

Investigation on Potentially Hazardous Hexavalent Chromium and Heavy Metals in Leather Products

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Abstract

Humans are prone to get exposed to heavy metals, a well-known potential health hazard, through common consumer products such as leather. Hazardous hexavalent chromium or Cr (VI), along with other heavy metals, gets added into the leather products during tannery operations. Leather products with improper hazard screening can enter the market in the absence of proper regulatory measures. In this study we investigated the presence of Cr (VI), lead, cadmium, arsenic, antimony, barium and selenium in 30 different leather samples from the Sri Lankan market. The limit of detection (LOD) for Cr (VI) was 0.013 ppm whereas the limit of quantification (LOQ) was 0.034 ppm. For arsenic, barium, cadmium, chromium, lead, antimony and selenium, the LOD and LOQ were 0.028, 0.026, 0.003, 0.002, 0.006, 0.023, 0.030 ppm and 0.099, 0.092, 0.009, 0.009, 0.021, 0.082, 0.106 ppm respectively according to the method of analysis. 25% of samples exceeded the permitted level of Cr (VI) (3 ppm) whereas soluble Cr found in 85% of the samples was greater than the permitted limit (60 ppm). The results very clearly show that among all Cr is the core metal that could potentially pose a health hazard to leather consumers of Sri Lanka.

Keywords: Hexavalent Chromium, Soluble Chromium, Heavy Metals, Leather, Health Hazard.

Introduction

The production of leather and leather goods are a highly relevant economic activity in many developing countries in the world. Leather market has become extremely diverse where it is a difficult task to determine the origin of leather products because part of the production might take place in one country while the final production process might take place in another country. Sri Lanka, too produces leather domestically as well as import from various neighboring countries. Cattle hides, goat and sheep skins are the three most abundantly used types of raw materials in the leather industry (Grote & Stamm, 2007), which undergo many processes such as unchaining, liming,

DE liming and bating, pickling, tanning, neutralizing, dyeing, fat liquoring, drying and finishing before sale or further product manufacturing. During tanning, which is the most chemically complex process, *collagen* forms stable complexes with the ligand present in the chromium complex (Mann & McMillan, 2010). It is reported that 90% of the tanneries in the world, including Sri Lanka, use significant amount of Cr, particularly chromium sulfate, as the main source of tanning (Aslan, 2009; Chaudhuri et al., 2003).

Cr and other heavy metals are believed to be retained in the treated animal skins mostly after the tanning and dyeing process, which are the steps that gives the skins the most chemical exposure (Zhenji, 2001). Hexavalent chromium (Cr (VI)) is one of the major and injurious chemical forms of Cr in leather products. Not only chromium, but other heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), antimony (Sb), barium (Ba) and selenium (Se) could also get added into the leather products during the post tannery operations including coloring and finishing process. These are also termed as xenobiotic, i.e., with no useful function in human physiological processes, typically posing toxicity at trace levels. They tend to persist in some storage sites like the liver, bones, and kidneys, for years or decades, causing serious injuries to human health (Sheehan et al., 1991; Elliott et al., 2000; Flora et al., 2012; Vinceti et al., 2001; Guishen et al., 2012; Yang, 2009).

Large amount of Cr present in the leather auxiliaries paves the path for the generation of Cr (VI) during leather production. One of the possible sources of hexavalent chromium is the pigmentation process of leather based on lead chromate (Font et al., 1998) and the use of contaminated Cr salts (Chaudhuri et al., 2003; Chaudhuri & Sarkar, 2001). Apart from the direct methods there could be significant conversion of trivalent chromium (Cr (III)) into Cr (VI). The presence of strong oxidizing agent at low pH and mild oxidizing agents at high pH are major sources that can generate Cr (VI) from Cr (III) (Candar, 2001; Pastore et al., 2004). Ammonia treatment, thermal and photo ageing of leather, adhesives used in product making and fat liquoring can be some of the other sources (Sheehan et al., 1991; Font, 1999; Babu, 2005).

