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Portable EDXRF and principal component analysis for inorganic element determination and provenance of eye shadows

EDXRF portátil e análise de componentes principais para a determinação de elementos inorgânicos e proveniência de sombras para os olhos

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Abstract

Nowadays cosmetic products play an important role in the life of almost all people. Men and women devote much time, resources and efforts to cultivate personal hygiene and the best possible look along their lives. One of the most widely used kind of cosmetics is eye shadow. X-ray fluorescence (XRF) is a well-established technique, known for its ability to identify and quantify inorganic species in a simple, fast and non-destructive way, however, it is not extensively used in cosmetic analysis. In order to show the potentiality of the technique, portable energy-dispersive X-ray fluorescence spectrometry has been employed in the quantification of inorganic elements in 40 Brazilian eye shadows. It was possible to identify and quantify the elements Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn and Bi. Using principal component analysis, specific manufacturers could be distinguished. The X-ray fluorescence methodology associated with principal component analysis proved to be a valuable tool for the discrimination and characterization of cosmetics.

Keywords: EDXRF. Principal component analysis. Cosmetics.

Resumo

Nos dias de hoje, produtos cosméticos desempenham um importante papel na vida de quase todas as pessoas. Homens e mulheres dedicam muito tempo, recursos e esforços para cultivar a higiene pessoal e a melhor aparência possível ao longo de suas vidas. Um dos tipos de cosméticos mais utilizados é a sombra para os olhos. A fluorescência de raios X (XRF) é uma técnica bem estabelecida, conhecida por sua capacidade de identificar e quantificar espécies inorgânicas de maneira simples, rápida e não-destrutiva, no entanto, não é amplamente utilizada em análises de produtos cosméticos. A fim de se mostrar a potencialidade da técnica, fluorescência de raios X por dispersão em energia portátil foi empregada na quantificação de elementos inorgânicos em 40 sombras para os olhos brasileiras. Foi possível identificar e quantificar os elementos Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn e Bi. Utilizando a análise de componentes principais, foi possível distinguir os diferentes fabricantes. A metodologia de fluorescência de raios X associada à análise de componentes principais provou ser uma ferramenta valiosa para a discriminação e caracterização de produtos cosméticos.

Palavras-chave: EDXRF. Análise de componentes principais. Cosméticos.

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Introduction

The use of cosmetics predates written history. Makeup products were created thousands of years ago to give people a more attractive look, to protect their bodies and also as medical care (PARISH; CRISSEY, 1988. WESTMORE, 2001). Nowadays, there are various reasons why cosmetic products continues being an important part of almost everyone's life (WESTMORE, 2001). The improvement in quality of life and the increase in longevity of the population make men and women devote more time, resources and efforts to cultivate personal hygiene and the best possible look along their lives.

Although cosmetics for the purpose of beautifying, perfuming, cleansing or rituals have existed since the antiquity, only in the last century a great progress has been made in the diversification of products and in the safety and protection of the consumer. Consumers have become more and more knowledgeable and demanding, and cosmetics have become more sophisticated, innovative and safe (BAREL; PAYE; MAIBACH, 2009).

One of the most widely used kind of cosmetics are eye shadows. They are cosmetics designed to impart color, mainly to the upper eyelid and it is used to make the eyes of the wearer stand out or look more attractive.

The elemental characterization of a cosmetic product may be important for many reasons, including quality assurance in industry of raw materials or final products and supervision by regulatory agencies. In addition, it has direct application in forensic science (MISRA *et al.*, 1992. MURPHY *et al.*, 2012. SHIMAMOTO; TERRA; BUENO, 2013), as in the analysis of cosmetic residues in crime scenes. Elemental characterization may be verified by analytical methods like X-ray fluorescence spectroscopy.

