

## DETERMINATION OF HEAVY METALS IN TEXTILE MATERIALS BY ATOMIC ABSORPTION SPECTROMETRY: VERIFICATION OF THE TEST METHOD

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### Abstract:

*The objective of this research was to identify the analytical steps affecting the quantitative assessment for the determination of heavy metals in textile materials and to test the selected extraction conditions, 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. The method was applied to a textile materials dyed with a chromium dyestuff at two different concentrations. The metals analyzed were total Cr and Cr VI. The extraction was carried out 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 extract was filtered under vacuum and analyzed by means of atomic absorption spectrometry for total Cr and UV-Visible spectroscopy for Cr VI. The tests were carried out varying some extraction parameters as temperature of the solution, time of contact and material-to-liquor ratio extraction. Finally the metal extraction profit was derived by the determination of total chromium in the ashes. The results show that the quantity of total chromium and CrVI 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. The percentage of metal extraction profit vary according to the extraction conditions, from 32% to 44%.*

### Key words:

*Heavy metals, textiles, atomic absorption spectrometry*

### Introduction

The past decade has been marked by a growing interest on the characteristic of the toxicological and ecotoxicological qualities of the textile products. Considering the interaction of the textiles with the human skin, the chemical substances content in textile manufactures can cause allergenic and toxic effects and they may represent a health hazard to consumers [1].

Among them there are carcinogenic amines, toxic heavy metals, pentachlorophenol and free formaldehyde [2], contained in dyes and finishers. Heavy metals often are used in different textile processes, as dyeing and printing [3], and they are present above all in metal complex dyes. In particular the fast black dyeing on wool and nylon is carried out using chromium based dye. In fact one of the most widely used dyes in the world is the chromium dye C.I. Mordant Black 11, but in the future it will probably be replaced by newly developed dyes containing less toxic metals like iron [4-5]. The determination of metal content of different textile materials is very important not only for the safety of the workers exposed during the production process, but also for the consumers.

Toxic effects of heavy metals on human safety are very well known: negative effects on metabolism, damages to organs, heart disease, disorder to nervous system and allergies. Moreover, the accumulation of heavy metals in body tissues and binding to enzymes may disrupt the correct functioning of the cells, with tumours [6] and mutations [7] development.

However the use of metals and metal complex dyes isn't prohibited in textile industry, because their abandoning would result in a loss of some important shades like turquoise, brilliant green, violet, blue or navy shades [5]. Actually the heavy metals 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. 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 [8]. 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 [9] 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. In particular, according to the requirements of Oeko - Tex the products are controlled for pH, formaldehyde, dyes that can release aromatic amines or can cause allergies to the skin, extractable heavy metals, pentachlorophenol and pesticides [10]. 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 shared methods. In many cases, moreover, official methods are not available and therefore the individual laboratories apply in-house or non-standard methods [11].

Because heavy metals may represent a health hazard to consumers and there are some problems regarding intra and inter-laboratory reproducibility of the methods for their determination in textiles, the aim of this study was to investigate the method for the analytical determination of extractable heavy metals from textile products in an acid perspiration solution.

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 nickel determination in handmade textiles of different fibers composition and colour. The results are interesting [12] 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 analysis of the analytical procedure used in the laboratories seems to indicate the phase of the metal removal from the fibrous matrix into the extraction solution as the critical passage of the method.

The second step of the work was 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. 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 tests were carried out on a pure wool top, dyed with black chromium dyestuff at two different concentrations. 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.

### Reagents

All the chemicals (chlorohydrate L-istidine monohydrate, sodium chloride, sodium dihydrogen phosphate dihydrate, sodium hydroxide, 1,5-diphenylcarbazine, nitric acid) used for this research work were p.a. grade, supplied by Sigma Aldrich, Fluka e Carlo Erba. The chromium standard solution used for calibration was prepared by diluting a stock solution of 1000

mg/l supplied by Perkin Elmer. Distilled water was used for all dilutions.

### Instrumentation

A perkin Elmer Analyst 4100 ZL atomic absorption spectrometer was used in this study. Total Cr in the extraction solution was determined by THGA graphite furnace using argon as inert gas. In Table 1 are reported the instrumental parameters and operating conditions. The determination of the hexavalent chromium content in the solution was carried out using ultra-violet-visible spectroscopy (UV-Vis).

Table 1. Instrumental parameters and operating conditions.