Various analytical techniques such as electrochemical techniques (Bergamini et al., 2007; Kalender et al., 2011), fluorimetry (Paleologos et al., 1998), chromatography (Guishen et al., 2012) and chemiluminescence (Gammelgaard et al., 1997) have been developed for the investigation of Cr and other heavy metals. In this study spectrophotometric methods; UV/Visible absorption spectroscopy and inductively couple plasma optical emission spectroscopy, are employed for the analysis of heavy metals in the leather materials collected from the production market. The main objective of this research is to determine the levels of heavy metals of those leather materials to investigate if they are within the safer limits for the use of consumers and contribute towards regulatory framework on safe limits for leather materials to be adopted by relevant Sri Lankan authorities.

Methodology

Reagents and instrumentation

Membrane filter (0.45 μm made up with polytetrafluoroethylene) and polypropylene cartridges filled with reversed phase materials (RP 18) from Sigma-Aldrich, all reagents used were analytical grade from Sigma – Aldrich with more than 95% purity, deionized water in accordance with ISO 3696 were used in all experiments. The instruments used include pH meter with an accuracy of measuring 0.1 pH units from Cole-Parmer, mechanical shaker and shaker water bath to constantly agitate the mixture at a temperature of 37 ± 2 ° C from Thermo Fisher Scientific, Shimadzu UV - 1700 UV-Visible spectrophotometer, Varian inductively coupled plasma – optical emission spectrophotometer (ICP-OES: 730-ES).

Leather sample collection and preparation for analysis

Leather samples were collected from the Sri Lankan leather distribution market where imported and domestic raw leather materials were sold before they were converted to different consumer products. The samples collected were separately stored in polythene packs until analysis to avoid possible cross contamination. The leather samples were cut into 5 x 5 mm² squares from the areas of thinnest material cross section in order to ensure a surface area of the test pieces to be as large as possible in proportion to their mass.

Determination of hexavalent chromium (Cr (VI))

The method specified in the International Standard (ISO 17075, 2007) was followed with appropriate modifications to extract and determine the Cr (VI) leached from leather under defined conditions. This method is

suitable to quantify the Cr(VI) content in all types of leather up to 3 ppm (as Cr(VI)), which is the standard maximum permissible limit (Rezić & Zeiner, 2009).

A mass of 3.00 ± 0.01 g was weighed and transferred to a 250 ml conical flask followed by addition of 100 ml of the degassed extraction solution; phosphate buffer (pH 8.0). Properly sealed conical flask was mechanically shaken for 3 hours to extract the Cr (VI). Immediately after the completion of the extraction, the contents were filtered into another clean screw capped conical flask. The pH of the extracted solution was ensured to be in the range of 7.5 - 8.0 at the end of extraction process.

RP 18 cartridges were pretreated by flushing with 5 ml of methanol followed by 5 ml of distilled water and with 10 ml of the extraction solution prior to removal of any colored dyes of extract. A 10 ml portion of the extracted solution was passed through the cartridge and collected into a 25 ml volumetric flask. Then the flask was filled up to 75% with the original extraction solution and 0.5 ml of phosphoric acid solution followed by 0.5 ml of diphenylcarbazide solution. Then the flask was made up to the mark with original extraction solution and mixed well. Similarly the blank solution was prepared without Cr (VI). Then the solutions were allowed to stand for 15 ± 5 minutes to develop the red-violet color and the absorbance was measured by using the UV-Visible Spectrophotometer at 540 nm and 4 cm path length.

Determination of soluble metals

The soluble metal test was conducted to check if the leather samples would comply with the European Standard: EN-71 which specifies the safety of toys and other materials produced out of materials including leather as per CPSA (2008). A mass of 0.2 g was measured into a clean dry glass test tube, and 10 mL of 0.07 M HCl was pipetted in and the pH was ensured to be at 1 – 1.5 using 1.0 M HCl solution. The test tubes were then capped and placed in the water bath at $37 \pm 2^\circ$ C, and constantly shaken for 1 hour in the dark. Once the shaking time is over the samples were immediately filtered using filter paper (0.45 μ m pore size) to directly analyze using the ICP-OES (ASTM E1613 2004) to see if they meet the standard limits for the maximum soluble migrated levels of heavy metals specified for the safe use of the consumers (Table 1).

The ICP-OES was calibrated using the standards that contained the lowest detectable levels of the elements as stated by the manufacturer. The lowest calibration standard used for Cr, Cd were 0.01 ppm and Pb was 0.04 ppm, while the other metals were 0.1 ppm that are well below that the maximum permissible limits of metals in a given sample. The highest calibration standard for all the metals were 4 ppm that demonstrated an excellent linearity.

