Coll. Antropol. **35** (2011) 1: 89–92
Original scientific paper

Determination of Total Chromium in Tanned Leather Samples used in Car Industry

Michaela Zeiner[1], Iva Rezić[2], Darko Ujević[3] and Ilse Steffan[1]

[1] University of Vienna, Faculty of Chemistry, Vienna, Austria (at time of research)
[2] University of Zagreb, Faculty of Textile Technology, Department of Applied Chemistry, Zagreb, Croatia
[3] University of Zagreb, Faculty of Textile Technology, Department of Clothing Technology, Zagreb, Croatia

A B S T R A C T

Despite the high competition of synthetic fibers leather is nowadays still widely used for many applications. In order to ensure a sufficient stability of the skin matrix against many factors, such as microbial degradation, heat and sweat, a tanning process is indispensable. Using chromium (III) for this purpose offers a multitude of advantages, thus this way of tanning is widely applied. During the use of chromium tanned leather as clothing material as well as for decoration/covering purposes, chromium is extracted from the leather and may then cause nocuous effects to human skin, e.g. allergic reactions. Thus the knowledge of the total chromium content of leather samples expected to come into prolonged touch with human skin is very important. In car industry leather is used as cover for seats, steering wheel and gearshift lever. The chromium contents of ten chromium tanned leather samples used in car industry were determined. First all samples were dried at 65°C overnight and then cut in small pieces using a ceramic knife, weighed and analyzed by inductively coupled plasma – optical emission spectrometry (ICP-OES) after acidic microwave assisted digestion. The total chromium amounts found were in the range from 19 mg/g up to 32 mg/g. The extraction yield of chromium from leather samples in sweat is approximately 2–7%. Thus especially during long journeys in summer chromium can be extracted in amounts which may cause nocuous effects for example on the palm of the hands or on the back.

Key words: *chromium, leather, car textiles, seat covers, contact allergy*

Introduction

People can be exposed to chromium on the one hand through breathing, eating or drinking and on the other hand through skin contact with chromium or chromium compounds for example via the every day's contact with different textile objects made of leather. Leather is the major industrial product made from a natural fabric, the skin. This product is created through the tanning of hides and skins of animals, primarily cattle hide.

Leather is still a unique material although many synthetic fibers are nowadays used in textile industry. Two important properties of leather which have rendered it irreplaceable by other materials are its visco-elasticity, pore size distributions, the ability to breathe and readjust to volume fluctuations[1]. But leather has also an important disadvantage, i.e. the required tanning process which renders the skin matrix stable against microbial degradation, heat, sweat and other parameters.

Tanning is a process with long history. After evolving the practice and skill the underlying chemical principles of the art and science of tanning were understood. Whereby in the beginning tanning with plant and organic materials may have been found accidentally, the increasing demand for aesthetic appeal and softer types of leathers as well as the need for reduction in process time, alternative methods had to be developed. The use of chromium salts in leather tanning dates back to the middle of the 19th century and is today the industry standard. Although many alternative mineral tanning materials have been explored, chromium based tanning methods in the manufacture of light and softer types of leathers are still the preferred[1]. Approximately 90% of global leather production of 16.7 billion m^2 uses the conventional chrome-tanning process for tanning leather, causing serious environmental concerns[2]. The remaining part is tanned

Received for publication May 20, 2009

principally using synthetic aldehydes or vegetable extracts[1]. In the western world the leather industry is leading in using chromium chemicals, in the USA it is on the second place after wood preservation[3].

During extended skin contact with chromium tanned leather samples chromium is extracted with sweat from textiles. Chromium(VI) is extremely toxic and known to cause various health effects. It may lead to liver damage, pulmonary congestion, skin irritation and carcinogenesis[4]. As compound in leather products it may cause contact allergic dermatitis on the skin and also be a trigger for many diseases. Thus the presence of chromium in chromium-tanned leather represents a considerable health problem. Allergic contact dermatitis caused by chromium(VI) resulting from oxidation of Cr(III) during the tanning process has been reported[5]. F. Mignini and colleagues studied the effects of hexavalent chromium on the immunological pattern of shoe, hide, and leather industry workers[6]. Similar results were obtained of N. K. C. Babu and colleagues concluding that any leather auxiliary containing 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[7]. The limits for extractable total chromium and Cr(VI) in leather samples are 50 mg/kg and 3 mg/kg, respectively[8].

