

Article

Portable EDXRF for Quality Assurance of Cosmetics

Fábio Luiz Melquiades *, Paulo Sérgio Parreira †, Lucas Yoshimi Endo, Geiele dos Santos, Luana Wouk and Otávio Portezan Filho †

Physics Department, Universidade Estadual de Londrina, Campus Universitário, PR 445, km 380, P.O. Box 10011, Postal code 86057-970, Londrina, Brazil; E-Mails: parreira@uel.br (P.S.P.); lucasyendo@yahoo.com.br (L.Y.E.); geielle@hotmail.com (G.S.); luanawouk@yahoo.com.br (L.W.); otavio@uel.br (O.P.F.)

† These authors contributed equally to this work.

* Author to whom correspondence should be addressed; E-Mail: fmelquiades@uel.br; Tel.: +55-43-3371-4266; Fax: +55-43-3371-4166.

Academic Editor: Amparo Salvador-Carreño

Received: 25 April 2015 / Accepted: 11 August 2015 / Published: 18 August 2015

Abstract: Portable Energy Dispersive X-ray Fluorescence is a viable, cost and time effective analytical technique for qualitative and quantitative evaluation of a wide range of samples. The objective of this study is to present a methodology for quantification of nail polishes, eye shadows, lipsticks and lip gloss using thin film geometry. The samples were applied over thin films, simulating its use on face and nails. It was possible to quantify S, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr, Ba and Bi. The methodology is viable and could be useful to forensic science, quality control on industry of raw materials or final products and supervision by regulatory agencies.

Keywords: X-ray fluorescence; cosmetic; heavy metal

1. Introduction

X-ray Fluorescence (XRF) in its various forms is a powerful, well established and mature technique with a wide range of application, like geology, chemistry, environment, industry, forensic, pharmaceuticals, archaeology, biology and others. Specifically, Energy Dispersive X-ray Fluorescence (EDXRF) is one of the atomic spectrometric techniques that allow portable use on field [1]. It is

remarkable how quickly hand-held and mobile EDXRF instrumentation has developed in the last 3 years in different areas and applications [2,3], providing a viable, cost and time effective approach for on-site analysis of a variety of samples. Also, an important industrial use of XRF is in the routine on-line analysis of raw materials and final products.

The physical principle is based on the fact that elements present in a sample, after been irradiated by an energetic external X-ray beam, have a certain probability of emitting characteristic X-rays which are detected and evaluated, conducting to qualitative and quantitative knowledge of the chemical elements in the sample.

EDXRF offers simultaneous determinations of chemical elements from Na to U (typically used for metals determination), high speed measurements (time ranging from 5 to 1000 s depending on the sample and goals) and even the advantages and limitations are well understood. Its instrumentation has viable costs and is easy to operate comparing to others analytical techniques. EDXRF is a non-destructive technique that can be applied to any kind of liquid or solid sample (thick, intermediate or thin thickness, in small quantities starting from 0.1 mg), with reduced steps of samples preparation or even eliminating handling. It has sufficient sensitivity for qualitative and quantitative determination reaching detection limits of tenths of ppm from trace elements depending on the measurements conditions.

In the literature, the use of XRF applied to cosmetic samples, encompasses a wide variety of products, although it is not vast. There are some scientific papers related to the use of this technique for characterization of face powder [4], lip and eye products [5,6] nail polish [7,8], presenting the concentration results of several metals, including toxic elements. A detailed study about the quantification of inorganic elements in sunscreen and the determination of solar protection factor due to Ti or Zn contents in sunscreen products were developed by Melquiades *et al.* [9] and Melquiades *et al.* [10] using a portable EDXRF system.

The objective of this paper is to present the advantages and the possibilities of portable EDXRF as a qualitative and quantitative methodology for elemental characterization of a great variety of cosmetic samples. Specifically, a methodology for quantification of nail polishes, eye shadows, lipsticks and lip gloss using thin film geometry, is presented using a portable home made EDXRF system.

