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ASSESSMENT OF THE RISKS POSED BY HEAVY METALS CONTAINED IN CONSUMER PRODUCTS USING THE BIOINDICATIVE MEASURING METHOD

Renata SALERNO-KOCHAN[1]

[1] Cracow University of Economics, Faculty of Commodity Science, Cracow, Sienkiewicza 4, Poland. E-mail: salernor@uek.krakow.pl

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Abstract

The problem dealt with in this research work refers to not unequivocally defined safety requirements that relate to consumer products such as clothes, shoes, toys, upholstered furniture and decorative items. The aim of the study was to find out if any of the so-called heavy metals included in products as components of chemical substances used during finishing processes might pose a real risk to consumers. For the realisation of the research purpose the samples of materials in which high quantities of heavy metals were detected have been subjected to extraction in different kinds of solution extracts and then the extracts were analysed for the presence of such elements as nickel, copper, lead, cadmium and chrome. To verify the toxicity effect of extracts, the bioindicative measuring method based on ciliate sp. test organisms was applied. Changes in test organisms' behaviour were analysed based on microscopic observations and spectrophotometric measurements.

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Introduction

Consumer products comprise a large and diverse group of common or daily use items available on the market that are ordinarily bought by individuals for private consumption. Quite a considerable group of these products, such as clothes, shoes, toys, upholstered furniture, decorative items are made of fibres or leather. Leather and natural fibres are perceived as rather friendly raw materials, while synthetic materials and especially chemical additives that are used in manufacturing processes to improve the product appearance or its utility properties may pose health problems for consumers. Among substances that cause a number of scientific problems are the so-called heavy metals such as arsenic, cadmium, chromium, copper, lead, mercury or nickel. These ele-

ments and their compounds are known for their toxic effect on live organisms. They may have a negative influence on human metabolism and internal organs. They may cause heart disease, disorder to the nervous system or allergies (Senczuk, 2006; Shekhawat, Chatterjee, and Joshi, 2015). Due to their known negative impact on human beings the use of heavy metals is banned or limited by legal regulations. The most restrictive requirements are defined in the REACH regulation (Regulation (EC) No 1907/2006). In accordance with this document, such elements as arsenic, cadmium, mercury and lead should not be used as substances, constituents of preparations or colorants in textile and leather materials. Another approach to the presence of heavy metals in textiles and leather is presented in:

- standard EN 71-3+A1: 2014-12 that relates to toys
- and ecological requirements defined in:
  - criteria for the OEKO-TEX® Standard 100 that is a comprehensive, third-party testing and certification system for textile products at all stages of production (https://www.oeko-tex.com/de/business/business_home/business_home.xhtml),
  - EU Ecolabel criteria introduced with Commission Decision of 5 June 2014 establishing the ecological criteria for the award of the EU Ecolabel for textile products (OJ L174/45 13.06.2014).

They allow for the presence of heavy metals in these materials and specify limits values for element migration from a product into the acid sweat solution. In accordance with ecological criteria, depending on the kind of heavy metal and product purpose, the migration limits vary from 50 mg/kg for Cu in decoration materials, through 1 – 2 mg/kg for Cr; 0.2 – 1 mg/kg for Pb; 0.1 mg/kg for Cd to 0.02 mg/kg for Hg.

The presented above different approach to the requirements of heavy metal content in consumer products raises the question related to the real risk that these elements may pose to human beings, so the aim of this research was to find out if the heavy metals included in products as components of chemical substances used during finishing processes, might pose a real risk to consumers.

Material and methods

Samples

Experiments were carried out on 3 textile materials of the following intended use and raw material composition:

– SAMPLE A: clothing knitted fabric made of polyamide (PA), navy blue colour;

– SAMPLE B: furniture woven fabric made of polyester fibres and coated by polyvinyl chloride (PET & PVC), red colour;

– SAMPLE C: furniture woven fabric made of polyamide fibres and coated by polyvinyl chloride (64%) and polyurethane (34%) (PA & PVC+PU),

and on 1 footwear leather material:

– SAMPLE D: cow split leather, natural colour.