PARAMETER	Cr
Wavelength (nm)	357.9
Slit width (nm)	0.7
Lamp current (mA)	30
Gas flow (ml/min)	250
Sample volume (µl)	20
HEATING PROGRAM TEMPERATURE °C (ramp time (s), hold time (s))	
Drying 1	110 (1, 20)
Drying 2	130 (5, 30)
Ashing	1500 (10, 20)
Atomization	2300 (0, 5)
Cleaning	2400 (1, 2)

### Extraction procedure

The textile sample was dried in an oven at  $105 \pm 2$  °C for a minimum of 4 hours. Afterwards  $1.00 \pm 0.01$  g of the sample was introduced into the acid solution and shook at constant temperature.

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, dissolving chlorohydrate L-istidine monohydrate (0,5 g/l), sodium chloride (5 g/l), sodium dihydrogen phosphate dihydrate (2,2 g/l) in distilled water. The pH was adjusted to 5,5 with sodium hydroxide (0,1 mol/l).

The eluted solution was filtered under vacuum with a 0,45 µm membrane; the total chromium content was determined by GFAAS spectrometry and the chromium hexavalent was determined by Uv-Vis analysis as a colored complex with 1,5-diphenylcarbazine [13], using appropriate reference solutions containing known concentrations of Cr tot and CrVI .

Table 2. 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

The tests were carried out varying some extraction parameters as temperature of the solution, time of contact and material-to-liquor ratio extraction (Table 2).

**Analysis 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 [14]. 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:

$$Me_x (mg / kg) = \frac{Me (\mu g / L) \times V (mL)}{P (g)}$$

where:  $Me_x$  is the concentration of the total or hexavalent chromium in the textile sample; Me is the concentration of the total or hexavalent chromium in the analysed solution, as obtained from the GFAA or UV-Visible analysis; V is the volume of artificial acid perspiration solution used to extract the metal; P is the dry weight of sample.

**Result and discussion**

**Determination of total chromium**

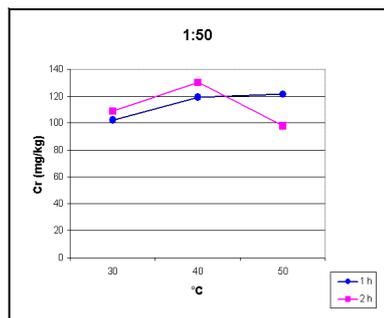
The operational development of the research consisted in the determination of the quantity of the metal extracted from the wool top. Each extraction was performed in double.

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

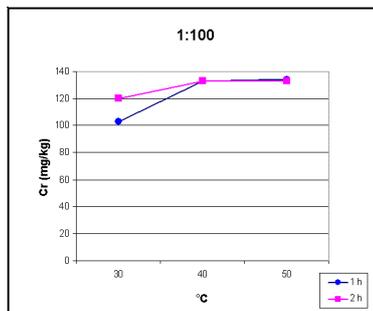
About the extraction of chromium from textile material dyed with dyestuff at high chromium concentration, the influence of the temperature and liquor ratio is significant. After one hour of contact, for a liquor ratio of 1:50, raising the temperature of the extraction from 30 to 40°C, the extractable metal content increases of about 17% and than further increases of about 2% raising the temperature to 50°C. For the liquor ratio 1:100, the value increases of about 29% passing from 30 to 40°C and

**Table 3.** Mean value of total chromium concentration.

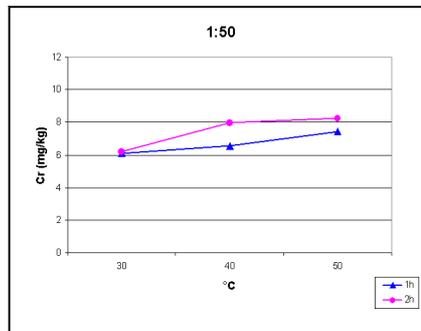
TEST	T (°C)	Liquor ratio	Concentration (mg/kg)							
			High concentrated dyestuff				Low concentrated dyestuff			
			1 h	CV%	2 h	CV%	1 h	CV%	2 h	CV%
1	30°C	1: 50	102.08	5.8	108.62	2.3	6.09	1.6	6.19	1.6
2	30°C	1:100	103.04	6.7	120.00	0.2	6.56	3.0	8.36	2.4
3	40°C	1: 50	119.20	0.2	130.18	1.2	6.54	1.5	7.99	5.0
4	40°C	1:100	132.96	0.8	132.78	3.2	9.04	1.1	9.95	3.0
5	50°C	1: 50	121.18	3.2	97.80	0.2	7.44	5.4	8.25	2.4
6	50°C	1:100	134.32	4.6	133.16	8.9	10.78	7.4	10.92	4.6