X-ray fluorescence (XRF) is a well-established technique, known for its ability to identify and quantify inorganic species in a simple, fast and non-destructive way, specially using its energy-dispersive variant, energy-dispersive X-ray fluorescence (EDXRF). In last decades, XRF has been employed in the elemental analysis of cosmetics. Misra *et al.* (1992) applied energy-dispersive X-ray fluorescence spectrometry in the quantitative analysis of nail polishes. Briggs-Kamara (2012) used energy-dispersive X-ray fluorescence spectrometry to determine the elemental composition of epidermal cosmetic creams. Kulikov, Latham and Adams (2012) employed wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry for multi-elemental analysis of mineral and traditional ingredient cosmetic powders. Murphy *et al.* (2012) employed a handheld XRF unit to measure the total mercury content of skin-whitening creams. DaSilva, David and Pejović-Milić (2015) applied total reflection X-ray fluorescence (TXRF) spectrometry in quantification of total lead in lipstick specimens. Melquiades *et al.* (2015) applied a portable EDXRF system for the elemental concentration determination in different kinds of cosmetics. Classification of samples which contain S in nail polish were determined by Melquiades and da Silva (2016) using EDXRF and multivariate analysis. Santos *et al.* (2018) employed energy dispersive X-ray fluorescence for inorganic elements quantification in eye shadows.

The Principal Component Analysis (PCA) is one of the most important modern methods of treating multivariate data. It is an important data compression tool that make possible original dimensionality reduction while preserving the relevant information. In PCA the original information is transformed into a more compact and summarized set of information than the previous one. These qualities make the PCA a suitable tool for analysis of the multi-elemental data from XRF. Through the graphical representation of the principal components, it is possible to verify the relations between the different variables, to detect and to interpret a pattern among the samples, gathering the similarities and differences among them (WOLD; ESBENSEN; GELADI, 1987).

Considering that EDXRF method is a well-known procedure; has an attractive cost-benefit ratio, allows field application and not requires complex sample preparation, like sample digestion, as in other methodologies, like LIBS (Laser Induced Breakdown Spectroscopy) and ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) (GONDAL *et al.*, 2010. BATISTA; DOS SANTOS AUGUSTO; PEREIRA-FILHO, 2015. DOS SANTOS AUGUSTO; BATISTA; PEREIRA-FILHO, 2016. MCINTOSH *et al.*, 2016), the main idea of this paper is to show the potentiality of the technique in cosmetic samples analysis. In this way, a portable EDXRF system was employed in the quantification of inorganic elements in eye shadows. Subsequently, the set of EDXRF spectra was analyzed by PCA with the objective to observe similarities among the different manufacturers and suppliers of eye shadows.

Materials and Methods

Sample collection and preparation

In this study, 40 eye shadows acquired from four Brazilian manufacturers and suppliers, representing different colors and shades were analyzed. Each sample has been assigned a code: the letters indicate the manufacturer and the numbers represents the product number in the set of samples from the same manufacturer.

The samples in loose powder form were prepared in triplicate without any kind of chemical preparation. The powder was applied over a thin paper (silk paper), placed on conventional 32 mm diameter XRF cup (Chemplex Industries Inc.). It was used an appropriate brush in such way that the samples fits in the thin film geometry (VAN GRIEKEN; MARKOWICZ, 2001). Figure 1 shows a sample properly mounted on the XRF cup and Table 1 shows some characteristics of the analyzed samples, i.e., their color, mass applied to the XRF cup and surface density.

Thin-film mono-element standards supplied by Micromatter™ were also examined for elementary sensitivity determination.

Figure 1 – Eye shadow sample properly mounted on the XRF cup.

Source: The authors.

Table 1 – Color (informed by the manufacturer), mass applied to the XRF cup and surface density of the samples analyzed.

