

## The Negative Effect of the Use of Disinfectants on Shoes Containing Oxidizers

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### Abstract:

The issue of hexavalent chromium the toxic agent occurring in the environment is widely discussed worldwide. The paper is focused on hexavalent chromium that is considered to be carcinogenic contained in leather goods in low concentrations, especially in shoes, and deals with its negative effects on human organism. In this contribution a new possible risk connected with the use of disinfectants on shoes containing oxidizers is presented. People vulnerable to the emergence of dermatological diseases are often recommended to disinfect the inner area of their shoes. Several disinfectants intended specifically for disinfecting footwear containing hydrogen peroxide were found in a survey of disinfectants available in the Czech Republic. The authors' assumption of the risk is based on the fact that one of the prerequisite factors for the conversion of trivalent to hexavalent chromium is the presence of oxidizing agents. The main purpose to destroy bacteria using such a disinfectant should be fulfilled, but more serious health risk might be caused due to the repeated procedure. The oxidation is supported by experimental data gained by UV-visible spectrophotometry. An innovative analytical method Raman spectroscopy is proposed for identification of the valence state of chromium present in examined material. Results indicate that the method can be successfully applicable. Another potential risk, the relationship between an increase of kidney and urinary tract cancer and wearing shoes of disputable quality, mainly on bare feet is introduced.

**Keywords:** disinfectants, footwear, health risk, hexavalent chromium, Raman spectroscopy

### 1. Introduction

Chromium compounds are commonly occurring in nature. It can be found in rocks, volcanic dust, gases, sea water, but also as a part of living organisms including human bodies. In the environment chromium occurs in several different forms. The most common form of chromium in chromium compounds is trivalent (CrIII) and hexavalent (CrVI).

Biological effects of chromium are strongly dependent on the valence, in which chromium enters into the body. Trivalent chromium is largely beneficial and necessary part of daily diet. Trace amounts are needful for humans for glucose and lipid metabolism. CrIII is benign due to poor membrane permeability in general (Eastmond 2008). On the contrary hexavalent chromium can negatively affect human health. It is very toxic and is considered a carcinogen (Hang 2011; Kolomaznik 2008; Shi 1994). In commercially available sources is often

mentioned increase risk of irritation or damage to the respiratory tract and lung cancer when CrVI is inhaled in a large extend and also allergic contact dermatitis when coming into contact with skin.

When hexavalent chromium react with biological reductants free radicals participating in reactive oxygen species production are generated (Hang 2011). Excessive production of reactive oxygen species may cause DNA and proteins damage. These mutagenic characters can lead to cancerous growths in respiratory tract (Shi 1994; Aizar 1991).

Generally it should be emphasized that the implementation of health studies should include control of not only the total content of chromium (both trivalent and hexavalent) in the environment, but especially in what form it comes into contact with organisms. In this paper other possible threats to human health relating to ways of wearing and treating footwear, the object of our daily use, will be discussed.

Chromium salts are often used to manufacture, among other things, paints, cements, surface coatings, anti-corrosives, or leather products. Dangerous hexavalent chromium is still used in some industries for chrome plating, stainless steel welding or the production of chromate pigments and dyes and a lot of workers come into direct contact with the chemical (Kirk, 1992).

In the leather tanning industry trivalent chromium is used as a tanning agent that stabilizes the hide by crosslinking the collagen fibers and supply required qualities. However, under various conditions trivalent chromium contained in leather can be in small amounts converted to hexavalent form. The possibility of the spontaneous oxidation of CrIII into CrVI can occur both in alkaline and acidic medium in the wide range of pH what complicate concrete conditions specification (Kolomaznik 2008).

Prerequisite factors for the formation of CrVI in leather are known (Graf 2001):

- Oxidizing agents – the fundamental for the conversion is presence of oxygen.
- Energy in a form of heat and ultraviolet light, because the conversion requires energy supply.
- Fatty acids as catalysts for peroxide formation.

Although knowledge of CrIII to CrVI conversion is well described in literature, the precise mechanism of the conversion is complex and details are not yet clearly explained (Chaudhuri 2003). The conversion can happen during the processing but these conditions may incidentally involve the normal use or ordinary care of leather items (e.g. drying wet things in the sun). That is why for instance gloves, footwear, clothing, luggage or upholstery – leather items that come into direct contact with skin should be regularly assessed for the hexavalent chromium presence.