The samples designed for mineralization were disintegrated by grinding and kept at a temperature of 60°C for 1 hour. Afterwards a 1g sample was placed in a Teflon vessel and 6ml of 70% nitric (V) acid was added. Then the samples were mineralized in a WX-6000 microwave oven. After mineralization and cooling dihydrogen peroxide was added, and then after the nitric oxides volatilised, water solutions of samples were prepared and subjected to FAAS analysis (EN 14084:2004).

For the realisation of the research purpose the samples in which high amount of heavy metals were detected have been subjected to extraction at three different extract solutions: water, HCl solution at concentration of 0.07 mol/L and 0.9% NaCl solution (physiological saline). The use of water as an extract was to simulate the contact of wet materials with the human skin. When using clothes or other textile products it does happen that textile is wetted more or less occasionally. Thus, it is necessary to investigate if such an event could lead to migration of harmful metals from wetted textile to the human body through contact with the skin. The use of hydrochloric acid was to determine a possibility of migration of trace elements in gastric acid that may be important in the context of children's products (e.g. toys) that may be swallowed. In turn the use of sodium hydroxide extract was to simulate conditions where a material is exposed to human sweat that is composed mainly of this compound (Salerno-Kochan, 2016).

The samples designed for extraction were prepared according to the procedure specified in EN 71-3+A1:2014-12. This consisted in placing 1 g of a sample in 50 ml of extracting solution and incubation at 37 ± 2°C for 2 hours. The next step was to separate solids from the solution by using a membrane filter.

Analytical method

The mineralized samples and extracts were analysed by using *Flame Atomic Absorption Spectroscopy* (FAAS) for the presence of such elements as nickel, copper, lead, cadmium and chrome. Only extracts from samples where metals were found in its mineralizates were subject to FAAS analysis for the presence of these elements on the Thermo Scientific iCE 3000 spectrophotometer.

Bioindicative method

To verify the toxicity effect of extracts the strain *Tetrahymena pyriformis* (Ehrenberg) Wolff 1947 of reference number CCAP 1630/1W, coming from the Culture Collection of Algae and Protozoa, Ambleside UK, was used. These organisms were selected due to the fact that *Tetrahymena pyriformis* meets most requirements for test organisms and is one of the bioindicators commonly used in laboratory tests. *Tetrahymena* belonging to protozoans is a unicellular organism with cell membrane of quite different structure than those of bacteria, yeasts or algae that form a barrier to toxic compounds. In the case of *ciliate sp.,* the interior of the cell is separated from its environment with a thin cell membrane only, thus causing ciliates to be very sensitive even to the trace presence of toxic compounds in their environment. In addition, in terms of vital functions, cellular structures and also gene functionality, *Tetrahymena* cells are closer to human cells than other model microorganisms (Gutierrez J.C. et. al., 2003).

Changes in test organisms' behaviour were analysed based on (Salerno-Kochan, 2011):

– direct readings of solution absorbance (optical density) measured at 330 nm after 4, 6, 8 and 24 hours;

– microscope observations of *Tetrahymena pyriformis* behavior in extracts;

– organoleptic assessment of color changes for cell vitality indicator.

The measurements were also performed for *Tetrahymena pyriformis* culture solutions in spring water and HCl and NaCl solutions. These measurements were treated as so-called control groups.

Results and discussion

Results of analytical measurements

The results of heavy metals contents in mineralized samples are presented in Table 1 and the amount of these elements in the extract solutions are presented in Figure 1.

