

Determination of extractable chromium from leather

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Abstract People are exposed to chromium ions from leather materials due to everyday contact with different textile objects. The problem is that Cr(VI) is extremely toxic and may cause contact allergic dermatitis on the skin and may also be a trigger for many diseases. Huge amounts of chromium ions are released by waste waters to rivers after chromium-tanning processes in the leather industry; the presence of chromium is not only a problem for human health, but also for the environment. For this reason it is extremely important to monitor the presence of chromium as Cr(VI) and as total chromium. This study aims to present an appropriate analytical method for monitoring Cr(VI) and the total chromium present on leather materials. Applying this method to chromium-tanned leather samples, it was observed that the amounts of total chromium as well as of Cr(VI) are higher than prescribed and recommended by different regulations. Chromium(VI) exceeded the limit of 3 mg/kg in the majority of tested materials, while the total chromium exceeded the limit of 50 mg/kg in all tested samples. For this reason, it is recommended to avoid direct and prolonged contact of those materials with the skin.

Keywords Spectroscopy · UV/VIS spectroscopy · Metal complexes · Tanned leather · Chromium

Introduction

Today around 90% of the global leather production of 16.7 billion m² uses the conventional chrome-tanning process for tanning leather, causing serious environmental concerns [1]. Although tanning is a very important process that provides stability to the skin matrix, allowing it to resist microbial degradation, heat, sweat, and other parameters [2], the problem lies in the fact that after the wood preservation industry, the leather industry uses the highest amounts of chromium chemicals (Table 1) [3], which afterwards are released into the environment or remain in and on the product.

The presence of chromium in chromium-tanned leather represents a considerable health problem. It is proven that it may lead to allergic contact dermatitis caused by Cr(VI) resulting from oxidation of Cr(III) during the tanning process [4]. The effect of hexavalent chromium on the immunological pattern of shoe, hide, and leather industry workers was investigated by Mignini et al. [5]. They found Cr(VI) values exceeding the levels allowed. The results were similar to those reported in the study of Babu et al. [6]. Their conclusion was that any leather auxiliary containing a potential oxidizing functional group can lead to the conversion of considerable quantities of Cr(III) in chrome-tanned leather to Cr(VI) even under unfavorable pH conditions. They also confirmed the role of certain leather auxiliaries in the formation of Cr(VI) above the permissible limits.

Chromium(III) is used in tanneries as chromium sulphate, which may be converted into Cr(VI) in the effluent. The hexavalent chromium has higher toxicity and can lead to liver damage, pulmonary congestion, skin irritation, and carcinogenesis [7]. Hafez and El-Manharawy [8] proved that the chromium content in chromium effluents ranges

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Table 1 Chromium chemicals used by different industries [3]

Industry	Europe (%)	USA (%)
Wood preservation	15	52
Leather tanning	40	13
Metal finishing	17	13
Pigments	15	12
Refractory	3	3
Other	10	7

between 1,300 and 2,500 mg [Cr(VI)]/l. Irrigation of fields with polluted waste waters causes a significant increase of Cr in soil, which poses a threat to future crop production [9]. The leather industry is marked as one of the prime pollution sources in terms of different toxic conventional parameters such as sulfide, chromium, oil and grease, biological oxygen demand (BOD) and chemical oxygen demand (COD), and ammonia concentration (Table 2) [10].

Due to the toxicity of chromium, major environmental and biological concerns have arisen. It is known that only 20% of wet salted leather skin can be converted into commercial leather, and 25% of the material becomes waste, representing a big environmental problem [11]. Attempts at different kinds of chromium removal have been made with physical adsorption, chemical and biochemical processes. In order to optimize the adsorption conditions for trivalent chromium removal from the wastewater stock of the leather industry, different materials have been used: activated carbon from co-mingled low-grade coal, biomass, and petroleum wastes. The studies resulted in reliable adsorption data: rate constants, activation energies, thermodynamic equilibrium constants, entropies, enthalpies, and free energies [12].