Sample	Color	Mass [g]	Surface density [g.cm^{-2}]
A1	Pearly green	0.00098	0.000219
A2	Military green	0.00100	0.000220
A3	Matte brown	0.00112	0.000227
A4	Shimmering gold	0.00106	0.000217
B1	Yellow/gold	0.00219	0.000525
B2	Light green	0.00352	0.000820
B3	Purple	0.00256	0.000602
B4	White	0.00292	0.000736
B5	Light brown	0.00231	0.000556
B6	Bronze	0.00289	0.000768
B7	Light purple	0.00330	0.000786
B8	Light pink	0.00441	0.001015
B9	White	0.00218	0.000476
B10	Brown	0.00371	0.000797
B11	Gray	0.00406	0.000822
B12	White	0.00387	0.001175
B13	Dark blue	0.00259	0.000544
B14	Black	0.00526	0.001097
B15	Ivory	0.00170	0.000379
B16	Light brown	0.00231	0.000533
B17	Red earth	0.00326	0.000743
B18	Brown	0.00451	0.001091
C1	Pearly blue	0.00162	0.000412
C2	Royal blue	0.00186	0.000440
C3	Water green	0.00168	0.000468
C4	Bluish green	0.00172	0.000429
C5	Peach pink	0.00218	0.000829
C6	Green	0.00141	0.000437
C7	Yellow	0.00158	0.000499
C8	Brown	0.00168	0.000395
D1	Green	0.00167	0.000505
D2	Orange	0.00132	0.000336
D3	Sky blue	0.00110	0.000304
D4	Yellow	0.00113	0.000360
D5	Pink	0.00203	0.000615
D6	Light purple	0.00159	0.000509
D7	Greenish blue	0.00109	0.000323
D8	Light green	0.00133	0.000491
D9	Light pink	0.00225	0.000786
D10	Ivory	0.00150	0.000525

Source: The authors.

Sample analysis

The data acquisition was carried out with a self-made portable EDXRF system (PARREIRA, 2019), which consists of a mini X-ray tube (Ag target, 4 W, Moxtek Inc., Orem. UT. USA) with a 50 μm thick Ag filter and the X-123 complete X-ray spectrometer with Si-PIN detector (FWHM 153 eV for Mn 5.9 keV line, 12.7 μm Be window, Amptek Inc., Bedford, MA, USA) with a 3 mm diameter Al collimator.

For each sample, twelve measurements were performed. Four measurements for each triplicate, by rotating the sample cup in 90 degree to ensure complete irradiation of the sample area.

The measurements conditions were: 28 kV and 10 μA, with acquisition time of 500 s. The spectra were analyzed using the software WinQXAS, from IAEA.

The inorganic elements quantification was performed based on the experimental calibration curve, obtained from the Micromatter™ standards, and employing the follow equation (1) for thin film samples (VAN GRIEKEN; MARKOWICZ, 2001):

$$I_i = c_i.S_i.A \tag{1}$$

where I_i is the characteristic X-ray net intensity (cps), c_i the concentration (g.cm^{-2}), S_i the elementary sensitivity (cps.cm^2.g^{-1}), determined from the calibration curve, and A the absorption factor. For this methodology, the absorption factor A was set to the unity since the samples were classified as thin film samples (VAN GRIEKEN; MARKOWICZ, 2001). The detection limit (DL) was obtained using Currie's equation (2) (CURRIE, 1968):

$$DL = \frac{3}{S_i}\sqrt{\frac{I_{bgi}}{t}} \tag{2}$$

where I_{bgi} is the background intensity (cps), and t the measurement time.

The EDXRF results were also processed using MATLAB software (Mathworks Inc., MA, USA). For the PCA analysis a matrix was constructed in such way that the columns refer to the variable (energy) and the lines correspond to each samples.

In order to test the methodology applied in cosmetic analysis, as there is no certified reference material (CRM) available for eye shadows, the same samples were also analyzed by a well-stablished commercial benchtop equipment. The benchtop equipment used is the energy dispersive X-ray spectrometer model EDX-720, from Shimadzu Corp., equipped with a Rh X-ray tube and a Si(Li) detector. The measurements conditions were: 15 kV (for the elements from Na to Sc) and 50 kV (for elements from Ti to U), current automatically determined by the measuring system, with acquisition time of 100 s. The quantitative methodology was performed using a routine pre-established by spectrometer software, based on the fundamental parameters equation (VAN GRIEKEN; MARKOWICZ, 2001). For each sample, three measurements were performed. A t-test with 95% confidence level was applied for the results comparison.