2. Experimental Section

2.1. X-ray Fluorescence Physical Principles

XRF phenomenon is based on photoelectric effect. When an external beam of X-rays impinges on a sample it will interact with the atoms and, if the X-ray energy is sufficient to remove an inner shell electron, the atom will be in an excited or ionized state. The instability of the atom, leads to a set of transitions, in which an electron from outer orbital shell fills the vacancy left by the ejected electron, thus generating a new vacancy that will be filled by another electron and so on. Each electron transition is accompanied by emission of a characteristic X-ray whose energy is equal to the difference between the orbital levels involved in the transition. The emission probability of characteristics X-rays is denoted as fluorescence yield and it has different behavior for each atom. For example, Auger electrons emission dominates over characteristics X-ray emission for low atomic number elements ($Z < 15$) [11].

The coherent and incoherent scattering also occurs in XRF as a consequence of the incident X-ray beam interaction with matter. The scattering contributes to the background radiation and to the increase detection limit. The probabilities of both kinds of scatterings depend on the incident beam energy and the composition of the sample, mainly the incoherent scattering, also known as Compton scattering, could be used to perform corrections of non-homogeneous samples, its moisture, and infer some implicit parameters of the samples [12].

EDXRF measurements generate a spectrum with characteristics X-ray peaks, scattering peaks and the continuum background. Qualitative results are obtained identifying the element that corresponds to each peak and quantification results, *i.e.*, the concentration, is proportional to the number of X-rays detected, obtained from the net area of the characteristics peaks. Due to multielement determination interferences and enhancement among elements are the main effects that must be evaluated in order to obtain accurate results.

2.2. Instrumentation

XRF instrumentation comprises an external radiation source, commonly an X-ray tube, the sample holder and a detection system. Geometry is one of the main precautions to be considered in EDXRF measurements to guarantee reproducibility and robustness of results.

The equipment used in this study is a home-made EDXRF system composed by a mini X-ray tube (Ag target, 4 W, Moxtek Inc., Orem, UT, USA), with 50 μm thick Ag filter and a Si-PIN X-ray detector (FWHM 221 eV for Mn 5.9 keV line, 25 μm Be window, Amptek Inc., Bedford, MA, USA), with miniaturized conventional electronics for data acquisition. At the detector entrance, a 3 mm diameter Ag collimator was used. The measurement conditions were: 28 kV, 10 μA , and measurement time ranging from 200 to 500 s.

As the X-ray tube spot is about 0.7 cm diameter, four measurements were performed by rotating the sample cup to guarantee irradiation of the complete sample area in the XRF cup. The results are the average of these measurements.

In all the cases presented in this study were performed analyses at the laboratory, although the equipment could be used on field.

2.3. Samples

The samples were obtained in the local market of Londrina municipality, Brazil, and comprise the most used brands and colors of different cosmetics. Samples of lipsticks, glitter lipsticks, nail polishes and eye shadows were analyzed without any kind of chemical preparation, just applying each sample over thin films placed on conventional 32 mm diameter XRF cups, according to the following description:

Nail polish: A total of 32 samples of 16 different brands of several colors and types. The samples were applied in a parchment paper using the brush of its own flask.

Eye shadow: A total of nine samples from the same makeup case of 9 different colors. The samples were applied over parchment paper using the brush of its own flask.

Lipstick: A total of 32 samples from 20 different brands of several colors. A thin layer of each lipstick sample was applied over a 6 μm Mylar film placed on a conventional XRF cup.

Lip gloss: Just two samples of glitter were analyzed because there is a drying problem with the samples due to the viscosity of the material. The samples were applied over 6 μm Mylar film using the brush of its own flask.

This sample preparation procedures avoid digestion or dilution of the samples and are in agreement with Green Chemistry principles. It is simple and fast.

