitfalls, and precautions to preserve the Cr speciation as initially in the sample. This mini-review also discusses a few examples of relevance for human health, including skin contact with chromated steels (treated with Cr^{VI} as surface treatment), inhalation of Cr^{VI}-containing welding fume nanoparticles, and skin contact with Cr-tanned leather and cement.

2. Some features of chromium speciation used in analytical methods

Two main distinguishing factors are used in most chromium speciation methods for both solid and liquid state chromium speciation: a difference in oxidation state and a difference in charge. In the solid state, the difference in oxidation state, which in this mini-review is denoted with superscript Roman numerals, such as Cr^{III} and Cr^{VI}, can be probed for solid state materials using spectroscopic methods, such as X-ray-based or vibrational spectroscopy methods. For liquid state Cr, the oxidation state can be probed through the presence or absence of oxidation reactions. The charge is relevant for liquid state Cr and conventionally denoted by Arabic numerals followed by a + or − sign, such as $CrO_4{}^{2-}$ and $Cr_2O_7{}^{2-}$ (the two most common aqueous Cr^{VI} species). Cr^{VI} is not stable in aqueous solutions in any cationic form (metal ions with an oxidation state equal or greater than IV form oxyanions in water). This distinguishes it in many cases from aqueous Cr^{III} species, which often form cations in water. This distinctive feature is used in some analytical methods, especially in chromatography and pre-separation techniques. For more insights into the nomenclature related to the oxidation state and charge of Cr species, the reader is referred to the excellent technical note by Kozlica and Miloševe.[9]

3. Selected legal frameworks and standardized tests for Cr^{VI} in aqueous solutions

Cr^{VI} is restricted in numerous applications, workplaces, and products across many countries and jurisdictions. Examples are occupational exposure limits for airborne particles, the European Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS),[10] the European Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH),[11,12] the Californian Proposition 65,[13] and the Canadian Environmental Protection Act,[14] to name a few. In most of these legal frameworks, the restriction limits have decreased drastically over time. For example, since 2017 (binding from 2025), the occupational exposure limit for Cr^{VI} in welding fume is 5 μg/m^3 in the European Union's member countries, down from significantly higher previous values of 50–100 μg/m^3.[15]

Table 1 shows some selected standardized tests used to test materials for compliance with these and other regulations. Generally, almost all standardized methods for Cr^{VI} are based on aqueous Cr^{VI}, often after extraction from solid samples. Quantitative analytical methods for Cr^{VI} in solid state samples are still too unreliable, inaccessible, or expensive to be used for regulatory compliance. A common cause of legal, scientific, and chemical debates has been the choice of extraction methods, which risks changing the speciation of Cr from the solid state to the liquid state in the extractant, further discussed in the next section. The other major difference among the standardized methods is the detection and determination limits, which range more than three orders of magnitude.

One commonly used (for ISO standards 16740 and 17075, and EN 196-10) and simple analytical method is a colorimetric method utilizing a color reaction specific to aqueous Cr^{VI}, with the reagent 1,5-diphenylcarbazide (DPC), which oxidizes to diphenylcarbazone through reaction with Cr^{VI} resulting in a pink complex with Cr^{III}.[16] This method is typically used for samples with expected higher levels of Cr^{VI} (cement, stainless steel welding fume nanoparticles, Cr-tanned leather), whereas other sample types require more sensitive methods, such as chromatographic methods coupled with inductively coupled plasma mass spectrometry (ICPMS). Even lower determination limits, as low as 20 ng/L, can be achieved with differential pulse adsorptive cathodic stripping voltammetry (DPAdCSV) utilizing electrochemical detection of a Cr^{III} complex with diethylenetriaminepentaacetate that specifically and time-dependently forms after reaction of Cr^{VI}.[17,18]Fig. 1 shows examples of the DPAdCSV electrochemical peak of a 0.16 μg/L Cr^{VI} water sample, determined by standard addition, and the pink color of a DPC-based calibration curve (up to about 1000 μg/L Cr^{VI}). The latter method does not even require any equipment, as the pink color is visible to the naked eye from a concentration of about 60 μg/L Cr^{VI}. This is likely the reason why it is widely used in international standard test methods, which have high requirements for relatively simple and affordable equipment and applicability across different laboratories.

4. When a result is misleading: dynamic change between species

Estimating the content of Cr^{VI} in solid samples through an extraction method risks a change of Cr speciation during the sample preparation. Similarly, a typical exposure scenario includes drastic chemical environment changes resulting in the change of Cr speciation and consequently changed hazard profiles over time. The two main factors are solution pH and the presence of reducing or complexing agents (only Cr^{III} forms complexes in aqueous solutions). Any factors increasing reaction rates, and oxidation rates in particular, such as sunlight, temperature, and solution agitation, matter as well. For example, pulverizing solid samples in air, a common sample preparation method prior to extraction tests, can increase the analyzed Cr^{VI} content.[28] A recent study showed that the pH and composition of the extraction solution and co-released antioxidants (reducing agents) of the solid sample resulted in less detected Cr^{VI} in solution than its initial values.[29] Vegetable-tanned leather samples were able to completely reduce up to 2000 μg/L Cr^{VI} during 24 h, inde-

Table 1. Selected standardized testing methods for Cr^{VI} for various materials/samples.

Standard	Purpose, sample	Analytical method used	Comments
ISO 16740[19]	Airborne particles (workplace air)	Extraction for soluble and insoluble Cr^{VI} compounds, followed by ion chromatography combined with DPC reagent	Warns about the possible oxidation of Cr^{III} to Cr^{VI} during extraction for insoluble Cr^{VI} compounds.
ISO 17075-1[20]	Cr-tanned leather	Extraction for soluble Cr^{VI}, followed by DPC-based colorimetric method	Solid phase extraction needed as pre-treatment to reduce color interferences from leather samples.
ISO 17075-2[21]	Cr-tanned leather	Extraction for soluble Cr^{VI}, followed by ion-exchange chromatography with UV–VIS detection	Coupling to a more sensitive detection method than UV–VIS, such as ICPMS, can decrease the detection limit further.
EN 196-10[22]	Cement	Extraction for soluble Cr^{VI}, followed by DPC-based colorimetric method	Compares to European restriction limit of 2 mg water-soluble Cr^{VI} per kg dry weight of cement.
EN 71-3[23]	Toys	Extraction for soluble Cr^{VI} (and total Cr and many other metals). Cr^{VI} is analyzed by chromatography coupled to ICPMS.	Specifies sampling methods for a wide range of materials. Acidic extraction risks the reduction of any available Cr^{VI} to Cr^{III}. Specifies migration limits of between 0.005 and 0.02 mg Cr^{VI} per kg of toy material, depending on the type of material.
OSHA method ID-215 (version 2)[24]	Airborne samples (particles collected on filters)	Extraction for Cr^{VI} using an alkaline buffer (pH 8), chemical selection of Cr^{III} and Cr^{VI}, followed by DPC-based colorimetric method.	Magnesium sulfate is added to the buffer solution to avoid unintended oxidation of Cr^{III} in the solid sample by the alkaline hot plate extraction.
NIOSH method 7605[25]			Similar to OSHA method ID-215 but without the magnesium sulfate.
NIOSH method 7703[26]			For field sampling. Uses an ultrasonic bath instead of a hot plate for the extraction. Strong anion exchange solid phase extraction instead of ion chromatography.

pendent of the extraction solution (artificial sweat or phosphate buffer ranging from pH 4.7 to 8.0).[29] A study comparing different standardized tests, where one was using magnesium sulfate to avoid interferences from Cr^{III} and iron from the samples, concluded only minor impacts for airborne samples from Cr plating facilities and suggested that magnesium sulfate in the pH 8 extraction solution was resulting in false-negative (too low) rather than false-positive (too high) Cr^{VI} detection in these samples.[30] Generally, most biological samples, containing high amounts of organic matter and a neutral or acidic pH, would result in the stabilization of Cr^{III} and a risk of reducing any initially present Cr^{VI}—a risk of false-negative detection that is elevated when using extraction solutions as compared to solid state detection methods. In contrast, for strongly alkaline extraction methods (pH 10 and higher), there is a risk of oxidation of Cr^{III} to Cr^{VI}, resulting in false-positive detection of Cr^{VI}. This pH dependence is exemplified by Fig. 2.

