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DETERMINATION OF TRACE HEAVY METALS IN SOME TEXTILE PRODUCTS PRODUCED IN TURKEY

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ABSTRACT. The concentrations of trace heavy metals in textile samples collected from Tokat, Turkey, were determined by flame and/or graphite furnace atomic absorption spectrometry after microwave digestion. The relative standard deviations for the determinations were found to be lower than 10 %. The concentrations of trace metals in analyzed textile samples were found to be in the range of 0.76-341 μg g^{-1} for Cu, 0.10-0.25 μg g^{-1} for Cd, 0.63-4.84 μg g^{-1} for Zn, 1.02-2.50 μg g^{-1} for Mn, 3.55-34.3 μg g^{-1} for Fe, and 1.20-4.69 μg g^{-1} for Ni, respectively. Copper and cadmium contents in textile products analyzed were found to be higher than limit values given by Oeko-Tex. The results of the present work for textile products are compared with literature values.

KEY WORDS: Trace metals, Textile samples, Atomic absorption spectrometry, Microwave digestion, Turkey

INTRODUCTION

Because of positive and negative effects and the toxicity of trace heavy metals on human health and the environment, many researchers have studied the analysis of the trace metal contents of the environmental and industrial samples including textile products [1-5]. Textile is one of the main industries in developing countries. Quality of textile productions is very important for export. People want to be able to buy clothing, bedding and household textiles that have been tested and are not dyed in any way with harmful substances [6-8]. Textile products contain some organic and inorganic substance including trace metal ions. Especially, reactive and pigment dyes contain trace heavy metals at high level. Trace metals may be health risks for human even at low concentrations in textile products [7]. Traces of heavy metals are often present in different textile process such as metal complex dyes, dye stripping agents, oxidizing compounds, antifungal, odor-preventive agents and mordant reactive [9]. Toxic and allergic metals including cadmium, copper, nickel, zinc, and chemicals like formaldehyde and chlorinated hydrocarbons can exist in natural structures of textiles or they can penetrate into the textiles during the production, dying process or via the protection agents used for the storage of these textiles [9, 10]. The most important standard in Europe is Oeko-Tex Standard 100 [11].

Trace metal contents of textile samples including cotton, polyester, etc., have been studied in the literature [7, 12, 13]. Studies on the trace heavy metal contents of Turkish textile products are limited. The determination of trace heavy metals in textile productions is very important not only for the safety of consumers but also for the textile industry.

The reliability of trace heavy metals determination in its complex matrices mainly depends on the dissolution process used. Both the wet and dry ashing procedures are slow and time consuming. In recent years, microwave digestion procedures in closed vessels have been developed as a rapid and reproducible sample preparation method for a great variety of complex matrices [5, 14, 15].

Instrumental techniques like inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometriy (ICP-MS) are used for the

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determination of metal ions in real samples at traces levels [16-23]. Atomic absorption spectrometry including flame or graphite furnace techniques is also the most widely used technique, because most of the concentrations of metals in the environmental and textile samples are determined using this technique [5, 7, 21-24].

In this study, the levels of trace metals in textile products collected from Tokat, Turkey, were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion.

EXPERIMENTAL

Sampling

The textile samples were collected from the various textile plants in Tokat, Turkey. The samples were dried at 105 ºC for 24 h. Dried samples were homogenized using an agate homogeniser and stored in pre-cleaned polyethylene bottles until analysis.

Reagents

All the reagents were of analytical reagent grade unless otherwise stated. Double deionised water (Milli-Q Millipore 18.2 $M\Omega cm^{-1}$) was used for all dilutions. HNO_3 and H_2O_2 were of suprapure quality (E. Merck). All the plastic and glassware were cleaned by soaking with the contact overnight in a 10 % (w/v) nitric acid solution and then rinsed with deionized water. The element standard solutions used for calibration were prepared by diluting a stock solution of 1000 mgL^{-1} of the given element supplied by Sigma and Aldrich, USA.