Results

Method development for Cr (VI) determination

The wide linear dynamic range from 0.005 – 0.6 ppm was employed for the calibration resulting a regression coefficient (R^2) of 0.9973. Also with the $p = 0.0136$, the regression demonstrated that there is a significant linear correlation between absorbance and concentration in the calibration (Figure 1). The standard method specifies a lowest detectable concentration of 0.02 ppm while this study yielded a lowest detectable concentration of 0.005 ppm, an increment of the sensitivity by four folds compared to the standard method. With the blank measurement showing no Cr (VI), the measurements made with good precision and accuracy using the sensitive calibration curve developed.

The extracts were spiked with various amounts of Cr (VI) standard, from 0.24 – 0.01 ppm, in order to identify the possible matrix effects existing at low and high concentrations from the standard Cr solution. The average recovery of 91% was obtained when the samples were spiked with 0.02 ppm of Cr (VI) resulting a limit of detection (LOD) of 0.013 ppm and LOQ of 0.034 ppm. The LOD was calculated by 3 times the standard deviation (σ) of lowest concentration level that is determined to be statistically different from a blank (99% confidence level, $n=5$) with signal to noise ratio greater than 3. The limit of quantification (LOQ) is calculated 10σ of the results for a series of replicates ($n=5$) used to determine a justifiable limit of detection. Therefore the Cr (VI) of each sample could be quantified with great precision and accuracy.

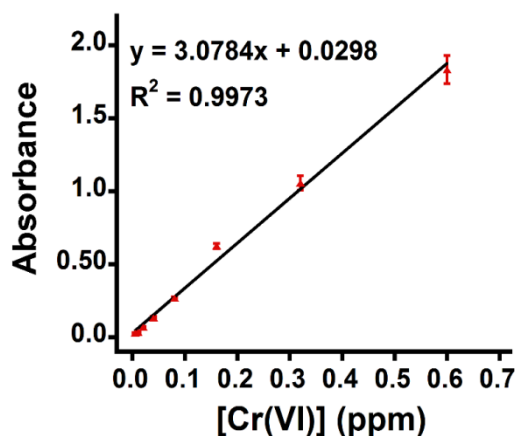


Figure 1. Calibration plot for the Cr (VI) determination using standards in the concentration range from 0.005 – 0.60 ppm.

The adsorption of Cr (VI) was found to be retarded by the inorganic ligands, and more pronounced by $H_2PO_4^-$ in the extraction solution at low pH in previous work (Naidu & Kookanal, 1998; Naidu et al., 1998) and thus has been maintained at higher levels to attribute such problems as per the method in this research. The excellent recovery rates indicates that the extract does not cause any transformation of the Cr (VI) spiked to Cr (III). It is also unlikely that the Cr (VI) to be retained in the cartridge column used to remove color from dye and wax containing samples, because the loss of the analyze in the standards tested for calibration were negligible after running through the similar columns.

Cr (VI) levels in leather samples

The extraction process using phosphate buffer with the pH range employed leads to negligible amount of Cr (VI) generation and hence is an interference free method for Cr (VI) extraction as reported in literature (Long et al., 2000; Chaudhuri et al., 2004). The uniqueness of this approach allowed to determine Cr (VI) accurately and specifically in the presence of other components in a sample matrix under the stated conditions of the test. All the samples resulted colored extracts with a die or wax paint except for samples numbers 31, 32, 33 and 34. Cr (VI) analysis was conducted in triplicates and the average results quantified as per the standard are presented in table 2. According to Figure 2 about 25% of the samples tested were above the limit of Cr (VI), 3 ppm as specified by the standard, confirming that there is a possible health effect that can be caused by Cr (VI) in the leather used in various parts of the country. It is indeed clear that most of the leather production strategies employed are not very well controlled and standardized before they release the leather products to the market for consumption.

