

Evaluation of the mineral profile of textile materials using inductively coupled plasma optical emission spectrometry and chemometrics

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ABSTRACT

The content of Al, Ba, Ca, Cr, Cu, Fe, Ni, P, Zn, Cd and Pb was determined in textile material samples after microwave-assisted decomposition in a cavity oven and extraction with an artificial sweat solution. Radial viewing inductively coupled plasma optical emission spectrometry (ICP OES) was the main detection technique, but Cd and Pb were determined by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) to increase the sensitivity. Principal components analysis (PCA) was applied to the data sets to characterize the samples with respect to their geographic origin and color difference. The PCA for Brazilian single-color samples showed separation, with one group consisting of blue and green textiles and another with all the other materials evaluated. The geographic origin study showed a clear separation between Brazilian and Chinese textiles. The metals amount extracted with sweat extractable solution were lower than limits values pointed by the International Testing and Certification System for Textiles, Öko Tex Standard 100, in the all considered classes. Recoveries varied from 85 to 112% for additions ranging from 3.0 to 25 mg kg⁻¹ for Ca and from 0.3 to 7.0 mg kg⁻¹ for all other analytes through the microwave-assisted decomposition procedure.

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1. Introduction

During the manufacture of textiles, different treatments are necessary to produce materials with attractive appearance and soft touch. However, some chemical substances used in such treatments can be harmful to the health of consumers and produce toxic wastes. The main chemical pollutants of the textile industry are pigments that contain carcinogenic amines, toxic elements (mainly metals), pentachlorophenol, chlorine bleach, halogen carriers, free formaldehyde, biocides, fire retardants and softeners [1].

The presence of inorganic elements in textiles is derived from processing and even the raw material, such as cotton [2,3]. Aluminum, Ca, Mg, Fe, Si, Na, Cu, Mn and Zn are often present in raw cotton, and this material can absorb metals from the environment [4]. Another source of metal is wet processing, and metals such as Co, Cr, Cu and Ni are frequently used as part of fabric dyes. Cationic dyes also contain Zn and trace concentrations of Hg, Cd, and As [5].

The exposure of humans to some metals and/or metal compounds can cause health problems, for example lung cancer in chromium-pigment workers, rabbits skin and eye irritation caused by Ba and allergic skin reactions (dermatitis) caused by Ni. Determination of the inorganic elements in textiles is important to evaluate the quality of these materials [6–9].

Rezic and Steffan quantified the content of elements present in textile materials of different origins by inductively coupled plasma optical emission spectrometry (ICP OES) after an extraction procedure in an artificial acidic sweat solution followed by microwave digestion using 7 mol L⁻¹ of nitric acid. The authors did not pose health hazards to consumers according to various standards [2]. Brushwood and Perkins determined the levels of K, Mg, Ca, Na, Cu, Mn, Zn, Pb and Cd in African, Chinese and Pakistani raw cottons by flame atomic absorption spectrometry after ashing. The effects of factors such as growing season, growing location and cotton variety on metals content were evaluated. The highest concentrated metal in the cotton samples was K, followed by Ca and Mg. Cadmium and Pb were not detected in any of the cotton samples studied. The metals content varied with the factors studied [3].

Chemical analyses in conjunction with pattern recognition techniques provide interesting tools for the study of the quality and origin of products [10]. Fernandes et al. used pattern recognition analyses to differentiate some important features in coffee and

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Table 1
Instrumental parameters for analytes determination by ICP OES.

Instrumental parameter	Radial ICP OES
RF generator power (kW)	1.3
Nebulizer gas flow rate (L min ⁻¹)	0.6
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	1.5
Nebulizer type	V-Groove
Chamber type	Sturman Master
Height of observation (mm)	15
Emission lines ^a (nm)	Al (II) 396.152 Ba (II) 493.408 Ca (II) 396.847 Cr (I) 267.716 Cu (II) 324.760 Fe (II) 238.204 Ni (I) 231.604 P (I) 213.618 Zn (II) 213.857

^a (I): atomic lines; (II): ionic lines.

cachaça samples, like geographical origin and production mode, based on their metal contents [11].