Due to the above listed reasons monitoring the chromium content of leather textiles which are intended for long skin contact is mandatory. In cars leather textiles are used as covers for seats, steering wheels and gearshift levers. While the time of use of the gearshift lever is relatively short, extended skin contact is given for seat covers and steering wheel covers. Thus the objective of the presented study was the quantification of the total chromium content of ten leathern textiles produced for car industry for these applications. Knowing the extraction yield of total chromium it is possible to estimate the risk for humans.

Materials and Methods

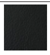
Chemicals

All acids used (nitric acid p.a., hydrochloric acid p.a.) and the chromium standard (1 g/L) were purchased from Merck, Darmstadt, Germany.

Samples

The tests covered 10 leather samples used in car industry for decoration/covers (Table 1). All the samples taken for the purpose of this investigation were produced in Croatia. They were chromium tanned and afterwards dyed in different colours.

TABLE 1
LEATHER SAMPLES ANALYZED

Number	Picture	Sample description	Number	Picture	Sample description
1		Calf leather	6		Cow leather
2		Cow leather	7		Calf leather
3		Cow leather	8		Calf leather
4		Cow leather	9		Beef leather
5		Cow leather	10		Beef leather

Sample preparation

First all samples were dried at 65°C overnight and then cut in small pieces using a ceramic knife. In order to receive the total chromium amount the samples were weighed and analyzed after microwave assisted digestion of the entire sample. The digestion was performed in triplicate using about 0.3 g of each sample applying a mixture of concentrated nitric acid (5 mL) and concentrated hydrochloric acid (1 mL). The working program used was the following: 5 min at 150°C (power 250 W), 15 min 180°C (300 W) and 20 min at the maximum temperature of 200°C (350 W). The resulting solutions were then filled to 10 mL in volumetric flasks with 2% nitric acid.

Instrumentation

The inductively coupled plasma-optical emission spectrometer used was a Perkin Elmer Optima 3000 XL. The instrument was equipped with a standard one piece extended torch with a quartz injector tube, a cyclone spray chamber and a concentric nebulizer (Table 2). A closed-vessel microwave digestion system MLS 1200 Mega (produced by Milestone) equipped with a temperature control was used for the sample digestion.

Measurements

Each digest solution was measured three times by ICP-OES using the method described in a previous

TABLE 2
INSTRUMENTAL PARAMETERS FOR ICP-OES OPTIMA 3000 XL

View	Axial view
Optical system	Echelle
Detector	solid state detector
RF frequency/MHz	40.68
Power/W	1 300
Plasma gas flow/L min^{-1}	15.0
Auxiliary gas flow/L min^{-1}	0.5
Nebulizing chamber	cyclone
Nebulizer	concentric
Sample flow rate/L min^{-1}	0.8

TABLE 3
TOTAL CHROMIUM CONTENT OF THE LEATHER SAMPLES [mg/g]

Sample	Chromium content	RSD [%]	Sample	Chromium content	RSD [%]
1	20.1	1.9	6	21.1	1.8
2	31.2	1.1	7	19.2	1.4
3	32.0	1.9	8	30.4	1.5
4	22.4	0.9	9	18.7	1.6
5	27.7	1.5	10	26.6	1.7

work[9]. The concentration of Cr was determined at four different emission lines, namely 205.560 nm, 206.149 nm, 267.716 nm, and 357.896 nm. The limits of detection for the lines used were 0.7 μg/L, 1.7 μg/L, 0.1 μg/L, and 0.4 μg/L, respectively. The accuracy of the method was ascertained by measuring certified reference materials: NIST 1643 (trace elements in natural water) and NIST 1640 (trace elements in water) for checking the ICP-OES measurements as well as IAEA-V-9 (cotton) for the digestion procedure. The Cr concentrations obtained were in good agreement with the certified values (recoveries 97–102%). The precision of the method is below 1.5%, the day-to-day reproducibility 2.4% and the uncertainty of measurement was estimated to be 4%.

Results and Discussion

The concentrations of total chromium in the ten samples analyzed are listed in Table 3. They range from 18.7 up to 32.0 mg/g. These values are comparable with previously found results for total chromium in tanned leather[10]. Although only chromium(VI) causes noxious health reactions, the knowledge of the total amount of chromium in leather samples is important, since during usage oxidation of chromium(III) to chromium (VI) may take place. The pH-value is one a the factors which determine the amount of oxidized chromium(III). Higher pH-values favor the oxidation. In alkaline solutions the possibility for oxidation is much higher than in acidic ones. Since the pH-value of human sweat varies from about 5 to 8, chromium(III) in the leather may be oxidized to chromium(VI) during handling of leathern materials. Also the extraction yield of chromium from leather depends on the pH of sweat[10], being higher in sweat with lower pH (pH 5:4–7%) than in more alkaline sweat solutions (pH 8.8:2–3%). Calculating the amount of possibly extracted total chromium using only 2% leads to values all beyond the limit of 50 mg/kg of total chromium extracted prescribed in the international Hess Natur Quality Guideline[8]. All samples analyzed may impose serious problems to human health. It could be shown that even the traditional textile material leather is not as harmless as always assumed.

