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► **To cite this version:**

Mónica Gisel Arellano-Sánchez, Christine Devouge-Boyer, Marie Hubert-Roux, Carlos Afonso, Mélanie Mignot. Chromium Determination in Leather and Other Matrices: A Review. *Critical Reviews in Analytical Chemistry*, 2022, 52 (7), pp.1537-1556. 10.1080/10408347.2021.1890545 . hal-03161912

**HAL Id: hal-03161912**

**<https://hal.science/hal-03161912>**

Submitted on 1 Jun 2023

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## **Chromium Determination in Leather and Other Matrices: A Review**

Mónica Gisel Arellano-Sánchez<sup>a</sup>, Christine Devouge-Boyer<sup>a</sup>, Marie Hubert-Roux<sup>b</sup>, Carlos Afonso<sup>b</sup>, and Mélanie Mignot<sup>a\*</sup>

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# Chromium Determination in Leather and Other Matrices: A Review

Leather industry plays an essential role in the world's economy; however, it also has a negative environmental impact due to the generation of significant quantities of wastes, some of which are classified as hazardous chemicals.

Chrome tanning, the most popular tanning process, employs chromium salts, acids, and some other chemicals. Some dyes can be also a source of chromium. As a result, hexavalent chromium, a known carcinogenic and mutagenic, can be found in leather products and cause allergic dermatitis or trigger other diseases. For this reason, it is important to quantify the total amount of chromium in final leather goods, as well as the oxidation state in which this element is found. This paper aims to summarize chromium contamination due to the leather production processes, and to review the analytical methods that have been used to determine chromium's most abundant species: Cr(III) and Cr(VI) in leather and other matrices (foodstuffs, cosmetic products, environmental, and pharmaceutical samples). The international and European regulations are presented as well as the last academic developments to extract and quantify chromium species. The future outlook of pre-treatment and quantification techniques are also discussed in this work, with a special focus on chromium interconversions.

Keywords: trivalent chromium; hexavalent chromium; chrome tanning; speciation analysis; isotope dilution

## Introduction

Leather industry plays an essential role in world's economy. Leather and leather products are among the most extensively traded commodities globally. However, negative environmental impacts arise due to the generation of relevant quantities of wastes in the leather industry, and the use of hazardous chemicals in tanneries, such as chromium, synthetic tannins, oils, resins, biocides and detergents [1].

In average, 3.5 million tons of different chemicals are used for leather processing. Some of the chemicals used are lime, sodium sulfide, chromium salts, dyes, and acids (Figure 1). A huge fraction of these chemicals are discharged into the effluent.

Approximately, around 50 m<sup>3</sup> of liquid wastes are discharged per ton of raw hide treated [2].

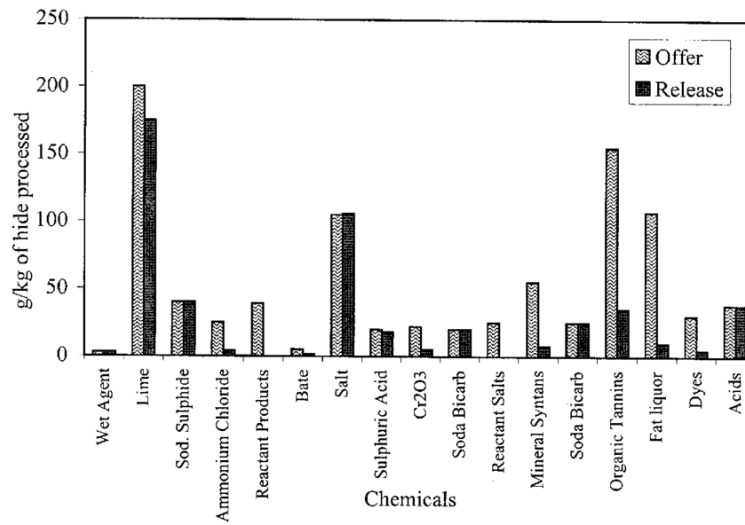


Figure 1. Major polluting chemicals used in leather processing. Obtained with permission from [2].

In the tanning process, trivalent chromium salts such as basic chromium sulfate ( $\text{Cr}_2(\text{OH})(\text{SO}_4)_3$ ) are widely used to transform raw skin into leather [3]. For chrome tanning, chromium waste emissions amount from 3.0 to 7.5 kg per ton of processed hide (Table 1) [2]. About 90% of all hides are treated with trivalent chromium salts [4].

Table 1. Waste emissions per leather manufacturing process. Modified from [2].

	<i>Soaking</i>	Liming	Deliming	Pickling	Chrome Tanning	Dyeing & Fatliquoring	Composite (incl. Washing)
BOD*	8.3-18.8	17.5-35.0	1.5-4.5	0.3-0.5	0.5-1.2	1.5-3.0	35.0-105.0
COD**	22.5-45.0	35.0-87.5	3.8-10.5	0.8-2.3	1.5-3.8	3.8-10.5	87.5-280.0
Total Solids	262.5-415.5	105.0-175.0	6.0-15.0	26.3-52.6	45.0-90.0	60-15.0	528.0-875.0
Solids suspended	22.5-52.5	21.0-70.0	2.3-6.0	0.8-2.3	1.5-3.8	0.9-1.5	70.0-140.0
Solids chlorides as Cl <sup>-</sup>	112.5-225.0	14.0-28.0	1.5-3.0	1.5-3.8	23.0-38.0	0.8-1.5	210.0-332.5
Chromium (total) as Cr	-	-	-	-	3.0-7.5	-	3.5-8.8

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(All values are expressed in kg/ton of hide processed).

\* BOD: Biochemical Oxygen Demand. \*\*COD: Chemical Oxygen Demand

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Nevertheless, even if Cr(III) is not considered as toxic, a fraction of this chromium can be oxidized into Cr(VI), a hazardous species. This unintentional oxidation of Cr(III) into Cr(VI) can be attributed to a high temperature, a dry atmosphere, and exposure to UV light [5]. Consequently, Cr(VI) can still be found in leather products and cause allergic dermatitis or trigger more serious illnesses. As many leather products are directly in contact with the skin, it is important to limit as much as possible the use of chromium salts as tanning agents.

It is important to remark that even if chromium tanning effluents contribute to a high concentration of chromium in the soils, this represents a minimal risk to crops. To delve more deeply into this subject, both chromium species can be absorbed by plants, yet, Cr(VI) is preferred due to sulfate carriers. In the roots, Cr(VI) is reduced to Cr(III) by the action of Fe(III) reductase enzymes [6]. Therefore, even if crops are irrigated with contaminated effluents, Cr(VI) is not likely to be transferred to foodstuffs. Antioxidants also contribute to limit the presence of Cr(VI) species in foodstuffs, which is the case of tea leaves and infusions, since they have a high content of flavonoid compounds [7]. Additionally, in the acidic conditions of the stomach, hexavalent chromium is likely to be reduced to trivalent chromium, representing no major risk to human health [8].

However, due to the dangerous effects of hexavalent chromium in leather, European and international agencies have adopted directives that limit its content in final products. Standard protocols have been developed in order to regulate the extraction and determination of Cr(VI). This review provides a summary of the pre-treatment techniques and the analytical methods that have been used for chromium

speciation in leather, as well as in other matrices such as foodstuffs, cosmetic products, environmental, and pharmaceutical samples. The latest developments and the future outlooks on chromium speciation are also discussed herein. Abbreviations used in this article are given in Table 2.

Table 2. Full names and abbreviations.

<b>Abbreviations</b>	<b>Full names</b>
ATR-FTIR	Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy
CE	Circular Economy
CE-ICP-MS	Capillary Electrophoresis - Inductively Coupled Plasma - Mass Spectrometry
COD	Chemical Oxygen Demand
CPE	Cloud Point Extraction
CRMs	Certified Reference Materials
CrPic	Chromium Picolinate
CSTEE	Scientific Committee on Toxicity, Ecotoxicity and the Environment
DCTA	1,2-cyclohexanediaminetetraacetic acid
DPC	1,5-diphenylcarbazide
DPCO	1,5-diphenylcarbazone
DRS-FTIR	Diffuse Reflectance - Fourier Transform Infrared Spectroscopy
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EEAA	Egyptian Environmental Association Affair
EMSL	Environmental Monitoring Systems Laboratory
EPA	Environmental Protection Agency
ESI-MS	Electrospray Ionization - Mass Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HBIG	2-hydroxybenzaldiminoglycine
HPIC-ICP-MS	High-Performance Ionic Chromatography - Inductively Coupled Plasma - Mass Spectrometry
HPLC-ICP-MS	High-Performance Liquid Chromatography - Inductively Coupled Plasma - Mass Spectrometry
HR-CS AAS	High-Resolution Continuum Source Atomic Absorption Spectrometry
IARC	International Agency for Research on Cancer
IC-DAD	Ion Chromatography - Diode Array Detector
IC-ICP-MS	Ion Chromatography - Inductively Coupled Plasma - Mass Spectrometry
IC-MS/MS	Ion Chromatography Tandem Mass Spectrometry
IC-UV-Vis	Ion Chromatography - UV-Visible Detection
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
IDL	Instrument Detection Limit
IDMS	Isotope Dilution Mass Spectrometry
ISO	International Organization for Standardization

IUPAC	International Union of Pure and Applied Chemistry
KED	Kinetic Energy Discrimination
LC-ICP-MS	Liquid Chromatography - Inductively Coupled Plasma - Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
MDL	Method Detection Limit
PDCA	2,6-pyridinedicarboxylic acid
PQL	Practical Quantification Limit
SEC	Size-Exclusion Chromatography
SIDMS	Speciated Isotope Dilution Mass Spectrometry
SM&T	Standard, Measurement and Testing Programme
SPE	Solid Phase Extraction
TBAH	Tetrabutylammonium Hydroxide
TDS	Total Dissolved Solids
Tris	Tris(hydroxymethyl)aminomethane
UV-Vis	UV-Visible Spectroscopy

### **Leather production processes**

The leather manufacturing process can be divided into four main steps: 1) preservation of hides and skins storage, 2) beam house operations, 3) tanning, and 4) post-tanning and finishing operations. A process diagram is shown in Figure 2.