In this work, determination of inorganic elements in Brazilian and Chinese textiles of different colors and prints was carried out by ICP OES and thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) [12] after two sample preparation procedures, microwave-assisted decomposition and extraction with an artificial sweat solution in order to observed the possible toxicity regarding the metals lixiviation. Also, an exploratory analysis was performed to characterize the samples in relation to geographic origin and color in order to supply important information regarding the identification and quality of the Brazilian and Chinese textile products.

2. Experimental

2.1. Reagents and samples

All dilutions were prepared using ultra pure water (18.2 MΩ cm) obtained in a Milli-Q[®] system (Millipore, Bedford, MA, USA). All glassware items were immersed in 10% (v v⁻¹) HNO₃ for 24 h and rinsed with water.

For total sample decomposition, concentrates of 65% (m v⁻¹) HNO₃ (Merck, Darmstadt, Germany) and 30% (m v⁻¹) H₂O₂ (Mallinckrodt, Mexico) were employed. For extraction in the artificial sweat solution the reagents sodium chloride, ammonium chloride, sodium hydroxide, acetic acid, lactic acid and urea were used, all of them obtained from Merck.

The multi-elemental Al, Ba, Ca, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Si and Zn reference solutions were prepared after successive dilutions from 1000 mg L⁻¹ stock solutions (Merck Titrisol[®]).

Six multicolored Chinese, and one multicolor Brazilian and fourteen single-color Brazilian fabrics were acquired at a local fabric store and analyzed in this work.

2.2. Instrumentation

A Vista PRO-CCS inductively coupled plasma optical emission spectrometer with radial view configuration (Varian, Australia) was used to determine the presence of the analytes. The parameters employed are shown in Table 1.

The determination of Cd and Pb was performed by TS-FF-AAS. A Varian SpectrAA-800 flame atomic absorption spectrometer equipped with a deuterium lamp for background correction was used. An oxidizing air/acetylene flame was used in all experiments. The other operational parameters, such as gas flow rates

Table 2
Microwave heating program.

Step	Power (W)	Time (min)
1	300	2.0
2	0	3.0
3	650	4.0
4	850	5.0
5	1000	5.0
6	Vent.	15.0

and lamp current, were those recommended by the manufacturer. This arrangement, proposed by Gaspar and Berndt [12], consists of a Ni tube (10 cm length) placed on a standard burner head of an FAAS spectrometer. A volume of 200 μL of sample was introduced into the tube via a ceramic capillary (typically with 0.5 mm i.d.) by a carrier (HNO₃ 0.01 mol L⁻¹) line with a flow rate of 0.5 mL min⁻¹. Transient signals were recorded during 100 s.

2.3. Sample preparation

2.3.1. Extraction in the artificial sweat solution

The textile samples were dried during 48 h at 60 °C before analysis, and afterwards were cut and weighed. A mass of 1.5 g of each sample was mixed in the circulating bath water (Marconi MA-470/1300, Piracicaba, Brazil) for 2 h at 40 °C using 25 mL of artificial sweat solution, which was prepared according to the ISO 3160/2 standard. It was prepared with a dilution of 20 g L⁻¹ sodium chloride, 17.5 g L⁻¹ ammonium chloride, 5 g L⁻¹ acetic acid and 15 g L⁻¹ lactic acid. The pH was adjusted to 4.7 with NaOH 0.1 mol L⁻¹ [13]. After filtration, the solutions were analyzed by ICP OES and TS-FF-AAS.

2.3.2. Microwave decomposition

To compare the analytes obtained with the extraction conditions, microwave-assisted decomposition of all the evaluated textile samples was carried out in a cavity oven. The samples were dried during 48 h at 60 °C, cut with plastic scissors and weighed. Sample masses of 375 mg were put into PFA digestion vessels of the microwave oven (Multiwave, Anton Paar, Graz, Austria) and digested using 2 mL of 7 mol L⁻¹ HNO₃ plus 1 mL of H₂O₂ of 30% (m v⁻¹). The microwave oven heating program was performed in five steps (Table 2). After decomposition, the solutions were transferred to 15 mL volumetric flasks and diluted with water.

