BJRS

BRAZILIAN JOURNAL
OF
RADIATION SCIENCES
09-01A (2021) 01-13

Elementary Analysis of Nail Polishes

Narloch[a] D.C., Paschuk[a] S. A., Torres[a] C. A. P., Corrêa[b] J. N.

[a] *Graduate Course in Electrical Engineering and Industrial Informatics/Federal Technological University of Paraná, 80230-901 Curitiba, Paraná, Brazil*

[b]*Civil Construction Academic Department/Federal Technological University of Paraná, 81280-340 Curitiba, Paraná, Brazil*

daninarloch@hotmail.com

ABSTRACT

Brazil is considered the 4th largest Cosmetics Toiletriesand Perfumary (CT&F) Market in the world. In 2017, the country earned R$ 102.5 billion, which means an increase of 3.2% over the year 2016. According to Associação Brasileira da Indústria de Higiene Pessoal, Perfumaria e Cosméticos (ABIHPEC), this information is provided by Strategic Research Institute for Consumer Markets, the Euromonitor. The composition of cosmetics produced should be in accordance with the recommendations presented in ANVISA RDC Resolution No. 83 of June, 2016. Prohibited elements in the RDC Resolution No. 83 are Cl, Ni, As, Be, Cd, Cr, I, P, Pb, Hg, Se, Zr, Co, Te, Tl and radioactive substances. The main purpose of this work was to characterize some nail polishes using EDXRF method. The analyses were made using EDXRF method at the Laboratory of Applied Nuclear Physics of the UTFPR. The AMPTEK portable X-ray equipment is composed of mini X-ray tube, model MINI X, with Ag and Au targets, as well as silicon drift detector, SDD-123 model. Qualitative analyses indicate Na, Mg, Al, Si, P, Na, S, Cl, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ba and Bi elements in the nail polishes analyzed. Some prohibited elements such as Cl, Ni and P were presents in nail polishes. It is shows that EDXRF method is very efficient in detecting the chemical elements present in these samples. Besides, these results enable to compare elements presents in sample and recommendation stablish in Resolution No. 83.

Keywords: **Cosmetics, Toxic metals, X-ray fluorescence.**

ISSN: 2319-0612
Accepted: 2020-11-15

1. INTRODUCTION

Nail polishes are cosmetics classified as category 1 according to Brazilian Health Regulatory Agency (ANVISA). These products present basic or elementary properties, which do not require initially of verification detailed information, because they have minimal risk [1].

Brazil is considered the 4th largest Cosmetics Toiletries and Perfumary (CT&F) Market in the world. In 2017, the country earned R$ 102.5 billion, which means an increase of 3.2% over the year 2016. According to Associação Brasileira da Indústria de Higiene Pessoal, Perfumaria e Cosméticos (ABIHPEC), these informations are provided by Strategic Research Institute for Consumer Markets, the Euromonitor [2].

Because the increase of consumption of cosmetics in Brazil it becomes necessary to know more about the safety of these products. Nail polish is composed of color pigment, volatile solvent and nitrocellulose. Two components can be added to nitrocellulose such as the resin and tosylamide formaldehyde, also known as toluene sulfonamide formaldehyde resin (TSRF). Both components can cause allergic contact dermatitis in some individuals. Hypoallergenic nail polishes minimize the risk of allergy, because it does not contain TSRF. This resin is replaced by polyester resin or cellulose acetate butyrate [3]. In nail polishes elementary composition is possible to find the elements such as V, Mn, Ni, Cu, Zn, As, Br, Ag, I, Ba, Hg, Pb, Bi, Cr, Co, Al, S, Ti and Fe in different amounts [4-7]. Although some elements are not toxic, if present in the human body in high concentrations can become toxic and cause health damage [8].

In the case of nail polishes, individuals are exposed by contact with the skin and / or inhaled during the nail polishes application, as well as when the nails are bitten or chewed, and the nail polishes ingested [7].

There are around 50 elements present in biological systems, which can be classified as essential, environmental microcontaminants and essential elements and simultaneously environmental microcontaminants. The essential elements can be subdivided into macroelements, trace elements and elements in ultra-trace. Macroelements are Na, K, Mg and Ca because they are in the human organism in the order of a few grams. On the other hand, trace elements Fe, Zn, Cu, Mn are in the order of a few milligrams. These elements may be toxic if they present concentrations higher than those necessary to provide for the operation of biological systems. The elements V, Cr, Mo, Co, Ni, Si, As, Se and B, are ultra-trace because they are in the order of a few microgram-nanograms [8].