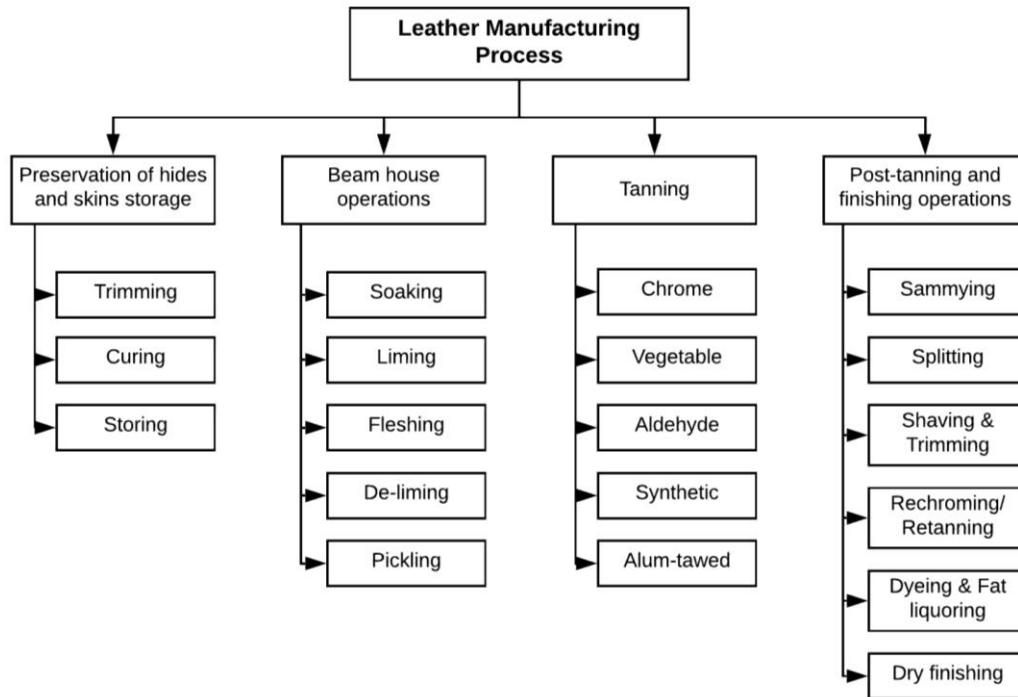


Figure 2. Leather manufacturing process.

### ***Preservation of hides and skins storage***

In this step, skins and hides are sorted and trimmed. A curing process is then implemented in order to prevent their decomposition, usually by salting and drying the raw material. This allows the skins and hides to be stored in ventilated or cooled areas for further processing [9].

### ***Beam house operations***

In the first instance, hides are soaked to get rid of salts and other solids, as well as to re-hydrate. Subsequently, a liming process (using lime liquors along with sodium sulfide) is performed to facilitate the removal of hair, flesh, fat, and inter-fibrillary protein.

Hides are then fleshed to remove excess tissues, muscles and fat. In a de-liming procedure, pH is adjusted around 8.0 in order to convert some proteins to soluble forms.

Pickling is required to correct the pH suitable to the tanning procedure (pH 2.8-3.0) with the use of a brine solution and sulfuric acid [1, 9, 10].



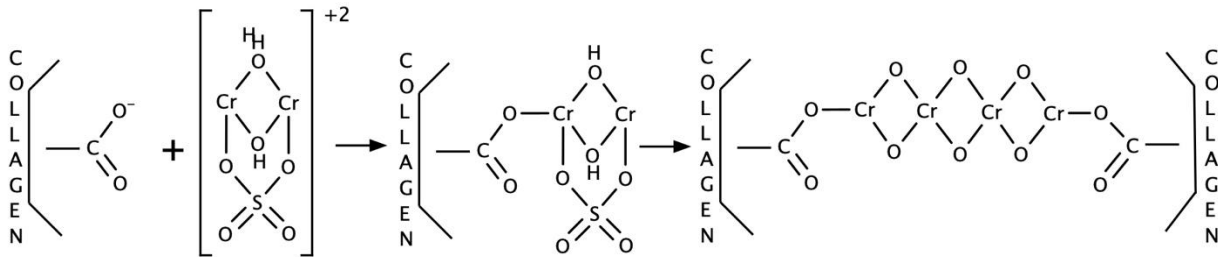
## ***Tanning***

The purpose of tanning is to transform raw hide into leather. There are several tanning methods, among which are chrome tanning, vegetable tanning, aldehyde tanning, synthetic tanning, and alum-tawing; being chrome and vegetable tanning the most widespread techniques [1].

The electronic structure of chromium ( $[\text{Ar}]3d^54s^1$ ) makes it a perfect tanning agent due to its incomplete 3d orbitals that can host additional electrons to form coordination complexes, which is one of the reasons why chrome tanning is the most common tanning system [11, 12]. Chrome tanning is performed with trivalent chromium salts, which ensures an excellent quality of the final product in terms of mechanical and hydrothermal resistance, attributable to the high rate of infiltration of Cr(III) salts into the interfibrillar spaces of the skins [4].

Collagen, the most abundant protein in the skins, consists of three polypeptide chains in the form of a helix. Aspartic and glutamic acid, some of the principal amino acids of collagen, provide amine ( $\text{R-NH}_2$ ) and carboxyl ( $\text{R-COOH}$ ) groups that are essential for chrome tanning [11]. During this process, pickled skins are treated with basic chromium sulfate,  $(\text{Cr}_2(\text{OH}(\text{SO}_4)_3)_3$ , (6-8%) and water as the medium. The first step is carried out in acidic medium (part of the pickling bath) permitting carboxyl groups to protonate. The objective of this step is to allow the chromium salts to penetrate homogeneously in the skin. Subsequently, the pH of the bath is raised to 3.8-4.0 with 10% alkali solution. In this step, carboxylate ions ( $\text{R-COO}^-$ ) are liberated from collagen, and chromium creates coordinate covalent bonds with the radicals containing the ionized carboxyl groups. After a self-polymerization reaction, this results in the formation of chromium-collagen complexes [10–12]. An example of a coordinate complex between collagen and chromium is shown in Figure 3.

Successful crosslinking of collagen in hides results in outstanding properties of the leather [13]. The duration of chrome tanning is around 6 hours. After this process,



leather is called wet blue [10].

Figure 3. Interaction of chromium with collagen.

On the other hand, vegetable tanning, one of the most ancient tanning methods, works through the action of water infusions of tannins or tannic acid [14]. Vegetable tanning agents are leached from wood, bark, leaves, roots, etc.[15] They may be described as a mixture of polyphenols which bind to collagen in order to confer resistance to the hides. Vegetable tanning materials can be divided into two groups [14]:

- (1) Pyrogallol group. They provide a yellow to light brown deposit (ellagic acid) to the leather and improve wearing properties and water resistance. Examples: sumach, chestnut, myrabolams, divi-divi, oak-wood, oak galls valonia, oak-barks.
- (2) Catechol group. They provide a pink to red sediment (phlobaphenes) to the leather and the resultant leather is more solid. Examples: gambier, hemlock, quebracho, mimosa, mangrove, pine, oak-bark.

Although vegetable tanning is a greener technology, chrome tanning reaction is faster (6 hours instead of 3 weeks), confers high hydrothermal stability, alters the structure of collagen in only a small way, makes collagen more hydrophobic (hence,

water-resistant) and allows the retention of colorants since Cr(III) can act as a dye fixing agent [16].

### ***Post-tanning and finishing operations***

Post-tanning operations include the removal of excess moisture (sammying), splitting the material into the desired thickness, mechanical shaving and trimming, and re-chroming or semi-chroming to improve the chromium content in leather. Subsequently, pH is neutralized and leather is dyed. Finally, the leather is fat-liquored and finished to obtain softness and fullness [9].

During the dyeing process, the leather is colored using: acid dyes, basic dyes, direct dyes, mordant dyes, premetallized dyes, reactive dyes or sulfur dyes. Azo dyes are organic colorants containing the azo group (N=N), usually bonded with chromophores. The azo group contributes to the delocalization of electrons in the chromophore, therefore, to the generation of color [16]. Orange II, shown in Figure 4, is an example of an azo dye widely used in the leather industry.

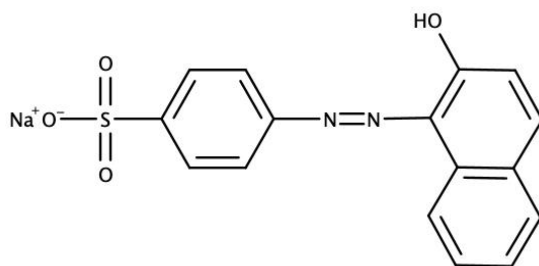


Figure 4. Molecular structure of Acid Orange 7 (Orange II).

These synthetic colorants are very popular in leather processing, though, its toxicity has been extensively investigated. Several azo dyes, specially benzidine-based colorants, have been reported to have a negative effect on human health, causing allergies or even triggering cancer [17, 18].

The European Union, after consulting the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) concerning the carcinogenicity of some azo dyes, provided a list of 22 prohibited aromatic amines. Azo dyes which may release these toxic aromatic amines in detectable concentrations, above 30 ppm, should not be used in textile and leather articles coming into contact with the human skin. This list includes the following aromatic amines: biphenyl-4-ylamine; benzidine; 4-chloro-o-toluidine; 2-naphthylamine; o-aminoazotoluene; 5-nitro-o-toluidine; 4-chloroaniline; 4-methoxy-m-phenylenediamine; 4,4'-methylenedianiline; 3,3'-dichlorobenzidine; 3,3'-dimethoxybenzidine; 3,3'-dimethylbenzidine; 4,4'-methylenedi-o-toluidine; 6-methoxy-m-toluidine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-oxydianiline; 4,4'-thiodianiline; o-toluidine; 4-methyl-m-phenylenediamine; 2,4,5-trimethylaniline; o-anisidine; 4-aminoazobenzene [19].

Besides azo dyes, premetallized dyes are another class of colorants that are widely used in the leather industry. Its concept relies on avoiding the two-step mordanting-dyeing process. Consequently, premetallized dyes are beforehand prepared by complexing a metal atom, usually chromium, with the molecules of the dye. These premetallized dyes exhibit interesting properties such as: increased fastness, good penetration and levelness of coloring, high fixation, etc.[16] An example of a premetallized dye (Acid Blue 158) is shown in Figure 5. Evidently, the use of these type of colorants contributes to the total content of chromium, which could pose a problem in case of an unintentional oxidation of Cr(III) into Cr(VI).

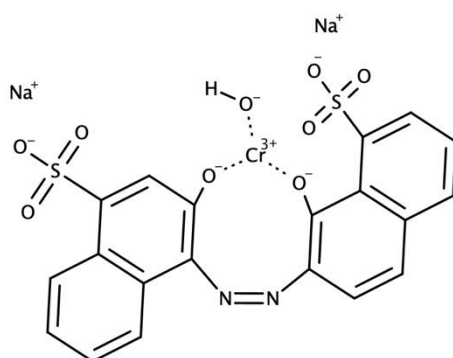


Figure 5. Molecular structure of a premetallized dye: Acid Blue 158.

Apart from the toxicity of some colorants, another inconvenient can emerge when hexavalent or trivalent chromium is determined through colorimetric methods. Some colorants (examples shown in Table 3) absorb in the same wavelength as some complexes used for chromium determination. Hence, for chromatographic applications, the efficiency of the pre-column or guard column is of great importance.

Table 3. Wavelengths of maximum absorbance of different colorants used in leather industry. Modified from [11].