Apparatus

A Perkin Elmer AAnalyst 700 model AAS with deuterium background corrector was used in this study. Cadmium in samples was determined by HGA graphite furnace using argon as inert gas. Other measurements were carried out in an air/acetylene flame. The operating parameters for working elements were set as recommended by the manufacturer. A Milestone Ethos D closed vessel microwave digestion system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Teflon reaction vessels were used in all the digestion procedures.

Microwave digestion

Milestone Ethos D microwave closed system was used in this study. 1.0 g of sample was digested with 6 mL of HNO_3 (65 %) and 2 mL of H_2O_2 (30 %) in microwave digestion system and diluted to 10 mL with deionized water. A blank digest was carried out in the same way. Digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, ventilation: 8 min, respectively. Then the analytes concentrations were determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The detection limit is defined as the concentration corresponding to three times the standard deviation of ten blanks. The detection limit values of the elements as $\mu g\ mL^{-1}$ in flame AAS were found to be 0.005 for Cu, 0.009 for Zn, 0.008 for Fe, 0.007 for Mn, and 0.006 for Ni. Cadmium was below detection limit of flame AAS. Cd was determined using graphite furnace

AAS. The absolute sensitivity is defined by the mass of an element, which gives a peak absorbance of 0.0044; it was found 0.6 pg for Cd.

In order to validate the procedure presented, the recovery tests for the analyte ions were performed by a microwave digested textile sample (double fabric cotton-polyester, reactive dye (Foron), Brand B). The results are given in Table 1. It can be seen that the recovery of investigated trace metals by the microwave digestion method was generally quantitative. The relative standard deviations for the determinations were found to be lower than 10 %. According to the light of these results, the concentrations of analytes in the textile samples produced in Turkey have been analyzed by atomic absorption spectrometry after microwave digestion. The results, which were repeated four times, are given in Table 2 and Figure 1. All the investigated metal concentrations were determined on a dry weight basis. According to these data, copper has the highest concentration and followed by iron, nickel, manganese, zinc and cadmium.

Table 1. Recovery of trace metals from double fabric cotton-polyester, reactive dye (Foron), Brand B using present method, N = 4.

Element	Added (µg mL^{-1})	Found (µg mL^{-1})	Recovery (%)
Cu	-	2.44 ± 0.10	-
	1.00	3.35 ± 0.18	97
	2.00	4.23 ± 0.21	95
	4.00	6.25 ± 0.36	97
Cd	-	0.12 ± 0.01	-
	0.05	0.17 ± 0.01	100
	0.10	0.21 ± 0.02	95
	0.20	0.31 ± 0.02	97
Zn	-	4.84 ± 0.30	-
	0.50	5.40 ± 0.42	101
	1.00	5.75 ± 0.35	98
	2.00	6.93 ± 0.50	101
Mn	-	1.23 ± 0.10	-
	1.00	2.19 ± 0.14	98
	2.00	3.10 ± 0.23	96
	4.00	5.30 ± 0.26	101
Fe	-	5.38 ± 0.28	-
	1.00	6.12 ± 0.35	96
	2.00	7.20 ± 0.42	99
	4.00	9.08 ± 0.31	97
Ni	-	1.33 ± 0.10	-
	1.00	2.28 ± 0.18	98
	2.00	3.24 ± 0.26	97
	4.00	5.12 ± 0.37	96

People are exposed to different chemical substances coming from textile materials due to daily contact with textiles like clothes, bed linen and similar products. Many of the chemicals applied on textiles may represent a health hazard for consumers, so it is crucial that the quantity of those substances is as low as possible. The metal content of natural fibers is also important for textile industry, because many elements contribute to problems during processing of textiles [9].

Table 2. Trace metal concentrations (μg g^{-1}) in analyzed textile samples, N = 4.