Table 1

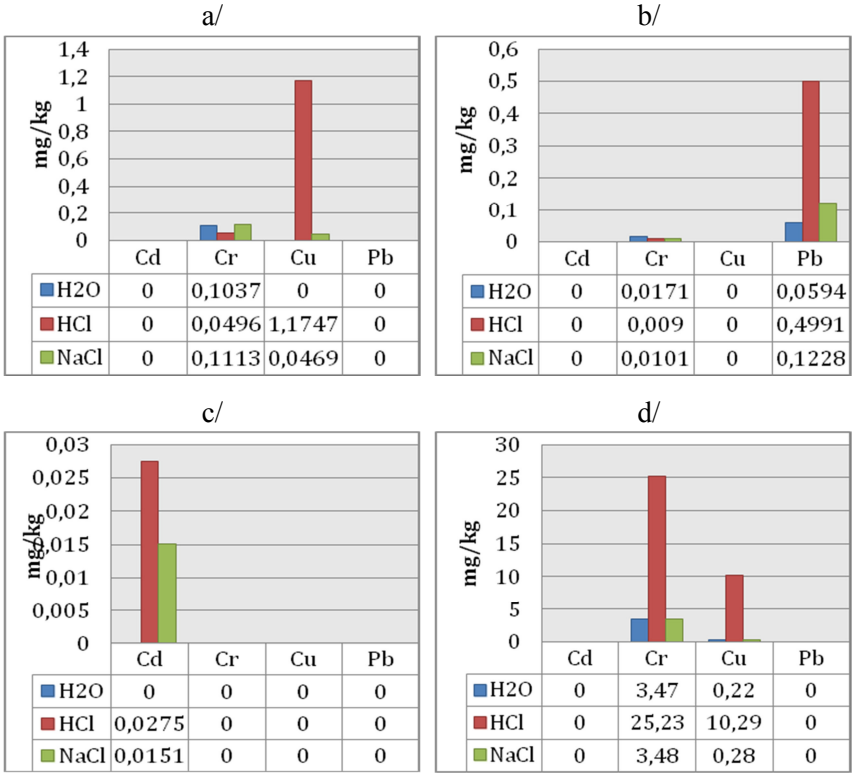
Heavy metals contents in the mineralized samples

Element	Heavy metals contents (mg/kg)			
	SAMPLE A	***SAMPLE B***	***SAMPLE C***	***SAMPLE D***
Cd	0.51	0	10 537.26	0
Cr	285.67	1 042.19	0	18 437.81
Cu	335.06	6.00	2.78	1 088.18
Pb	0	6 466.91	0	0

Source: *own research.*

The data presented in Table 1 demonstrate the presence of heavy metals in all mineralized samples and indicate that these materials do not meet the requirements of the REACH regulation. It should be underlined that the content of banned elements in these materials was extremely high, especially in such materials as SAMPLE D, in which almost 18 500 mg/kg of chromium was detected, SAMPLE C which contains more than 10 000 mg/kg of cadmium and SAMPLE B, in which there were found lead and chromium in high concentrations.

Considering in turn the results presented in Figure 1, related to the amounts of these elements in the extracts of analysed materials, there was observed significantly low content of heavy metals in extract solutions.



Source: *own research.*

Fig. 1. Heavy metal content in samples' extracts: a/ extracts of SAMPLE A; b/ extracts of SAMPLE B; c/ extracts of SAMPLE C; d/ extracts of SAMPLE D

The amount of detected elements in the extracts didn't exceed 0.1% value of harmful elements found in mineralized samples. The highest migration capability has copper, contained in SAMPLE A. Compared to the content of this element in the mineralized sample, its presence in hydrochloric acid solution extract was at the level of 0.5% of copper content in the mineralized sample. Also chromium shows high migration capability and it easily extracts into aqueous environment and sodium chloride solution. In turn, in SAMPLE C, despite a significant cadmium content subjected to mineralization (10 537 mg/kg) the content of this element in extracts was 0.0275 mg/kg and 0.0151 in HCl and NaCl extracts, i.e. 0.00026% and 0.00014%, respectively, with reference to the cadmium concentration in the mineralized sample.

It has also been stated that among the three extract solutions used in the experiment, the hydrochloric acid solution shows the highest extraction capability, while the lowest amounts of harmful elements were extracted into water.

When analysing the research results related to extracts in the context of environmental requirements for textile and leather materials one should conclude that the amount of heavy metals detected in three of the analysed samples reached values substantially below the specified requirements limits. Only SAMPLE D does not comply with ecological requirements due to the high amount of total chromium content in all extract solutions used in the experiment.

Results from the bioindicative method

The fundamental experiment aimed at estimating the toxicity effect of sample extracts on test organisms was preceded by the examination of HCl and NaCl solutions impact on *Tetrahymena pyriformis*. It showed the negative effect of these solutions on test organisms, so the main observations with the use of bioindicative method were performed only in water extracts. The results of spectrophotometric measurements are presented in Table 2.