It is important to consider even short-lived Cr^{VI} species for health considerations. However, these are analytically challenging to detect in biological systems. Estimates focused on Cr content in red blood cells have been used as a proxy to understand any past presence of Cr^{VI} in a human body or animals, as Cr^{VI} is taken up at a much higher rate by red blood cells compared to Cr^{III}.[32] However, even nanoparticles containing other forms of Cr could be taken up by cells (resulting in false-positives),[33–35] or the Cr^{VI} of interest never reaches the blood, for example, when it is already converted in dendritic (skin) cells or in the skin (resulting in false-negatives).[5,36–38] Therefore, solid state chromium speciation methods, as direct evidence of potentially available Cr^{VI}, are important to assist in chemical/material hazard assessments.

5. Solid state chromium speciation

5.1. Colorimetric methods

Within dermatology, the DPC-based colorimetric method has also been used semiquantitatively for solid state analysis of potential Cr^{VI}-containing solid samples.[39,40] It is a quick, inexpensive method that can be applied outside of a lab and by patients (with suitable instructions) to determine the culprit sources (at work or at the patient's home) of diagnosed Cr contact allergy. It can be applied by using cotton sticks or by directly dropping the reagent solution onto the material to be tested. The following analysis kit and instructions have been prepared by one of the authors (YSH) at the Centre for Occupational and Environmental Medicine, Stockholm, Sweden, for patients and occupational hygienists to assist in their culprit material search.

Analysis kit:

1. Fill a closed, brown (non-transparent, to avoid oxidation by light) 1 mL clean glass vial/bottle with 0.01 g of 1,5-diphenylcarbazide powder. Keep it closed and dry.

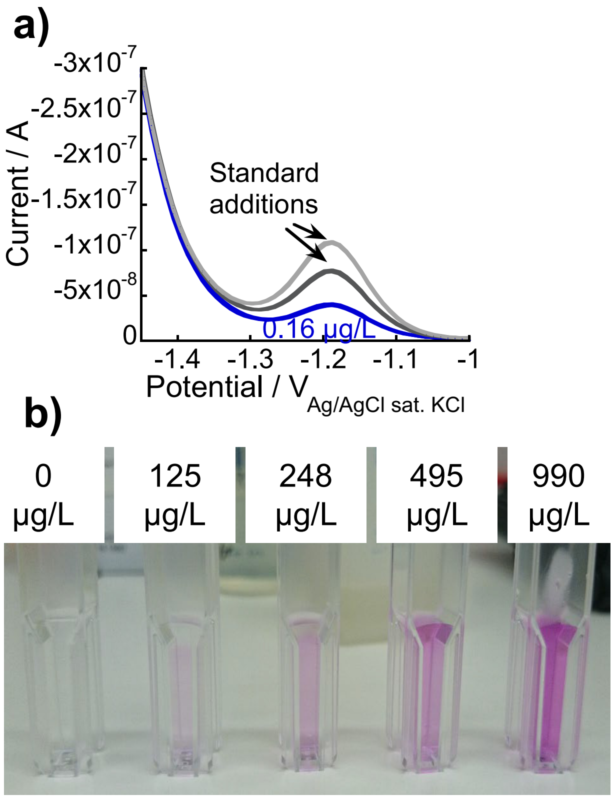


Fig. 1. (*a*) Example of DPAdCSV peak of a 0.16 µg/L Cr^{VI} water sample, to illustrate a technique with a low determination limit (0.02 µg/L Cr^{VI}–double the value of a recognizable peak), and (*b*) calibration standards of 0–990 µg/L Cr^{VI} using the DPC colorimetric method, to illustrate a technique with a detection limit of about 60 µg/L Cr^{VI}. The figure is partially using data and a picture from previous studies,[18,27] both of which are published under a CC-BY license.

2. Fill another closed, brown 1 mL glass vial with 1 mL of acetone and one small drop (about 20 µL) of glacial acetic acid.
3. Add a small pipette (one-time use), a few cotton sticks, one-time use plastic gloves, and a few plastic bags to lay the reacted cotton sticks on. Note that tissue paper can contain Cr^{VI} and should be avoided for use as a substrate.

Instructions for Cr-allergic patients:

1. Pour the liquid from the bottle containing the liquid into the empty bottle with the powder, close it, mix it by gently shaking it, and wait a few minutes.
2. Drop a small droplet onto the material to be investigated. You can also drop a droplet on a cotton stick and then gently rub the material to be investigated with the wet cotton stick. The latter is preferred if the material is colored or if you do not want it to become pink (but this could happen anyway).
3. If your material or the cotton stick becomes pink within 5 min, Cr^{VI} is detected. If it becomes pink within 24 h or later, Cr^{III} is detected. Avoid skin contact with anything that has become pink.

Some examples of positive, unclear, and negative Cr^{VI} readings using the DPC solid state colorimetric test from our laboratories are shown in Fig. 3.

As is the case with the DPC test in the liquid state,[16] there is a risk of false-positive Cr^{VI} detection in the presence of Cr^{III} due to oxidation of DPC to diphenylcarbazone–a risk that certainly increases in the presence of air. The presence of zinc, corrosion reactions, and Cr^{III} have also been reported to lead to false-positive readings for Cr^{VI} using the DPC cotton stick test.[42] Therefore, a quick (<5 min after application) reading is required, and alternative laboratory methods are required to validate results.

5.2. Electrochemical methods

Electroanalytical methods are extremely powerful for various solid species of Cr. Originally developed for aqueous species of Cr,[2] solid samples can be directly analyzed by electroanalytical methods through attaching powders (the samples) to various types of carbon-based electrodes or even directly for solid samples (like sheets with a thin oxide of the Cr species of interest), although the latter is difficult due to the low signal. Powder-based electroanalytical methods have been used for metal speciation.[43–52] To the best of our knowledge, Cr speciation of solid powder samples has been limited to a few samples in our own laboratory, which are discussed in the following. The Cr speciation of solid powder samples by cyclic voltammetry is so powerful that it is hard to assign the peaks, since the exact reference materials needed often do not exist. A few Cr-specific parameters that influence the peak positions, areas, and shape are:

- Substrate and type of working electrode (if the sample is a powder and needs to be attached to a working electrode)
- Oxide thickness and location of the Cr species within the oxide
- Oxidation state and exact species, including whether it is a pure or a mixed oxide
- Degree of crystallinity of Cr species
- Concentration of Cr species

As for all electroanalytical techniques, other important factors are the solution pH and buffer capacity, the agitation or rotation speed (for rotating disc electrodes), the scan rate, and the temperature. It is important to, whenever possible, choose a pH and a suitable buffer to allow for solid−solid transitions of the Cr species of interest, so that a peak can be detected and evaluated. To determine the speciation in the sample, the starting potential should be the open circuit potential and the sample should then be reduced followed by oxidation, and a separate sample should be oxidized followed by reduction.