Sample type	Cu	Cd	Zn	Mn	Fe	Ni
Double fabric cotton-polyester, reactive dye (Foron), Brand A	3.16±0.20	0.10±0.01	1.30±0.12	2.22±0.10	34.3±2.10	4.44±0.32
Double fabric cotton-polyester, reactive dye (Foron), Brand B	2.44±0.10	0.12±0.01	4.84±0.30	1.23±0.10	5.38±0.28	1.33±0.10
100 % cotton, reactive dye (Indanthrene), Brand A	1.28±0.10	0.14±0.01	0.69±0.04	1.61±0.12	4.08±0.23	3.58±0.20
100 % cotton, reactive dye (Indanthrene), Brand B	1.23±0.10	0.16±0.01	0.63±0.05	1.87±0.10	4.96±0.30	1.99±0.10
100 % cotton, pigment dye (Pigma color), Brand A	4.86±0.32	0.18±0.01	0.67±0.03	1.02±0.10	15.4±1.30	1.32±0.10
100 % cotton, pigment dye (Pigma color), Brand B	212±16	0.25±0.02	1.39±0.10	2.50±0.20	17.5±1.40	2.45±0.21
100 % cotton, reactive dye (Cibacron), Brand A	341±21	0.19±0.01	0.84±0.07	1.40±0.10	6.81±0.41	1.50±0.10
100 % cotton, reactive dye (Cibacron), Brand B	0.99±0.08	0.20±0.02	0.66±0.03	1.13±0.10	3.55±0.20	1.25±0.10
100 % cotton, reactive dye (Cibacron), Brand C	128±11	0.15±0.01	1.64±0.10	1.38±0.11	15.6±1.20	1.52±0.10
100 % cotton, reactive dye (Dirimaren), Brand A	78.7±6.1	0.12±0.01	0.77±0.05	1.65±0.12	3.80±0.32	4.69±0.30
100 % cotton, reactive dye (Levafix), Brand A	0.76±0.05	0.17±0.01	0.78±0.04	1.23±0.10	6.08±0.44	1.53±0.10
100 % cotton, reactive dye (Everzol), Brand A	81.6±7.6	0.16±0.01	1.45±0.10	1.10±0.10	9.32±0.55	1.20±0.10
Cotton-polyester, reactive dye (Diresul–S), Brand A	3.37±0.20	0.10±0.01	1.12±0.10	1.88±0.13	5.70±0.30	2.48±0.20

Cadmium, iron, copper, manganese, zinc and nickel were chosen as representative trace metals whose levels in the environment represent a reliable index of environmental pollution. Most of the problems arise from trace metal complex dyes which could be extracted from the fabrics by sweat solutions [7]. The concentrations of trace metals in analyzed textile samples were found to be in the range of 0.76-341 μg g^{-1} for Cu, 0.10-0.25 μg g^{-1} for Cd, 0.63-4.84 μg g^{-1} for Zn, 1.02-2.50 μg g^{-1} for Mn, 3.55-34.3 μg g^{-1} for Fe, and 1.20-4.69 μg g^{-1} for Ni, respectively. Copper and cadmium contents in samples were found to be higher than limit values given by Oeko-Tex. The highest copper values were found 100 % cotton, reactive dye (Everzol), Brand A; 100 % cotton, reactive dye (Dirimaren), Brand A; 100 % cotton, reactive dye (Cibacron), Brand C; 100 % cotton, reactive dye (Cibacron), Brand A; 100 % cotton, pigment dye (Pigma color), Brand B samples. The highest cadmium values were found 100 % cotton, pigment dye (Pigma color), Brand B and 100 % cotton, reactive dye (Cibacron), Brand B samples. Nickel values were found to be within the normal limits. There is no any information about iron, manganese and zinc limit values given by Oeko-Tex. The lower limit values have been reported for babies in Oeko-Tex. standards. Generally, trace metal concentrations in this study were found to be higher than literature values (Table 3). So, Turkish textile samples should be analyzed more often with respect to trace metal.