Table 2

The proliferation rate of test organisms in extracts obtained from spectrophotometric measurements

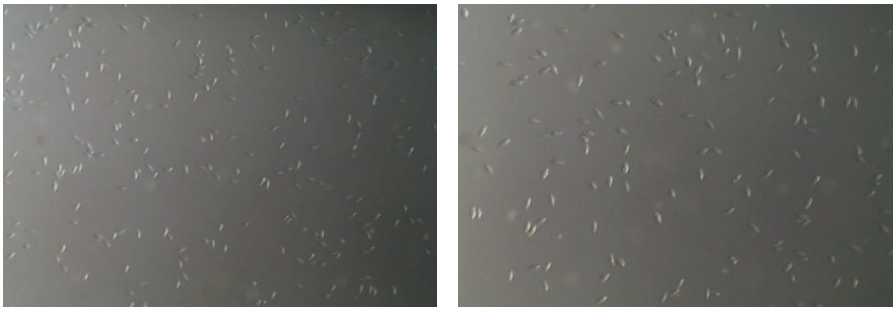
Water extracts of the samples	Proliferation rate of *Tetrahymena pyriformis*, % of control			
	Obtained from the measurement of optical density		Obtained from the measurement of colour change	
	after 6h of incubation	after 24h of incubation	after 6h of incubation	after 24h of incubation
A	100	100	100	100
B	100	100	100	100

C	0	0	0	0
D	0	0	0	0

Source: *own research.*

The bioindicative method showed the negative impact of SAMPLES C and D water extracts on test organisms. The proliferation rate of *Tetrahymena pyriformis* culture growth in these two extracts, computed for spectrofotometric measurements, reached 0% of the control group (test organisms incubated in spring water), while in the extracts of SAMPLE A and B there was not observed any inhibition in test organism growth, what is more, the proliferation rate and behaviour of *Tetrahymena sp.* in these extracts was comparable to those in spring water (Figure 2a & 2b).

a/ b/



c/

Source: *own research.*

Fig. 2. The microscopic observations of the test organism proliferation after 24h incubation in water extracts of the samples in comparison to *Tetrahymena pyriformis* proliferation in spring water: a/ test organisms in spring water, b/ test organisms in extract of SAMPLE A, c/ test organisms in extract of SAMPLE C (as well as D)

The negative effect of the extract of SAMPLE C on test organisms confirmed the harmfulness of this material, evaluated on the base of analytical measurements performed on the mineralized sample. As mentioned before, the FAAS method showed the high content of cadmium in this sample. On the other hand, it is worth underlining that in SAMPLE C there were not detected any amounts of heavy metals, even cadmium, as a result of their migration into the water. So, the question arises, why was there such strong impact of this extract on test organisms (the lack of living cells in the extract), visible in Figure 2c? To answer this question other analytical methods siutable for analysing other hazardous substances that were beyond this research subject (e.g. azo dyes, amines) should be applied.

The lack of *Tetrahymena pyriformis* culture in the extract of SAMPLE D (Figure 2c) may testify to its high toxicity to living organisms resulting from the chromium content (probably the presence of Cr(VI)) in leather as well as the high susceptibility of this element to the migrafion into aqueous environment from material that was proved by analytical measurements.

Conclusions

The research has shown that the so-called heavy metals, e.g. copper, lead, chromium or cadmium might not pose high risk to consumers. Despite the substantial amount of heavy metals in mineralised samples, their content in extracts may be significantly low and their toxicity effect on test organisms may be unnoticeable.

The study has revealed the usefulness of the bioindicative measuring method for safety assessment of nonfood products. This method may indicate the presence of harmful elements within materials that are susceptible to migration into aqueous environment and may inform us if the product poses or not a real risk to living organisms.

The safety assessment of textile and leather materials as components of nonfood products, depends on the method of their analysis and requirements taken under consideration. It was stated that materials which do not meet legal reqiurements may comply with ecological or standard requirements, and may have no toxic effect on living organisms.

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