The presence of chromium in leather is so detrimental to human health and the environment that an appropriate monitoring is mandatory. A fast, simple, and reliable analytical method is needed for determining the presence of chromium. A recent study by Monteiro et al. [13] proved that different methods can be applied for this purpose: the colorimetric method with 1, 5-diphenyl-carbazide (metal

Table 2 Characteristics of waste waters after the leather tanning process [10]

Parameter ($\mu\text{g/ml}$)	EPA subcategory I	EPA subcategory II
BOD ₅	213–4,300	100–3,920
COD	182–27,200	370–31,500
TSS	24.8–36,100	118–7,650
Chromium	3–345	0.02–140
Sulfide	–	0.8–198
TKN	90–626	39–750

complexation), graphic furnace atomic absorption spectrometry (GF AAS), and flame atomic absorption spectrometry (FAAS). Another study by Cespón-Romero et al. [14] employed a flow injection system comprising chelating ion-exchange and flame atomic absorption spectrometry showing low detection limits and good precision for different amounts of chromium. Still, traditional methods for the speciation of inorganic chromium are relatively time consuming; they involve species separation based on different solid phase or solvent extractions, co-precipitation, electrochemical separation, ion exchange, or selective volatilization in combination with graphite furnace atomic absorption spectrometry [15]. Methods applied for reducing possible interferences from Cr(III) organic complexes are 1,5-diphenyl-carbazide spectrophotometry, organic extraction with methyl isobutyl ketone, and co-precipitation with iron and bismuth salts, since many organic ligands (proteins, amino acids, and organic acids) react with the investigated Cr(III) [16]. Walsh et al. proved that the spectrophotometric method suffers minor interferences attributable to a non-specific turbidity effect, while two other methods (methyl isobutyl ketone extraction and co-precipitation) suffer many severe interferences with Cr(III)–protein complexes. On-line separation and pre-concentration of chromium species in seawater were performed by a combination of ultrasonic nebulization inductively coupled plasma optical emission spectrometry (UN-ICP-OES) with high-performance liquid chromatography (HPLC) as reported by Posta et al. [17]. The method provides an accurate and precise means for discriminating Cr(III) and Cr(VI) as well as for pre-concentration of Cr(VI). Comparison among ICP-OES, FAAS, and UV–VIS (1,5-diphenyl-carbazide method) was performed by Balasubramanian and Pugalenthi [18]. The results showed that the UV–VIS is the most suitable method: other methods suffered from severe matrix effects arising from high concentrations of mineral acids and electrolytes [18]. For this reason, UV–VIS was chosen for monitoring the Cr(VI) and the total chromium contents in this study. The results of chromium concentrations found are compared to the permissible limits presented in Table 3 [19].

Results and discussion

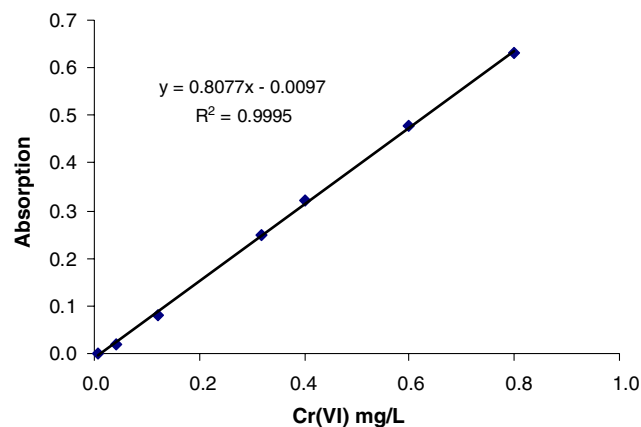
Monitoring chromium content in extracts from leather materials is extremely important because people are exposed to its impact during every day usage of leather textile materials. There have been many case reports of contact allergic dermatitis caused by chromium on leather. Our previous investigations proved that the total chromium amounts can range from 100 $\mu\text{g/g}$ to 30 mg/g on untreated cow skin and in chromium-tanned leather, respectively [20]. The problem is the chromium in the final leather

Table 3 Limits for heavy metals on leather materials presented in (mg/kg) [19]

Heavy metal	Limit (mg/kg)
Al (aluminum)	500.0
As (arsenic)	1.0
Cd (cadmium)	0.2
Co (cobalt)	5.0
Cr (chromium total)	50.0
Cr VI (chromium VI)	3.0
Hg (mercury)	0.2
Ni (nickel)	5.0
Pb (lead)	1.0
Ti (titanium)	500.0
Zr (zirconium)	500.0
Sb (antimony)	10.0

products used every day. It is important to monitor the toxic Cr(VI) with the most suitable analytical procedure. As described by Balasubramanian and Pugalenthi [18], UV–VIS does not suffer from severe matrix effects and is recommended as an appropriate analytical procedure. The UV–VIS 1,5-diphenyl-carbazide spectrometry method has a low detection limit of 15 µg/l for chromium determination, which is an advantage of this analytical method. The disadvantage is the relatively low linear working range, which is presented in Fig. 1.