Description	Acid Red 97	Acid Red 131	Brown HH 469
CAS Number	10169-02-5	70210-37-6	94933-05-8
$\lambda_{max}$	530 nm	550 nm	540 nm
Structure			

### Evolution of chromium content during leather products' life-cycle

As we mentioned before, chrome-tanned leather can represent a risk to human health due to the unintentional oxidation of Cr(III) into Cr(VI).

In 2014, Hedberg et al[20] characterized four differently tanned leather samples and exposed them to artificial sweat and phosphate buffer for chromium extraction, observing that co-released leather-specific species can reduce released hexavalent chromium. Therefore, no Cr(VI) was found in artificial sweat or phosphate buffer. However, leather samples with no reduction capacity and fewer aromatic groups, identified by Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR), revealed Cr(VI) at the surface.

Some years later, in 2018, the International Organization for Standardization (ISO) published a thermal pre-ageing procedure that permits to predict the evolution of hexavalent chromium content in tanned leather. The ISO 10195 standard requires the sample to be heated in an oven for a specific period of time (60° and relative humidity <20%, or 80° and relative humidity <10%, 24 hours). Nevertheless, this method does not simulate real conditions and only provides a tendency for the oxidation of Cr(III) into Cr(VI) [21].

In order to study the different storage conditions that could influence the evolution of hexavalent chromium content in leather, Fontaine et al.[5] studied natural and accelerated ageing in 4 bovine leather samples. A factorial design of experiment was performed with the following factors: temperature (40° or 80°), relative humidity (20% or 50%), presence or not of UV light, and exposure duration (24h or 48h). The experiments showed that temperature, relative humidity, and exposure to UV light had a great impact on Cr(VI) formation, having UV light a predominant role. In parallel, the same leathers were naturally aged for 12 months at room temperature and analyzed for hexavalent chromium content. They found out that the conditions that best simulate

natural ageing are the following: 1) 40°C, 50% relative humidity, presence of UV light, 48h, and 2) 40°C, 20% relative humidity, presence of UV light, 24h. Finally, they analyzed the same leather samples after undergoing through ISO 10195 artificial ageing, concluding that this standard does not accurately reflect what happens during natural ageing. Therefore, UV light should be taken into consideration for artificial ageing tests.

### **Regulations on hexavalent chromium**

Because of the dangerous effects of hexavalent chromium in human health, its content in leather products should be closely monitored.

As a result of an increment in chromium allergy, 16 228 patients with dermatitis patch tested between 1985 and 2007 at the Department of Dermato-Allergology, Getofte Hospital (Denmark), were studied to determinate the possible causes of this allergy. In particular, this study showed that around 55% of 197 patients with chromium allergy tested between 1995 and 2007 had been exposed to leather products (shoes, gloves and other sources) [22] .

Further determinations of hexavalent chromium in leather goods performed in Germany and Denmark between 2007 and 2008 showed that more than 30% of these leather articles contained above 3 mg/kg of hexavalent chromium [23].

In 2012, the Danish government submitted a report in which they proposed to the European Chemicals Agency a maximum hexavalent chromium content of 3 ppm in leather products sold in the European Union [23, 24].

Consequently, in 2014 the European Union adopted the restriction proposed by the Danish government, limiting the content of hexavalent chromium to 3 mg/kg of the total dry weight in leather articles coming into contact with the skin; otherwise these products could not be commercialized [25].

Currently, the ISO 17075 standard is the only internationally recognized procedure to determine the content of hexavalent chromium in leather via a colorimetric (part 1) [26] and a chromatographic (part 2) analysis [27]. This standard requires a previous selective extraction of Cr(VI) with  $K_2HPO_4 \cdot 3H_2O$  at pH 8.0, and it is suitable for concentrations above 3 mg/kg. The colorimetric analysis requires a reaction between Cr(VI) and DPC, and the detection of the resulting complex by UV-Vis spectroscopy at 540 nm. Concerning the chromatographic analysis, it can be performed by direct detection of the chromate peak at 372 nm, or through a post-column reaction with DPC. Post-column reaction offers more sensitivity and should be preferred in case the sample may contain reducing species that interfere with the analyte [28, 29]. Though, an inconvenience can surge when using post-column reaction due to the interference of colorants that may absorb at the same wavelength as the complex analyzed.

### **Chemistry of chromium**

Chromium is a transition metal that, after being processed, occurs in several chemical species: metallic chromium, trivalent chromium and hexavalent chromium [30].

Metallic chromium, chromium 0, can be found in alloys and coatings. As a coating, chromium exhibits anti-wear and anticorrosion properties, and can also be used as decoration. It is obtained as a result of an electrochemical reduction of chromium salts [31, 32].

Trivalent chromium, Cr(III), exists as cationic species ( $Cr^{3+}$ ,  $Cr(OH)^{2+}$ ,  $Cr(OH)_2^+$ ) [6] and has been considered as an essential nutrient involved in the regulation of glucose [33, 34], due to its participation in the activation of an insulin receptor [35, 36]. It can be frequently found in the form of chromium picolinate in dietary supplements. Nonetheless, some studies suggest no relevant benefits in certain populations [37]. Though, more studies on proper dosage and length of time of



supplementation should be performed in order to accurately define the advantages of chromium picolinate supplementation [38].

By the other hand, hexavalent chromium, Cr(VI), exists as anionic species ( $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HCr}_2\text{O}_7^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ), and it is a known mutagenic, classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans [39]. For this reason, it is of great importance the selective determination of Cr(VI).

As shown in the Eh-pH diagram from Figure 6, in aqueous systems, the oxidation state of chromium is determined by redox potential and pH [40].

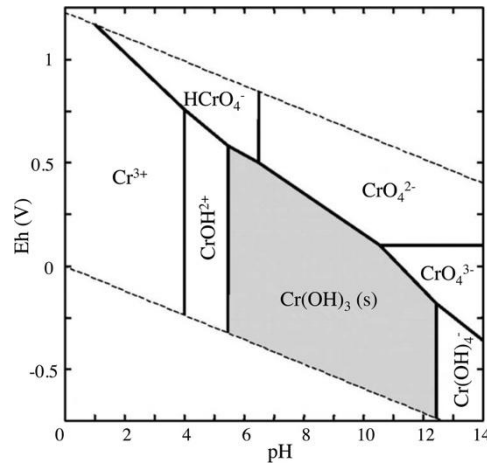
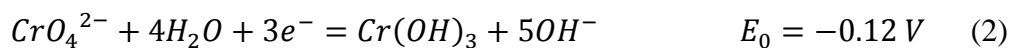


Figure 6. Eh-pH diagram of chromium. Reproduced of [40] with permission from Elsevier.

The reduction process in acidic solution can be expressed as [41]:



and in alkaline solution:



As we can see, interconversions can take place between the oxidation state of chromium. Cr(VI) can be reduced to Cr(III) under acidic conditions; by the other hand,

Cr(III) can be oxidized to Cr(VI) in the presence of oxygen under alkaline conditions [3].

Dias da Silva et al.[4], after performing an extraction scheme that will be further described, noticed that in one of the steps (oxidizing conditions) about 48%, 5%, and 0.9% of chromium (percentages from three different samples) were converted into Cr(VI). Martone et al.[42], knowing the possibility of this type of transformations, employed isotopic dilution techniques to follow species interconversions during the analysis of Cr(VI) in dietary supplements. The results showed that 11 samples contained a highly reductive matrix that transformed all the spiked  $^{53}\text{Cr(VI)}$  into  $^{53}\text{Cr(III)}$ . For 14 samples, the phosphate buffer extraction (basic media) caused an oxidation of Cr(III) to Cr(VI) that ranged from 0.3 to 47.9%.

This poses a difficulty in the speciation of chromium, as the sample preparation protocols can lead to an interconversion between Cr(III) and Cr(VI), thus distorting the results [43, 44]. Therefore, the real challenge is to preserve, as much as possible, the initial distribution of both chromium species throughout the pre-treatment and analysis stages. Protocols should guarantee that no Cr(VI) is generated from the oxidation of Cr(III). In the same way, no Cr(VI) should be masked by its reduction to Cr(III) during its extraction and determination.

### ***Complexing agents***

The use of complexing agents can be a useful tool to achieve trivalent and hexavalent chromium separation. Some of the most popular chelating agents are 1,5-diphenylcarbazide (DPC), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), 2,6-pyridinedicarboxylic acid (PDCA), 1,2-cyclohexanediaminetetraacetic acid (DCTA), and 2-hydroxybenzaldiminoglycine

(HBIG). Some of them can form a complex with Cr(III), or with Cr(VI) after oxidation of the organic agent. The main examples are presented below.

### *DPC*

In acidic medium, Cr(VI) oxidizes DPC to 1,5-diphenylcarbazone (DPCO), resulting in a violet Cr(III)-diphenylcarbazone complex that can be detected by UV-Vis spectroscopy at 540 nm [26, 45, 46]. The reaction is shown in Figure 7.

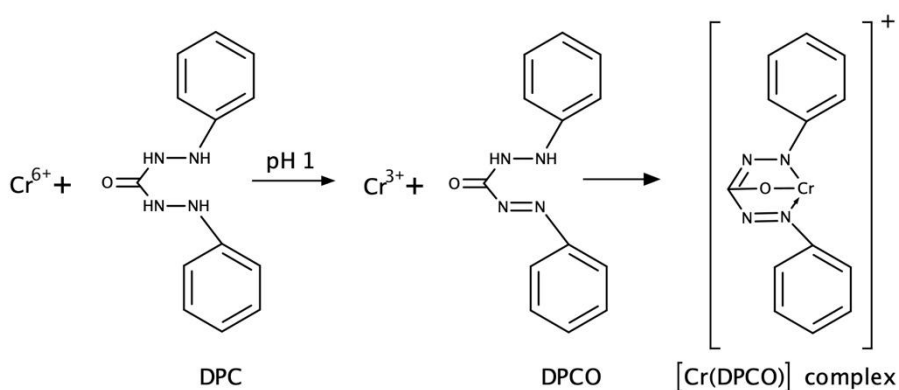


Figure 7. Complexation of Cr(VI) with DPC.

### *EDTA*

EDTA can form colored complexes with some cations. In slightly acidic medium, EDTA can react with Cr(III) to form a violet Cr(III)-EDTA<sup>-</sup> complex (anionic species) that absorbs strongly at 540 nm [45]. Due to the slow rate of complexation at room temperature, solutions are frequently heated to accelerate the reaction [47, 48].

### *DTPA*

Similarly to EDTA, DTPA can react with trivalent chromium to produce the [Cr(DTPA)]<sup>2-</sup> complex. Yet, poorer stability has been reported for [Cr(DTPA)]<sup>2-</sup> [49].

### *PDCA*

PDCA is also used to complex Cr(III) due to its high selectivity compared to other ligands, resulting in a  $[\text{Cr}(\text{PDCA})_2]^-$  complex [50]. The reaction between Cr(III) and 2 molecules of PDCA is described in Figure 8.  $[\text{Cr}(\text{PDCA})_2]^-$  can be quantified through direct UV detection at 335 nm and 535 nm [46].