Toxic substances should require strict limitations. In many countries the CrVI contamination of drinking water, of the air and other materials as e.g. leather is monitored in recent years and is governed by regulatory standards. However, they are different and changing. The allowed range of hexavalent chromium in leather is in ppb to ppm orders. The most common concentration limit in European countries is 3 mg/kg. In Germany has been adopted zero tolerance of CrVI in leather. However, confirming the absence of CrVI may be problematic, since the test method does not have such detection limits.

There exist several methods for analysis of low concentrations of hexavalent chromium in different ambient. The widespread method is UV-visible spectrophotometric method. This

method is also an official method for determining CrVI in solutions leached from leather under defined conditions. Among other methods can be named e.g. inductively coupled plasma mass spectrometry together with liquid chromatography or flame atomic absorption spectrometry for water analyses, ultrasonic extraction in combination with a strong anion-exchange solid-phase extraction or differential pulse polarography for workplace and environmental air testing (Gómez 2006).

Because of the fact that CrVI and CrIII can normally coexist in the first instance is for testing in some cases needed valence state identification. The authors of (Hua 2009) detected the CrIII and CrVI compounds in electronic and electrical components and products by energy dispersion X-ray fluorescence spectrometry (EDXRF), quantitative UV-VIS spectroscopic analyses followed. Another paper dealing with the identification of different forms of chromium on electrical and electronic equipment (Kikuchi 2005) used Raman spectroscopy. Raman spectroscopy has a lot of advantages and is a potential method for material identification (Vaskova 2011). Qualitative analyses were already proved even on leather samples in our laboratories but more demanding quantification is going to be developed in a near future.

## 2 Problem Formulation

As was already said one of the prerequisite factors for the formation of CrVI in leather is the presence of oxidizing agents. Hydrogen peroxide and its compounds are strong oxidants often used for disinfection or the process of sterilization. Oxidation kinetics of CrIII to CrVI in the presence of hydrogen peroxide at normal temperature was studied. During the reaction hydrogen peroxide decomposes according the following equation:



*O* is highly reactive oxygen with the oxidation state -1, which can be also acquired by the effect of ultraviolet radiation as mentioned in the introduction:



The conversion of all trivalent to hexavalent chromium occurred very quickly particularly in alkaline medium what is also confirmed in (Kirk, 1992). This is very important result because of further consequences.

It is often recommended for people vulnerable to the emergence of dermatological diseases (e.g. fungal infection) to regularly disinfect the inner area of their shoes. We made a survey of disinfectant available in the Czech Republic recommended specifically for disinfection of footwear. There were found several containing hydrogen peroxide. One of them readily available in pharmacy was used for the experiment.

The aim of this paper is to highlight that is important attentively choose a disinfectant to be free of strong oxidizing agents as peroxides. Otherwise the main purpose to destroy bacteria would be probably fulfilled, but more serious health risk could be caused due to the repeated procedure.

### 3 Materials and methods

#### 3.1. Materials

Ten different leather samples (nine chrome-tanned and one aldehyde-tanned) were used as a source of trivalent chromium to verify effects of disinfectant containing hydrogen peroxide to increase the level of hexavalent chromium. A description of the samples is shown in table 1. The disinfecting agent with the 0,1 g H<sub>2</sub>O<sub>2</sub> per 100g of the product was purchased in a pharmacy.

**Table 1** Description of the samples

No.	Sample designation	Form	Colour
1	A	Aldehyde-tanned, bovine hide	pale creame
2	B	Cr-tanned, bovine hide	red
3	C	Cr-tanned, bovine hide nubuck	beige
4	D	Cr-tanned, bovine hide	pink
5	E	Cr-tanned, bovine hide nubuck	dark brown
6	F	Cr-tanned, pig skin	light beige
7	G	Cr-tanned, pig skin, wet-blue	light blue
8	H	Cr-tanned, bovine hide	beige
9	I	Cr-tanned, pig skin	light beige
10	J	Cr-tanned, pig skin, wet-blue	light blue

#### 3.2 Methods

##### UV-visible spectrophotometry

UV-visible spectrophotometric method was applied on our leather samples. Basically it is a colorimetric technique using 1,5 diphenylcarbazide reacting with the CrVI extracted from leather to form colored - magenta complexes that are consequently measured on spectrophotometer at a wavelength of 540 nm. Detection limit of this method is about 50µg/l. Opponents of this method has expressed reasonable doubts about the reliability of the method. They argue that CrIII to CrVI oxidation can occur just by the extraction.

The disinfectant was applied on three-gram pieces of leathers several times always in quantities of 1.25 ml and with the same intervals. The ambient conditions were maintained at the same level. Samples were left to air 24hours and then placed in distilled water for 120 hours. One more set of measurements was done without disinfection application to determine the content of CrVI on the untreated samples. Solutions were assessed according to standard CSN ISO 11083.