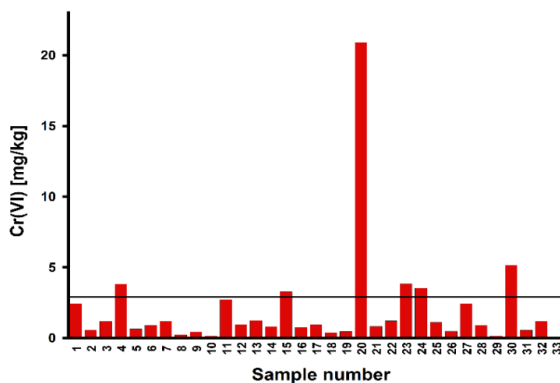


Figure 2. The amount of Cr (VI) present in the leather samples in Sri Lankan market. The solid line drawn across states the maximum limit of Cr (VI): 3 ppm that is specified by ISO 17075.

Quantified levels of soluble metals

An added forecast of this assessment was to check if the leather samples would comply with the European Standard: EN-71 which specifies the safety of toys and related materials produced out of leather as mentioned in CPSA. These requirements have been established to minimize children’s exposure to heavy metals in toys made of leather as accessible substrate material. The criteria to be considered as accessible is that the toy materials are likely to be sucked, mouthed or ingested. Soluble elements are extracted from leather samples, under conditions that simulate the situation in which the materials stay four hours in the alimentary tract in contact with the stomach acids after swallowing. The content of the soluble elements in the extracts were determined quantitatively by ICP-OES. Samples detecting metal content lower than the lowest calibration standard values are considered as not detected (N/D) during result interpretations (Table 2). A recovery study was performed by spiking 10 randomly selected samples with 0.04 ppm for Cr, Cd and Pb and 0.10 ppm the rest of the metals to assess the accuracy of the testing method. The obtained recoveries of >90% for all the metals studied prove the accuracy of the method used in this experiment (Table 1).

Table 1. Results of recovery studies performed in sample matrices (n = 10).

Heavy metal	[Spiked] /ppm	[Recovered] /ppm	Recovery (%)
As	0.10	0.093	93
Ba	0.10	0.090	90
Cd	0.04	0.039	98
Cr	0.04	0.038	95
Pb	0.04	0.039	98
Sb	0.10	0.096	96
Se	0.10	0.089	89

The calculated LOD and LOQ for each metal at 99% confidence levels are summarized in Table 2. The QC sample containing 1.00 ppm each of the metals under study was used to validate the calibration procedure. The mean sample values of QC used for the soluble and total metal check results are mentioned in Table 2. A student t-test was carried out at 95% confidence level to check if the sample means have a significant difference from 1 ppm. Since the p-values are greater than 0.05, the sample means are not significantly different from 1.00 ppm. Therefore, the calibration can be considered suitable to test the heavy metals of samples in a bias free manner.

Table 2. Mean values, resulted p-values from student t-test (paired two sample for means at 95% confidence level) performed for the results of quality check sample (n=5) that validated the linear dynamic range during calibration, and LOD and LOQ calculated for soluble metal analysis. The specified permitted maximum soluble migrated levels for each metal under study (16 CFR Part 1303, 2008).

Heavy metal	Mean (ppm)	p-value	($\alpha = 0.05$)	Linear calibration range (ppm)	LOD (ppm)	LOQ (ppm)	Permitted soluble level (ppm)
As	1.001 ± 0.002	0.474		0.1 – 4.0	0.028	0.099	25
Ba	1.004 ± 0.008	0.315		0.1 – 4.0	0.026	0.092	1000
Cd	1.001 ± 0.005	0.737		0.01 – 4.0	0.003	0.009	75
Cr	1.003 ± 0.006	0.302		0.01 – 4.0	0.002	0.009	60
Pb	1.007 ± 0.008	0.063		0.04 – 4.0	0.006	0.021	90
Sb	1.003 ± 0.007	0.276		0.1 – 4.0	0.023	0.082	60
Se	1.003 ± 0.006	0.286		0.1 – 4.0	0.030	0.106	500

According to the results in table 3 none of the samples contained soluble as or Cd, and few samples showed the presence of Ba, Sb and Se in levels lower than limits specified by 16 CFR 1303 regulation (Table 2). However the soluble Cr level in most of the samples were not in agreement with the limits. More than 90% of the samples of finished leather contained greater than 60 ppm of soluble Cr. Hence they accounted for Cr, including Cr (VI), which can be adversely affecting the consumers. Out of all the samples, 20 seem to be exceptionally unsuitable for use due

to its high content of soluble Cr as well as Cr (VI). Also more than 50% of samples displayed detectable levels of soluble Pb, but were within the safer limits.