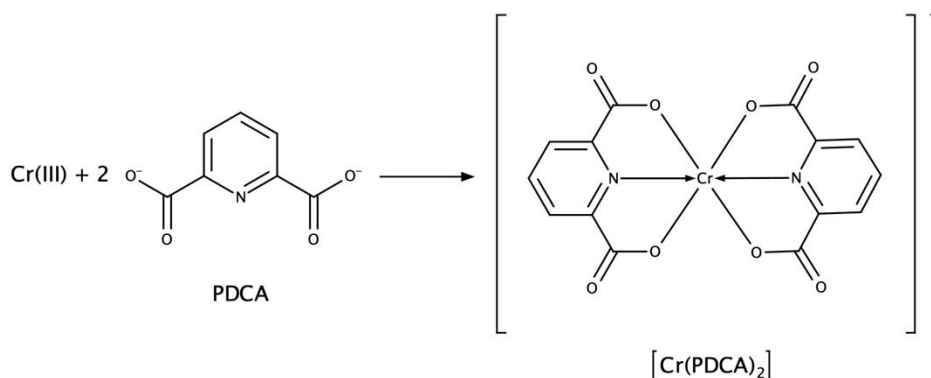


Figure 8. Complexation of Cr(III) with PDCA.

### *DCTA*

In a slightly acidic medium (pH 6.5 - 7.0), Cr(III) can be chelated with DCTA to produce a single charged Cr-DCTA<sup>-</sup> complex [36]. This reaction occurs slowly at room temperature but can be warmed up to 60 °C to speed up the rate of reaction. The Cr-DCTA<sup>-</sup> complex can be measured through UV detection at 210 nm [51].

### *HBIG*

HBIG has also showed potential to chelate Cr(III). Complexation occurs instantaneously at pH 7.5, and requires the use of a buffer solution: disodium hydrogen orthophosphate (0.01 M) and sodium hydrogen orthophosphate (0.01 M). The chromium(III)-HBIG complex has a maximum absorbance a 565 nm [52]. This method is selective and sensitive.

Nevertheless, UV detection is not a very selective method and some other compounds, especially when working on complexes matrices, can be extracted and

absorb at the same wavelength than the complex formed between chromium and the ligand.

### Pre-treatment and determination methods

Due to the nature of the samples, chromium speciation in leather requires a treatment before approaching its determination. Concerning leather products, only few pre-treatment and analytical methods have been reported. Therefore, this section presents a review of pre-treatment and determination methods for chromium species in leather, but also includes chromium speciation studies in environmental and pharmaceutical samples, foodstuffs, and cosmetic products. In this way, we can see what is being done with other matrices, and what can be implemented when working with leather. Table 4 provides a summary of the reported literature of chromium speciation. It is arranged by analytical technique, and includes an exhaustive revision of pre-treatment and analytical methods. The way in which the different analytical figures of merit were calculated is specified in Table 5 (NA whenever the author did not specified the calculation).

### Sample pre-treatment

Depending on the extraction conditions (i.e. pH, concentration, etc.), chromium can be encountered in different forms as specified in Table 6.

Table 6. Dominant Cr species in different aqueous conditions.

Cr oxidation state	Aqueous conditions	Dominant aqueous Cr species
Cr(III)	pH < 3.5	Cr <sup>+</sup>
	pH > 3.5	CrOH <sup>2+</sup>
	Increased pH	Cr(OH) <sub>2</sub> <sup>+</sup>
	Increased pH	Cr(OH) <sub>3</sub> <sup>0</sup> (Aq)
	Increased pH	Cr(OH) <sub>4</sub> <sup>-</sup>
	Higher Cr concentrations	Cr <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>
	Higher Cr concentrations	Cr <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup>
Cr(VI)	pH < 6.5 & conc. < 30 mM	HCrO <sub>4</sub> <sup>-</sup>
	pH < 6.5 & conc. > 30 mM	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>
	pH > 6.5	CrO <sub>4</sub> <sup>2-</sup>

As previously described, ISO established a normalized method in which hexavalent chromium is leached from leather samples by means of a phosphate buffer ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ) at pH 8.0 [26, 27]. This pre-treatment method was also implemented by Rezić and Zeiner[53] for Cr(VI) extraction from leather. Pastore and his colleagues[44] evaluated the normalized method and presented evidence of Cr(VI) formation, after the oxidation of Cr(III) by peroxides. As a consequence of the results obtained, they proposed a more suitable extraction solution consisting of a 0.1M phosphate solution (0.1M  $\text{NaH}_2\text{PO}_4$  and 0.1M  $\text{H}_3\text{PO}_4$ ) at pH 4.4 in presence of 5% NaCl.

Costa et al.[54] tried an alkaline extraction of Cr(VI) in leather using a NaOH 0.1M solution. A different approach was studied by Dias da Silva et al[4] on which tanned leather shavings were pre-treated using the SM&T (Standard, Measurement and Testing Programme) sequential extractions scheme. Considering Cr concentrations, the extracted fractions can be ordered as follows: oxidizable > exchangeable > reducible > residual. The oxidizable fraction was tested to determine the concentration of Cr(VI). For this fraction, they observed that a part of the released chromium was oxidized to from Cr(III) to Cr(VI), which exposes the danger of the disposal of this type of waste under oxidative conditions.

For soils, sludges, sediments, and similar waste materials, the SW-846 Environmental Protection Agency (EPA) 3060A method defines an extraction protocol for hexavalent chromium using 0.28M  $\text{Na}_2\text{CO}_3$ /0.5M NaOH, a phosphate buffer (0.5M  $\text{K}_2\text{HPO}_4$ /0.5M  $\text{KH}_2\text{PO}_4$ ) and  $\text{MgCl}_2$  [55].  $\text{Mg}^{2+}$  serves to suppress oxidation of Cr(III) into Cr(VI). Petrucci and Senofonte[56] adapted the EPA 3060A method for cosmetic products pre-treatment. This alkaline digestion has been employed for traditional Chinese medicines as well [57].

An alkaline extraction of hexavalent chromium with  $\text{NH}_4\text{OH}$  is frequently used when working with foodstuffs (milk, cheese, yoghurt, cereal products, chocolate, vegetables, fruits, meat, fish, eggs, and beverages) [58–60]. Some other selective alkaline extractions of Cr(VI) require the use of 0.1M  $\text{Na}_2\text{CO}_3$  [61, 62] or 0.01M NaOH / 1M  $\text{NH}_4\text{NO}_3$  [63].

Cloud Point Extraction (CPE) has been used for separation and preconcentration of metallic ions, among them chromium [64–66]. Kiran et al. [67] reported the determination of Cr(III) in industrial wastewater, natural water, and spiked water samples after its complexation with bis-[2-hydroxynaphthaldehyde] thiourea using CPE. For the determination of Cr(VI) in turmeric samples, Tiwari et al. [68] complexed Cr(VI) with DPC and then used the non-ionic surfactant Triton X-100 for the determination of Cr(VI) by CPE. Likewise, Solid Phase Extraction (SPE) has also permitted the preconcentration of Cr(VI) on Amberlite XAD-1180 resin after its reaction with DPC, as reported by Narin et al. [69]

For total chromium determination in siliceous matrices, organic matrices, and other complex matrices, the SW-846 EPA 3052 method proposes a microwave digestion with  $\text{HNO}_3$  and HF. HCl and  $\text{H}_2\text{O}_2$  can be alternatively used [70].

### ***Determination methods***

#### *UV-Visible detection*

Regarding hexavalent chromium determination in leather, ISO proposes a colorimetric analysis by UV-Vis spectroscopy at 540 nm after the reaction between Cr(VI) and DPC, as well as a chromatographic analysis (using an anion exchange column and a pre-column) by direct detection of the chromate peak at 372 nm, or after a post-column reaction with DPC by measuring the absorption peak at 540 nm [26, 27]. Similarly, the SW-846 EPA 7196A method describes a UV-Visible determination of hexavalent

chromium in groundwaters based on the same reaction[71]. In order to evaluate the ISO standardized protocol, Pastore et al.[44] performed Ion Chromatography and post-column reaction with DPC, and obtained a limit of quantification (LOQ) of 0.15 mg/kg after changing to a more suitable extraction solution to avoid Cr(III) oxidation into Cr(VI) (0.2 g of leather and 100 mL of 0.1M phosphate solution at pH 4.4, and 5% NaCl). For this study, they used an anion exchange Dionex IonPac AG7 guard column. To eliminate any interference of colorants, they employed SPE C18 cartridges that were activated before injection.

UV-Visible determination through Cr(VI) and DPC complexation has been extensively executed by several authors. Rezić and Zeiner[53] analyzed leather products from different chromium tanning processes and obtained a limit of detection (LOD) of 15 µg/L for Cr(VI). They also quantified total Cr after oxidation of Cr(III). Costa et al.[54] evaluated leather samples using this complexation together with a colorimetric analysis of digital images by means of a mobile phone and PhotoMetrix App, achieving a LOD of 0.6 mg/kg. Dias da Silva et al.[4] determined extractable hexavalent chromium in leather samples, in the oxidizable fraction of the SM&T extractions scheme, by UV-Visible detection through the DPC reaction.

For drinking water, groundwater, and industrial wastewater effluents, Ion Chromatography (anion exchange Dionex IonPac AS7 column and NG1 guard column capable of removing strongly absorbing organics) with UV-Vis detection after post-column reaction with DPC has been reported in the SW-846 EPA 7199 method with a method detection limit (MDL) of 0.3-0.4 µg/L [72] and by the Environmental Monitoring Systems Laboratory (EMSL) obtaining a MDL of 1 µg/L [73]. For soil and wastewater samples, Phesatcha et al.[74] isolated Cr(III) by derivatization with PDCA on a pre-column and complexed Cr(VI) by post-column reaction with DPC. Both



complexes were analyzed using an ion exchange Dionex IonPac CS5A column and a CG5A guard column. The detection was set at 335 nm from 0.0 to 4.7 min for Cr(III), and at 530 nm from 4.7 to 8.0 min for Cr(VI). Tiwari et al.[68] detected the same reddish-violet complex at 540 nm by Diffuse Reflectance - Fourier Transform Infrared Spectroscopy (DRS-FTIR) with a LOD of 1.22 µg/mL for Cr(VI) in turmeric samples.

#### *Off-line analytical techniques*

Certain off-line techniques that have been used for chromium speciation in various matrices are Flame Atomic Absorption Spectrometry (FAAS) [67, 69], Electrothermal Atomic Absorption Spectroscopy (ETAAS) [63], Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [62] and High-Resolution Continuum Source Atomic Absorption Spectrometer (HR-CS AAS) [61]. Nevertheless, these techniques do not allow the separation of species and require a selective extraction of either one of the two species. Generally, the other species is calculated by subtraction of the extracted species from the total content of chromium.