2.4. Exploratory analyses

A data matrix with 84 rows (textile samples in triplicates) and 9 columns (analyte concentration) was organized and principal component analysis (PCA) was applied using the Pirouette software (InfoMetrix, Woodinville, USA), version 4.0. The data were auto-scaled due to different order of magnitude among the variables.

2.5. Addition and recovery tests

To evaluate the accuracy of the digestion procedure, samples of white Brazilian fabric were spiked with the evaluated elements at three levels: low (3.0 mg kg⁻¹), medium (15 mg kg⁻¹) and high (25 mg kg⁻¹) for Ca and 0.3, 2.0 and 7.0 mg kg⁻¹ for all other elements. After addition, the samples were submitted to the microwave-assisted decomposition procedure.

3. Results and discussion

To evaluate the mineral profile of the textile materials, ICP OES analysis of the sample solutions provided by the microwave-assisted decomposition and simulated extraction solution was

Table 3
Mineral profile of cavity oven microwave-assisted decomposition samples (mg of mineral kg⁻¹ of textiles).

Samples	Al	Ba	Ca	Cr	Cu	Fe	Ni	P	Zn
Light green	32.3 ± 2.26	19.9 ± 2.36	206 ± 11.6	2.60 ± 1.22	30.0 ± 1.09	27.7 ± 0.58	2.00 ± 0.50	41.0 ± 6.63	3.74 ± 1.05
Dark green	23.7 ± 0.71	12.2 ± 1.66	184 ± 4.45	2.05 ± 0.82	157 ± 2.29	20.5 ± 3.10	5.10 ± 0.62	23.3 ± 7.69	3.43 ± 0.27
Moss green	30.5 ± 2.29	8.42 ± 0.56	273 ± 11.8	<1.09	273 ± 4.37	16.9 ± 1.28	<2.00	30.2 ± 11.1	3.53 ± 0.72
Light yellow	30.7 ± 1.75	8.02 ± 0.55	257 ± 2.34	<1.09	<1.20	19.4 ± 0.80	<2.00	42.7 ± 6.22	1.36 ± 0.22
Dark yellow	36.3 ± 0.57	6.62 ± 0.57	206 ± 16.2	<1.09	<1.20	20.2 ± 1.44	<2.00	31.3 ± 5.59	1.2 ± 0.37
Brown	21.4 ± 0.83	6.54 ± 0.58	234 ± 9.11	<1.09	14.2 ± 0.31	18.9 ± 0.84	<2.00	37.6 ± 7.34	2.96 ± 0.73
Red	23.8 ± 2.54	3.42 ± 0.40	181 ± 6.95	<1.09	<1.20	19.95 ± 0.70	<2.00	61.6 ± 5.88	2.93 ± 0.75
Pink	27.4 ± 3.30	3.01 ± 0.65	265 ± 11.9	<1.09	<1.20	27.5 ± 0.89	<2.00	78.6 ± 0.67	3.32 ± 0.58
Light blue	31.8 ± 0.96	7.85 ± 0.56	410 ± 7.05	1.61 ± 0.50	2.30 ± 0.46	25.8 ± 0.30	<2.00	32.3 ± 12.1	10.9 ± 0.69
Black	30.1 ± 1.32	3.65 ± 1.01	317 ± 5.02	<1.09	<1.20	33.4 ± 1.91	<2.00	52.9 ± 2.63	2.33 ± 0.33
Light blue	24.6 ± 1.80	6.44 ± 0.39	212 ± 6.79	1.28 ± 0.56	115 ± 4.47	20.0 ± 0.76	2.51 ± 0.25	<15.60	1.46 ± 0.11
Orange	36.0 ± 1.04	4.34 ± 0.29	349 ± 7.38	<1.09	<1.20	25.8 ± 0.16	<2.00	25.0 ± 3.99	2.07 ± 0.72
Purple	26.4 ± 5.91	4.53 ± 0.21	308 ± 8.40	<1.09	<1.20	14.9 ± 0.15	<2.00	153 ± 7.35	4.11 ± 0.57
White	21.1 ± 2.20	3.41 ± 0.08	241 ± 10.5	<1.09	<1.20	12.1 ± 0.36	<2.00	64.5 ± 5.40	<1.2
Brazilian multicolor	31.7 ± 1.37	4.33 ± 0.49	341 ± 8.34	<1.09	52.2 ± 2.67	23.1 ± 0.37	<2.00	22.2 ± 3.34	4.08 ± 0.64
Chinese multicolor	20.8 ± 4.78	6.52 ± 1.65	1268 ± 48.28	<1.09	1.41 ± 0.47	27.9 ± 1.33	<2.00	73.7 ± 2.52	3.57 ± 0.71
Chinese multicolor	126 ± 2.71	87.4 ± 5.15	1848 ± 91.68	<1.09	3.97 ± 0.05	66.1 ± 1.41	2.54 ± 0.32	88.0 ± 2.84	3.16 ± 0.28
Chinese multicolor	75.6 ± 3.36	4.61 ± 0.78	1073 ± 11.68	<1.09	2.22 ± 0.92	41.3 ± 1.10	<2.00	145 ± 11.3	3.30 ± 0.48
Chinese multicolor	17.6 ± 1.66	2.05 ± 0.28	1508 ± 10.75	<1.09	1.20 ± 0.10	38.5 ± 0.11	<2.00	70.6 ± 0.08	2.56 ± 0.39
Chinese multicolor	117.5 ± 4.26	102 ± 4.84	1850 ± 47.48	<1.09	<1.20	64.1 ± 1.67	2.26 ± 0.56	93.1 ± 1.63	2.41 ± 0.13
Chinese multicolor	21.4 ± 1.09	3.94 ± 0.52	1410 ± 26.29	<1.09	<1.20	34.6 ± 0.22	1.84 ± 0.66	77.8 ± 3.93	4.39 ± 0.39