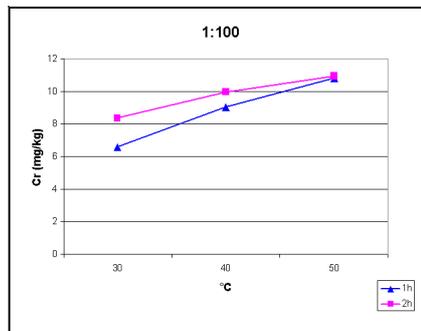
**Figure 1.** Total chromium extracted with material-to-liquor ratio extraction 1:50, to different condition of time and temperature, for high concentrated chromium dyestuff.



**Figure 2.** Total chromium extracted with material-to-liquor ratio extraction 1:100, to different condition of time and temperature for high concentrated chromium dyestuff.



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



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

that further increases of about 1% raising the temperature to 50°C. 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 (Figure 1-2).

About the determination of chromium in textile material dyed with dyestuff at low chromium concentration, the temperature and liquor ratio affect the extraction in a significant way. 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 7% and than further increases of about 14% raising the temperature to 50 °C. For the liquor ratio 1:100, the value increases of about 38% passing from 30 to 40 °C and that further increases of about 19% raising the temperature to 50 °C.

In this case also the efficiency of the metal extraction is a function of the liquor-ratio. So it is possible to affirm that only adequate quantity of solution, available to wet uniformly all the fibers, can exert the extractive function in a reproducible and complete way.

The influence of the contact time is significant too. In fact the increase of the contact time leads to a better extraction efficiency. For liquor ratio 1:50 the metal concentration increase of 2% at 30 °C, of 22% at 40 °C and of 11% at 50 °C. At the same temperatures and with a liquor ratio 1:100 the metal concentration increases of about 27% at 30 °C, of 10% at 40 °C and of 1% at 50 °C (Figure 3-4).

**Analysis of hexavalent chromium**

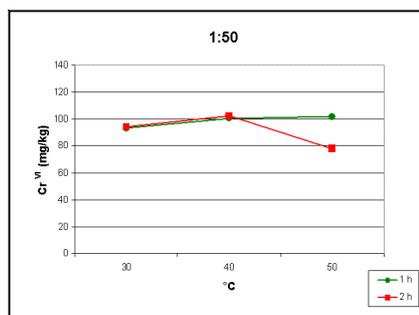
It has been reported that the hexavalent chromium is toxic, cancerogenic and dangerous for the human safety [15]. Therefore it was considered necessary to determine the value of the extracted CrVI from the sample. Each determination was performed in double.

The analytical results were expressed as mean of two lectures with their coefficient of variation (CV%) and they are reported in Table 4. For both of the chromium concentrations in dyestuff (high and low), the temperature and liquor ratio affect the metal extraction in a significant way.

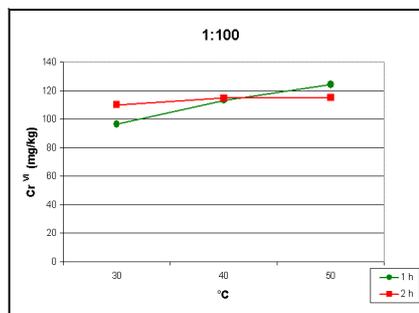
In the first case, after one hour of contact, for a liquor ratio of 1:50 raising the temperature of the extraction from 30 to 40 °C the extractable metal content increases of about 8% and than further increases of about 1% raising the temperature to 50 °C. For the liquor ratio 1:100, the value increases of about 17% passing from 30 to 40 °C and than further increases of about 10% raising the temperature to 50 °C.