##### Raman spectroscopy

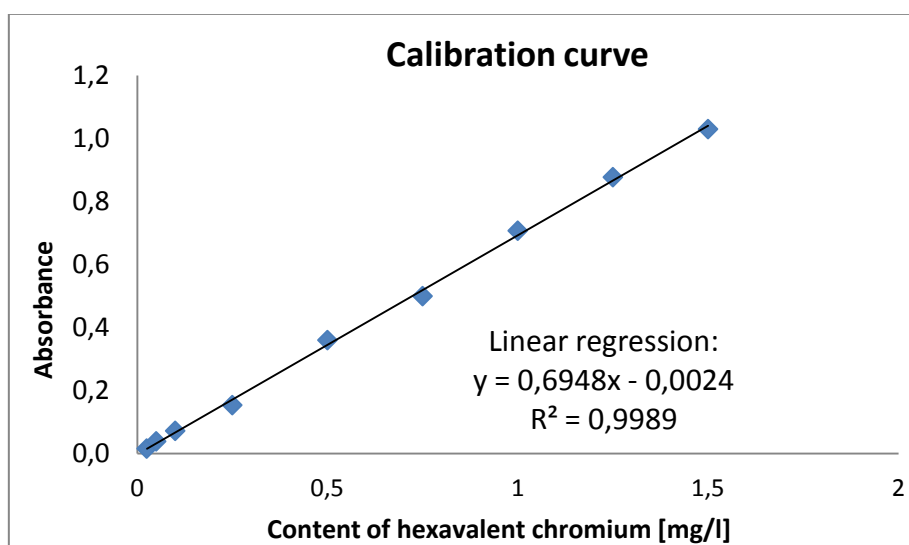
Raman spectroscopy is an innovative analytical tool that becomes a valuable part of laboratories around the world lately. Its applications bring effective results in many scientific disciplines and industrial sectors. In principle, Raman spectroscopy has the potential to answer a number of questions related to chemical details of molecular structure what makes this technique definitely proper for material identification. Raman spectroscopy provides very

specific chemical „fingerprint” of every single chemical substance in the form of the Raman spectrum. Indisputable advantages as non-destructiveness, rapidity, contactless measurements or no special requirements for sample preparation makes this method attractive, convenient and support the growth of its popularity.

## 4 Results and discussion

### 4.1 Spectrophotometric method

Firstly a calibration curve, the dependence of absorbance on hexavalent chromium was measured. The dependence is linear. The calibration curve is displayed in Fig. 1. The table 2 shows the specifications of individual sets of measurements.



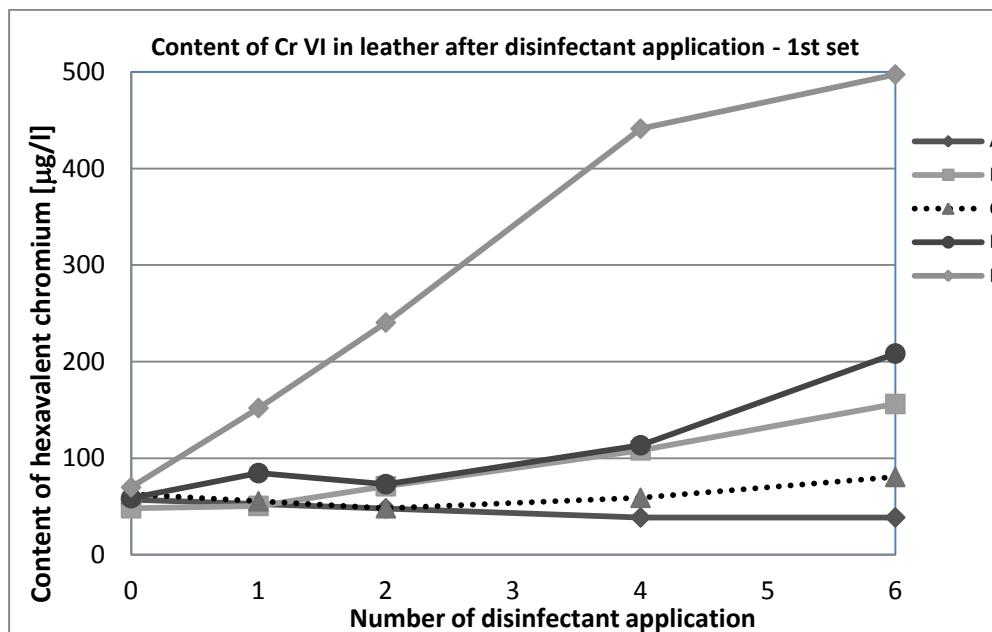
**Fig. 1** Calibration curve – absorbance dependence on hexavalent chromium content in solution