Environmental microcontaminants can be natural origin and / or human activity. The elements with these characteristics are Pb, Cd, Hg, Be, Tl, Sb, W, Al, Sn and Ti. The essential elements and simultaneously environmental microcontaminants are Cr, Mn, Ni, Fe, Zn, As, Mo and Co [8]. Nickel element present in some nail polishes can also cause adverse reactions to individuals [9].

Aluminum is a metal found abundantly in the earth's crust. Therefore, exposure to aluminum becomes frequent. One of the forms of exposure is through the use of cosmetics. Bioaccumulation of this element may result in neurological damage and bone problems [8].

Due to the risks caused by the bioaccumulation of metals and other chemical substances in the human organism, there are national and international resolutions about limits to cosmetic compositions and list with prohibited substances [10-14].

ANVISA RDC Resolution No. 79 of August 28, 2000, allows the use of artificial organic dyes provided that the maximum amounts of metal impurities for cosmetics, such as 500 ppm (parts per million) for barium chloride, 3 ppm for arsenic, 20 ppm for lead and 100 ppm for heavy metals [10].

ANVISA RDC Resolution No. 83 of June, 2016, invalidates some provisions of RDC Resolution No. 48 of March 16, 2006 [11, 12]. Resolution updated increased number of substances prohibited in personal care products, cosmetics and perfumes, based on the list of substances prohibited in the European Union document. Elements such as Cl, Ni, As, Be, Cd, Cr, I, P, Pb, Hg, Se, Zr, Co, Te, Tl and radioactive substances are in the list [11, 13].

On the other hand, Canadian legislation establishes that toxic metals such as Pb, As, Cd, Hg and Sb should not be used as ingredients. However, because of presence these metals in the environment and mineral ore they may be found as impurities. In this way, the legislation allows the limit of 10 ppm for impurities [14].

Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF) is widely used for characterization of materials (solid, liquid, metallic or non-metallic). One of the advantages of this method is that it does not usually require preparation of the samples, that is, a non-destructive analysis [15].

In this context, there are few studies in the literature about the nail polishes elementary characterization [4-7; 16-17]. Besides new nail polishes are produced and sold on the market. Wherefore, the main of this work was to characterize nail polishes of Brazilian market using EDXRF method.

2. MATERIALS AND METHODS

Present survey was performed using 44 samples of cream nail polishes marketed in Brazil, which were analyzed using EDXRF method at the Laboratory of Applied Nuclear Physics of the Federal University of Technology of Paraná (UTFPR), located at city of Curitiba, Brazil. Samples were chosen as follows: light pink (10 brands), white (9 brands), red (9 brands), purple (7 brands), light brown (5 brands) and gray (4 brands). Each sample was deposited in acetate containers with the supplied brush of the nail polish, in order to avoid contamination and to ensure the homogeneity of the samples. The measurements were performed after the nail polishes were dried. Each sample has an area of 1.5 cm^2 and thickness of 0.2 cm.

Samples were identified with a letter and a number. The letter identifies the brand and associated number indicates the color. For example, “A1” sample means that it belons to “A” brand and it has white color (see Tables 1, 2 and 3).

The AMPTEK portable X-ray equipment is composed of mini X-ray tube, model MINI X, with silver (Ag) and gold (Au) targets, as well as silicon drift detector, SDD-123 model, together with the DP5 digital signal processor (Figure 1). In this work, the Ag and Au X-ray tubes were used.