Table 3. The levels of heavy metals (ppm) detected from the leather samples.

Heavy metal contents (ppm) determined																	
S.No	Cr(VI)	Cr	As	Ba	Cd	Pb	Sb	Se	S.No	Cr(VI)	Cr	As	Ba	Cd	Pb	Sb	Se
1	2.5	509	N/D	N/D	N/D	N/D	3.2	28	16	0.8	306	N/D	8.3	N/D	40	1.7	17
2	0.6	591	N/D	N/D	N/D	2.7	3.2	27	17	0.9	332	N/D	2.9	N/D	N/D	2.1	18
3	1.2	107	N/D	N/D	N/D	N/D	N/D	5.9	18	0.4	357	N/D	4.5	N/D	2.8	2.1	20
4	2.4	404	N/D	5.12	N/D	6.4	2.3	23	19	0.5	597	N/D	N/D	N/D	3.1	3.3	26
5	0.6	127	N/D	N/D	N/D	1.3	N/D	7.6	20	20.9	1324	N/D	N/D	N/D	1.6	6.9	62
6	0.9	276	N/D	N/D	N/D	1.2	N/D	14	21	0.8	411	N/D	10.7	1.2	6.3	2.6	24
7	1.2	410	N/D	N/D	N/D	3.4	1.9	19	22	1.2	5.0	N/D	5.7	N/D	N/D	N/D	N/D
8	0.2	949	N/D	11	1.4	N/D	5.8	54	23	2.8	64	N/D	6.1	0.6	31	N/D	4.1
9	0.4	1342	N/D	N/D	N/D	N/D	N/D	N/D	24	2.5	1258	N/D	4.7	N/D	5.0	6.4	57
10	0.2	146	N/D	N/D	N/D	1.4	N/D	9.2	25	1.1	198	N/D	3.9	N/D	1.2	2.8	11
11	1.8	840	N/D	7.3	0.8	39	4.9	45.5	26	0.5	901	N/D	N/D	N/D	1.3	5.3	43
12	1.1	385	N/D	N/D	N/D	N/D	2.0	22	27	1.7	289	N/D	13.1	2.1	1.9	1.9	16
13	1.2	313	N/D	N/D	N/D	2.9	1.8	17	28	0.9	149	N/D	N/D	N/D	N/D	7.5	63
14	0.8	532	N/D	N/D	N/D	2.5	3.1	31	29	0.2	226	N/D	5.1	N/D	N/D	1.9	11
15	2.4	306	N/D	N/D	N/D	N/D	1.8	17	30	3.2	0.3	N/D	N/D	N/D	N/D	N/D	N/D

*N/D indicates the presence of heavy metals below the detection limit

Conclusion

The tanning industry is a growing source of income for many developing South Asian countries including Sri Lanka accounting for a reasonable share of the export market. The quality control parameters followed by the tanners while they manufacture raw leather will be vital for the employees as well as the consumers. Though presence of Cr (VI) is one of the safety parameters of EN420 and of European Eco-label for footwear, no systematic investigation has been done in Sri Lanka on leather products. This investigation alarms the presence of Cr (VI) in leather products used in Sri Lanka. Since the reported levels of Cr (VI) is hazardous for reasonable amount of samples, preventive measure need to be taken to avoid its exposure. Use of vegetable tanning (Barnhart, 1997) is preferred over the chrome tanning in this regard. Also reducing agents such as sodium bisulfite, sodium met bisulfite (Candar, 2001) may be used in the final washing of leather to retard Cr (VI) exposure. A higher moisture content during storage of the leather is another positive method for lowering or preventing formation of Cr (VI) (Font, 1999).

In summary, 30 leather samples were collected for this study and it is noteworthy to mention that neither of the leather types were documented in any catalog. Furthermore, both the merchants and the consumers were not aware of the content of hazardous chemicals in the leather products. Unfortunately, the workers in tanneries are exposed to higher levels of hazardous chemicals due to lack of awareness on the hazardous materials and lack of usage of personal protective equipment. Information revealed in this study is vital for the policymakers to strengthen the safety of the tannery workers, leather product manufacturers and the consumers. Otherwise prolong exposure to chemicals such as Cr can have a severe impact to the society.

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Conflict of interest

The authors declare no conflict of interest

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Art work