Figure 4 exemplifies the complexity and potential of using electroanalytical methods for solid and thin oxide speciation of Cr in complex samples. The reference samples $K_2Cr_2O_7$ and Cr_2O_3 have distinct electrochemical profiles (Fig. 4*a*). However, the Cr^{III}-rich surface oxide on gas-atomized stain-

Fig. 2. pH-potential diagram of Cr species (ion concentration of 1 μmol/L) at 25 °C and 1 atm of pressure in water (ionic strength of 0 mol/L), as calculated by Hydra/Medusa[31] (redrawn for clarity). The potential is plotted against the standard hydrogen electrode (SHE). Only the dominant species in and around the stable water area are shown here. The typical redox potentials of water (such as surface water, rainwater, and tap water) are between the two green dotted lines. More negative potentials than the lower green dotted line correspond to the presence of reducing agents (such as hydrogen gas or antioxidants from biological matter), and more positive potentials than the upper green dotted line correspond to the presence of oxidants (such as oxygen gas or hydrogen peroxide). $HCrO_4^-$ and CrO_4^{2-} (in the upper part of the diagram) are the two dominant Cr^{VI} species, while all other species within the stable water area are Cr^{III} species. In typical water, Cr^{III} species are the stable species in neutral and acidic conditions, whereas Cr^{VI} species are stable in alkaline conditions.

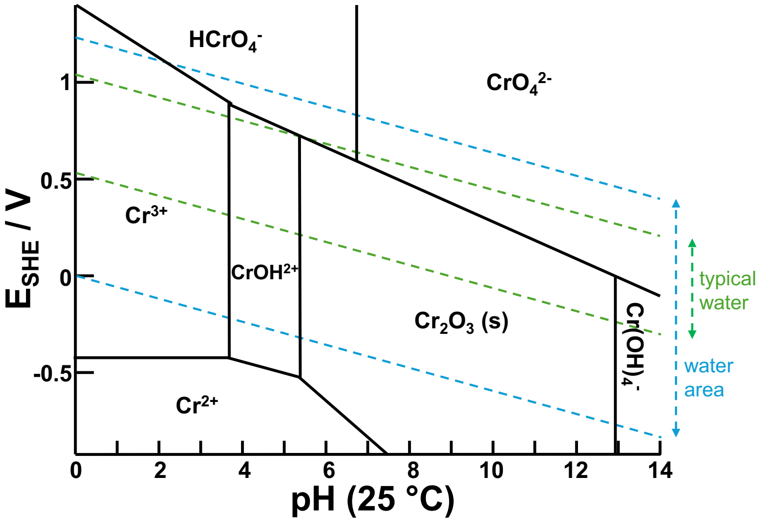
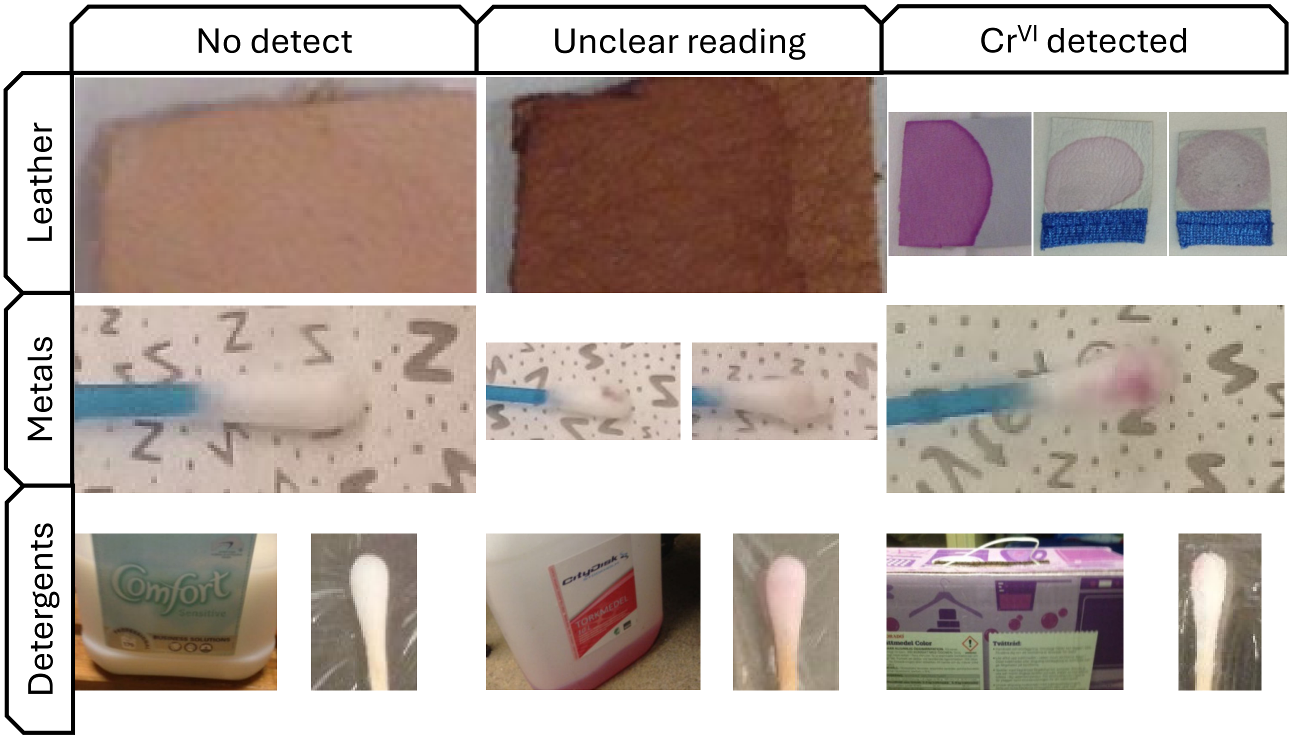


Fig. 3. Examples of negative (no detect), unclear (due to color interferences), and positive detections of Cr^{VI} from solid or liquid samples (leather, metal objects, and liquid or powder detergents) tested through the DPC colorimetric test directly on the material or through a cotton stick (spot test). The leather images have been published through a CC-BY license in previous work,[27,41] whereas the other results and images are unpublished.



less steel powder (Fig. 4*b*) is shifted compared to Cr_2O_3 (Fig. 4*a*). The Cr^{VI}-rich surface oxide on water-atomized stainless steel (Fig. 4*b*), which is an almost insoluble Cr^{VI} form embedded in silicate-rich matrix in a rapidly cooled, thermodynamically unstable surface oxide, has some resemblance with the $K_2Cr_2O_7$ reference sample in Fig. 4*a*, although its oxidative dissolution isn't equally pronounced. In contrast, the Cr^{VI}-rich oxide in stainless steel flux-cored wire welding fume nanoparticles (Fig. 4*c*), which is a highly soluble form in a mixed oxide containing Fe, Mn, Bi, K, Na, F, and Si, showed a completely different reduction peak and no oxidation peak or oxidative dissolution. In all these cases, many other analytical techniques had to be utilized to unambiguously assign these peaks and identify the Cr species in these samples. Still, cyclic voltammetry of solid samples has great potential in aiding the Cr speciation of solid samples. Future studies focusing on Cr speciation should explore a buffered electrolyte at pH 8–10, which is more suitable for Cr speciation, as it avoids reductive dissolution of Cr^{VI} species to $Cr(OH)_4^-$ (see Fig. 2).

5.3. Vibrational spectroscopy and X-ray diffraction

What follows is a discussion on two of the most commonly accessible and used solid state chromium speciation techniques; vibrational spectroscopy, such as Fourier transform infrared spectroscopy[55,56] or Raman spectroscopy[57–65], and X-ray diffraction. These lab-based methods have been widely used in studies aimed at assessing the presence of Cr^{VI} species in solids, including welding fume particles.[54,56,66–69] They are powerful, qualitative techniques for clean samples with significant amounts of Cr^{VI}, however, for mixed samples with missing reference samples, e.g., for the commonly high-temperature formed thermodynamically unstable and possibly amorphous mixed oxide phases, they can be misleading. Both technique classes have relatively high detection limits (0.1 to a few wt.%), which makes them less suitable for Cr^{VI} trace analysis in solids. Modern devices and best practices, in combination with a favorable sample (low interferences, pure Cr^{VI} compounds), can lower the limit of detection. X-ray diffraction, at least for lab-based techniques, requires crystallinity and a certain crystal size. These sample requirements are rarely fulfilled for our most common Cr^{VI} environmental sources; for rapidly cooled oxides, such as in welding fume and fly ash particles, trace Cr^{VI} in an organic matrix, such as in detergents and leather, chromate-passivated metal surfaces, or Cr^{VI}-contaminated soil.

