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.
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 continue 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.

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.

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   | 0.001109                |
| 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.
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 following equation (1) for thin film samples (VAN GRIEKEN; MARKOWICZ, 2001):

\[ I_i = c_i S_i A \]  

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):

\[ DL = \frac{3}{S_i} \sqrt{\frac{I_{bg}}{t}} \]  

where \( I_{bg} \) 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-established 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\(_3\)Si\(_4\)O\(_{10}\)(OH)\(_2\)) with pigments and zinc (Zn(C\(_{18}\)H\(_{35}\)O\(_{23}\))) or magnesium (Mg(C\(_{18}\)H\(_{35}\)O\(_{23}\))) stearate used as a binder. Kaolin (Al\(_2\)Si\(_2\)O\(_5\)(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\(_2\)O\(_3\)) and hydrate (Cr(OH)\(_3\)), manganese violet (NH\(_4\)MnP\(_2\)O\(_7\)), copper powder and iron blue (C\(_{18}\)Fe\(_7\)N\(_{18}\)) 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 (KAl\(_2\)(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.
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] | Zn [µg/g] | Bi [µg/g] |
|--------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| A1     | 20,000±5,000 | 42,000±6,000 | 2,900±30  | 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     | 100,000±30,000 | 7,200±1,300 | 11,100±1,700 |
| B4     | 53,000±4,000 | 2,760±170 | 8,200±800 |
| B5     | 56,000±4,000 | 29,000±2,000 | 11,000±1,000 |
| B6     | 142,000±18,000 | 730,000±50,000 | 16,200±1,300 |
| B7     | 65,000±7,000 | 4,000±400 | 6,000±500 |
| B8     | 30,000±2,000 | 1,700±150 | 7,400±1,300 |
| B9     | 39,000±6,000 | 2,600±400 | 14,400±1,600 |
| B10    | 10,000±3,000 | 220,000±30,000 | 7,600±800 |
| B11    | 43,000±2,000 | 15,000±1,200 | 6,900±400 |
| B12    | 34,000±4,000 | 1,700±300 | 5,000±1,000 |
| B13    | 100,000±20,000 | 250,000±50,000 | 12,000±5,000 |
| B14    | 180,000±40,000 | 14,000±3,000 | 13,000±2,000 |
| B15    | 48,000±3,000 | 40,000±4,000 | 12,000±5,000 |
| B16    | 390,000±40,000 | 15,300±1,700 |
| B17    | 39,000±3,000 | 175,000±3,000 | 6,390±130 |
| B18    | 11,000±5,000 | 2,500±1,100 | 25,000±11,000 | 15,000±7,000 |
| C1     | 11,000±5,000 | 2,500±1,100 | 25,000±11,000 | 15,000±7,000 |
| C2     | 2,000±2,000 | 1,300±400 | 1,600±400 | 1,800±500 |
| C3     | 1,100±100 | 2,070±180 |
| C4     | 8,000±16,000 | 1,700±400 | 1,400±200 |
| C5     | 6,000±8,000 | 1,510±160 | 1,250±130 |
| C6     | 9,000±6,000 | 2,800±700 | 1,400±400 |
| C7     | 15,600±1,100 | 2,900±300 | 2,100±1,200 |
| C8     | 13,000±700 | 73,000±12,000 | 1,050±190 |
| D1     | 49,000±19,000 | 37,000±16,000 | 17,000±7,000 |
| D2     | 31,400±1,300 | 4,200±600 |
| D3     | 5,050±70 | 1,430±130 |
| D4     | 3,000±900 |
| D5     | 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     | 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.

After 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<sup>TM</sup>, 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.

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.

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.

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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