

EXTRACTABLE HEAVY METALS IN DYED TEXTILES: VERIFICATION OF THE TEST METHOD.

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ABSTRACT

The growing interest on the characteristic of the toxicological and ecotoxicological qualities of the textile products makes indispensable the availability of laboratory methodologies that are sufficiently sensitive, specific and reproducible for testing toxic substances in textile materials.

Heavy metals in textiles are actually regulated by mandatory environmental standards and textile eco-labels. In particular some ecolabelling voluntary schemes impose heavy metals requirements based on the extraction of the metals by means of a saline solution simulating the human acid perspiration.

This method suffer from an inadequate reproducibility of the analytical data and our attention was focused on the identification of the analytical steps affecting the quantitative assessment.

The method was applied to a textile material dyed with a chromium dyestuff. The metals analyzed were total Cr and Cr^{VI} extracted by means of the artificial perspiration solution, according to the standard adopted by the most important textile ecolabelling schemes operating in the European market. The metal was quantified in the solution by means of atomic absorption spectroscopy for total Cr and UV-Visible spectroscopy for Cr^{VI}.

The extraction method was investigated in depth and the critical passage was identified with the extraction phase of the metal from the fibres into the saline solution. The tests were carried out varying some extraction parameters and the results show that the quantity of chromium extracted is affected principally by the temperature of the solution and by the material-to-liquor ratio extraction and less by the time of contact.

Therefore the method needs a better understanding of the chemical and physical mechanism that controls the release of the metals of interest from the textile matter to the solution, in order to produce analytical data that could have definite and acceptable reproducibility levels.

INTRODUCTION

Beginning from the 1990s, the interest on the characteristic of the toxicological and ecotoxicological qualities of the textile products is grown. Some causes for concern began to emerge on the possible negative effects of textile products on the environmental and on the health of sector workers and consumers [1].

In particular an increase in the number of cases of skin allergies and other dermatological pathologies was reported. Such increases can be partially attributed to the chemical substances used in textile production and released during usage, and then during disposal of the finished products at the end of their life cycles [2].

As a result, action has been taken at the institutional and private levels [3-4]. International authorities and organizations are developing strategies and regulations to protect the consumers and the workers exposed during the production process.

In this respect, in the past 10 years, the EU issued a considerable amount of regulations, that have been implemented in Italy as in most Member Countries. Some examples are: the Directive 1999/45/EC [5] on general product safety; the Directive 94/27/EC, that sets limits on the permitted levels of nickel in textile products destined for skin contact; the Directive 91/338/EC, that established the permitted levels of cadmium used to give stability to PVC materials; and the Directive 02/19/EC on prohibition for use of azo-dyes that can form aromatic cancerogenic amines in final product.

In the same vein, in 2000, the EU has produced a provision that sets the criteria for awarding environmental labels to different categories of commercial products [6]. The most common labels in the textile industry are the Ecolabel and the Oeko-Tex Standard 100. Ecolabel is a voluntary label and sets specific quality criteria to textile product [7]. The quality criteria are both ecological in nature and based on the performance of the product. In addition to environmental parameters, the Ecolabel establishes limits on the permitted levels of pesticides, heavy metals and other toxic substances.

The Oeko – Tex label [8] was conceived to protect safety of the consumers, is applied to textile sector and to finished products with a subdivision into “products for a generic use” and “products with skin contact”. In that last case, there is a further subdivision into “products for children” and “products for grown-up people”. The Oeko – Tex Standard 100 prohibits or limits the use of some chemical substances that are dangerous for the human safety.

The application of these provisions, however, has also highlighted some technical problems regarding the availability of laboratory methodologies that are sufficiently sensitive, specific and reproducible for testing chemicals safety on textile materials. There is an insufficient intra-laboratory and inter-laboratory reproducibility of the analytical techniques and there are not unequivocal and condensible methods. In many cases, moreover, official methods are not available and therefore the individual laboratories apply in-house or non-standard methods.