This means that the absence of Cr^{VI} vibration modes (Cr–O–Cr or $Cr–O_4$) or the absence of diffraction peaks corresponding to a crystalline and pure Cr^{VI} species does not mean the absence of Cr^{VI} at relevant concentrations for health considerations. For vibrational spectroscopic methods, interferences, especially with various silicon oxide species, might make assignments challenging for common mixed oxides. However, these techniques can be used for complex samples in conjunction with other solid state speciation techniques and extraction methods.

5.4. X-ray photoelectron spectroscopy (XPS)

XPS is now a well-established vacuum-based surface analysis technique capable of providing elemental and chemical state information from the outer 5–10 nm of a solid surface. For Cr, detection limits range from 0.03 at.% in a light element matrix (e.g., C, Al, and Si) to 0.3–1.0 at.% in heavier element matrices.[70]

Normally, chemical state analysis in XPS is accomplished by monitoring shifts in the binding energy (BE) position of the strongest core photoelectron peak. For Cr, the strongest peak and the peak utilized for chemical state analysis is the Cr $2p_{3/2}$ peak, ranging in BE position from ∼574–580 eV. Complications in chemical state analysis arise for transition metals with unpaired electrons, in this case Cr^{III} ([Ar]$3d^3$), which exhibit a phenomenon called multiplet splitting, which both broadens and adds structure to the XPS spectrum. Different Cr^{III} compounds will have differing BE positions and unique peak shapes,[71,72] which can allow for the differentiation of the various Cr^{III} species present on the surface of a sample. Cr^{VI}, which has no unpaired electrons ([Ar]), does not exhibit multiplet splitting and gives a sharp single Cr $2p_{3/2}$ peak at ∼579.5 eV.[71,72]

Using carefully controlled curve-fitting procedures, which mimic the Cr $2p_{3/2}$ peak spectral positions and shapes for specific Cr species (e.g., Cr metal, Cr_2O_3, $Cr(OH)_3$, $FeCr_2O_4$, and $PbCrO_4$), one can quantify the various Cr species present, including the metal, Cr^{III}, and Cr^{VI} components.[71,72] Due to a slight overlap of the Cr^{VI} envelope with a portion of the Cr^{III} multiplet split peak shapes, detection limits for Cr^{VI} in a mostly Cr^{III} matrix are approximately 5% of the total Cr present.[71,72]

Figure 5 shows quantitative results of these types of curve-fitting procedures. Figure 5*a* shows approximately 6% Cr^{VI} species in a mixture of Cr metal (8%), Cr_2O_3 (31%) and $Cr(OH)_3$ (55%). Figure 5*b* reveals 17% Cr^{VI} at the surface with 49% Cr_2O_3 and 34% $Cr(OH)_3$. Detection of Cr^{VI} species in samples containing Cr^{III} compounds other than the oxide or hydroxide can be more problematic. One example is shown in Fig. 5*c*, which is basic Cr^{III} sulfate, a commonly used tanning agent for Cr-tanned leather. This and similar compounds, such as Cr^{III} sulfate hydrate, show multiplet structures at higher binding energies than those seen for Cr_2O_3 and $Cr(OH)_3$. This higher binding energy multiplet structure more strongly overlaps with the single peak for Cr^{VI} species, effectively worsening detection limits for Cr^{VI} substantially.

5.5. X-ray absorption near-edge spectroscopy (XANES)

XANES is a species-sensitive technique and particularly powerful to distinguish Cr^{III} and Cr^{VI} species because of a characteristic sharp pre-edge peak for Cr^{VI} species (Fig. 6).[73–75] The samples can be investigated in their original state and do not need to be crystalline;[73] however, their Cr^{VI} content (accessible to the detection mode) needs to be in sufficiently high concentration, especially when Cr^{III} is also present.[76] The weak pre-edge features in the total electron yield (TEY) of Cr^{III}, which is in a distorted octahedral structure, comes from the Cr 1 s to Cr 3d/O 2p transition, where

Fig. 4. Cyclic voltammograms of different samples, (*a*) $K_2Cr_2O_7$ and Cr_2O_3 reference samples (unpublished) using a graphite paste electrode, (*b*) Cr^{VI}-containing water-atomized and Cr^{III}-containing gas-atomized 316 L powder using a graphite paste electrode,[53] and (*c*) Cr^{VI}-containing welding fume nanoparticles ("F1" in a previous study[54]) attached to a paraffin-impregnated graphite electrode. All were reduced or oxidized (as indicated by the arrows) from open circuit potential (marked with an X) at 0.5 mV/s and in 8 mol/L NaOH (pH 13) electrolyte. Published data have been replotted, normalized to the same reference electrode, and are reproduced using a CC-BY licence.