2.4. Quantification Procedure

The quantitative evaluation of element concentrations in EDXRF methodology is given by the relationship between the fluorescence intensity of the characteristic Ka or La line and the concentration of an element in the sample, according to fundamental parameters equation [13]:

$$I_i = C_i \cdot S_i \cdot A \quad (1)$$

in which I_i is the characteristic X-ray net intensity (cps), C_i the concentration ($\mu\text{g}\cdot\text{g}^{-1}$), S_i the elementary sensitivity of the analyzed element i ($\text{cps}\cdot\text{g}^{-1}\cdot\text{cm}^2$), and A the absorption factor. This equation considers the X-ray source as a monochromatic radiation and the absent of inter-element effects. Also, specifically in this study, it can be considered the samples in thin film geometry (as the samples were spread over thin films), which makes the A factor equal to 1. The maximum surface density to guarantee thin film geometry is $0.0135 \text{ g}\cdot\text{cm}^{-2}$ [12]. In this study all the samples satisfy this condition.

To quantify the samples, mono-elements standards on polycarbonate membranes from MicroMatter were irradiated, and the known concentration of each metal is correlated with its peak intensity for sensitivity determination. The media differences among Micromatter blank, mylar and parchment paper were evaluated and peak to background ratio are equivalent up to 10 keV. For higher energy values the background increases for parchment paper, but in this study it was not an impediment.

The detection limits (DL) and quantification limits (QL) were determined according to equations detailed by Currie, 1968 [14], which consider 3 times and 10 times, respectively, the square root of the background divided by the sensitivity and measurement time [15].

The performed analysis is considered a semi-quantitative procedure due to the use of Micromatter standards as a reference for sensitivity determination. The real-world samples are prepared on different media and thicknesses and consequently will have a small difference in the response.

3. Results and Discussion

Portable EDXRF allows on-line qualitative results of the elements present in the samples according to the different peaks in the measured spectra. Figure 1 shows the overlapped spectra of the different matrix analyzed in this study. The main difference is on the final part of the spectra, which includes the scattering peaks from the X-ray source target, Ag in this case. The intensity and shape of this region is related with the density and composition of the basic raw material used in each cosmetic.