On the other hand, there are standard methods that are remarkably complex to apply and that are able to produce exact and reproducible analytical results only if applied by qualified specialized laboratories that operate according to quality standards.

According to that stated earlier, it was deemed relevant to initiate a research project to examine the problems regarding intra and interlaboratory reproducibility of the methods for the determination of toxic substances in textiles. In particular, the investigation regarded the analytical determination of extractable heavy metals from textile products in an acid perspiration solution.

Heavy metals were chosen because their presence in textiles is not regulated by binding national or European standards, but these parameters are included in and regulated by almost all voluntary environmental labels. Furthermore, toxic effects of heavy metals on

human safety were demonstrated. Heavy metals cause negative effects on metabolism, damages to organs, heart disease, disorder to nervous system and allergies. Moreover, the direct inhibition of enzymatic system, the indirect alteration of the essential metal-ions equilibrium and the consequent inhibition of their biological availability prevent from correct functioning of the cells, with tumours [9] and mutations [10] development. Heavy metals in textile materials principally come from some colouring agents, activators and stabilizers used to produce some synthetic fibers; then they also are used to produce metal accessories for finished textile products.

Heavy metals presence in textile products can be certified by two different criteria:

- the valuation of the product tendency to release heavy metals during the use, above all by skin contact;
- the determination of the particularly toxic heavy metals presence in the fibers.

About that, the UE and some Nations issued laws on nikel and cadmium content in handmade textiles. The Ecolabel sets limits on antimony presence into the polyester fibers, on heavy metals content into dyestuff and pigments, on chromium and other metals concentration into the waste waters. Finally, the Oeko – Tex Standard 100 imposes heavy metals requirements based on the extraction of the metals by means of a saline solution simulating the human acid perspiration.

A specific regulation doesn't exist, so the saline solution concentration and the parameters applied refer to ISO 105 E/04 on colour fastness tests.

The first step of the work was based on the collaboration of five different laboratories belonging to organizations that operate, in varying degrees, in the textile industry and thus are technically competent to carry out all the relevant operations correctly.

The project, that was funded by the Italian National Institute for Occupational Safety and Prevention (ISPESL) and carried out for 17 months, concerned chromium, cobalt, copper and nikel determination in handmade textiles of different fibers composition and colour. The results are interesting [11] and reveal discrepancies between analytical data produced from the same sample, with a shared method, by the participating laboratories and also within the laboratories themselves. The data are reproducible only in a small percentage of cases, and the analysis of the analytical procedure used in the laboratories seems to indicate the most probable source for the lack of reproducibility to be in the phase of the metal removal from the fibrous matrix into the extraction solution.

Thereby it was considered necessary to investigate in depth the extraction method at single laboratory level and to study the parameters that could affect the heavy metals release into saline solution. Particularly, the attention was focused on the determination of total chromium and its hexavalent form, because the previous work showed that, between all the metal analysed, the chromium extraction results were the less reproducible. Moreover, the metal extraction profit was derived by the determination of total chromium in the ashes, to verify the efficiency of the debugged method.

The objective of this research was to identify the critical passage of the analytical procedure, with the intent of developing a standardized and shared method that would help promote textile products, both in terms of safety for the environment and health of citizens, and of safety for workers exposed during the production process and for end users.

EXPERIMENTAL

Sample

The sample analysed is a pure wool top, dyed with black chromium dyestuff. Dyeing was carried out in the laboratory, using a suitable dyeing apparatus, under controlled process conditions to guarantee a substantial homogeneity in the absorption and distribution of the dye on the fibers.

Total and exavalent chromium were extracted by means of a saline solution simulating the human acid perspiration. The determination of the metal content in the solution was carried out using graphite furnace atomic absorption spectroscopy (GFAA) for total Cr and ultraviolet-visible spectroscopy (UV-Vis) for Cr^{VI} (Fig. 1-2).



Figure 1: Atomic absorption spectrometer (GFAA)



Figure 2: UV-Visible spectrometer

Extraction procedure

The analytical method is based on the textile matter extraction by means of an acid saline solution (pH 5.5) simulating human perspiration. The preparation of the solution was based on UNI EN ISO 105-E04 standard – Colour fastness to acid perspiration – adopted also by Oeko –Tex private eco-label.