performed. Tables 3 and 4 present the mineral profile obtained with microwave decomposition and simulated sweat extraction, respectively, as determined by ICP OES. Some toxic elements (such as Ni, Cr, and Ba), trace elements (Cu and Zn) and macronutrients (Ca, Fe and P) were determined. Considering the extraction in the artificial sweat solution, as expected, Ca, Fe and P were present in higher concentrations than the other evaluated analytes. Relatively high amounts of aluminum, Ba, and Zn were extracted as well, while hardly any Cr, Cu, and Ni were extracted. In both sample preparation procedures, Cd and Pb were not detected even with the employment of TS-FF-AAS (instrumental detection limits of 1.13 and 16.5 µg L⁻¹ for Cd and Pb, respectively), indicating that these elements were present in very low concentration or were not present in the samples, as previously described by Brushwood and Perkins [3].

The obtained metals amount for all evaluated elements were lower than limits values pointed by the International Testing and Certification System for Textiles, Öko Tex Standard 100, for sweat extractable solution in all the evaluated samples, independent of the geographical origin. Cadmium and Pb amount were lower than the limit of detection of the employed technique (Table 5) [14].

3.1. Principal component analysis (PCA)

This study was divided into three steps. In the first one the Brazilian single-color microwave-assisted decomposition samples were compared to evaluate the possible mineral profile for each color. In the second step, microwave decomposition solutions were used to generate the profile of all samples and compared according with their origin. Finally, the availability of elements in each textile material was analyzed, considering the extraction with the simulated sweat solution. In all analyses the analyte concentration values were auto-scaled to attribute the same importance to each variable.