Results and Discussion

The inorganic elements present in the eye shadow samples and the detection limits for each set of samples are shown in Table 2.

The variations in mass fraction are related to the characteristics of each sample as its coloring and hue, brightness, opacity and skin adhesion capability. The composition of eye shadows is predominantly talc ($Mg_3Si_4O_{10}(OH)_2$) with pigments and zinc ($Zn(C_{18}H_{35}O_2)_2$) or magnesium ($Mg(C_{18}H_{35}O_2)_2$) stearate used as a binder. Kaolin ($Al_2Si_2O_5(OH)_4$) or calcium carbonate ($CaCO_3$) may be added to improve oil absorption and increase the adhesion of the cosmetic on the skin. The pigments play a fundamental role in makeup products because they provide the chromatic modifications necessary for these qualities. Iron oxides, titanium dioxide (TiO_2), chrome oxide (Cr_2O_3) and hydrate ($Cr(OH)_3$), manganese violet ($NH_4MnP_2O_7$), copper powder and iron blue ($C_{18}Fe_7N_{18}$) are some of the pigments used in current makeup applications. In addition to diversity in eye shadow color, variation in eye shadow surface characteristics is also available. The surface appearance can vary from matte to a pearled shine. A dull surface texture is produced through the addition of titanium dioxide (TiO_2), while a pearled shine is obtained using mica ($KAl2(AlSi_3)O_{10}$) or bismuth oxychloride (BiOCl) (DRAELOS, 2001).

The differences in the detection limits, for a given element, can be explained due to the non-homogeneity of the surface density in the analyzed samples. In addition, variations in the chemical composition of the samples produce small changes in the scattering profile of the X-rays (background of the spectrum), contributing to obtain different detection limits among the different sets of samples analyzed.

The inorganic elements present in the eye shadow samples, obtained from measurements with the benchtop system are shown in Table 3.

The quantification of Cl could not be performed from measurements with the benchtop equipment. The overlapping of the Cl peaks with the Rh peaks (from the X-ray tube) made impossible to quantify Cl in the studied samples.

The results for all detected elements were submitted to a t-test with 95% confidence level. For K, which was detected in fourteen samples, the results proved be statistically equal only for the samples B11, B13, B15 and B16.

Table 2 – Results of the elemental analysis of the eye shadows, obtained with the portable system.