**Table 4.** Mean value of hexavalent chromium concentration.

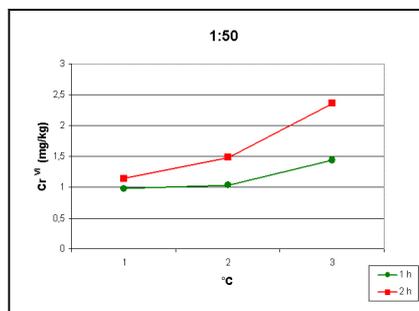
TEST	T (°C)	Liquor ratio	Concentration (mg/kg)							
			Hight concentrated dyestuff				Low concentrated dyestuff			
			1 h	CV%	2 h	CV%	1 h	CV%	2 h	CV%
1	30 °C	1: 50	93.28	0.5	94.24	0.2	0.98	4.1	1.14	8.8
2	30 °C	1:100	96.34	0.1	110.04	11.9	1.39	7.2	1.87	5.3
3	40 °C	1: 50	100.78	10.2	102.44	3.6	1.03	9.7	1.48	6.8
4	40 °C	1:100	113.25	0.8	114.68	1.2	1.59	1.3	2.00	5.0
5	50 °C	1: 50	102.00	4.3	77.84	0.1	1.44	6.9	2.36	8.5
6	50 °C	1:100	124.44	2.1	115.12	6.2	2.38	1.7	2.63	7.6



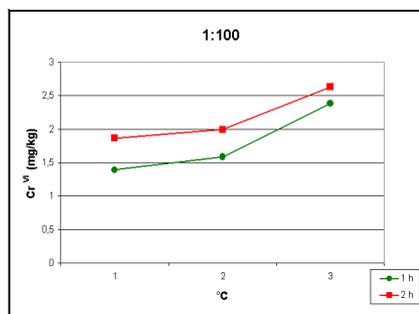
**Figure 5.** Cr<sup>VI</sup> extracted with material-to-liquor ratio extraction 1:50, to different condition of time and temperature, for high concentrated chromium dyestuff.



**Figure 6.** Cr<sup>VI</sup> extracted with material-to-liquor ratio extraction 1:100, to different condition of time and temperature, for high concentrated chromium dyestuff.



**Figure 7.** Cr<sup>VI</sup> extracted with material-to-liquor ratio extraction 1:50, to different condition of time and temperature, for low concentrated chromium dyestuff.



**Figure 8.** Cr<sup>VI</sup> extracted with material-to-liquor ratio extraction 1:100, to different condition of time and temperature, for low concentrated chromium dyestuff.

In the second case, 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 CrVI content increases of about 5% and than further increases of about 40% raising the temperature to 50 °C. For the liquor ratio 1:100, the value increases of about 14% passing from 30 to 40 °C and than further increases of about 49% raising the temperature to 50 °C.

About the influence of the contact time on the extraction efficiency, there are discrepancy between high and low chromium concentrated dyes.

For high chromium content, doubling the contact time the extraction efficiency increase is not sig-

nificant and the anomaly of experiment n°5 and 6 is confirmed (Figure 5-6).

For low chromium content, the extraction efficiency seems to be affected positively increasing the contact time. For liquor ratio 1:50, passing from one hour to two hours of contact, the metal concentration increases of 16% at 30°C, of 44% at 40°C and of 64% at 50°C. At the same temperatures for the liquor ratio 1:100 the metal concentration increases of about 34% at 30°C, of 26% at 40°C and of 10% at 50°C (Figure 7-8).

### Analysis 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 for high chromium concentrated dye, and of 21.66 mg/kg for low chromium concentrated dye. The results are reported in Table 5.

Table 5. Percentage of metal extraction profit.

TEST	T (°C)	Liquor ratio	Profit %			
			Hight concentrated dyestuff		Low concentrated dyestuff	
			1 h	2 h	1 h	2 h
1	30°C	1: 50	33.4	35.6	28.1	28.6
2	30°C	1:100	33.8	39.3	30.3	38.6
3	40°C	1: 50	39.0	42.6	30.2	36.9
4	40°C	1:100	43.6	43.5	41.7	45.9
5	50°C	1: 50	39.7	32.0	34.3	38.1
6	50°C	1:100	44.0	43.6	49.8	50.1

The percentage of metal extraction profit vary according to the extraction conditions, from 32% to 44% for high metal content in dye, and from 28% to 50% for low metal content in dye.

### Conclusion

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 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. This was verified for textiles dyed with dyestuff both high and low chromium concentrated.

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.

In both high and low chromium case, the conditions that lead to a better extraction efficiency seem to be a temperature of 50°C and a liquor-ratio of 1:100. Moreover, in the high chromium case it is recommended to maintain the contact with the saline solution for 1 hour, in the low chromium case for 2 hours. This is right for the determination of total chromium and for the analysis of the hexavalent form too.

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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