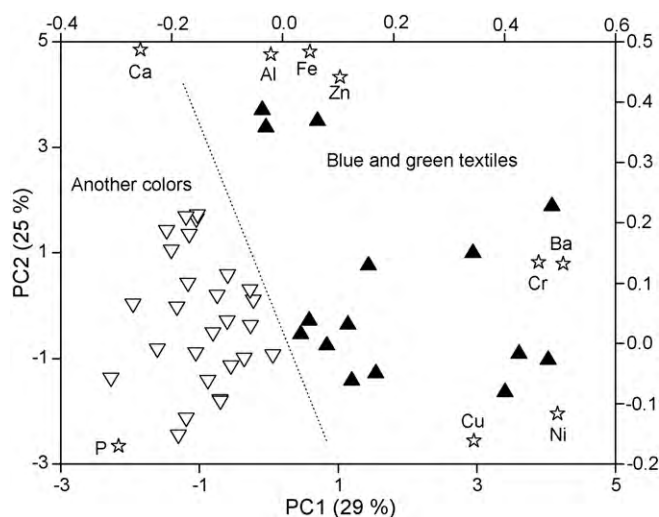
The results of the first study, the mineral profile of the Brazilian single-color microwave decomposition, are shown in Fig. 1. Few components were necessary to explain the total data variance. The first two components describe 54% of the total variance. The first component (PC1) is responsible for 29% and the second (PC2) explains 25% of the total information. The score plot (see Fig. 1) shows separation of the all shades of green and blue samples (black triangles), with positive PC1 scores, from other colors (white triangles), which have negative PC1 scores. Aluminum, Ca, and P are

Table 4
Mineral profile of extracted samples by artificial sweat solution (mg of mineral kg⁻¹ of textiles).

Samples	Al	Ba	Ca	Cr	Cu	Fe	Ni	P	Zn
Light green	<1.2	<0.33	112 ± 0.88	<0.47	<0.45	0.26 ± 0.06	<0.83	34.1 ± 4.15	<0.50
Dark green	<1.2	<0.33	96.0 ± 1.84	<0.47	<0.45	1.91 ± 0.11	<0.83	18.9 ± 0.90	<0.50
Moss green	<1.2	<0.33	192 ± 0.84	<0.47	0.95 ± 0.11	0.47 ± 0.12	<0.83	22.9 ± 0.27	<0.50
Light yellow	<1.2	<0.33	<2.34	<0.47	<0.45	<0.66	<0.83	6.09 ± 3.42	<0.50
Dark yellow	1.75 ± 0.18	1.62 ± 0.08	198 ± 2.14	0.21 ± 0.01	<0.45	1.19 ± 0.26	<0.83	15.4 ± 1.73	<0.50
Brown	<1.2	<0.33	178 ± 1.69	<0.47	<0.45	0.43 ± 0.01	<0.83	32.2 ± 3.42	0.52 ± 0.06
Red	<1.2	<0.33	171 ± 1.58	<0.47	<0.45	3.41 ± 0.52	<0.83	54.0 ± 3.65	0.73 ± 0.11
Pink	2.81 ± 0.07	2.98 ± 0.05	252 ± 1.16	0.48 ± 0.08	<0.45	6.80 ± 0.15	<0.83	47.8 ± 3.54	1.01 ± 0.01
Light blue	7.53 ± 2.54	2.49 ± 0.07	324 ± 0.48	<0.47	<0.45	3.74 ± 0.34	<0.83	<6.00	4.45 ± 0.16
Black	1.73 ± 0.65	2.91 ± 0.34	271 ± 8.44	0.18 ± 0.03	<0.45	8.23 ± 0.32	<0.83	34.1 ± 1.50	0.73 ± 0.01
Light blue	<1.2	<0.33	<2.34	<0.47	<0.45	<0.66	<0.83	<6.00	<0.50
Orange	2.08 ± 1.28	1.82 ± 0.22	273 ± 11.6	<0.47	<0.45	4.14 ± 0.31	<0.83	<6.00	<0.50
Purple	<1.2	<0.33	151 ± 2.46	<0.47	<0.45	1.05 ± 0.10	<0.83	103 ± 2.02	1.39 ± 0.19
White	9.44 ± 0.06	3.42 ± 0.88	288 ± 13.0	<0.47	<0.45	2.76 ± 0.31	<0.83	44.1 ± 4.60	<0.50
Brazilian multicolor	2.89 ± 0.96	0.63 ± 0.08	167 ± 5.60	0.22 ± 0.00	1.08 ± 0.01	2.50 ± 0.11	0.21 ± 0.14	6.22 ± 4.38	1.84 ± 0.29
Chinese multicolor	2.23 ± 0.95	1.55 ± 0.42	730 ± 4.94	0.29 ± 0.04	0.75 ± 0.05	5.30 ± 0.48	0.48 ± 0.24	31.8 ± 0.20	1.45 ± 0.28
Chinese multicolor	36.0 ± 2.88	66.2 ± 5.85	892 ± 27.6	0.20 ± 0.04	0.53 ± 0.02	5.05 ± 0.76	<0.83	26.5 ± 0.17	<0.50
Chinese multicolor	16.9 ± 1.15	<0.33	448 ± 4.34	<0.47	0.52 ± 0.11	3.74 ± 0.19	<0.83	47.1 ± 4.30	0.61 ± 0.04
Chinese multicolor	2.51 ± 0.30	1.19 ± 0.01	769 ± 32.7	0.13 ± 0.03	<0.45	7.68 ± 0.42	<0.83	27.7 ± 1.11	0.76 ± 0.04
Chinese multicolor	25.2 ± 2.18	62.8 ± 3.80	715 ± 32.6	0.13 ± 0.01	<0.45	2.49 ± 0.19	<0.83	20.0 ± 1.76	<0.50
Chinese multicolor	3.73 ± 0.49	<0.33	682 ± 23.9	<0.47	<0.45	5.14 ± 0.19	0.54 ± 0.21	31.4 ± 1.45	1.72 ± 0.27