By UV–VIS spectrometry it is possible to easily determine the concentration of chromium present on leather material. Several different leather materials have been tested, and the results for Cr(VI) ranged from 0.30 to 0.33 mg/kg for the first group of samples (Table 4) and from 2.0 to 3.14 mg/kg for the second group of samples (Table 5). The majority of the materials tested in the second group of samples (subgroups III–VI) exceed the permissible values of extracted 3 mg of Cr(VI) per kg leather material according to CEN/TS 14 995 and [19]. The

**Fig. 1** Calibration curve for chromium UV–VIS determination**Table 4** Results for the first two groups of tested chromium materials

Group	Cr(VI) (mg/kg)
I	0.32 ± 0.03
II	0.30 ± 0.02

Table 5 Cr(VI) content extracted from leather material

Group	Absorbance	Cr(VI) (mg/kg)
III	0.010	3.04 ± 0.08
IV	0.004	2.12 ± 0.11
V	0.01	3.30 ± 0.05
VI	0.01	3.19 ± 0.12

results for the total chromium content measured in the solutions obtained after permanganate oxidation are presented in Table 6. They all exceed the permissible value of 50.0 mg/kg (Table 3).

This study has proven that in majority of the leather samples tested, the quantities of extractable Cr(VI) and of total chromium exceed the recommended values. For this reason, they may pose a serious health problem. It is recommended to avoid prolonged contact with the leather materials containing higher chromium amounts. There is an urgent need for checking such products prior to bringing them on the market.

Experimental

Samples

The samples were final leather products taken from several different chromium-tanning processes that were intended to be used in textile industry.

Extraction and sample preparation

Triplicates of 2.00 ± 0.01 g of dried and cut leather samples were placed into a 250-ml flask, and 100 ml of K₂HPO₄ solution was added. The reagent solution was prepared by dissolving 22.8 g of the salt in 1,000 ml of bidistilled water and adjusting the pH value to 8.0 ± 0.1. The flask was tightly sealed and the solution mixed on an automatic shaker for 3 h at room temperature.

Table 6 Total Cr content extracted from leather materials

Groups	Total Cr (mg/kg)
I, II, and III	59 ± 1
IV, V, and VI	53 ± 2

After mixing, the pH value of the solution obtained was checked again in order to maintain 8.0. Afterwards the samples were filtered, and the filtrates were analyzed for their Cr contents. Blank solutions were prepared in the same way without leather samples.

UV–VIS determination

Ten microliters of the filtered solution was placed in a 25-ml flask, and 0.5 ml of the 1, 5-diphenyl-carbazide solution was added. The reagent solution was prepared by dissolving 1.0 g of reagent in 100 ml of acetone and acidifying with glacial acetic acid; 0.5 ml of orthophosphoric acid solution in bidistilled water (7:10 parts per volume) was added. After filling up to volume, the solution was left for 15 min in order to form a stable colored metal complex. The absorption was then measured by UV–VIS spectrophotometry at 540 nm using a Cary 3 Varian instrument.

Calibration

The calibration was performed using a stock standard Cr(VI) solution prepared by dissolving 2.829 g of $K_2Cr_2O_7$ (dried for 16.5 h at 102 °C) in 1,000 ml of bidistilled water. One microliter of this stock solution was diluted up to 1,000 ml, and the resulting solution was used for preparing the calibration standards in a concentration range from 50 µg/l to 1 mg/l. The colored complex was generated in the same way as for the samples.

The total chromium content was determined after oxidation of Cr(III) with $KMnO_4$ in acidified solution. The oxidized samples were prepared and measured in the previously described manner.

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