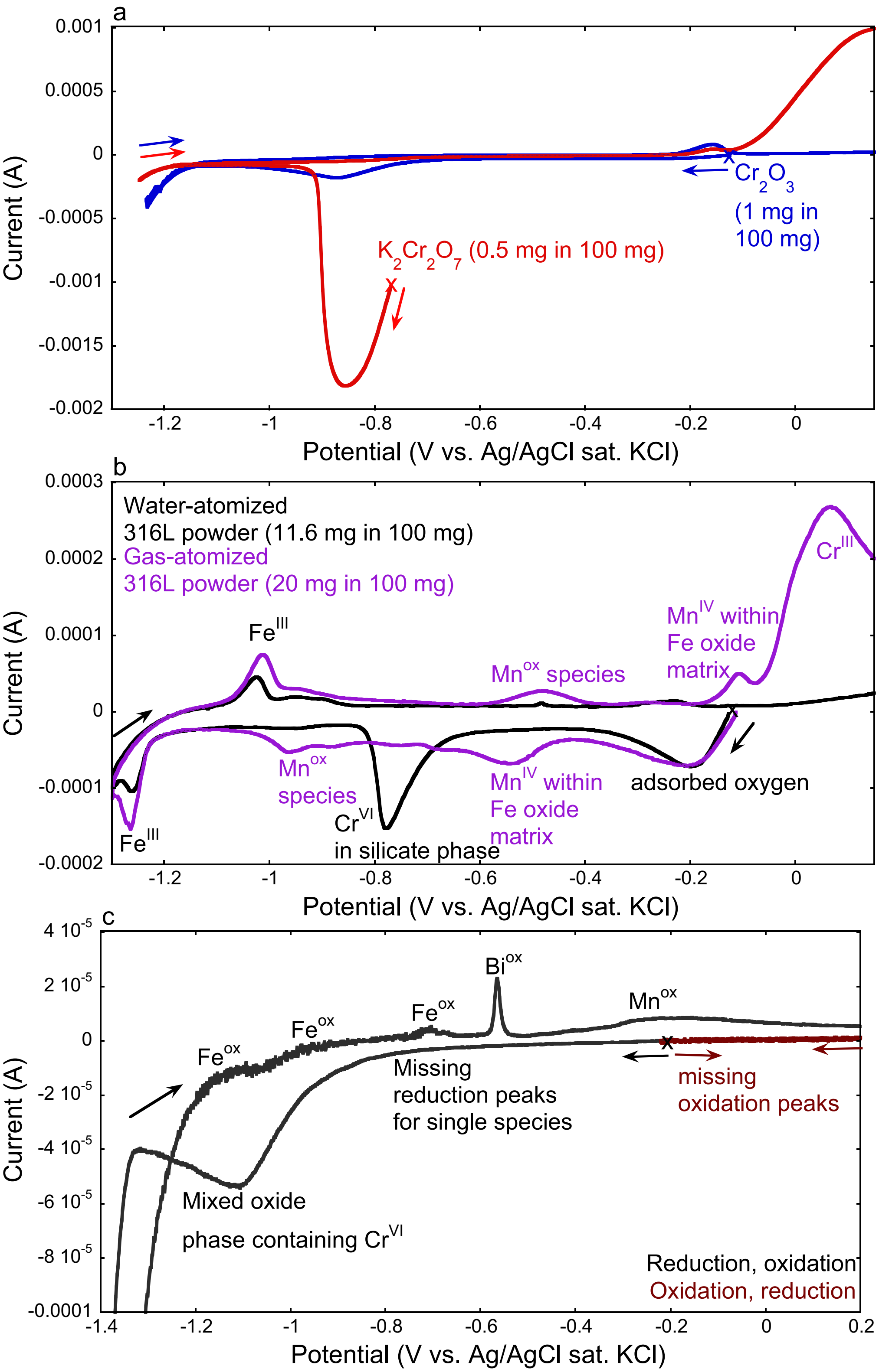


Fig. 5. Unpublished examples of Cr 2p XPS peaks (with fitted species in the Cr $2p_{3/2}$ peak using a Shirley background, CasaXPS software v. 2.3.2.6.) of (*a*) an atomic layer deposited Cr oxide coating on silicon, (*b*) a steel alloy surface that has been treated with a structural adhesive primer that contains strontium chromate, and (*c*) the tanning agent basic Cr^{III} sulfate, $CrSO_4OH$, obtained from a European tannery (peak fitting parameters in Table 2). The dashed vertical line in (*c*) indicates 579.5 eV, the position where the single Cr^{VI} peak would be expected. Relevant instrument settings: Kratis AXIS Ultra Spectrometer, monochromatic Al Kα source (15 mA, 14 kV), with the instrument work functions calibrated to the Au $4f_{7/2}$ at 83.96 eV BE, instrument base pressure at 8×10^{-10} Torr, high-resolution analyses with an analysis area of 300 μm × 700 μm at 20 eV pass energy, with the Kratos charge neutralizer system on, the samples mounted electrically isolated from the instrument sample holder, and the spectra charge-corrected to the aliphatic carbon signal at 284.8 eV BE. The legend in (*c*) corresponds to (*a*) and (*b*) as well.

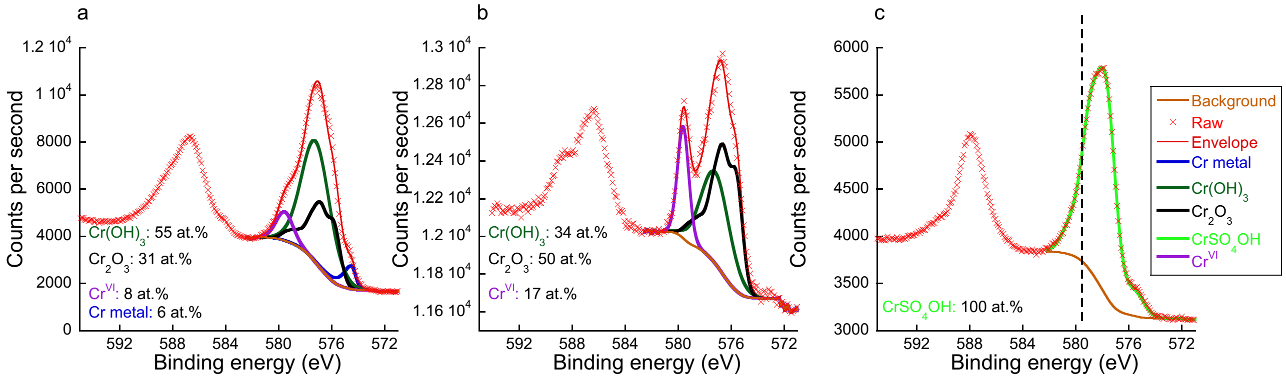


Table 2. Used (in Fig. 5*c*) curve-fitting parameters for basic Cr^{III} sulfate ($CrSO_4OH$). All peaks have a full width at half maximum of 1.65 eV.

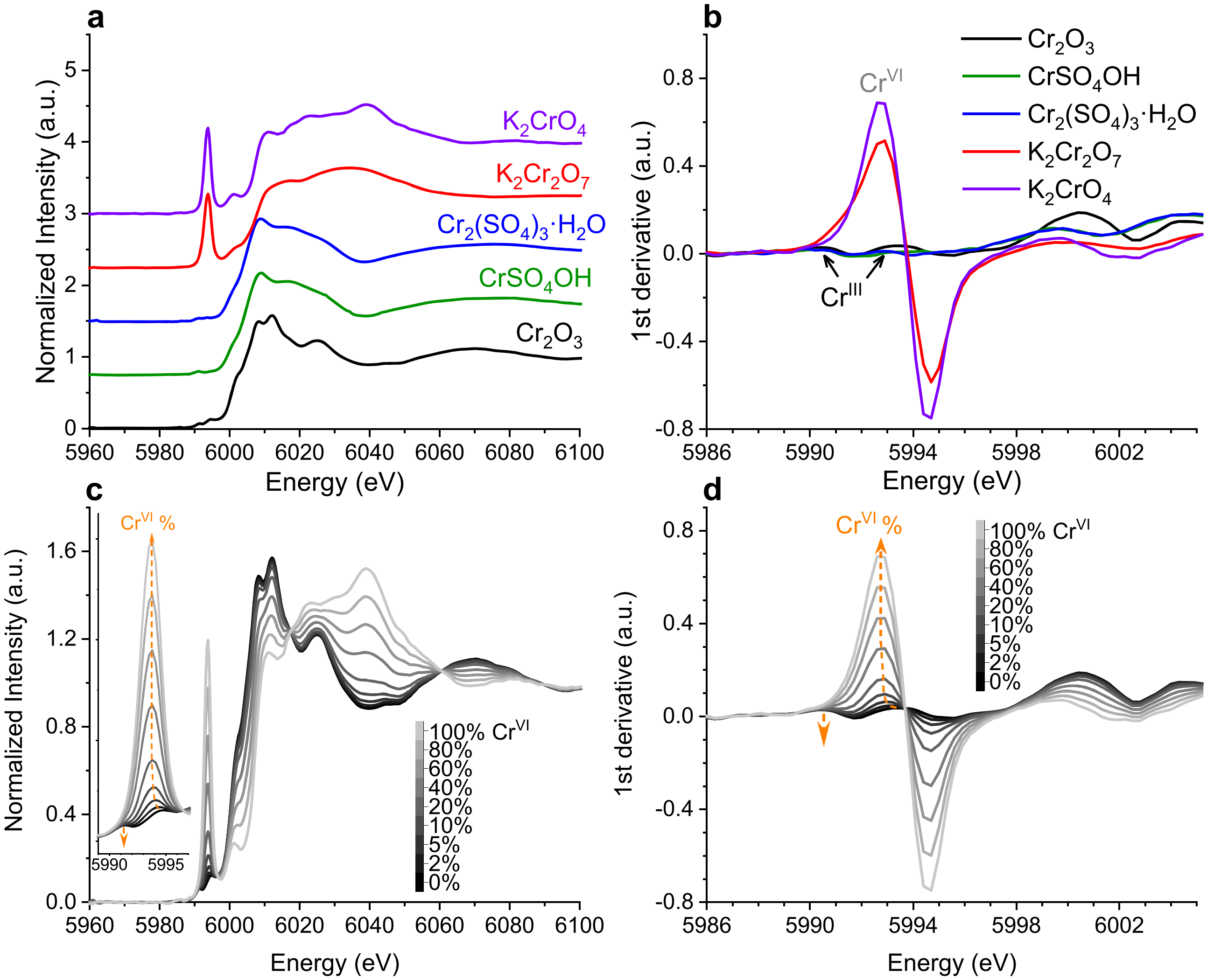
Peak	Binding energy (eV)	Area (%)
1	575.5	6.4
2	577.8	50.9
3	579.0	36.1
4	580.6	6.6