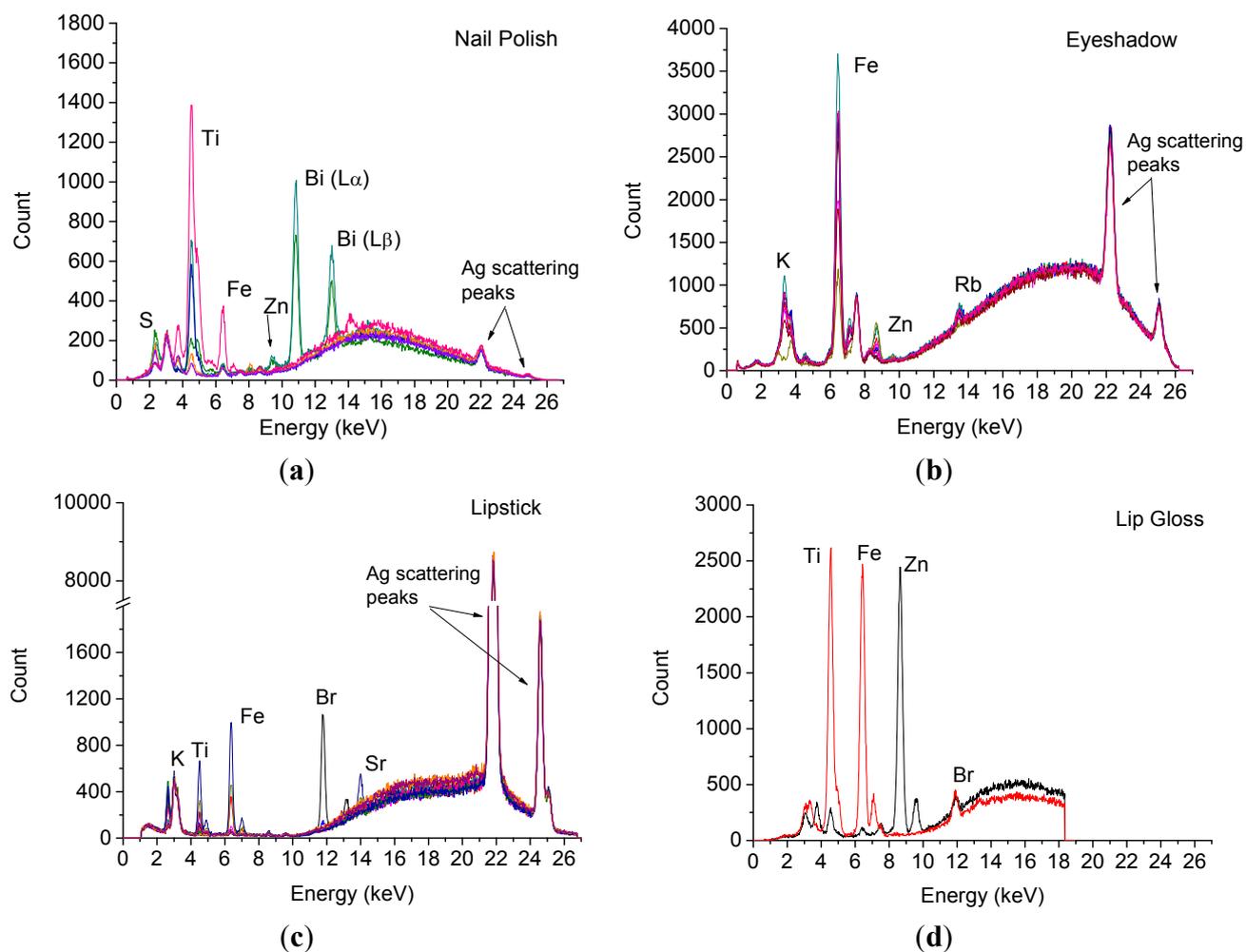


Figure 1. Overlapped Energy Dispersive X-ray Fluorescence (EDXRF) spectra of different cosmetic matrix (a) six spectra of nail polishes, (b) nine spectra of eye shadow, (c) 12 spectra of lipstick, (d) two spectra of lip gloss.

3.1. Nail Polish

The concentration results from nail polishes samples are presented at Table 1. The great significant difference in elemental composition is due to the expressive difference between samples. For example, one of the samples is a magnetic nail polish in which the Fe concentration is two magnitude orders greater than the other samples. The presence of S in almost all the samples indicate the presence of TSFR compound that is responsible for contact dermatitis in people with sensibility to this element [16]. Bismuth is not so common, although it has been increasingly used as a compound for pearlescent pigment or lubricating agent effect [17].

Table 1. Range of concentration for nail polishes with the respective detection limit (DL) and quantification limit (QL). Values in $\text{mg}\cdot\text{kg}^{-1}$.

Element	Range of Concentration	Number of Samples	DL	QL
S	14,077–121,782	28	239	797
Ca	69–23,039	22	7.4	25
Ti	329–58,421	27	4.1	14
Fe	23–98,353	28	1.4	4.6
Cu	19–337	13	1.3	4.3
Zn	7–269	19	0.8	2.8
Bi	935 ± 11 1,644 ± 17	2	1.9	6.4

3.2. Eye Shadow

Results for the eye shadows samples set are at Table 2. In this case, the aim is to show the concentration variation due to different colors of the same set of samples. For example the presence of Cu was verified in green eye shadow indicating the contribution of an inorganic pigment based on this element. The presence of Rb is related with the origin of the raw material used as base matrix of the powder. Variations in K, Ti and Fe concentration are correlated, decreasing with the tone of the shadows, on which the high concentrations are related to the dark coloring of these samples.

Table 2. Range of concentration for eye shadows with the respective detection limit (DL) and quantification limit (QL). Values in $\text{mg}\cdot\text{kg}^{-1}$.