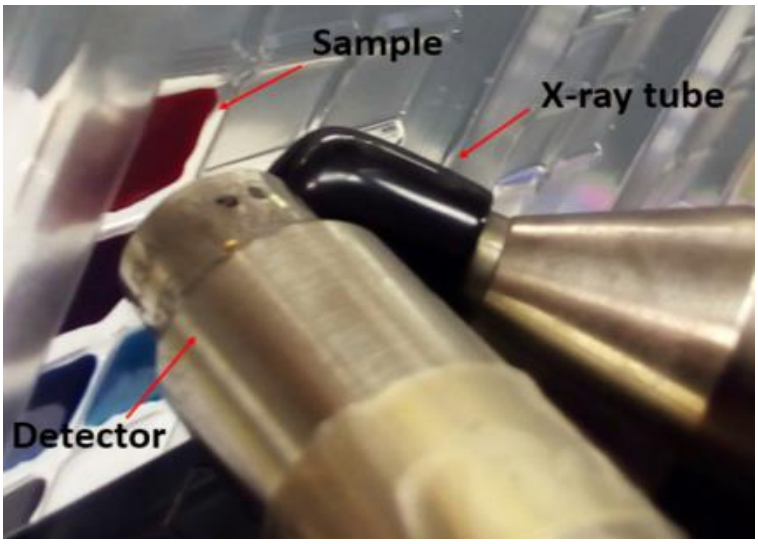

Figure 1: The AMPTEK portable X-ray equipment and sample
Source: Own authorship

The samples were submitted to measurements at three different points with energy of 40 kV, current of 15 μA, acquisition time of 900s and collimator of 1 mm in diameter. These parameters were chosen because is necessary to identify all possible elements presents in samples.

3. RESULTS AND DISCUSSION

EDXRF method allowed to identify the elements present in the nail polishes of different brands and colors by qualitative analysis. The choice of using the two X-ray tubes (Au and Ag target) was fundamental to obtain the results more complete. Tables 1, 2 and 3 show all detected elements with EDXRF method.

Table 1: Detected elements in nail polishes samples with EDXRF methods

Brand	Color	Color Code	Elements
A	White	1	Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn.
B			Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn.
C			Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn.
D			Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn.
E			Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn.
F			Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn
G			Al, Si, S, Ca, Ti, Fe, Ni.
H			Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn.
I			Al, Si, S, Ca, Ti, Fe, Ni, Cu.
J			
A	Gray	4	Mg, Al, Si, Cl, K, Ca, Ti, Fe, Ni, Cu
B			
C			Mg, Al, Si, S, Cl, K, Ca, Ti, Fe, Ni, Cu
D			Mg, Al, Si, S, Cl, K, Ca, Ti, Fe, Ni, Cu
E			
F			
G			Mg, Al, Si, Cl, K, Ca, Ti, Fe, Ni
H			
I			
J			

Table 2: Detected elements in nail polishes samples with EDXRF methods

Brand	Color	Color Code	Elements
A	Pink	7	Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
B			Mg, P, Al, Si, Ca, Ti, Fe, Ni, Cu, Bi
C			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
D			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
E			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
F			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
G			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
H			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
I			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
J			Mg, Al, Si, Ca, Ti, Fe, Ni, Cu
A	Brown	10	
B			Mg, P, Al, Si, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Ba
C			Mg, Al, Si, Cl, K, Ca, Ti, Fe, Ni, Cu, Zn, Ba
D			Mg, P, Al, Si, Cl, K, Ca, Ti, Fe, Ni, Cu, Zn
E			
F			Mg, P, Al, Si, Cl, Ca, Ti, Fe
G			Mg, P, Al, Si, Cl, K, Ca, Ti, Fe, Mn, Ni
H			
I			
J			
A	Red	13 e 14	Mg, Al, Si, P, S, Cl, Fe, Ni, Cu, Zn, Ba, Sr
B			Mg, Al, Si, S, Cl, K, Ca, Cr, Fe, Ni, Ba, Sr
C			Mg, Al, Si, S, Cl, K, Ca, Fe, Ni, Cu, Zn, Ba, Sr
D			Mg, Al, Si, S, Cl, K, Ca, Fe, Ni, Cu, Zn
E			Mg, Al, Si, S, Cl, K, Ca, Cr,Ti, Fe, Ni, Cu, Zn
F			Mg, Al, Si, S, Cl, Ca, Fe, Ni, Ba
G			Al, Si, S, Cl, K, Ca, Fe, Ba
H			Mg, Al, Si, S, Cl, Ca, Cr, Fe, Ni, Zn, Ba, Sr
I			Mg, Al, Si, S, Cl, Ca, Cr, Fe, Ni, Cu, Zn, Ba
J			

Table 3: Detected elements in nail polishes samples with EDXRF methods

Brand	Color	Color Code	Elements
A	Purple	16	Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn
B			Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, Ba
C			Mg, Al, Si, S, Cl, Ca, Ti, Fe, Ni, Cu, Zn
D			Mg, Al, Si, S, Cl, Ca, Ti, Fe, Ni, Cu, Zn
E			
F			
G			
H			Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, Ni, Cu
I			Mg, Al, Si, S, Ca, Ti, Fe, Cu, Mn
J			Mg, Al, Si, S, Ca, Ti, Fe, Ni, Cu, Zn

All the white nail polishes analyzed have in their formulation the following elements Al, S, Ca, Ti, Fe and Ni. The Cu and Zn elements are present in 8 and 7 samples, respectively. Only the H1 sample does not contain the Si element. Figure 2 shows EDXRF spectra from white nail polishes with Au target.