Conclusion

Monitoring total chromium contents in leather materials is extremely important because people are exposed to its impact during every day usage of leather textile materials. Numerous case reports of contact allergic dermatitis caused by chromium on leather have been already reported. Due to the tanning process and possible dying using chromium containing dyes, chromium is in the final leather products used every day in non negligible amounts as proven by the results obtained in this study. High chromium contents in leather lead to concentrations of extractable chromium which exceed the prescribed limits.

Thus it is adviseable to avoid prolonged contact with leather materials containing high chromium amounts. Furthermore there is an urgent need for checking such products before they are brought on the market.

REFERENCES

1. SREERAM KJ, RAMASAM T, Conserv Recycling, 38 (2003) 185. — 2. SUNDAR VJ, RAO JR, MURALIDHARAN C, J Clean Prod, 10 (2002) 69. — 3. BARNHART J, Regul Toxicol Pharm, 26 (1997) 3. — 4. SRIVASTAVA S, THAKUR IS, Bioresource Technol, 97 (2006) 1167. — 5. LIERDE VV, CHÉRY CC, MOENS L, Vanhaecke F, Electrophoresis, 26 (2005) 1703. — 6. MIGNINI F, STRECCIONI V, BALDO M, VITALI M, INDRACCOLO U, BERNACCHIA G, COCCHIONI M, Prev Med, 39 (2004) 767. — 7. BABU NKC, ASMA K, RAGHUPATHI A, VENBA R, RAMES R, SADULLA S, J Clean Prod, 13 (1995) 1189. — 8. Hess Natur quality guidelines leather version 2.0 — 9. REZIC I, STEFFAN I, Microchem J, 85 (2007) 46. — 10. ZEINER M, REZIC I, STEFFAN I, Toxicol Lett, 164 (2006) 187.

M. Zeiner

University of Natural Resources and Life Sciences, Department of Chemistry, Mathgasse 18, 1190 Vienna, Austria
e-mail: michaela.zeiner@boku.ac.at

ODREĐIVANJE UKUPNOG KROMA U UZORCIMA ŠTAVLJENE KOŽE IZ AUTOMOBILSKE INDUSTRIJE

S A Ž E T A K

Unatoč jakoj konkurenciji sintetskih materijala, u automobilskoj se industriji koža učestalo rabi u razne svrhe. Kako bi se osigurala potrebna stabilnost kožne matrice tokom utjecaja raznih parametara poput mikrobiološkog utjecaja, topline ili znoja, proces štavljenja ima nezamjenjivu ulogu. Uporaba kroma u štavljenju kože ima mnoge prednosti, pa je štavljenje kože pomoću kroma proces koji se učestalo rabi. Za vrijeme uporabe štavljenih materijala u odjevnoj, pokrovnoj, dekorativnoj ili bilo kojoj drugoj primjeni, krom se ekstrahira s kože pa u doticaju s ljudskim organizmom može izazvati neželjene posljedice poput alergijskih reakcija. Stoga su informacije o ukupnoj količini kroma koji se otpušta s kožnih materijala te dolazi u dugotrajni doticaj s ljudskom kožom izrazito važne. Kožni se materijali u automobilskoj industriji koriste za pokrivanje sjedala, volana te mjenjača. Ti su materijali bili predmet istraživanja u ovom radu kako bi se odredio ukupan krom koji se otpušta tokom njihove uporabe. Uzorci su na početku ispitivanja bili sušeni preko noći na 65°C, a zatim su pomoću keramičkog noža izrezani na sitne dijelove, razoreni pomoću mikrovalne pećnice te analizirani pomoću induktivno spregnute plazme – optičke emisijske spektroskopije (ICP-OES). Koncentracija ukupnog kroma bila je u rasponu od 19 mg/g do 32 mg/g. Od ukupne količine krom postupkom ekstrakcije u umjetnoj otopini znoja uklonilo se 2–7% kromovih iona. Ove količine mogu biti znakovite i to poglavito za vrijeme ljetnih mjeseci kada se veće količine kromovih iona mogu ekstrahirati te uzrokovati razne neželjene promjene na ljudskoj podlaktici ili vratu.