Sample	Cl [μg/g]	K [μg/g]	Ca [μg/g]	Ti [μg/g]	Cr [μg/g]	Fe [μg/g]	Cu [μg/g]	Zn [μg/g]	Bi [μg/g]
A1	–	–	–	21,500±1,500	43,000±1,100	2,150±100	–	7,530±180	21,100±600
A2	38,000±9,000	–	–	13,400±1,200	–	170,000±14,000	–	7,900±500	33,800±1,300
A3	37,000±9,000	18,000±2,000	–	< DL	–	232,000±6,000	–	11,500±600	38,900±1,700
A4	54,000±9,000	23,000±2,000	–	14,900±1,000	–	147,000±5,000	–	20,400±700	60,500±1,200
Detection Limit	32,500	16,400		4,700	2,500	1,600		800	1,600
B1	–	21,000±2,000	< DL	59,100±1,500	–	11,290±190	–	8,700±190	–
B2	–	–	< DL	82,000±2,000	–	7,810±130	–	7,090±170	–
B3	–	9,500±1,500	< DL	111,000±6,000	–	6,900±300	–	12,900±400	–
B4	–	5,700±700	< DL	55,000±1,000	–	2,190±60	–	9,100±300	–
B5	–	22,000±2,000	< DL	63,300±1,900	–	29,100±500	–	12,500±200	–
B6	–	12,100±1,300	< DL	109,000±4,000	–	497,000±11,000	–	12,000±400	–
B7	–	6,400±800	< DL	67,000±2,000	–	3,580±110	–	6,660±170	–
B8	–	–	< DL	33,600±1,600	–	1,880±90	–	9,000±300	–
B9	–	–	3,200±1,400	44,000±3,000	–	2,190±180	–	17,000±800	–
B10	–	< DL	< DL	1,650±180	–	215,000±7,000	–	8,100±300	–
B11	–	12,800±1,200	< DL	50,300±900	–	16,100±400	–	8,700±300	–
B12	–	< DL	< DL	35,300±1,400	–	1,410±40	–	5,800±400	–
B13	–	10,000±3,000	< DL	129,000±16,000	–	340,000±60,000	–	20,000±3,000	–
B14	–	–	< DL	< DL	–	440,000±30,000	–	11,400±700	–
B15	–	30,000±4,000	< DL	208,000±8,000	–	14,200±500	–	16,300±400	–
B16	–	25,000±3,000	< DL	52,900±1,400	–	40,900±1,300	–	13,200±1,100	–
B17	–	8,200±1,000	< DL	< DL	–	330,000±6,000	–	14,000±300	–
B18	–	9,000±800	< DL	42,500±700	–	162,500±1,600	–	6,800±140	–
Detection Limit		5,500	3,000	1,500			500	200	
C1	–	–	5,200±400	9,900±1,700	–	1,800±200	22,000±3,000	13,400±1,800	–
C2	–	–	4,200±500	4,800±1,700	–	1,400±200	1,890±190	2,500±300	–
C3	–	–	< DL	< DL	–	800±60	< DL	2,590±110	–
C4	–	–	< DL	10,000±2,000	–	1,690±180	–	1,910±100	–
C5	–	–	< DL	7,600±300	–	1,530±50	–	1,480±60	–
C6	–	–	< DL	12,000±3,000	–	3,300±300	–	2,040±180	–
C7	–	–	3,800±500	14,200±1,300	–	2,600±200	–	2,000±300	–
C8	–	–	< DL	13,100±900	–	76,000±5,000	–	1,320±90	–
Detection Limit		3,200		2,200		700	400	400	
D1	26,000±5,000	–	< DL	7,300±700	–	41,000±4,000	34,000±3,000	16,800±1,700	–
D2	–	–	< DL	21,000±3,000	–	31,100±1,700	–	4,500±200	–
D3	–	–	< DL	17,800±1,100	–	6,430±130	–	2,030±120	–
D4	–	–	< DL	8,100±800	–	2,550±80	–	3,000±200	–
D5	–	–	< DL	28,000±3,000	–	2,600±200	–	1,310±100	–
D6	–	–	< DL	–	–	2,900±200	–	7,200±600	–
D7	–	–	< DL	–	–	10,510±190	1,610±120	2,200±130	–
D8	–	–	< DL	2,900±600	–	17,100±1,600	< DL	2,400±300	–
D9	–	–	< DL	–	–	5,100±300	–	1,860±130	–
D10	–	–	< DL	–	–	1,800±140	–	900±80	–
Detection Limit	14,000		3,600	2,400		700	400	400	

– element not detected
Source: The authors.

The divergence associated with the measurement of K is related to the overlap of spectral lines from different elements in the same region of K characteristic energy, which results in a less precise analysis of the element mentioned.

Ca was detected in four samples. In three samples (B9, C1 and C7), the results shown be statistically equal, only for the sample C2 the results disagreed.

Ti was detected in thirty-two samples. The t-test results showed that for eighteen samples – A1, A2, A4, B1, B2, B3, B4, B7, B9, B12, C1, C4, C6, C7, C8, D1 D4 and D5, the results proved to be statistically equivalent.