#### *Capillary electrophoresis*

A different approach was reported by Chen et al.[36] via Capillary Electrophoresis - Inductively Coupled Plasma - Mass Spectrometry (CE-ICP-MS), achieving the separation of Cr(III), Cr(VI) and Chromium Picolinate (CrPic) in nutritional food samples. This was accomplished by chelating Cr(III) with DCTA, allowing the separation of the single-charged Cr-DCTA<sup>-</sup> complex from the double-charged molecule CrO<sub>4</sub><sup>2-</sup> (Cr(VI)), and CrPic (no charge).

#### *Chromatographic methods coupled to Mass Spectrometry*

Coupling chromatographic methods with Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) has facilitated and increased speciation studies, allowing the separation and posterior quantification of trivalent and hexavalent chromium.

Hernandez and her team[58] analyzed Cr(VI) in dairy (milk, cheese, yoghurt) and cereal products by High-Performance Ionic Chromatography – ICP-MS (HPIC-ICP-MS) with an ion exchange Dionex IonPac CS5A column and a CG5A guard column, attaining the optimization of a sensitive and specific on-line method where no pre-concentration was required. In a further study, they determined Cr(III) in dairy products by in-situ complexation of EDTA and the determination of the Cr(III)-EDTA<sup>-</sup> complex by High-Performance Liquid Chromatography – ICP-MS (HPLC-ICP-MS) (using the same columns as in the previous study) [59]. Vacchina et al.[60] also worked with HPLC-ICP-MS (ion exchange Dionex IonPac CS5A column) to accomplish hexavalent chromium determination in dairy products, flour, chocolate, vegetables, fruits, meat, fish, eggs, and beverages. To study the interactions between Cr(VI) and the matrices, they employed size-exclusion HPLC-ICP-MS (gel filtration Superdex-200 HR 10/30 column). However, no Cr(VI) was found in any of the samples, attributing these results to the instability of Cr(VI) in food matrices.

HPLC-ICP-MS was also implemented for the analysis of Cr(III) and Cr(VI) in environmental samples. Jabłońska-Czapla et al.[75] accomplished chromium speciation in water and bottom sediments using an anion exchange Dionex IonPac AG7 guard column and 0.1M NH<sub>4</sub>NO<sub>3</sub> / 0.8M HNO<sub>3</sub> gradient elution after buffer extraction. According to Séby et al.[76], who worked with an ion exchange Dionex IonPac CS5A column and a CG5A guard column, they were not able to quantify Cr(III) in natural water samples due to its possible precipitation in alkaline medium. To avoid this problem, Hu and his colleagues[77] stabilized Cr(III) with EDTA, and were able to separate it from hexavalent chromium and polymeric Cr(III) using a reversed phase Spheri-5 C18 column, obtaining a LOD of 0.9 µg/L for both chromium species in wood leachates, surface waters, tap water, and wastewater. Li et al.[57] attained a good

recovery of Cr(VI) in traditional Chinese medicines by HPLC-ICP-MS using a weak anion exchange Agilent Bio WAX column and  $\text{NH}_4\text{NO}_3$  as mobile phase. Evaluating iron supplements, Araujo-Barbosa et al.[78] reported a fast chromatographic run (5 minutes) using 1.0mM tetrabutylammonium hydroxide (TBAH), 0.7mM EDTA and 5% methanol at pH 7.2. as mobile phase and a Phenomenex Kinetex reversed phase C18 column, allowing the separation of Cr(III) and Cr(VI).

Speciation in drinking water has been addressed by Ion Chromatography – ICP-MS (IC-ICP-MS) with minimal sample preparation using nitric acid as mobile phase and an anion exchange Dionex IonPac AG7 guard column for separation of both species, attaining low LOD (ng/g, pg/L) [79, 80]. Similar conditions were used by Kutscher et al.[81] for Cr(VI) quantification in toys and toy material with the aim of studying the migration of elements in these samples. IC-ICP-MS with an anion exchange Dionex IonPac AS7 column and an AG7 guard column was also employed by Petrucci and Senofonte[56], where they found that one of the 4 cosmetic products evaluated contained more than 5 mg/L of Cr(VI). Chen et al.[49] investigated wastewater by IC-ICP-MS using 20mM  $\text{NH}_4\text{NO}_3$  and 10mM  $\text{NH}_4\text{H}_2\text{PO}_4$  at pH 7.0 as mobile phase, an anion exchange Agilent G3154A/101 column, and a G3154A/102 guard column. Subsequently, they evaluated the stability of Cr(III) complexes with three aminopolycarboxylic acids (EDTA, DTPA and PDCA) by Electrospray Ionization - Mass Spectrometry (ESI-MS). They attained the separation of Cr(VI) and Cr(III) as  $\text{Cr(III)-EDTA}^-$ , and confirmed the kinetical stability of the chromium-chelate complex. Direct injection of the samples was possible and no  $\text{Cl}^-$  interferences were found. Hagendorfer and Goessler[82] studied chromium speciation in cement and homeopathic drugs by IC-ICP-MS without derivatization. This was attained by taking into account the distribution of Cr species in water and working in the window of pH where Cr(VI)

is not reduced and Cr(III) does not precipitate, which can be described as the gray shading in Figure 9. For this reason, they used a mobile phase of pH 3.5 (90 mM  $(\text{NH}_4)_2\text{SO}_4$  and 10 mM  $\text{NH}_4\text{NO}_3$ ) and a metal-free Rspak NN-814 PEEK column.

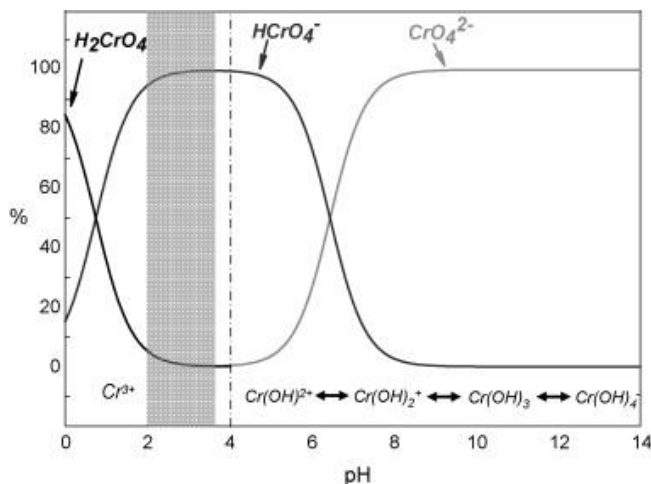


Figure 9. Distribution of Cr species in water. Reproduced of [82] with permission from Elsevier.

Gürleyük and Wallschläger[48] complexed Cr(III) with EDTA and achieved the separation of chromium species in CRMs (synthetic and estuarine water) by IC-ICP-MS using an anion exchange Dionex IonPac AS7 column, an AG7 guard column, a self-regenerating suppressor, and 50mM  $\text{NH}_4\text{NO}_3$  (pH 8) as eluent. They obtained an LOD of 12 ng/L for Cr(VI) and 5 ng/L for Cr(III).

When working with ICP-MS for Cr determination, it is important to precise that polyatomic interferences can arise with the presence of carbon or chlorine. For  $^{52}\text{Cr}^+$  the interferences could be  $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ ,  $^{35}\text{Cl}^{17}\text{O}^+$  and  $^{40}\text{Ar}^{12}\text{C}^+$ ; and for  $^{53}\text{Cr}^+$  the interferences could be  $^{37}\text{Cl}^{16}\text{O}^+$ ,  $^{40}\text{Ar}^{13}\text{C}^+$  and  $^{40}\text{Ar}^{12}\text{C}^1\text{H}^+$ . These interferences can be reduced by using collision/reaction cell and kinetic energy discrimination (KED) with He as collision gas[58, 83].

*Isotopic dilution techniques*

To improve the accuracy of chromium speciation, several authors have implemented isotope dilution techniques. The two different approaches of isotope dilution are Isotope Dilution Mass Spectrometry (IDMS) and Speciated Isotope Dilution Mass Spectrometry (SIDMS). While IDMS serves for total element determination through the addition of a known quantity of an enriched isotope, SIDMS is capable of tracing species interconversions by labelling each species with enriched isotopes.

The SW-846 EPA 6800 method describes a procedure for the implementation of IDMS and SIDMS, for the speciation of different elements, among which chromium is part of the list, in a variety of samples such as waters, solids, blood, foods, extracts or digests [84]. Mädler et al. implemented SIDMS by adapting the EPA 6800 method for trace (MDL of 0.007 µg/L)[85] and ultra-trace level analysis (MDL of 2 ng/L)[86] of Cr(VI) in environmental water and sediment samples by Ion Chromatography Tandem Mass Spectrometry (IC-MS/MS) through an anion exchange Dionex IonPac AS20 column and an AG20 guard column. <sup>50</sup>Cr(VI) and <sup>53</sup>Cr(III) tracers were used by Drinčić et al.[87] to follow possible interconversions in the determination of hexavalent chromium by HPLC-ICP-MS using an anion exchange Mono Q HR 5/5 column. However, Cr(VI) was not detected in river sediments. SIDMS has also been reported for teas, bread samples [43], and dietary supplements [42].

IDMS was studied by Fabregat-Cabello et al.[88], who quantified Cr(VI) in several Certified Reference Materials (CRMs) after microwave assisted extraction with 5mM EDTA (5 min at 90 °C and 5 min at 110 °C) by IC-ICP-MS using an anion exchange Dionex IonPac AS9-HC column. The CRMs analyzed in this work were: soil containing chromite ore processing residue, welding dust loaded on a filter, and sandy clay soil. In this work, only <sup>50</sup>Cr(VI) was added to the samples as Cr(III) was found to be stable in the extracting conditions. Guidotti et al.[89] modified these extraction

conditions (only one cycle of 5 min at 80 °C) to minimize Cr(VI) reduction during the analysis of soil samples from a contaminated area.  $^{53}\text{Cr(VI)}$  was traced to attain accurate quantification by Liquid Chromatography – ICP-MS (LC-ICP-MS) using the same column as Fabregat-Cabello et al.[88]. The application of both IDMS and SIDMS was reported by Wolle et al[90] in soil samples.

In the absence of CRMs for chromium speciation in leather samples, only spiking and isotope dilution techniques can help to improve the accuracy of the measurements. Therefore, these techniques that had been employed in other matrices should set the tone for what should be considered when working with leather.

Table 4. Pre-treatment and determination methods for chromium speciation in different matrices.