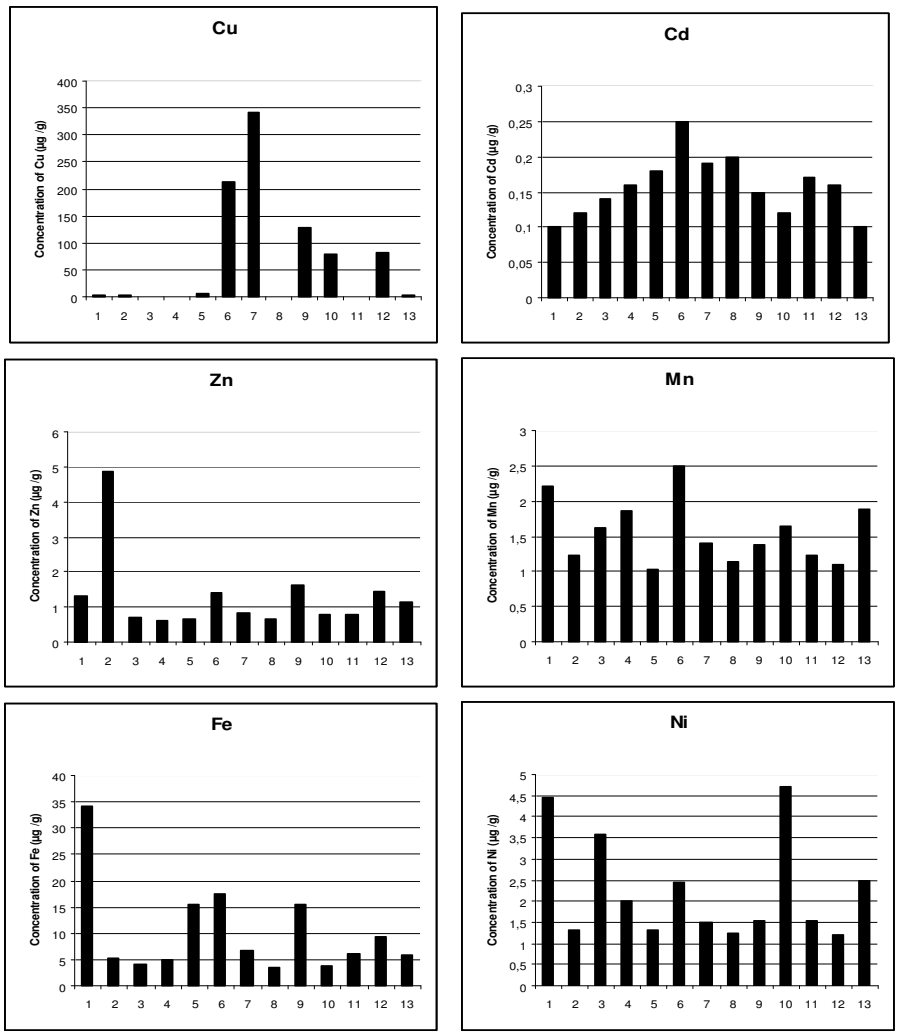

Figure 1. Copper, cadmium, zinc, manganese, iron and nickel concentrations in (1) double fabric cotton-polyester, reactive dye (Foron), Brand A, (2) double fabric cotton-polyester, reactive dye (Foron), Brand B, (3) 100 % cotton, reactive dye (Indanthrene), Brand A, (4) 100 % cotton, reactive dye (Indanthrene), Brand B, (5) 100 % cotton, pigment dye (Pigma color), Brand A, (6) 100 % cotton, pigment dye (Pigma color), Brand B, (7) 100 % cotton, reactive dye (Cibacron), Brand A, (8) 100 % cotton, reactive dye (Cibacron), Brand B, (9) 100 % cotton, reactive dye (Cibacron), Brand C, (10) 100 % cotton, reactive dye (Dirimaren), Brand A, (11) 100 % cotton, reactive dye (Levafix), Brand A, (12) 100 % cotton, reactive dye (Everzol), Brand A, and (13) Cotton-polyester, reactive dye (Diresul–S), Brand A.

Table 3. Literature values of trace metals (as μg g^{-1}) in textile samples.

Elements	Data from [7]	Data from [10]	Data from [9]	Present work
Cu	0.12-11.2	0.29-13	0.36-193.9	0.76-341
Cd	-	-	-	0.10-0.25
Zn	0.4-5.0	1.29-955	2.44-9.56	0.63-4.84
Mn	-	-	-	1.02-2.50
Fe	0.23-28.9	-	5.17-325.9	3.55-34.3
Ni	0.18-3.63	0.08-2.23	1.15-23.03	1.20-4.69

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