the electron configuration of Cr^{III} is [Ar]$3d^3$. The pre-edge feature becomes very sharp for Cr^{VI}, which is in a tetrahedral structure and has much lower symmetry than Cr^{III}, as well as a higher unoccupied density of states on its Cr 3d orbital ([Ar]).[76] For some samples, such as Cr-tanned leather, welding fume particles, and fly ash particle samples, access to air or oxidizing gases is essential to the formation of Cr^{VI}, which is hence found most prevalently on the surface of the sample. This requires surface-sensitive modes of detection, which in the case of XANES is the TEY mode. However, due to the often minor or trace amounts of Cr^{VI} and the concomitant presence of Cr^{III} in samples such as Cr-tanned leather and Cr-passivated metal surfaces, even the TEY-XANES data collection would require many scans and might not be sufficient to detect trace amounts of Cr^{VI} of relevance to health. Another complication is the requirement of conductive samples for the TEY mode of XANES.[77,78] Also, unknown Cr^{III} ligands might change, or even overlap, with the target Cr^{VI} analyte, since the ligand effect can change the pre-edge peaks drastically.[79,80] An alternative to the TEY mode would be the fluorescence yield (FLY) mode, which is more suitable for diluted samples (low amounts of total Cr), but less suitable for samples which have Cr^{VI} only on the surface with predominantly Cr^{III} in the bulk. FLY probes several orders deeper into the sample than TEY, but surface analysis by FLY could be achieved by adjusting the X-ray incident angle (glancing angle). However, core-hole lifetime broadening can significantly truncate the fine structures in FLY-XANES when measured with a traditional multi-element germanium detector. High-energy-resolution fluorescence detection (HERFD)[81] could overcome some of the main limitations of conventional FLY and transmission spectra in the hard X-ray region by providing higher resolved fine structures. TEY, FLY and HERFD can be chosen depending on the sample concentration, surface-bulk gradient of Cr^{VI}/Cr^{III}, and electronic conductivity.

6. Concluding remarks

Oxidizing and environments of high alkalinity generally can cause the formation of Cr^{VI}, unless there are reducing agents present in the environment. This is why even impurities of Cr in some occupational and household items can result in typical occupational and environmental Cr^{VI} sources, such as (i) Portland cement, which uses an oxidizing manufacturing process, has high alkalinity and no reducing agents, (ii) detergents, which have high alkalinity, and (iii) air- or ozone-exposed surfaces of some particles or products, e.g., welding fume, leather, and fly ash particles. Within metal toxicology, Cr is an unusual element, since most of its occupational and environmental exposure sources are unintentional, which means that the Cr^{VI} has not been intentionally added to the material or product. Some industrial and consumer products also see intentional additions, for example, for corrosion protection purposes, although this has been banned in many countries and products. The chemical nature

Fig. 6. X-ray absorption near-edge spectroscopy (XANES) spectra of Cr^{III} (Cr_2O_3, tanning agent $CrSO_4OH$, $Cr_2(SO_4)_3.H_2O$) and Cr^{VI} ($K_2Cr_2O_7$, K_2CrO_4) reference samples (unpublished); (*a*) Total electron yield (TEY) mode at the Cr K-edge, normalized (edge = 1) and off-set for clarity; (*b*) corresponding first derivative of the spectra to more clearly show their features and differences. Note the clear pre-edge peak (at around 5994 eV) for Cr^{VI}, but not Cr^{III}, species. These measurements were run at the SXRMB beamline of the Canadian Light Source (0.3 eV step in XANES region). The tanning agent $CrSO_4OH$ was the same as in Fig. 5*c*; all other standard samples were of analytical grade and purchased in Canada. Illustrative spectra of (*c*) TEY-XANES and (*d*) corresponding 1st derivative spectra with different weight ratios of $Cr^{VI}/(Cr^{III} + Cr^{VI})$ using the TEY of Cr_2O_3 and K_2CrO_4 from (*a*) as standards. It suggests that the detection limit for Cr^{VI} in a mixture of Cr^{III} and Cr^{VI} could be down to 2–5 wt.% of total Cr using XANES.



of Cr^{VI} formation and stability also results in exposure scenarios being more likely caused by surface-available Cr^{VI} and more likely combined with an alkaline pH. An alkaline pH is skin-irritating and increases the uptake. This requires sensitive and reliable determination methods for Cr^{VI} in trace levels on a wide variety of complex materials. This mini-review introduced liquid state and solid state determination methods, each of which has its drawbacks in terms of false positive or false negative detection and limiting sample requirements. Liquid state and extraction methods have been widely standardized, are often inexpensive and widely available, but their largest risk is the extraction method itself, which risks changing the speciation of Cr. For biological or organic samples extracted at a neutral, acidic, or weakly alkaline pH, the highest risk is the reduction of Cr^{VI} to Cr^{III}, resulting in false negatives. In contrast, the extraction at alkaline pH, or of samples containing oxidants, risks the false-positive detection of Cr^{VI} due to oxidation during the extraction process. Available liquid state detection methods have a wide range of detection ranges and can detect trace amounts (down to parts per trillion or ng/L), in contrast to solid state detection methods, which often require higher concentrations of the analyte. Because of the relatively high risk of interference with either Cr^{III} or other species, we recommend using at least two different analytical methods and investigating potential interfering elements/species. To combine solid and liquid state methods is highly recommended where the research question includes potential human exposure routes. For example, the false negative detection of Cr^{VI} using an extraction method that reduces initially present Cr^{VI} can give information on the duration of survival of Cr^{VI} or its likelihood to be stable long enough to be available in an exposure scenario. It is likely that exposure sources with concomitantly released/present antioxidants are less harmful over time than exposure sources that provide a perfect environment for Cr^{VI} to be stable. At the same time, even short-lived Cr^{VI} is potentially harmful and needs to be detected.

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References

(1) Sun, H.; Costa, M. Chapter 8 – Chromium. *In Handbook on the Toxicology of Metals (Fifth Edition)*; G. F. Nordberg M. Costa. Ed.; Academic Press, **2022**; pp. 197.
(2) Namieśnik, J.; Rabajczyk, A. *Crit. Rev. Env. Sci. Tec.* **2012**, *42*(4), 327. doi:10.1080/10643389.2010.518517.
(3) Ashley, K.; Howe, A. M.; Demange, M.; Nygren, O. *J. Environ. Monit.* **2003**, *5*(5), 707. doi:10.1039/b306105c. PMID: 14587839.
(4) Remy, L. L.; Byers, V.; Clay, T. *Environ. Health*, **2017**, *16*, 1. doi:10.1186/s12940-017-0222-8. PMID: 28049482.
(5) Hedberg, Y. S. Metal allergy: chromium. *In Metal allergy: from dermatitis to implant and device failure*; J. K. Chen J. P. Thyssen. Ed.; Springer International Publishing, **2018**; pp. 349. doi:10.1007/978-3-319-58503-1.
(6) Chou, T.–C.; Chang, H.–Y.; Chen, C.–J.; Yu, H.–S.; Wu, J.–D.; Sheu, S.–C.; Shih, T.–S. *Contact Dermatitis*, **2008**, *59*(3), 151. doi:10.1111/j.1600-0536.2008.01403.x. PMID: 18759895.
(7) Pedersen, B.; Thomsen, E.; Stern, R. *Ann. Occup. Hyg.* **1987**, *31*(3), 325. PMID: 3426032.
(8) Pastore, P.; Favaro, G.; Ballardin, A.; Danieletto, D. *Talanta*, **2004**, *63*(4), 941. doi:10.1016/j.talanta.2004.01.010. PMID: 18969521.
(9) Kozlica, D.; Milošev, I. *Corrosion*, **2021**, *77*(7), 696. doi:10.5006/3840.
(10) European Union. Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (recast) (Text with EEA relevance). *In Document 02011L0065-20250101*. Available from https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A02011L0065-20250101 [accessed December 2025]. **2011**.
(11) European Commission. **2007**. REACH–registration, evaluation, authorisation and restriction of chemicals. *In European Commission Environment Directorate General*. Available from http://ec.europa.eu/growth/sectors/chemicals/reach_en [accessed December 2025].