Matrix	Sample pre-treatment	Analytical technique	Analyte	Analytical Conditions	Analytical Figures of Merit	Important Remarks	Reference
Nutritional food samples	Extraction with 25% methanol solution under ultrasonic agitation.	CE-ICP-MS	Cr(III), Cr(VI), CrPic	CE voltage: 13 kV. 50 cm x 75 µm i.d. x 375 µm o.d. fused silica capillary	IDL: 0.10 ng/mL for Cr(VI), 0.18 ng/mL for Cr(III), 0.20 ng/mL for CrPic. MDL: 1.0 ng/g for Cr(VI), 1.8 ng/g for Cr(III), 2.0 ng/g for CrPic.	Cr(III) was chelated with DCTA to form a single charged Cr-DCTA <sup>-</sup> complex.	Chen et al.[36]
Turmeric samples	The Cr(VI)-DPC complex was extracted of using Triton X-100 as non-ionic surfactant. CPE was used as preconcentration process.	DRS-FTIR	Cr(VI)	Wavelength: 540 nm.	LOD Cr(VI): 1.22 µg/mL. LOQ Cr(VI): 4.02 µg/mL.	Cr(VI) is complexed with DPC prior to extraction.	Tiwari et al.[68]
Bread samples	Acid digestion (total Cr) and selective alkaline extraction of Cr(VI) with 0.01M NaOH and 1M NH <sub>4</sub> NO <sub>3</sub> .	ETAAS	Total Cr, Cr(VI)	Ashing temperature: 1600 °C. Atomization temperature: 2500 °C	LOD: 1.5 µg/kg for total Cr and 1.7 µg/kg for Cr(VI). LOQ: 4.95 µg/kg for total Cr and 5.60 µg/kg for Cr(VI).	From 152 bread samples, about 10% of the total Cr in bread is in the Cr(VI) form.	Soares et al.[63]
Industrial wastewater, natural water, and spiked water samples	Cr(III) is complexed with bis-[2-hydroxynaphthaldehyde] thiourea and extracted with the non-ionic surfactant Triton X-100.	FAAS	Total Cr, Cr(III)		LOD~0.18 µg/L.	Total Cr: determined after reducing Cr(VI) to Cr(III). Cr(VI): calculated by subtracting Cr(III) from the total Cr.	Kiran et al.[67]
Tap water, bottled mineral water, and red lentil	Cr(VI) is complexed with DPC. Then the Cr(III)-diphenylcarbazone complex was analyzed on Amberlite XAD-1180 resin.	FAAS	Total Cr, Cr(VI)	Elution with 1M HNO <sub>3</sub> in acetone.	LOD: 7.7 µg/L for Cr(VI) and 8.6 µg/L for total Cr.	Total Cr was determined after oxidizing Cr(III) to Cr(VI). Cr(III) was calculated by subtracting Cr(VI) from total Cr.	Narin et al.[69]
Tanned leather	Acid digestion (total Cr) and SM&T Sequential Extractions Scheme (oxidizable > exchangeable > reducible > residual).	FAAS, UV-Vis	Total Cr, Cr(VI)	Wavelength: 540 nm.		Cr was determined in each extracted fraction. Cr(VI) was determined in the oxidizable fraction by reaction with DPC.	Dias da Silva et al.[4]
Teas	Acid digestion (total Cr) and alkaline extraction of Cr(VI) with 0.1M Na <sub>2</sub> CO <sub>3</sub> .	GFAAS	Total Cr, Cr(VI)	Atomization temperature: 2500 °C.	LOD: 0.020 µg/g for Cr(VI). LOQ: 0.07 µg/g for Cr(VI) (tea samples).	Kinetic of Cr(VI) leaching from tea sample was also studied.	Mandiwana et al.[62]
Dairy (milk, cheese, yoghurt) and cereal products	Acid digestion (total Cr) and extraction of Cr(VI) with NH <sub>4</sub> OH.	HPIC-ICP-MS	Total Cr, Cr(VI)	Column: Dionex IonPac CG5A, CS5A (4x250 mm). Mobile phase: 2M HNO <sub>3</sub> , H <sub>2</sub> O. Gradient mode.	LOQ: 0.8 µg/kg (cereals), 0.6 µg/kg (dairy products) for Cr(VI).	Cr(VI) was not found in dairy and cereal products.	Hernandez et al.[58]
Iron supplement samples	Acid digestion (total As, Cr) and extraction with ultrapure water and microwave assisted radiation (for speciation).	HPLC-ICP-MS	Total As/Cr, As(III)/As(V), Cr(III)/Cr(VI)	Column: Phenomenex Kinetex C18 (4.6x100 mm). Mobile phase: 1.0mM TBAH, 0.7mM EDTA and 5% methanol at pH 7.2.	LOD: 0.029 µg/g for Cr, 0.014 µg/g for Cr(III), 0.04 µg/g for Cr(VI). LOQ: 0.089 µg/g for Cr, 0.5 µg/g for Cr(III), 0.14 µg/g for Cr(VI).	Fast chromatographic run (5 min).	Araujo-Barbosa et al.[78]
Dairy products, flour, chocolate, vegetables, fruits, meat, fish, eggs, and beverages	Acid digestion (total Cr) and extraction of Cr(VI) with NH <sub>4</sub> OH at pH 11.5.	HPLC-ICP-MS	Total Cr, Cr(VI)	SEC column: Superdex-200 HR 10/30 (10x300 mm). Ion exchange column: Dionex IonPac CS5A (4x250 mm). Mobile phase (SEC): 30mM tris buffer pH 7.5. Mobile phase (Ion exchange): 85mM HNO <sub>3</sub> .	LOD Cr(VI): 1 µg/L and 10 µg/kg. LOQ Cr(VI): 3 µg/L and 30 µg/kg.	SEC HPLC-ICP-MS for Cr(VI)/matrix(milk) interactions. Ion-exchange HPLC-ICP-MS for Cr(VI) quantification.	Vacchina et al.[60]
Natural waters samples	Filtration prior to analysis.	HPLC-ICP-MS	Cr(III), Cr(VI)	Column: Dionex IonPac CG5A (4x50 mm), CS5A (4x250 mm). Mobile phase: HNO <sub>3</sub> .	LOD: 0.19 µg/L for Cr(VI), 0.32 µg/L for Cr(III). LOQ: 0.6	Recovery of Cr(III) was not completely quantitative due to its	Séby et al.[76]

					$\mu\text{g/L}$ for Cr(VI), 0.9 $\mu\text{g/L}$ for Cr(III).	high reactivity in alkaline medium.	
Sediment samples	Acid digestion (total Cr) and Cr(VI) extraction with 2% NaOH + 3% $\text{Na}_2\text{CO}_3$ .	HPLC-ICP-MS	Total Cr, Cr(VI)	Column: Mono Q HR 5/5 (5x50 mm). Mobile phase: Linear gradient elution from 100% water to 100% 0.7M NaCl.	LOD: 1.25 $\mu\text{g/kg}$ for Cr(VI). LOQ: 4.0 $\mu\text{g/kg}$ for Cr(VI).	The addition of 0.4M $\text{MgCl}_2$ prevented oxidation of Cr(III). SIDMS was implemented.	Drinčić et al.[87]
Teas and bread samples	Acid digestion (total Cr) and alkaline extraction of Cr(VI) with 0.1M $\text{Na}_2\text{CO}_3$ or 0.01M NaOH/1M $\text{NH}_4\text{NO}_3$ .	HPLC-ICP-MS	Total Cr, Cr(III), Cr(VI)	Column: Mono Q HR 5/5 (5x50 mm). Mobile phase: Linear gradient elution from 100% water to 100% 0.7M NaCl .	LOD: 0.5 $\mu\text{g/kg}$ for total Cr, 0.03 $\mu\text{g/L}$ for Cr(VI), 0.02 $\mu\text{g/L}$ for Cr(III). LOQ: 1.7 $\mu\text{g/kg}$ for total Cr, 0.11 $\mu\text{g/L}$ for Cr(VI), 0.07 $\mu\text{g/L}$ for Cr(III).	Cr(VI) cannot exist in tea and bread samples due to the presence of organic matter and antioxidants. SIDMS was implemented.	Novotnik et al.[43]
Traditional Chinese medicines	Extraction with 0.28M $\text{Na}_2\text{CO}_3$ /0.5M NaOH, phosphate buffer (0.5M $\text{K}_2\text{HPO}_4$ /0.5M $\text{KH}_2\text{PO}_4$ ) and $\text{MgCl}_2$ .	HPLC-ICP-MS	Cr(VI)	Column: Agilent Bio WAX (4.6x250 mm). Mobile phase: 75mM $\text{NH}_4\text{NO}_3$ at pH 7.	LOD: 0.1 $\mu\text{g/L}$ . LOQ: 0.3 $\mu\text{g/L}$ .	Good recovery of Cr(VI) in the present of high amount of Cr(III).	Li et al.[57]
Water and bottom sediments	Acid digestion (total As, Cr, Sb), extraction with buffer (5mM $\text{Na}_2\text{HPO}_4$ and 50mM $\text{KH}_2\text{PO}_4$ pH 6.0), and extraction with deionized water.	HPLC-ICP-MS	Total As/Cr/Sb, As(III)/As(V), Cr(III)/Cr(VI), Sb(III)/Sb(V)	Column: Dionex IonPac AG7 (4x50 mm) for Cr; AS7 (4x250 mm) for As and Sb. Mobile phase: A: 0.1M $\text{NH}_4\text{NO}_3$ pH 4.0, B: 0.8M $\text{HNO}_3$ gradient mode for Cr; 1mM phthalic acid, 10mM $\text{EDTANa}_2$ pH 4.5 for As and Sb.	LOD: 0.11 $\mu\text{g/L}$ for Cr(III), 0.17 $\mu\text{g/L}$ for Cr(VI).	A guard column was used for separation of Cr species.	Jabłońska-Czapla et al.[75]
Wood leachates, surface waters, tap water, and wastewater	Filtration prior to analysis.	HPLC-ICP-MS	Cr(III), polymeric Cr(III), Cr(VI)	Column: PerkinElmer Spheri-5 RP-18 (4.6x220 mm). Mobile phase: 5% (v/v) methanol/0.5mM EDTA + 1 mM TBAH (pH 7.2).	LOD: 0.9 $\mu\text{g/L}$ for Cr(III) and Cr(VI).	EDTA was added to complex and stabilize monomeric Cr(III) during sample preparation and measurement.	Hu et al.[77]
Yoghurt and cheese samples	Acid digestion (total Cr) and extraction of Cr(VI) with $\text{NH}_4\text{OH}$ .	HPLC-ICP-MS	Total Cr, Cr(III), Cr(VI)	Column: Dionex IonPac CG5A, CS5A (4x250 mm). Mobile phase: 2M $\text{HNO}_3$ , $\text{H}_2\text{O}$ . Gradient mode.	LOD: 12.6 $\mu\text{g/kg}$ for Cr(III). LOQ: 38 $\mu\text{g/kg}$ for Cr(III).	In-situ complexation of Cr(III) with EDTA. Good agreement between Cr(III) and total Cr.	Hernandez et al.[59]
Bread and cereals	Acid digestion (total Cr) and alkaline extraction of Cr(VI) with 0.1M $\text{Na}_2\text{CO}_3$ .	HR-CS AAS	Total Cr, Cr(VI)	Pyrolysis temperature: 1200 °C. Atomization temperature: 2450 °C	LOD of Cr: 0.045 $\mu\text{g/g}$ .	Cr levels in bread do not exceed the daily maximum acceptable concentration.	Mathebula et al.[61]
Tanned leather	Extraction of Cr(VI) with 0.1M phosphate solution (0.1M $\text{NaH}_2\text{PO}_4$ and 0.1M $\text{H}_3\text{PO}_4$ ) at pH 4.4 in presence of 5% NaCl.	IC-DAD	Cr(VI)	Column: Dionex IonPac AG7. Mobile phase: 1) $\text{H}_2\text{O}$ , 2) 250mM $(\text{NH}_4)_2\text{SO}_4$ /100mM $\text{NH}_3$ (pH 8-8.5), 3) 2.5M $(\text{NH}_4)_2\text{SO}_4$ /1M $\text{NH}_3$ (pH 8-8.5). Gradient mode. Wavelength: 543 nm.	LOQ: 0.15 mg/kg.	Post-column reaction with DPC for Cr(VI) determination. Cr(III) was complexed with EDTA. Evidence of Cr(VI) formation (ISO 17075).	Pastore et al.[44]
Cement samples and homeopathic drugs	Acid digestion (total Cr) and Cr(VI) extraction with water or dissolution in 0.1M HCl for both species determination.	IC-ICP-MS	Total Cr, Cr(III), Cr(VI)	Column: Shodex Rspak NN-814 4DP (4x150 mm). Mobile phase: 90mM $(\text{NH}_4)_2\text{SO}_4$ and 10mM $\text{NH}_4\text{NO}_3$ (pH 3.0-3.5).	LOQ~0.5 $\mu\text{g/L}$ for both species.	Minimum sample preparation, no derivatization, multi-mode column.	Hagendorfer & Goessler[82]
Cosmetic products: face powder and eye shadow	Defatted samples (defatted with ethanol-hexane) are extracted with 0.28M $\text{Na}_2\text{CO}_3$ /0.5M NaOH.	IC-ICP-MS	Cr(VI)	Column: Dionex IonPac AS7 (2x250 mm), AG7(4x50 mm). Mobile phase: 0.25M $(\text{NH}_4)_2\text{SO}_4$ + 0.1M $\text{NH}_4\text{OH}$ .	LOQ: 0.11 mg/kg.	Cr(VI) was found in 1 out of 4 evaluated products.	Petrucci & Senofonte[56]
CRMs: soil containing chromite ore processing residue, welding dust loaded on a filter, and sandy clay soil	Cr(VI) is extracted with 50mM EDTA (Cr(III) complexation with EDTA).	IC-ICP-MS	Cr(VI)	Column: Dionex IonPac AS9-HC (4x250 mm). Mobile phase: EDTA 5mM (pH 10).		IDMS was implemented.	Fabregat-Cabello et al.[88]
CRMs: synthetic and estuarine water	Cr(III) is complexed with EDTA 0.2mM.	IC-ICP-MS	Cr(III), Cr(VI)	Column: Dionex IonPac AS7 (4x250 mm), AG7 (4x50 mm). Mobile phase: 50mM	LOD: 12 ng/L for Cr(VI) and 5 ng/L for Cr(III).	Self-regenerating suppressor was used.	Gürleyük & Wallschläger[48]