Cr was detected only in the sample A1, and Cu was detected in four samples (C1, C2, D1 and D7). The results obtained for these elements, when submitted to the t-test, shown be statistically equal.

Fe was detected in all analyzed samples. Af-

Table 3 – Results of the elemental analysis of the eye shadows, obtained with the benchtop system.

Sample	Cl [μg/g]	K [μg/g]	Ca [μg/g]	Ti [μg/g]	Cr [μg/g]	Fe [μg/g]	Cu [μg/g]	Zn [μg/g]	Bi [μg/g]
A1				20,000±5,000	42,000±6,000	2,900± 300		5,900±600	20,000±3,000
A2	*			12,800±1,400		130,000±40,000		5,900±1,300	29,000±7,000
A3	*	23,000±5,000				210,000±30,000		9,000±2,000	36,000±8,000
A4	*	29,700±1,600		15,100±1,100		146,000±18,000		17,700±1,900	67,000±3,000
B1		29,000±3,000		59,000±6,000		12,500±1,100		8,300±500	
B2				76,000±10,000		8,000±400		6,300±200	
B3		16,000±4,000		100,000±30,000		7,200±1,300		11,100±1,700	
B4		13,200±800		53,000±4,000		2,760±170		8,200±800	
B5		24,900±1,600		58,000±4,000		29,000±2,000		11,000±1,000	
B6		23,000±4,000		142,000±18,000		730,000±50,000		16,200±1,300	
B7		11,800±1,200		65,000±7,000		4,000±400		6,000±500	
B8				30,000±2,000		1,950±150		7,400±1,300	
B9			2,600±400	39,000±6,000		2,600±400		14,400±1,600	
B10				2,100±300		220,000±30,000		7,600±800	
B11		14,000±1,000		43,000±2,000		15,000±1,200		6,900±400	
B12				34,000±4,000		1,700±300		5,000±1,000	
B13		12,000±2,000		100,000±20,000		250,000±50,000		12,000±3,000	
B14						600,000±200,000		14,000±5,000	
B15		36,000±10,000		180,000±40,000		14,000±3,000		13,000±2,000	
B16		27,000±2,000		48,000±3,000		40,000±4,000		12,000±3,000	
B17		13,000±2,000				390,000±40,000		15,300±1,700	
B18		10,830±140		39,900±800		175,000±3,000		6,390±130	
C1			4,800±1,800	11,000±5,000		2,500±1,100	25,000±11,000	15,000±7,000	
C2			2,100±800	2,000±2,000		1,300±400	1,600±400	1,800±500	
C3						1,100±100		2,070±180	
C4				8,000±6,000		1,700±400		1,400±200	
C5				6,600±800		1,510±160		1,250±130	
C6				9,000±6,000		2,800±700		1,400±400	
C7			3,700±900	13,600±1,100		2,900±300		2,100±1,200	
C8				13,000±700		73,000±12,000		1,050±190	
D1				8,000±4,000		49,000±19,000	37,000±16,000	17,000±7,000	
D2				16,000±5,000		31,400±1,300		4,200±600	
D3				10,700±1,300		5,050±70		1,430±130	
D4				8,500±600		2,870±70		3,000±900	
D5				26,000±2,000		2,600±200		1,100±300	
D6						3,200±1,200		7,000±3,000	
D7						11,000±3,000	1,700±400	1,900±700	
D8				4,300±1,100		25,000±8,000		2,900±1,100	
D9						4,700±900		1,500±300	
D10						1,800±400		700±200	

*element not detected due to the overlapping of the Cl peaks with the peaks from the Xray tube

Source: The authors.

ter the t-test application, it was possible to verify that Fe results were statistically equal for 21 samples – A4, B2, B3, B5, B8, B10, B15, B16, C2, C4, C5, C6, C7, C8, D1, D2, D5, D6, D7, D9 and D10.