**Table 2** Specifications of sets of measurements

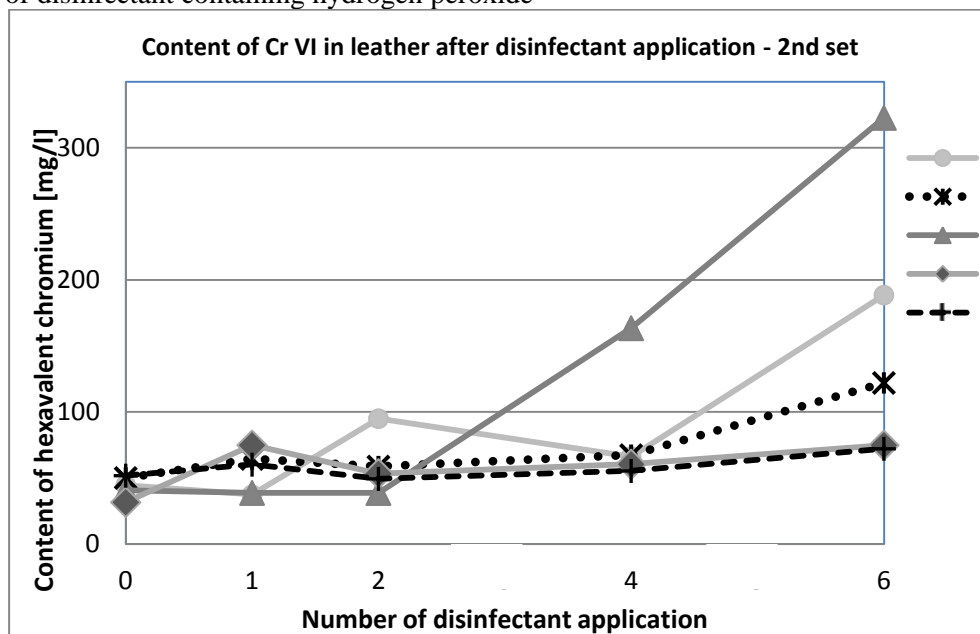
Experiment no.	Treated / untreated	No. of disinfectant application
1	untreated	0
2	treated	1
3	treated	2
4	treated	4
5	treated	6

Evaluated data are shown in Fig.2 and Fig.3. The data are listed in two sets/two figures for better clarity. Graphs show an increase in the content of CrVI in leather samples with repeated application of disinfectant containing the oxidizer. An increase trend is observed in eight cases out of ten. Some values are slightly below 50µg/l what correspond to detection limit. Values pertaining to six-times cured leather pieces are in maximum almost eightfold and on average quadruple in comparison with untreated samples. The Fig. 4 shows how many times the value of the content of CrVI in leather increased after repeated treatment of the samples.

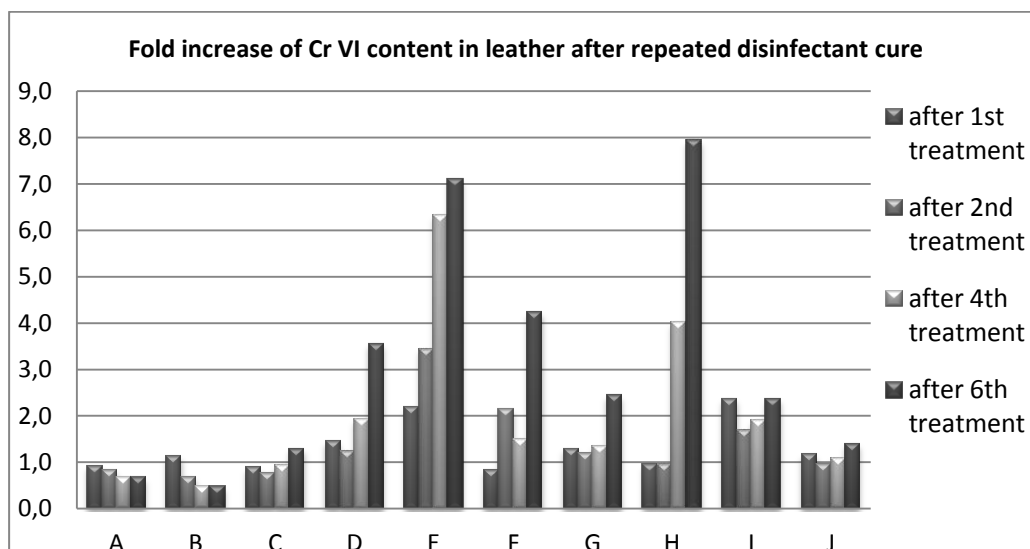
The results clearly confirm the fact, that strong oxidizing agents facilitate the conversion of CrIII to CrVI even in leather. Significant on submitted demonstration is that to this or similar situation may be people routinely exposed. With regard to the fact, that effects of repeated exposure, even to low concentrations, to CrVI have hazardous impact on human health it is necessary to take the issue of hexavalent chromium very seriously.