				NH <sub>4</sub> NO <sub>3</sub> (pH 8).			
Dietary supplements	Digestion through EPA 3052 (total Cr) or extraction through EPA 3060A (Cr(VI)).	IC-ICP-MS	Total Cr, Cr(III), Cr(VI)	Column: Hamilton PRP-X100 (4.6x150 mm). Mobile phase: A: 0.06M NO <sub>3</sub> <sup>-</sup> (pH 9.3), B: 0.06M NO <sub>3</sub> <sup>-</sup> (pH 1.2). Gradient mode.	LOD: 0.9 µg/L for Cr(III) and Cr(VI).	Total Cr determined by ICP-MS. Cr(VI) determined by IC-ICP-MS or EPA 7196A or 7199. Cr(III) determined by ICP-MS after Cr(VI) extraction. SIDMS was implemented.	Martone et al.[42]
Drinking water	No sample preparation.	IC-ICP-MS	Cr(III), Cr(VI)	Column: Dionex IonPac AG7 (2x50 mm). Mobile phase: 0.4M HNO <sub>3</sub> .	LOD: 0.20 pg/g for Cr(VI) and 0.38 pg/g for Cr(III).	A guard column was used for separation of both species.	Kutscher et al.[79]
Drinking water	Samples are acidified with HNO <sub>3</sub> .	IC-ICP-MS	Cr(III), Cr(VI)	Column: Dionex IonPac AG7 (2x50 mm). Mobile phase: 0.3M HNO <sub>3</sub> .	LOD: 4.0 ng/L for Cr(VI) and 9.0 ng/L for Cr(III).	A guard column was used for separation of both species.	Schmelzel et al.[80]
Soil samples	Digestion through EPA 3052 (total Cr and insoluble Cr species), extraction through EPA 3060A (Cr(VI)), EDTA extraction (Cr(VI) and soluble Cr(III)).	IC-ICP-MS	Total Cr, soluble Cr(III), Cr(VI), insoluble Cr species.	Column: Metrosep A Supp 4 (Metrohm), (4x250 mm). Mobile phase: 2mM EDTA pH 10.		IDMS and SIDMS were implemented.	Wolle et al.[90]
Toys & toy material	Samples are subjected to migration process and diluted (1eq of 1M NH <sub>4</sub> OH + 4eq of migration solution).	IC-ICP-MS	Total element quantification, Cr(VI)	Column: Dionex IonPac NG1 (2x50 mm), AG7 (2x50 mm). Mobile phase: 0.35M HNO <sub>3</sub> .	IDL: 0.9 ng/L for Cr(VI).	Cr(VI) was stable for at least 24h. Cr(III) was prone to hydrolysis and precipitation.	Kutscher et al.[81]
Contaminated waters	Direct injection of the samples.	IC-ICP-MS, ESI-MS,	Cr(VI)	Column: Agilent guard (G3154A/102) and separation (G3154A/101) columns. Mobile phase: 20mM NH <sub>4</sub> NO <sub>3</sub> and 10mM NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (pH 7.0).	LOD: 0.2 µg/L for Cr(III), 0.1 µg/L for Cr(VI).	Stability of Cr(III) complexes was studied by ESI. Separation was performed with IC.	Chen et al.[49]
Environmental water samples	Samples were preserved with NH <sub>4</sub> OH or NH <sub>4</sub> OH/(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , and filtered prior to analysis.	IC-MS/MS	Cr(VI)	Column: Dionex IonPac AG20 (2x50 mm), AS20 (2X250 mm). Mobile phase: 1) 30mM KOH, 2) 60mM KOH, 3) 30mM KOH. Gradient mode.	MDL: 2 ng/L. PQL: 0.010 µg/L.	Ultra-trace level analysis. SIDMS was implemented.	Mädler et al.[86]
Sediment samples	Alkaline digestion (0.28M Na <sub>2</sub> CO <sub>3</sub> /0.5M NaOH) and EDTA extraction.	IC-MS/MS, UV-Vis	Cr(VI)	Column: Dionex IonPac AG20 (2x50 mm), AS20 (2X250 mm). Mobile phase: 1) 30mM KOH, 2) 60mM KOH, 3) 30mM KOH. Gradient mode. Wavelength: 540 nm (CRMs).	MDL: 0.007 µg/L.	Trace level analysis. CRMs were additionally analyzed by UV-Vis (reaction with DPC). SIDMS was implemented.	Mädler et al.[85]
Drinking water, groundwater, and industrial wastewater effluents	Sample preparation through appropriate SW-846 method.	IC-UV-Vis	Cr(VI)	Column: Dionex IonPac AS7, NG1 (or equivalent). Mobile phase: 250mM (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 100mM NH <sub>4</sub> OH. Wavelength: 530 nm.	MDL: 0.3-0.4 µg/L.	Post-column reaction with DPC.	SW-846 EPA 7199[72]
Drinking water, groundwater, and industrial wastewater effluents	Not described.	IC-UV-Vis	Cr(VI)	Column: Dionex IonPac AS7, NG1. Mobile phase: 250mM (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 100mM NH <sub>4</sub> OH. Wavelength: 530 nm.	MDL: 1 µg/L.	Post-column reaction with DPC.	EMSL[73]
Leather	Extraction of Cr(VI) with K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O at pH 8.0.	IC-UV-Vis	Cr(VI)	Annex B (direct detection of chromate peak). Column: Anion exchange column (4,6 ×75 mm), 1 mm pre-column. Mobile phase: 25mM (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 1mM NaOH. Annex C (detection after complexation with DPC). Column: Anion exchange column (4x250 mm), guard column (4x35 mm). Mobile phase: 250mM (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 116mM	LOQ: 3 mg/kg.	Direct detection of chromate peak at 372 nm (Annex B) or post-column reaction with DPC by measuring the absorption peak at 540 nm (Annex C).	ISO 17075-2[27]

				NH <sub>4</sub> OH.			
Soil and wastewater samples	Digestion with HNO <sub>3</sub> and eluent stock (10x concentrate).	IC-UV-Vis	Cr(III), Cr(VI)	Column: Dionex IonPac CG5A (4x50 mm), CS5A (4x250 mm). Mobile phase: 2mM PDCA, 2mM Na <sub>2</sub> HPO <sub>4</sub> , 10mM NaI, 50mM NH <sub>4</sub> CH <sub>3</sub> CO <sub>2</sub> and 2.8mM LiOH. Wavelength: 335 (0.0-4.7 min) and 530 nm (4.7-8.0 min).		Cr(III) is complexed with PDCA (pre-column derivatization) and Cr(VI) reacts with DPC (post-column reaction).	Phesatcha et al.[74]
Tanned leather	Acid digestion (total Cr) and alkaline extraction of Cr(VI) with 0.1M NaOH.	ICP-OES, Mobile Phone, PhotoMetrix App	Total Cr, Cr(VI)	Wavelength: 540 nm.	LOD: 0.6 mg/kg for Cr(VI). LOQ: 2 mg/kg for Cr(VI).	Reaction with DPC for Cr(VI) determination.	Costa et al.[54]
Waters, solids, blood, foods, extracts or digests.	Sample preparation through appropriate SW-846 method.	IDMS, SIDMS	Multielements			Applicable to the determination of total elements, elemental and molecular species at ppb, ppt and sub-ppt levels.	SW-846 EPA 6800[84]
Soil samples	Cr(VI) is extracted with 50mM EDTA (Cr(III) complexation with EDTA).	LC-ICP-MS	Cr(VI)	Column: Dionex IonPac AS9-HC (4x250 mm). Mobile phase: EDTA 5mM (pH 10).		IDMS was implemented.	Guidotti et al.[89]
Groundwaters	Sample preparation through appropriate SW-846 method.	UV-Vis	Cr(VI)	Wavelength: 540 nm.		Reaction with DPC.	SW-846 EPA 7196A[71]
Leather	Extraction of Cr(VI) with K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O at pH 8.0.	UV-Vis	Cr(VI)	Wavelength: 540 nm.	LOQ: 3 mg/kg.	Reaction with DPC.	ISO 17075-1[26]
Tanned leather	Extraction of Cr(VI) with K <sub>2</sub> HPO <sub>4</sub> at pH 8.0.	UV-Vis	Total Cr, Cr(VI)	Wavelength: 540 nm.	LOD: 15 µg/L for Cr(VI).	Reaction with DPC for Cr(VI) determination. Total Cr was measured after oxidation of Cr(III).	Rezić & Zeiner[53]
Siliceous matrices, organic matrices, and other complex matrices	Microwave digestion with HNO <sub>3</sub> and HF.	Via appropriate SW-846 method.	Multielements			Alternative acid and reagent combinations (HCl and H <sub>2</sub> O <sub>2</sub> )	SW-846 EPA 3052[70]
Soils, sludges, sediments, and similar waste materials	Digestion with 0.28M Na <sub>2</sub> CO <sub>3</sub> /0.5M NaOH, phosphate buffer (0.5M K <sub>2</sub> HPO <sub>4</sub> /0.5M KH <sub>2</sub> PO <sub>4</sub> ) and MgCl <sub>2</sub> .	Via SW-846 EPA 7196A or 7199	Cr(VI)			Mg <sup>2+</sup> can suppress oxidation of Cr(III) to Cr(VI).	SW-846 EPA 3060A[55]

Table 5. Description of the calculation of LOD, LOQ, IDL, MDL, and/or PQL according to the different authors cited in Table 4.