Table 5
Limit values and fastness (Öko Tex Standard 100).

Product class	Baby	In direct contact with skin	With no direct contact with skin	Decoration material
Extractable heavy metals (mg kg ⁻¹)				
Sb	30.0	30.0	30.0	–
As	0.2	1.0	1.0	1.0
Pb	0.2	1.0	1.0	1.0
Cd	0.1	0.1	0.1	0.1
Cr	1.0	2.0	2.0	2.0
Cr (VI)	Under detection limit			
Co	1.0	4.0	4.0	4.0
Cu	25.0	50.0	50.0	50.0
Ni	1.0	4.0	4.0	4.0
Hg	0.02	0.02	0.02	0.02
Heavy metals in digested sample (mg kg ⁻¹)				
Cd	45.0	90.0	90.0	90.0
Pb	50.0	100.0	100.0	100.0

**Fig. 1.** PC1 versus PC2 scores and loading plots of Brazilian textile materials showing differentiation between textile colors. Blue and green textiles (black triangle), other colors (white triangles) and loading (asterisk).

present (see loading plots at Fig. 1) in the second group, while the first group is mainly composed of Ba, Cu, Cr, and Ni. Iron and Zn appear at the center of the loading plot, linked with both groups. In this study it is important to highlight that some compounds of Ni,

Table 6
Percentage of extracted and total mineral content ratio (%).

Samples	Al	Ba	Ca	Cr	Cu	Fe	Ni	P	Zn
Light green	0.0	0.0	36	0.6	0.0	0.6	0.0	55	5.3
Dark green	0.0	0.0	35	7.8	0.0	6.2	0.0	54	5.7
Moss green	0.8	0.0	75	0.0	0.3	4.2	0.0	88	19
Light yellow	5.7	1.4	36	0.0	0.0	5.7	0.0	29	5.9
Dark yellow	3.7	25	96	43	0.0	5.2	0.0	41	0.0
Brown	0.0	0.0	66	0.0	0.0	1.5	0.0	75	12
Red	0.2	28	94	0.0	0.0	17	0.0	68	31
Pink	8.9	99	95	52	0.0	25	0.0	67	27
Light blue	16	28	72	0.1	0.0	12	0.0	25	41
Black	13	80	85	59	0.0	24.6	0.0	72	34
Light blue	0.0	0.0	23	0.0	0.0	2.5	0.0	83	0.0
Orange	14	42	78	85	0.0	16	0.0	9.5	8.9
Purple	0.0	0.0	33	0.0	0.0	4.7	0.0	45	23
White	32	100	102	16	0.0	18	0.0	68	13
Brazilian multicolor	9.1	19	49	60	1.9	11	0.0	19	45
Chinese multicolor	73	0.0	37	9.1	26	15	0.0	64	28
Chinese multicolor	28	76	46	32	14	7.7	15	28	0.0
Chinese multicolor	4.2	34	66	0.0	31	13	0.0	22	44
Chinese multicolor	17	49	51	100	1.9	20	2.2	39	30
Chinese multicolor	21	61	39	25	1.0	3.9	0.5	21	0.0
Chinese multicolor	15	13	48	41	0.1	15	34	40	39