The acid saline solution was prepared in distilled water dissolving chlorohydrate L-istidine monohydrate (0,5 g/l), sodium chloride (5 g/l), sodium dihydrogen phosphate dihydrate (2,2 g/l). The pH was adjusted to 5,5 with sodium hydroxide (0,1 mol/l). The solution is not stable and must be prepared fresh daily or at the time the analysis is carried out.

A carefully weighed sample of textile material (1.00 ± 0.01 g), previously dried in an oven at 105 ± 2 °C for a minimum of 4 hours, was introduced into the acid solution and shaken at constant temperature.

The resulting solution was filtered under vacuum with a 0,45 µm membrane. The total chromium content in the eluate solution was determined by GFAAS spectrometry and the chromium exavalent was determined by UV-Vis analysis as a colored complex with 1,5-diphenylcarbazide [12], using appropriate reference solutions containing known concentrations of Cr^{tot} and Cr^{VI}.

The tests were carried out varying some parameter of the extraction process (Table 1), to verify which of them could affect the metal extraction from the textile material. The efficiency and the reproducibility of the method was checked.

Table 1: *Process parameters applied to the different tests*

TEST	TEMPERATURE (°C)	TIME (h)	LIQUOR RATIO
1	30	1-2	1 g : 50 ml
2	30	1-2	1 g : 100 ml
3	40	1-2	1 g : 50 ml
4	40	1-2	1 g : 100 ml
5	50	1-2	1 g : 50 ml
6	50	1-2	1 g : 100 ml

Determination of total chromium by means of ashing procedure

The total efficiency of the saline solution extraction method was verified comparing the metal content extracted into the solution with the metal content extracted from the textile material by ashing.

The ashing method was based on UNI 8047 [13]. The ashes were dissolved in nitric acid and distilled water and filtered on filter paper to obtain a clear solution. The total chromium content in the solution was determined by GFAA spectrometry.

The metal content (Me) was calculated as follows:

$$Me_x = \frac{Me \times V}{P}$$

where

Me_x (mg/kg) = concentration of the total or exavalent chromium in the textile sample;

Me (µg/L) = concentration of the total or exavalent chromium in the analysed solution, as obtained from the GFAA or UV-Visible analysis;

V (mL) = volume of artificial acid perspiration solution used to extract the metal;

P (g) = dry weight of sample.

RESULTS AND DISCUSSION

Determination of total chromium

The operational development of the research consisted in the determination of the quantity of the metal extracted from the wool top. Each extraction was performed in double.

The analytical results were expressed as mean of two lectures with their coefficient of variation (CV%) and they are reported in Table 2.

Table 2: Mean value of total chromium concentration

TEST	T (°C)	Liquor ratio	Concentration (mg/kg)			
			1 h	CV%	2 h	CV%
1	30°C	1:50	102.08	5.8	108.62	2.3
2	30°C	1:100	103.04	6.7	120.00	0.2
3	40°C	1:50	119.20	0.2	130.18	1.2
4	40°C	1:100	132.96	0.8	132.78	3.2
5	50°C	1:50	121.18	3.2	97.80	0.2
6	50°C	1:100	134.32	4.6	133.16	8.9

The influence of the temperature and liquor ratio is significant. After one hour of contact, for a liquor ratio of 1:50, raising the temperature of the extraction from 30 to 40°C, the extractable metal content increases of about 17% and then further increases of about 2% raising the temperature from 40 to 50°C. For the liquor ratio 1:100, the value increases of about 29% passing from 30 to 40°C and that further increases of about 1% raising the temperature from 40 to 50°C.