Zn is another element detected in all the samples. The results were statistically equivalent only for twelve samples – B10, B14, B16, C1, C7, D1, D2, D4, D5, D6, D7 and D8, according to the t-test.

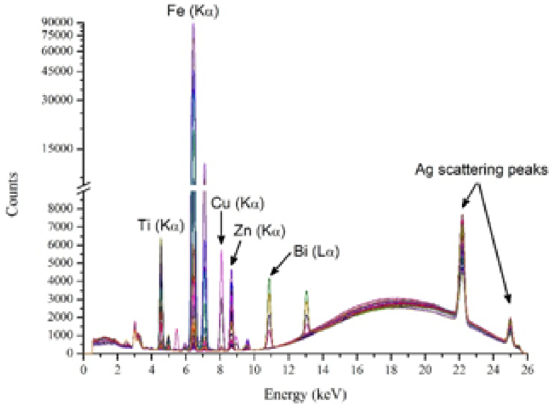
Bi was detected in the four samples from manufacturer A and the results for the samples A1 and A3 proved to be statistically equal after the t-test application.

It is important to emphasize that despite the same technique was used in the results comparison, the quantification procedure was different. While a calibration curve, obtained from mono-element standards from Micromatter™, was used for the portable system results, in the bench top equipment the quantification was performed based in the fundamental parameters, using the spectrometer software.

Principal Component Analysis

Figure 2 shows an overlap of the EDXRF spectra obtained for the 40 eye shadow samples. Each spectrum refers to the average spectrum of 12 measurements.

Figure 2 – Overlap of the EDXRF spectra from the samples analyzed.



Source: The authors.

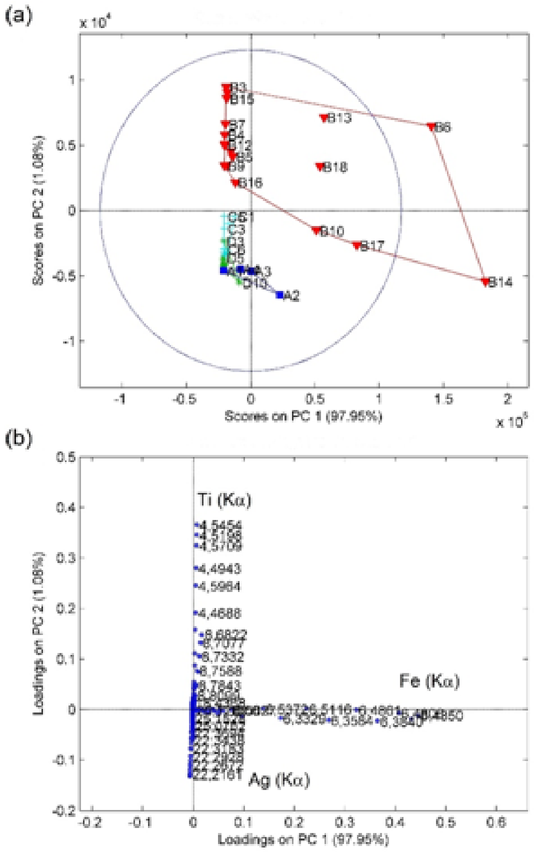
Relying on its multi-dimensional feature, the set of X-ray spectra was evaluated by PCA. The data were mean-centred before the analysis and leave-one-out cross-validation was applied. The entire X-ray spectrum has been considered in the analysis. Figure 3a shows the scores plot of PC1xPC2 and it is possible to verify a separation of the samples. The loadings plot, Figure 3b, shows the relevant variables that provided this separation.

The greater separation is due to the Fe content in each sample and is related to its colors and hues. The samples that stand out in the scores plot exhibit dark colors and hues. It is also possible to verify that the set of samples “B” is separated from the others due to Ti, whereas the sets of samples “A”, “C” and “D” are grouped due to X-ray elastic scattering intensity, expressed in the Ag peaks.