Cr and Cu, present in the second group, are used in the industry as green and blue dyes. Therefore, it can be inferred that dyes played a role in the content of these minerals in the textile samples.

The second study began with another classification assessed by PCA, now including all the textile samples evaluated. The objective was to study the mineral profile of the products according to origin between Brazilian and Chinese samples. Fig. 2 shows the scores and loading scatter plots of PC1 and PC2, which account for 63% of the total data variance. The first component accounts for 42% and the second explains 21% of the total information. Two groups can be suggested based on the distribution of samples along PC1: one of them (black square) with negative PC1 scores, composed of Brazilian samples and characterized mainly by Cu and Cr; and a second group (white circle), located at the positive side of PC1, composed of Chinese samples and characterized by Al, Ba, Ca, Fe, and P. Additionally, Ni and Zn, located at the center of PC1, characterize both groups.

Finally, to estimate the availability of elements in each textile material, the ratio between the results obtained by extraction and total mineral amount were calculated. These results indicate the percentage of each mineral that is extractable and available using artificial sweat solution extraction (Table 6). A new PCA was performed with these data, and the availability of elements according to these origins was assessed. Fig. 3 shows the score and loading scatter plots of PC1 and PC2, which account for 50% of the total data variance. The first component accounts for 31% and the sec-

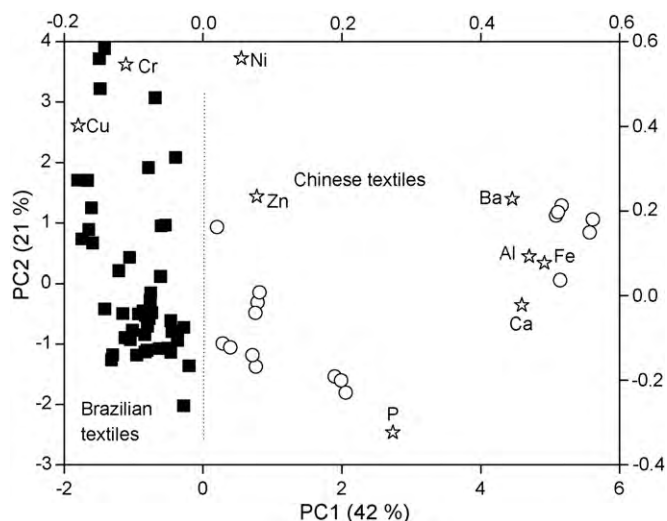


Fig. 2. PC1 versus PC2 scores and loading plots of textile materials showing differentiation between geographic origin. Brazilian textiles (black square), Chinese textiles (white circle) and loading (asterisk).

and explains 19% of the total information. As previously observed, two groups can be suggested based on the distribution of samples along PC2. The first group (black square), located on the negative part of PC2 (see Fig. 3), comprises the Brazilian samples and is characterized mainly by Cr, Fe, Ba, Ca and P (see loadings in Fig. 3), and a second group (white circle), composed of Chinese samples, is located in the positive part of PC2, characterized by Al, Cu, and Zn. These results show that some elements that characterize the Chinese samples (Ba, Ca, P, and Fe) when considering the total profile were more extracted by the artificial sweat solution in the Brazilian textile material, while Cu, which characterizes Brazilian samples, and Zn, which characterizes both groups according with the total profile, were more extracted by the artificial sweat solution in the Chinese textile materials. Nickel was not extracted from any of the samples. Thus, the availability of elements in the textile materials differs according to geographic origin.