(12) European Union. EU 301/2014 COMMISSION REGULATION (EU) No 301/2014 of 25 March 2014 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards chromium VI compounds. **2014**.

(13) Proposition 65. *Safe drinking water and toxic enforcement act of 1986*[25249.5 – 25249.14]. California Law; **1986**.

(14) Government of Canada. *Canadian Environmental Protection Act*. Available from https://laws-lois.justice.gc.ca/eng/acts/c-15.31/ [accessed December 2025]. **1999**.

(15) European Commission. *Annex III, Limit values and other directly related provisions (Article 16)*, Directive 2004/37/EC of 29 April 2004, European Parliament: 2025; 2004/37/EC. Available from https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:02004L0037-20240408 [accessed December 2025]. **2025**.

(16) Pflaum, R. T.; Howick, L. C. *J. Am. Chem. Soc.* **1956**, *78*(19), 4862. doi:10.1021/ja01600a014.

(17) Bobrowski, A.; Królicka, A.; Zarębski, J. *Electroanalysis*, **2009**, *21*(13), 1449. doi:10.1002/elan.200904582.

(18) Hedberg, Y.; Lundin, M.; Jacksén, J.; Emmer, Å.; Blomberg, E.; Odnevall Wallinder, I. *J. Appl. Electrochem.* **2012**, *42*(5), 349. doi:10.1007/s10800-012-0404-6.

(19) International Standards Organization. Workplace air–determination of hexavalent chromium in airborne particulate matter–method by ion chromatography and spectrophotometric measurement using diphenyl carbazide. *ISO 16740*, **2005**.

(20) International Standards Organization. *ISO 17075-1, leather–chemical determination of chromium(VI) content in leather–Part 1*, Colorimetric method; **2017**.

(21) International Standards Organization. *ISO 17075-2, leather–chemical determination of chromium(VI) content in leather–Part 2: chromatographic method*; **2017**.

(22) European Norm. EN 196-10:2016. *Methods of testing cement–Part 10: determination of the water-soluble chromium (VI) content of cement*; **2016**.

(23) European Norm. *Safety of toys–Part 3: migration of certain elements*; **2019**.

(24) Occupational Safety and Health Administration (OSHA). ID-215 (version 2). Available from https://www.osha.gov/sites/default/files/methods/osha-id215_v2.pdf [accessed September 1998, revised April 2006]. **2006**; T-ID215-FV-02-0604-M.

(25) National Institute for Occupational Safety and Health (NIOSH). *NIOSH method 7605*. Available from https://www.cdc.gov/niosh/docs/2003-154/pdfs/7605.pdf [accessed December 2025]. NIOSH Manual of Analytical Methods (NMAM), Fourth Edition. Prevention, Centres for Disease Control and Prevention; **2003**.

(26) National Institute for Occupational Safety and Health (NIOSH). *NIOSH method 7703*. Available from https://www.cdc.gov/niosh/docs/2003-154/pdfs/7703.pdf [accessed December 2025]. NIOSH Manual of Analytical Methods (NMAM), Fourth Edition. Prevention, Centres for Disease Control and Prevention; **2003**.

(27) Mathiason, F.; Lidén, C.; Hedberg, Y. *Contact Dermatitis*, **2015**, *72*(5), 275. doi:10.1111/cod.12334. PMID: 25630767.

(28) Glastonbury, R.; Van der Merwe, W.; Beukes, J.; Van Zyl, P.; Lachmann, G.; Steenkamp, C.; Dawson, N.; Stewart, M. *Water SA*, **2010**, *36*(1), 105. doi:10.4314/wsa.v36i1.50913.

(29) Wright, A.; Laundry-Mottiar, L.; Hedberg, Y. S. *Regul. Toxicol. Pharm.* **2022**, *133*, 105222. doi:10.1016/j.yrtph.2022.105222.

(30) Ashley, K. E.; Boiano, J. M.; Groff, J. H.; Sieber, W. K.; Wallace, M. E.; Wang, J. *J. Environ. Monit.* **2000**, *2*, 329. PMID: 11249787.

(31) Puigdomenech, I. *KTH Royal Institute of Technology* **2015**. Available from *https://www.kth.se/polopoly_fs/1.369371!/Eq-Calcs_32.zip* [accessed December 2025].

(32) Merritt, K.; Brown, S. A. *J. Biomed. Mater. Res.* **1995**, *29*(5), 627. doi:10.1002/jbm.820290510. PMID: 7622548.

(33) Park, E.–J.; Yi, J.; Kim, Y.; Choi, K.; Park, K. *Toxicol. in vitro*, **2010**, *24*(3), 872. doi:10.1016/j.tiv.2009.12.001. PMID: 19969064.

(34) Limbach, L. K.; Wick, P.; Manser, P.; Grass, R. N.; Bruinink, A.; Stark, W. J. *Environ. Sci. Technol.* **2007**, *41*(11), 4158. doi:10.1021/es062629t. PMID: 17612205.

(35) McCarrick, S.; Romanovski, V.; Wei, Z.; Westin, E. M.; Persson, K.–A.; Trydell, K.; Wagner, R.; Odnevall, I.; Hedberg, Y. S.; Karlsson, H. L. *Arch. Toxicol.* **2021**, *95*(9), 2961. doi:10.1007/s00204-021-03116-x. PMID: 34287684.

(36) Siegenthaler, U.; Laine, A.; Polak, L. *J. Invest. Dermatol.* **1983**, *80*(1), 44. doi:10.1111/1523-1747.ep12531034. PMID: 6184422.

(37) Polak, L.; Frey, J. R. *Int. Arch. Allergy Immunol.* **1973**, *44*(1), 51. doi:10.1159/000230917.

(38) Rytter, M.; Haustein, U. F. *Br. J. Dermatol.* **1982**, *106*(2), 161. doi:10.1111/j.1365-2133.1982.tb00925.x. PMID: 6174139.

(39) Bregnbak, D.; Johansen, J. D.; Hamann, D.; Hamann, C. R.; Hamann, C.; Spiewak, R.; Menné, T.; Zachariae, C.; Jellesen, M. S.; Thyssen, J. P. *Contact Dermatitis*, **2016**, *75*(2), 115. doi:10.1111/cod.12577. PMID: 27385521.

(40) Bregnbak, D.; Johansen, J. D.; Jellesen, M. S.; Zachariae, C.; Thyssen, J. P. *Contact Dermatitis*, **2015**, *73*(5), 281. doi:10.1111/cod.12406. PMID: 25919302.

(41) Hedberg, Y.; Lidén, C.; Odnevall Wallinder, I. *J. Hazard. Mater.* **2014**, *280*, 654. doi:10.1016/j.jhazmat.2014.08.061. PMID: 25222930.

(42) Reveko, V.; Lampert, F.; Din, R. U.; Thyssen, J. P.; Møller, P. *Contact Dermatitis*, **2018**, *78*(5), 315. doi:10.1111/cod.12955. PMID: 29341169.

(43) Mouhandess, M.; Chassagneux, F.; Durand, B.; Sharara, Z.; Vittori, O. *J. Mater. Sci.* **1985**, *20*(9), 3289. doi:10.1007/bf00545197.

(44) Mouhandess, M. T.; Chassagneux, F.; Vittori, O. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *131*(0), 367. doi:10.1016/0022-0728(82)87088-5.