Since the PC corresponding to the Fe content in the cosmetic samples can explain 97.95% of the data variance the same set of EDXRF spectra was evaluated by PCA once again, this time excluding the variables corresponding to Fe-Kα (≈ 6.40 keV) and Fe-Kβ (≈ 7.06 keV) peaks.

Figure 4a shows the scores plot of PC1xPC3. Together, these PCs account for over 65% of the variance contained in the data. A separation of the samples into groups is verified according to the manufacturer. The loadings plot (Figure 4b) shows the relevant variables that provided this separation, i.e., Ti, Zn, Bi and Ag scattering peaks.

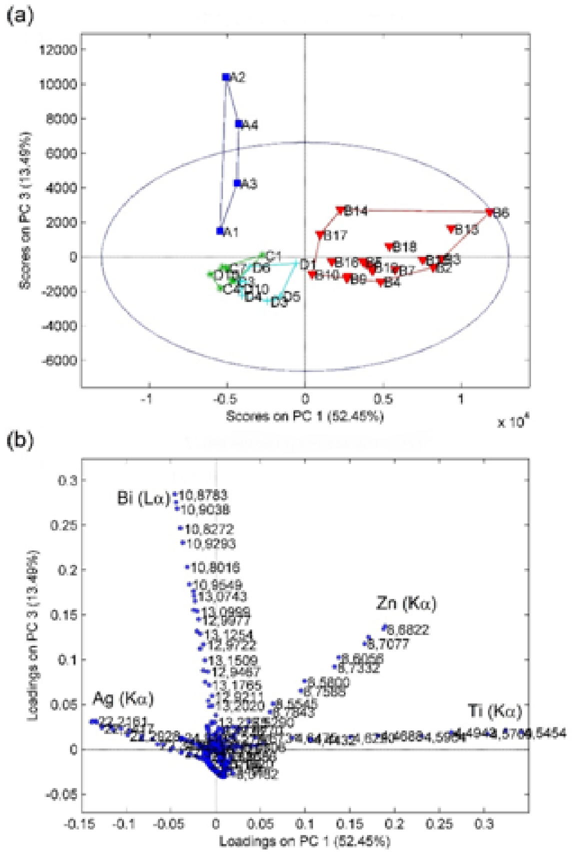
Figure 3 – The (a) scores plot and the (b) loadings plot associated with PC1 and PC2 from principal components analysis of the set of EDXRF spectra set.



Source: The authors.

Confronting the scores and the loadings plot, it is notable that Ti and Zn, and the probable presence of titanium dioxide and zinc stearate, are crucial when discriminating samples from manufacturer "B". The presence of Bi, associated with the additive bismuth oxychloride, is the decisive factor in the separation manufacturer "A" samples. The X-ray elastic scattering peak intensity is responsible for the manufacturers "C" and "D" samples separation, indicating that these samples have higher levels of organic compounds compared to the samples from the other brands. This procedure has direct applications in forensic science for brand identification, where the identification of a particular material can be essential to elucidate the sequence of events in a crime scene or to establish the relationship among subjects and facts.

Figure 4 – The (a) scores plot and the (b) loadings plot associated with PC1 and PC3 from principal components analysis of the set of EDXRF spectra, excluding the variables corresponding to Fe-Kα and Fe-Kβ peaks.



Source: The authors.

Conclusions

With the methodology presented in this study the total content of various inorganic elements were determined in the samples, either as carrier material or as pigments in the manufacture process of eye shadows. Also, the provenance of the cosmetics related to its manufacturer was differentiated.

Portable EDXRF systems present a high-speed analytical technique with minimum sample preparation as well as the possibility of in situ analysis. The X-ray fluorescence methodology associated with principal component analysis presents as a valuable tool for the differentiation and characterization of cosmetics samples. This methodology can be improved in order to be employed in the forensic area as well as in the quality assurance of industries and by the governmental agencies of inspection.

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