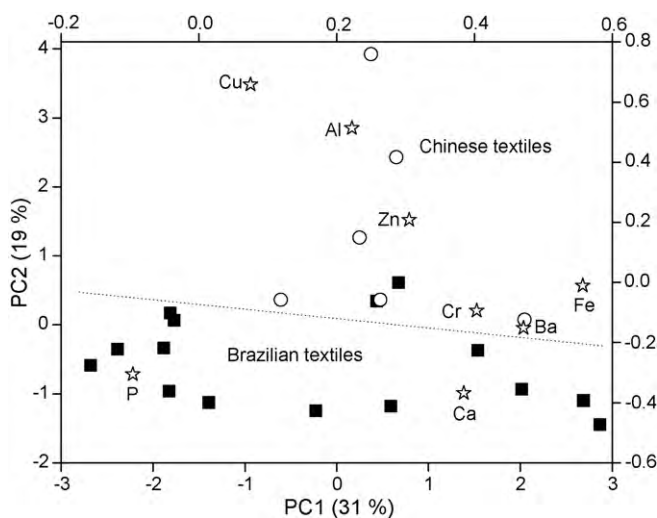


Fig. 3. PC1 versus PC2 scores and loading plots of availability of minerals in textile materials according to geographic origin. Brazilian textiles (black square), Chinese textiles (white circle) and loading (asterisk).

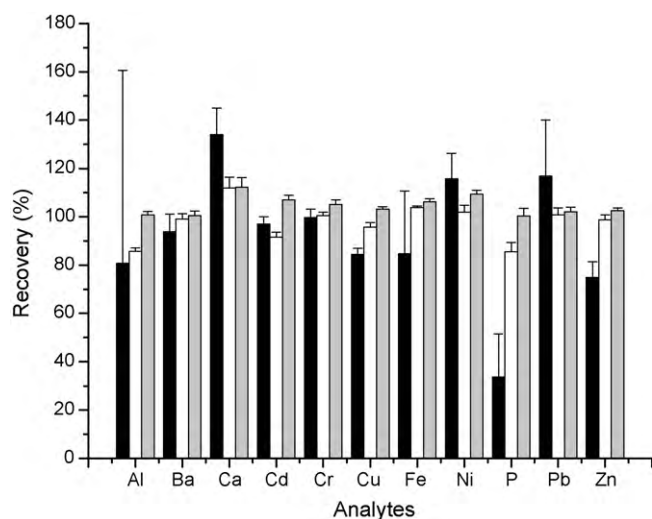


Fig. 4. Addition and recovery test. Low level (black bars), medium level (white bars) and high level (gray bars).

3.2. Addition and recovery tests

Fig. 4 shows the results obtained from addition and recovery tests after microwave-assisted decomposition. For most of the analytes evaluated, recoveries near 100% were obtained. P and Al, however, presented 40% of recovery and 79% of standard deviation, respectively, at the evaluated lower level, probably because the amounts of these analytes added were near the detection limits of the ICP OES technique.

4. Conclusion

The samples of textile materials of Chinese and Brazilian origin presented differences in the analyte contents. The Chinese samples were characterized by Al, Ba, Ca, Fe, and P, however Cu and Zn were more available from the artificial sweat extraction procedure, while the Brazilian samples were characterized by Cu and Cr in the total digestion procedure and the analytes Cr, Fe, Ba, Ca and P were more available from artificial sweat extraction. The study of the colors showed that the green and blue fabrics presented higher concentration of Cr, Cu and Ni. The dyes used probably contribute to the presence of these minerals. The extractable and total contents determined for all elements were lower than the limits values suggested by Öko Tex Standard 100.

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