Reference	LOD	LOQ	IDL	MDL	PQL
Chen et al.[36]			Concentration necessary to yield a net signal equal to 3 times the standard	Calculated from IDL and mass ratio of final solution used for CE-ICP-MS	

			deviation of the background ( $3\sigma/S$ )		
Tiwari et al.[68]	3SD/b for 3 times the standard deviation for 7 replicates and b the slope of the calibration curve	10SD/b			
Soares et al.[63]	3s/m where s is the standard deviation of the measurements of the blank and m is the slope of the calibration curve	10s/m			
Kiran et al.[67]	5 times signal-to-noise ratio				
Narin et al.[69]	3 times the standard deviation of the blank				
Mandiwana et al.[62]	3s/b for 3 times the standard deviation of 22 measurements of the blanks divided by the slope	10s/b			
Hernandez et al.[58]		Calculated through statistical method. Obtained from the intersection between acceptance and tolerance limits. Acceptance: set to $\pm 35\%$ (corresponding to an intermediate precision coefficient of variation estimated at 12% at $k=3$ ( $p=0.99$ )). Tolerance: calculated from the mean bias at each concentration level. Probability set to 90 or 85%.			
Araujo-Barbosa et al.[78]	$3\sigma/s$ , where $\sigma$ is the standard deviation of the measurements of the blank and s is the slope of the calibration curve	$10\sigma/s$			
Vacchina et al.[60]	3 times the standard deviation of 10 blanks	10 times the standard deviation of 10 blanks			
Séby et al.[76]	NA	NA			
Drinčić et al.[87]	Concentration that gives a signal equal to 3 times the standard deviation of 8 blanks	Concentration that gives a signal equal to 10 times the standard deviation of 8 blanks			
Novotnik et al.[43]	Concentration that gives a signal equal to 3 times the standard deviation of 8 blanks	Concentration that gives a signal equal to 10 times the standard deviation of 8 blanks			
Li et al.[57]	3S/N ratio	10S/N ratio			
Jabłońska-Czapla et al.[75]	3s/b, where s is the standard deviation and b the slope of the calibration curve				
Hu et al.[77]	NA				
Hernandez et al.[59]	3 times the standard deviation of 10 blanks	10 times the standard deviation of 10 blanks			
Mathebula et al.[61]	$x + 3s$ , where x is the signal of the blank sample and s is the standard deviation of the blank				
Pastore et al.[44]		NA			
Hagendorfer & Goessler[82]		Calculated from the calibration method			
Petrucci & Senofonte[56]		$10\sigma$ analyzing 10 blanks			

Gürleyük & Wallschläger[48]	3 times the standard deviation of the baseline noise				
Martone et al.[42]	NA				
Kutscher et al.[79]	Calculated from calibration curves				
Schmelzel et al.[80]	Calculated based on the standard deviation of the peak area of 15 injections of unspiked water				
Kutscher et al.[81]			3 $\sigma$ for the lowest concentration standard		
Chen et al.[49]	Signal/Noise = 3				
Mädler et al.[86]				Standard deviation of the analysis of multiple standard solutions multiplied by one-tailed student t-value ( $\alpha=0.01$ , $n=18$ ) of 2.567	Same approach as MDL
Mädler et al.[85]				Standard deviation of the analysis of multiple standard solutions multiplied by one-tailed student t-value ( $\alpha=0.01$ , $n=18$ ) of 2.567	
SW-846 EPA 7199[72]				NA	
EMSL[73]				NA	
ISO 17075-2[27]		NA			
Costa et al.[54]	Calculated according to IUPAC recommendations				
ISO 17075-1[26]		NA			
Rezić & Zeiner[53]	NA				

## **Future outlooks**

As a result of the environmental concerns regarding leather industry, researchers have been continuously trying to find ways to reduce wastes, as well as alternatives to conventional chrome tanning.

Recently, Md.A. Moktadir et al.[91] analyzed the challenges of implementing Circular Economy (CE) practices in leather industry. CE is a strategy that aims to limit the input of virgin materials and the production of wastes, creating a closed-loop system. This work revealed that the major challenge is the lack of financial support from the authorities, followed by the lack of technological advancement. According to them, financial support could help implement CE policies for environmental protection. Meanwhile, technological advancement could improve tannery effluent treatment, which would reduce wastes and protect the environment. The analysis of wastewater, solid waste, sulfide, Chemical Oxygen Demand (COD), ammonium salt, chloride and chromium with CE practices is essential to accomplish sustainable development of leather industry [92].

According to Abdel-Shafy et al.[93], the liming/unhairing operation produces highly polluted effluents (high levels of COD, BOD, TDS and sulfides) that should be treated separately before its discharge. They were able to develop a wastewater treatment based on the Fenton technique for the oxidation of organic matter in water employing  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  (Fenton reagent). This method was followed by membrane filtration and showed to be effective for the non-biodegradable portions of wastewater. The final effluent could meet the permissible limits of the unrestricted water reuse according to the Egyptian Environmental Association Affair (EEAA). El-Khateeb et al.[94] employed the electrocoagulation process assisted by chemical oxidation to treat chrome tanning effluents. The electrocoagulation treatment consists in forming an

agglomeration (that can be subsequently separated by filtration) of the suspended matter by means of an electrical current.  $H_2O_2$  was used to support the oxidation process. This methodology permitted a 99.99% of chromium removal and 99.97% of sulfides removal. In further studies, El-Khateeb et al.[95] combined chemical coagulation process (using  $FeCl_3$  and lime) and an aerobic reactor to treat effluents generated from beam house operations. The developed system efficiently reduced the COD, BOD and sulfides levels: 96.1%, 85.2% and 99.3% removal, respectively. The final treated effluent could be used for irrigation of trees or reused in the tanning industry.

Another option to minimize the environmental problems caused by chrome tanning is the extraction of chromium from leather scrap. Ferreira et al[96]. developed a method for the acidic extraction of chromium, using concentrated  $H_2SO_4$ , recovering 30-60% of chromium and rendering the residue suitable for anaerobic biodegradation. Similarly, Popielsky and her coworkers[97] achieved 98% of chromium removal from residual leather tannery via an EDTA ultrasound-assisted extraction. Additionally, they proposed EDTA's recovery by adding  $H_2SO_4$  to precipitate EDTA- $H_4$ .

On the other hand, alternatives to conventional chrome tanning have also been explored. Some of these alternatives include: high exhaustion chrome tanning using exhaust aids or high exhaust tanning salts [10, 98], ultrasound assisted chrome tanning which improves chromium requirement and reduces shrinkage [99], microwave/ultrasound assisted chrome tanning which additionally decreases tanning time [100], salt-free pickling chrome tanning which diminishes the discharge of COD and Total Dissolved Solids (TDS) [101], and enzyme assisted vegetable tanning which enhances the diffusion of vegetable tannins into the leather fibers [15].

Still, chrome tanning remains the preferred alternative due to the versatility of the resulting leather. Ultrasound assisted [99] and salt-free pickling chrome tanning

[101] seem to be promising alternatives as they maintain the good quality of the leather. On the other hand, high exhaustion and microwave/ultrasound assisted chrome tanning resulted in some properties that were inferior than the conventional technique, such as thermal stability and non-uniform distribution of chromium [10, 100].

Eco-friendly chrome-free tanning is another alternative to conventional chrome tanning. This approach has been attempted with different tanning agents such as titanium salts[102], natural and unnatural amino acids[103–105], and an aluminum sulfate - composite material[106]. Leathers obtained by way of these tanning agents have shown good qualities, comparable or superior to the properties of chrome-tanned leather. The exploitation of these promising approaches could help reduce the environmental impacts of tanning industry.

Regarding chromium determination, there is no current standard describing a technique to extract and quantify Cr(III) and Cr(VI) simultaneously in leather products coming from chrome tanning. Hence, it is of particular importance to develop a protocol that takes into account the possible interconversion processes, eventually through the use of SIDMS. The production of CRMs for speciation of Cr in leather articles would also represent a huge step on the mitigation of these obstacles.

## **Conclusion**

In the leather manufacturing process, chrome tanning is the most common tanning system due to the quality of the final products. However, the environmental impacts of this process have encouraged researchers to find cleaner alternatives to conventional chrome tanning. Even if only trivalent chromium salts are used during chrome tanning, hexavalent chromium can still be found in leather, which represents a risk to human health. Additionally, natural ageing of the leather could also favor its formation. The European regulation restricts Cr(VI) content to 3 mg/kg in leather articles coming into

contact with the skin. As the oxidation state of chromium is determined by redox potential and pH, the current international standard for hexavalent chromium determination in leather goods should consider any possible interconversion between Cr(III) and Cr(VI) during the extraction and analysis procedure. The introduction of isotope dilution techniques and the production of CRMs could help mitigate this struggle. The review of the analytical methods for chromium extraction and quantification showed that most of the studies have been performed in foodstuffs and environmental samples, which is comprehensible. However, more attention should be given to leather articles in order to develop more reliable analytical protocols that monitor possible interconversions and reveal the real health risk consumers are exposed to. Further regulations must also contemplate the evolution of hexavalent chromium over time.

### **Acknowledgments**

The authors gratefully acknowledge the support of CONACYT's grant (CVU 707668). This work was also supported by the European Regional Development Fund (ERDF) N° HN0001343, the Région Normandie, and the Laboratoire d'Excellence (LabEx) SynOrg (ANR-11-LABX-0029).

### **Conflict of interest**

The authors declare no conflict of interest.

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