(45) Mouhandess, M. T.; Chassagneux, F.; Vittori, O.; Accary, A.; Reeves, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *181*(1–2), 93, doi:10.1016/0368-1874(84)83622-9.

(46) Encinas, P.; Lorenzo, L.; Tascón, M. L.; Vázquez, M. D.; Sánchez-Batanero, P. *J. Electroanal. Chem.* **1994**, *371*(1–2), 161. doi:10.1016/0022-0728(93)03246-L.

(47) Encinas Bachiller, P.; Tascon Garcia, M. L.; Vazquez Barbado, M. D.; Sanchez-Batanero, P. *J. Electroanal. Chem.* **1994**, *367*(1–2), 99. doi:10.1016/0022-0728(93)03033-L.

(48) Chouaib, F.; Cauquil, O.; Lamache, M. *Electrochim. Acta*, **1981**, *26*(3), 325. doi:10.1016/0013-4686(81)85018-9.

(49) Doménech, A.; Doménech-Carbó, M. T.; Pasies, T.; Bouzas, M. C. *Electroanalysis*, **2011**, *23*(12), 2803. doi:10.1002/elan.201100577.

(50) Scholz, F.; Schröder, U.; Gulaboski, R. *Electrochemistry of immobilized particles and droplets*; Springer Verlag, **2005**. doi:10.1007/b137048.

(51) Grygar, T.; Bezdička, P.; Hradil, D.; Doménech-Carbó, A.; Marken, F.; Pikna, L.; Cepriá, G. *Analyst*, **2002**, *127*(8), 1100. doi:10.1039/B205199K. PMID: 12195953.

(52) Hedberg, Y. S.; Pradhan, S.; Cappellini, F.; Karlsson, M. E.; Blomberg, E.; Karlsson, H. L.; Odnevall Wallinder, I.; Hedberg, J. F. *Electrochim. Acta*, **2016**, *212*, 360. doi:10.1016/j.electacta.2016.07.017.

(53) Hedberg, Y.; Norell, M.; Linhardt, P.; Bergqvist, H.; Wallinder, I. O *Int. J. Electrochem. Sci.* **2012**, *7*(12), 11655. doi:10.1016/S1452-3981(23)16495-9.

(54) Hedberg, Y. S.; Wei, Z.; McCarrick, S.; Romanovski, V.; Theodore, J.; Westin, E. M.; Wagner, R.; Persson, K. A.; Karlsson, H. L.; Odnevall Wallinder, I. *J. Hazard. Mater.* **2021**, *413*, 125273. doi:10.1016/j.jhazmat.2021.125273. PMID: 33581669.

(55) Stammreich, H.; Bassi, D.; Sala, O.; Siebert, H. *Spectrochim. Acta*, **1958**, *13*(3), 192. doi:10.1016/0371-1951(58)80076-4.

(56) Vats, V.; Melton, G.; Islam, M.; Krishnan, V. V. *J. Hazard. Mater.* **2023**, *448*, 130862. doi:10.1016/j.jhazmat.2023.130862. PMID: 36708696.

(57) Maslar, J. E.; Hurst, W. S.; Vanderah, T. A.; Levin, I. *J. Raman Spectrosc.* **2001**, *32*(3), 201. doi:10.1002/jrs.687.

(58) Zuo, J.; Xu, C.; Hou, B.; Wang, C.; Xie, Y.; Qian, Y. *J. Raman Spectrosc.* **1996**, *27*(12), 921. doi:10.1002/(SICI)1097-4555(199612)27:12%3c921::AID-JRS57%3e3.0.CO;2-L.

(59) Maslar, J. E.; Hurst, W. S.; Bowers, W. J., Jr; Hendricks, J. H.; Aquino, M.; Levin, I. *Appl. Surf. Sci.* **2001**, *180*(1-2), 102. doi:10.1016/S0169-4332(01)00338-5.

(60) Vuurman, M. A.; Wachs, I. E.; Stufkens, D. J.; Oskam, A. *J. Mol. Catal.* **1993**, *80*(2), 209. doi:10.1016/0304-5102(93)85079-9.

(61) Lutz, H.; Müller, B.; Steiner, H. *J. Solid State Chem.* **1991**, *90*(1), 54. doi:10.1016/0022-4596(91)90171-D.

(62) Farrow, R.; Benner, R.; Nagelberg, A.; Mattern, P. *Thin Solid Films*, **1980**, *73*(2), 353. doi:10.1016/0040-6090(80)90499-X.

(63) Ramsey, J. D.; McCreery, R. L. *Corros. Sci.* **2004**, *46*(7), 1729. doi:10.1016/j.corsci.2003.10.010.

(64) Sudesh, T.; Wijesinghe, L.; Blackwood, D. *Appl. Surf. Sci.* **2006**, *253*(2), 1006.

(65) Hedberg, Y.; Norell, M.; Hedberg, J.; Szakálos, P.; Linhardt, P.; Odnevall Wallinder, I. *Powder Metall.* **2013**, *56*(2), 158. doi:10.1179/1743290112Y.0000000041.

(66) Floros, N. *Welding in the World*, **2018**, *62*(2), 311. doi:10.1007/s40194-018-0552-3.

(67) Sowards, J.; Lippold, J.; Dickinson, D.; Ramirez, A. *Weld. J.* **2008**, *87*(4), 106.

(68) Sowards, J.; Ramirez, A.; Dickinson, D.; Lippold, J. *Weld. J.* **2010**, *89*, 82.

(69) Moroni, B.; Viti, C. *J. Aerosol Sci.* **2009**, *40*(11), 938. doi:10.1016/j.jaerosci.2009.08.004.

(70) Shard, A. G. *Surf. Interface Anal.* **2014**, *46*(3), 175. doi:10.1002/sia.5406.

(71) Biesinger, M.; Brown, C.; Mycroft, J.; Davidson, R.; McIntyre, N. *Surf. Interface Anal.* **2004**, *36*(12), 1550. doi:10.1002/sia.1983.

(72) Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. *Appl. Surf. Sci.* **2011**, *257*(7), 2717. doi:10.1016/j.apsusc.2010.10.051.

(73) Gräfe, M.; Donner, E.; Collins, R. N.; Lombi, E. *Anal. Chim. Acta*, **2014**, *822*, 1. doi:10.1016/j.aca.2014.02.044. PMID: 24725743.

(74) Gaur, A.; Shrivastava, B. D. *Rev. J. Chem.* **2015**, *5*(4), 361. doi:10.1134/S2079978015040032.

(75) Ohta, A. *Geostand. Geoanal. Res.* **2015**, *39*(1), 87. doi:10.1111/j.1751-908X.2014.00292.x.

(76) Peterson, M. L.; Brown, G. E.; Parks, G. A.; Stein, C. L. *Geochim. Cosmochim. Acta*, **1997**, *61*(16), 3399. doi:10.1016/S0016-7037(97)00165-8.

(77) Stöhr, J.; Noguera, C.; Kendelewicz, T. *Phys. Rev. B*, **1984**, *30*(10), 5571. doi:10.1103/PhysRevB.30.5571.

(78) Muramatsu, Y.; Gullikson, E. M. *Anal. Sci.* **2020**, *36*(12), 1507. doi:10.2116/analsci.20P171. PMID: 32830159.

(79) Tromp, M.; Moulin, J.; Reid, G.; Evans, J. *AIP Conf. Proc.* **2007**, *882*(1), 699. doi:10.1063/1.2644637.

(80) Engemann, C.; Hormes, J.; Longen, A.; Dötz, K. *Chem. Phys.* **1998**, *237*(3), 471. doi:10.1016/S0301-0104(98)00260-2.

(81) De Groot, F. *Chem. Rev.* **2001**, *101*(6), 1779. doi:10.1021/cr9900681. PMID: 11709999.