**Fig. 2** 1<sup>st</sup> set of data, contents of hexavalent chromium in leather samples after application of disinfectant containing hydrogen peroxide



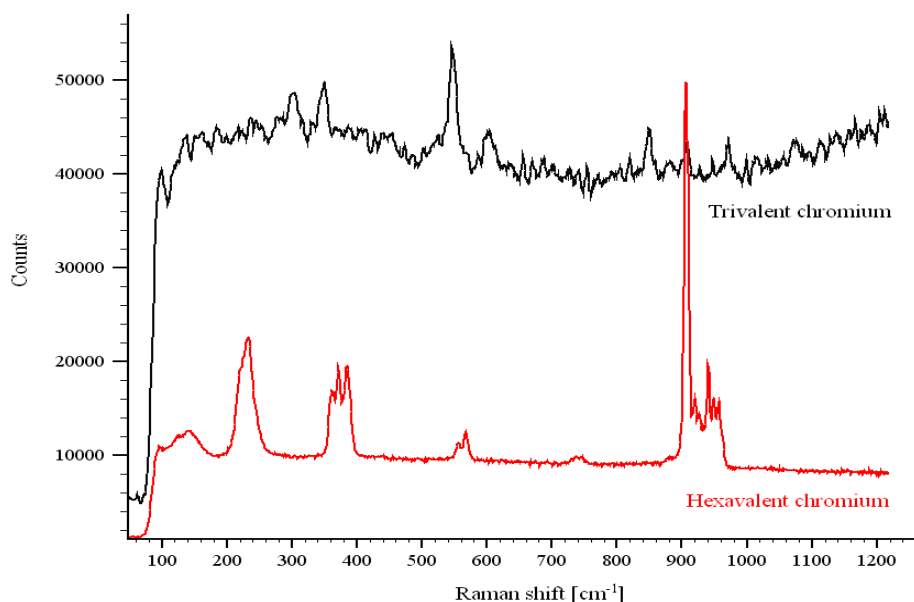
**Fig.3** 2<sup>nd</sup> set of data, contents of hexavalent chromium in leather samples after application of disinfectant containing hydrogen peroxide



**Fig. 4** Fold increase of Cr VI content in leather after repeated disinfectant application

#### 4.2. Raman spectra

Raman spectra of trivalent and hexavalent form of chromium were acquired by InVia Basis Raman microscope. Better results, shown in figure 2, were obtained using NIR laser (785nm) than with the use of visible (514nm) laser because of the reducing of fluorescence in NIR domain. Spectra indicate their diversity, what simplify identification of valence forms.



**Fig.5** Measured Raman spectra of leather containing trivalent and hexavalent chromium

#### 4.3. The impact of CrVI on human health

Another potential threat to the health could be hidden in chrome-tanned leather goods, mainly shoes, which are in daily contact with the human organism. If the goods contain even small amounts of carcinogenic chromium, there is a potential risk of cancer, especially kidney and

urinary tract (Kirk 1992). Upward trend in the incidence of urinary tract neoplasms not only in Czech Republic requires serious answer, if not caused by the content of hexavalent chromium in leather goods. According Kolomaznik (2008) there is a possible correlation between increasing mentioned cancer disease and rising import of relatively cheap and often disputable quality shoes. Hexavalent chromium can penetrate through the skin, amplified by the presence of sweat, into the organism, when wearing shoes on bare feet.

#### 4 Conclusion

The issue of chromium in connection with products of leather industry was discussed, also the impacts of repeated contact with the toxic form hexavalent chromium on human health. Another potential risk, the relationship between the increase of kidney and urinary tract and wearing shoes of disputable quality, mainly on bare feet was introduced. The main intention, however, concerned the possible risks associated with the use of disinfectants on shoes containing strong oxidizers by the reasons of mitigating the consequences of dermatological diseases as is supported by experimental data.

#### 5. Acknowledgements

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