The dyestuff is mainly concentrated on the fiber cortical surface but also penetrate into the fiber in the direction of the inner cortical structure. The kinetic of metal extraction from a textile dyed materials by means of a saline solution can be influenced by the solution temperature and concentration, all the other conditions (mechanical agitation, shape and weight of the sample) being equal. In this case also the ratio between the textile material and the volume of saline solution seems to play an important role because the efficiency of the metal extraction is a function of the volume of solution available to wet uniformly all the fibers. Probably a inadequate quantity of solution cannot effectively wet the textile, so that the solution is not able to exert its extractive function in reproducible and complete way.

The influence of the contact time seems to be significant but the overall results are not completely clear. It could be expected that the increase of the contact time will lead to a better extraction efficiency. This is true for liquor ratio 1:50, with a metal concentration increase of 6% at 30°C and of 9% at 40°C. At the same temperatures the liquor ratio 1:100 is more efficient at 30°C, with a metal concentration increase of about 16%, but there is no increase at 40°C. At 50°C the quantity of metal extracted after two hours decrease for both the liquor ratios. Doubling the time of contact between the sample and the solution, the sample wettability with liquor ratio 1:50 is improved and this lead to a better extraction efficiency. Increasing the contact time at higher temperature seems to affect negatively the extraction efficiency (Fig. 3-4).

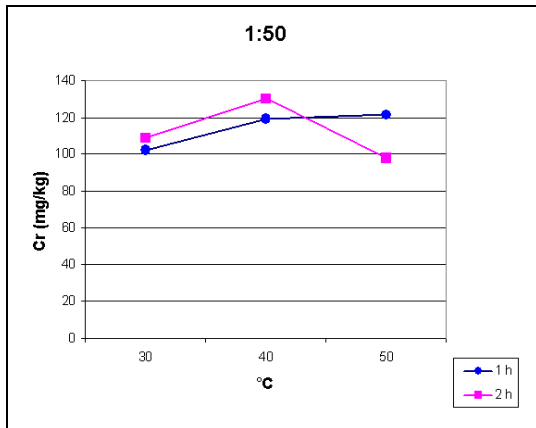


Figure 3: Total chromium extracted with material-to-liquor ratio extraction 1:50, to different condition of time and temperature.

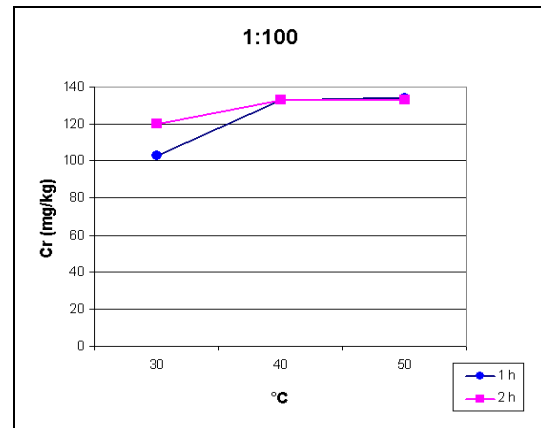


Figure 4: Total chromium extracted with material-to-liquor ratio extraction 1:100, to different condition of time and temperature.

Determination of exavalent chromium

It has been reported that the exavalent chromium is toxic, cancerogenic and dangerous for the human safety [14]. Therefore it was considered necessary to determine the value of the extracted Cr^{VI} from the sample. Each determination was performed in double.

The analytical results were expressed as mean of two lectures with their coefficient of variation (CV%) and they are reported in Table 3.

Table 3: Mean value of Cr^{VI} concentration

TEST	T (°C)	Liquor ratio	Concentration (mg/kg)			
			1 h	CV%	2 h	CV%
1	30°C	1:50	93.28	0.5	94.24	0.2
2	30°C	1:100	96.34	0.1	110.04	11.9
3	40°C	1:50	100.78	10.2	102.44	3.6
4	40°C	1:100	113.25	0.8	114.68	1.2
5	50°C	1:50	102.00	4.3	77.84	0.1
6	50°C	1:100	124.44	2.1	115.12	6.2

The influence of the temperature and liquor ratio is significant. After one hour of contact, for a liquor ratio of 1:50 raising the temperature of the extraction from 30 to 40°C the extractable metal content increases of about 8% and then further increases of about 1% raising the temperature from 40 to 50°C. For the liquor ratio 1:100, the value increase of about 17% passing from 30 to 40 °C and then further increases of about 10% raising the temperature from 40 to 50 °C.