Element	Range of Concentration	Number of Samples	DL	QL
K	2,287–29,320	9	226	765
Ca	3,995–10,923	9	165	546
Ti	308–1,264	9	83	269
Mn	105–346	9	31	101
Fe	4,871–14,689	9	31	90
Cu	138 ± 8	1	20	54
Zn	93–524	9	20	54
Rb	291–546	8	61	194

3.3. Lipstick

Table 3 presents the results for lipstick samples. The presence of Br, Bi and Ba deserve to be highlighted because they are considered heavy metals and toxic elements responsible for illness effect. Bromine is commonly used in red and purple lipstick. Bismuth as mentioned before is used in lipstick as lubricating agent. Barium in the form of barium sulfate is still used in some cosmetic formulations [18]. Although allowed by cosmetic rules in specific compounds, these elements are not essential for human health and under high exposition can cause disease.

Table 3. Range of concentration results from lipstick samples with the detection limit (DL) and quantification limit (QL). Values in $\text{mg}\cdot\text{kg}^{-1}$.

Element	Range of Concentration	Number of Samples	DL	QL
K	731–5,347	3	53	117
Ti	691–13,019	17	50	168
Mn	69–168	4	14	48
Fe	185–16,377	22	25	84
Zn	72–2,851	4	17	57
Br	510 \pm 93 2,258 \pm 450	2	64	212
Sr	254–1,170	4	62	205
Bi	14,138 \pm 2,827	1	160	532
Ba	58,170 \pm 11,634 90,506 \pm 18,101	2	324	1097

3.4. Lip Gloss

The results for two different brands of lip gloss are at Table 4. It is evident the differences on its elementary compositions. The chemical elements that were coincident have higher concentrations on sample 2. Gloss 1 is light rose color and is more liquid than Gloss 2 that is highly viscous and dark red. As mentioned for the lipstick, K, Ti and Fe concentrations have relation with the intensity of the colors.

Table 4. Concentration results for the two lip gloss samples with the detection limit (DL) and quantification limit (QL). Values in $\text{mg}\cdot\text{kg}^{-1}$.

Element	Gloss 1	Gloss 2	DL	QL
K	317 \pm 45	2,346 \pm 296	73	239
Ca	1,289 \pm 99	<QL	53	170
Ti	617 \pm 55	11,690 \pm 1,619	25	84
Mn	<QL	52 \pm 7	9	29
Fe	17 \pm 3	4,290 \pm 594	7	25
Zn	1,223 \pm 92	<QL	4	13
Br	68 \pm 5	197 \pm 23	9	28

4. Conclusions

Portable EDXRF is a viable technique for fast characterization of cosmetic samples. The cost-benefit of portable systems and the possibility of analysis on field without sample preparation are the main advantages. In this study, the samples were applied on thin films, simulating the real use of its product, which are rubbed on the eyes, lips or nails, but no consideration was done about the quantity of sample compared to the amount applied in the skin. The thin film geometry of analysis with calibration standards allows us to obtain very satisfactory results. It was possible to quantify S, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr, Ba and Bi. The main limitation is the quantification limits that are in the order of tenths of ppm. The procedure could be applied to forensic application, quality control on industry of raw materials or final products and supervision by regulatory agencies.

Acknowledgments

This work was sponsored by CNPq 483840/2013-0 (National Council for Scientific and Technological Development). The authors also thanks to the students: Lais Novaes Maia, Ana Carolina Gomes Mantovani, Rafael Molari and Guilherme Nogueira for their collaboration in samples preparation and measurements.