Doubling the contact time, the extraction efficiency increase is not significant and the anomaly of experiment n5 and 6 is confirmed (Fig. 5-6).

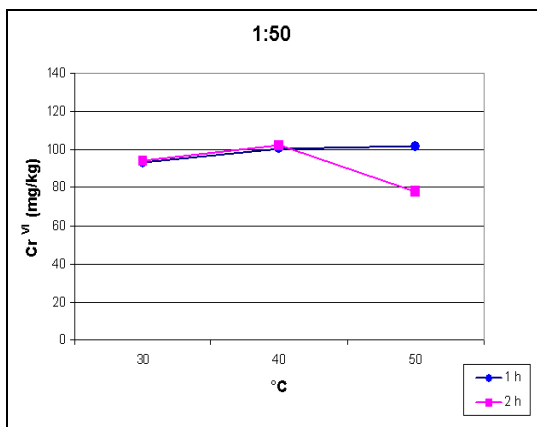


Figure 5: Cr^{VI} extracted with material-to-liquor ratio extraction 1:50, to different condition of time and temperature.

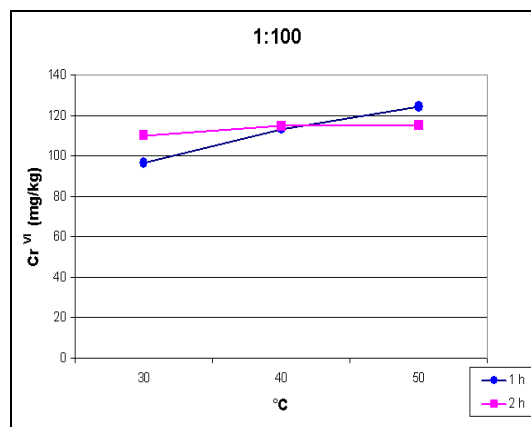


Figure 6: Cr^{VI} extracted with material-to-liquor ratio extraction 1:100, to different condition of time and temperature.

Determination of total chromium in the ashes

The total efficiency of the saline solution extraction method was verified comparing the metal content extracted into the solution with the metal content extracted from the textile material by ashing. The total chromium content in the textile materials was of 305.23 mg/kg. The results are reported in Table 4.

Table 4: Percentage of metal extraction profit

TEST	T (°C)	Liquor ratio	Profit (%)	
			1 h	2 h
1	30°C	1:50	33.4	35.6
2	30°C	1:100	33.8	39.3
3	40°C	1:50	39.0	42.6
4	40°C	1:100	43.6	43.5
5	50°C	1:50	39.7	32.0
6	50°C	1:100	44.0	43.6

The percentage of metal extraction profit vary according to the extraction conditions, from 32% to 44%.

CONCLUSIONS

The experimental results confirm that the determination of heavy metals from textile products with an acid perspiration solution can vary according to different analytical conditions and is affected by a low reproducibility.

The variation and dispersion of the results is mainly due to the extraction procedure, i.e. to the solubility of the heavy metal into the saline solution, which constitute the critical stage of the analytical method tested.

An increase of liquor ratio and temperature makes the extraction more efficient, but the doubling of the extraction time affect the metal concentration only in a little and non reproducible way.

The heavy metals extraction from textile materials by means of a saline solution in order to assess the bio-accessibility of the metal from a dyed material to the human skin is not actually regulated by national or EU standards but is included and regulated by almost all voluntary eco-labels.

On the other hand there is a lack of a regulated analytical method specifically aimed to quantify the heavy metals with the analytical procedure above tested.

This work has highlighted the need to improve the study of the chemical-physical mechanism that controls the release of the metals from the textile materials to the saline extraction solution, in order to develop a definite analytical standard.

The result would be an official analytical method that would really help promote textile products, both in terms of safety for the environment and health of consumers.

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