Author Contributions

Authors Paulo Sérgio Parreira, Otávio Portezan Filho and Fábio Luiz Melquiades designed the experimental protocol, supervised eye shadow, nail polish and lipstick analysis, respectively. Lucas Yoshimi Endo, Geiele dos Santos and Luana Wouk conducted the preparation, measurements and analysis, respectively. Fábio L. Melquiades wrote the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Melquiades, F.L.; Appoloni, C.R. Application of XRF and field portable XRF for environmental analysis. *J. Radioanal. Nucl. Chem.* **2004**, *262*, 533–541.
2. West, M.; Ellis, A.T.; Potts, P.J.; Strelci, C.; Vanhoof, C.; Wobrauschek, P. 2014 Atomic spectrometry update—A review of advances in X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.* **2014**, *29*, 1516–1563.
3. West, M.; Ellis, A.T.; Potts, P.J.; Strelci, C.; Vanhoof, C.; Wegrzynek, D.; Wobrauschek, P. 2013 Atomic spectrometry update—A review of advances in X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.* **2013**, *28*, 1544–1590.
4. Kulinov, E.; Latham, K.; Adams, M.J. Classification and discrimination of some cosmetic face powder using XRF spectrometry with chemometric data analysis. *X-ray Spectrom.* **2012**, *41*, 410–415.
5. Liu, S.; Hammond, S.K.; Rojas-Cheatham A. Concentration and Potencial Health Risks of Metal in Lip Products. *Environ. Health Perspect.* **2013**, *121*, 705–710.
6. Nnorom, I.C.; Igwe, J.C.; Oji-Nnorom, C.G. Trace metal contents of facial (make-up) cosmetics commonly used in Nigeria. *Afr. J. Biotechnol.* **2005**, *4*, 1133–1138.
7. Misra, G.; Sawhney, K.J.S.; Lodha, G.S.; Mittal, V.K.; Sahota, H.S. The Application of Energy-dispersive X-ray Fluorescence Spectrometry to the Analysis of Cosmetic Evidence in Indian Nail Polishes. *Appl. Radiat. Isot.* **1992**, *43*, 609–614.
8. Murphy, T.; Lim, S.; Huong, S.P.; Irvine, K.; Bayen, S.; Kelly, B.C.; Wilson, K. Application of Handheld X-ray Fluorescence Analyzers to Identify Mercury in Skin-Whitening Creams in Cambodia. *J. Health Pollut.* **2012**, *2*, 21–31.
9. Melquiades, F.L.; Ferreira, D.D.; Appoloni, C.R.; Lopes, F.; Lonni, A.G.; Oliveira, F.M.; Duarte, J.C. Titanium dioxide determination in sunscreen by energy dispersive X-ray fluorescence methodology. *Anal. Chim. Acta* **2008**, *613*, 135–143.

10. Melquiades, F.L.; Appoloni, C.R.; Lonni, A.G.; Ferreira, D.D.; Lopes, F. Determination of Inorganic Elements in Sunscreen by Using Energy Dispersive X-Ray Fluorescence. *Lat. Am. J. Pharm.* **2010**, *29*, 1000–1003.
11. Barnard, M.; Burgess, C.; Edwards, D.; Hill, S.J.; Jarvis, K.E.; Lord, G.; Sargent, M.; Potts, P.J.; West, M. Evaluation of analytical instrumentation. Part XX Instrumentation for energy dispersive X-ray Fluorescence. *Accredit. Qual. Assur.* **2006**, *11*, 610–624.
12. Van Grieken, R.E.; Markowicz, A.A. *Handbook of X-ray Spectrometry*, 2nd ed.; Marcel Dekker Inc.: New York, NY, USA, 2002.
13. Bertin, E.P. *Principles and Practice of X-ray Spectrometric Analysis*; Plenum Press: New York, NY, USA, 1970.
14. Curie, L.A. Limits for quantitative detection and quantitative determination. *Anal. Chem.* **1968**, *40*, 586–593.
15. Melquiades, F.L.; Parreira, P.S.; Appoloni, C.R.; Silva, W.D.; Lopes F. Quantification of metals in river water using a portable EDXRF system. *Appl. Radiat. Isot.* **2011**, *69*, 327–333.
16. Park, M.E.; Zippin, J.H. Allergic Contact Dermatitis to Cosmetics. *Dermatol. Clin.* **2014**, *32*, 1–11.
17. Patty-Beliles, R.P. The metals: Bismuth. In *Patty's Industrial Hygiene and Toxicology*, 4th ed.; Clayton, G.D., Clayton, F.E., Eds.; John Wiley & Sons: New York, NY, USA, 1994; Volume 2, pp. 1948–1954.
18. Rastogi, S.C.; Pritzl, G. Red lipstick: A source of barium to humans and the environment. *Bull. Environ. Contam. Toxicol.* **1998**, *60*, 507–510.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).