The gray nail polishes are composed of Mg, Al, Si, Cl, K, Ca, Ti, Fe and Ni. Only the G4 sample has no copper in its formulation or its quantity is below the detection limit. Sulfur is present in C4 and D4 samples.

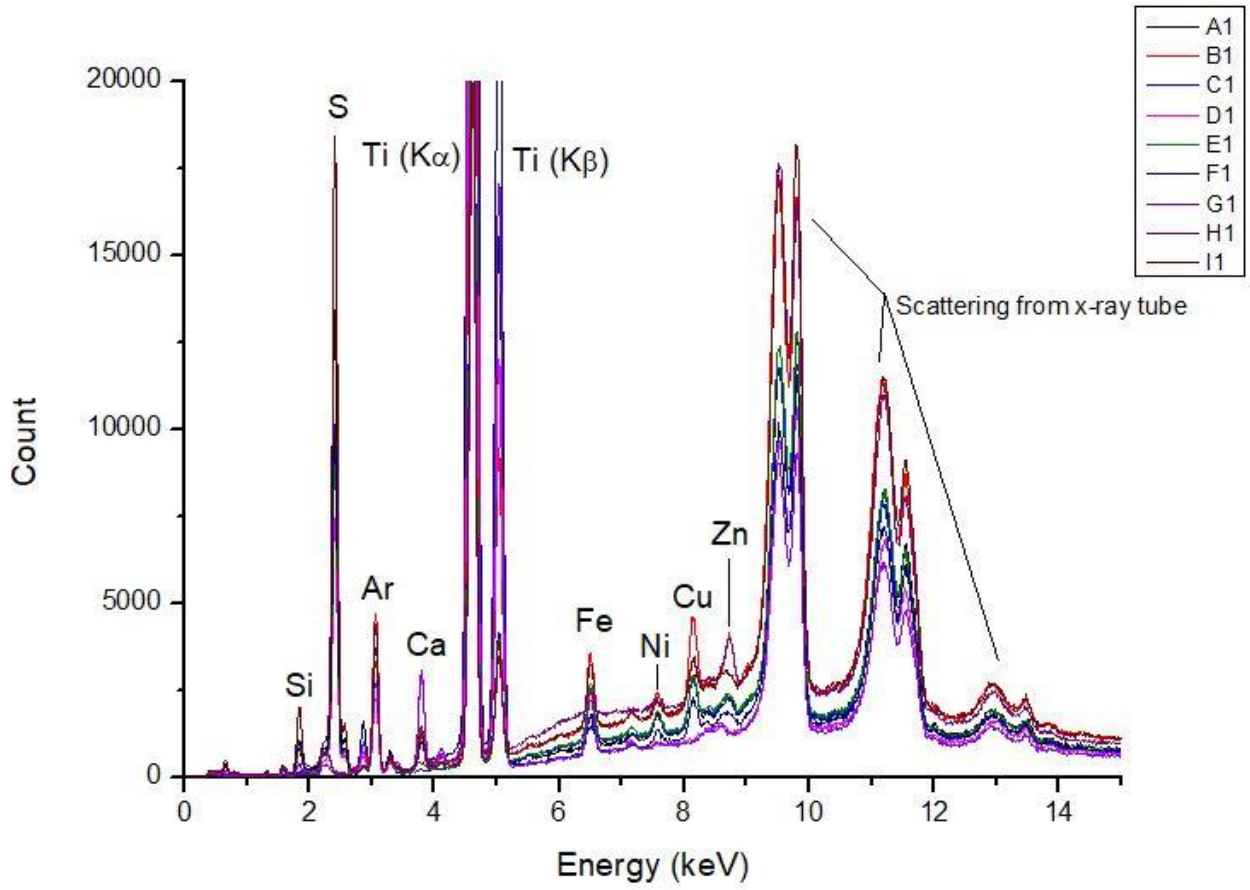

Figure 2: EDXRF spectra from white nail polishes
Source: Own authorship

The predominant elements in the pink nail polishes are Mg, Al, Si, Ca, Ti, Fe, Ni and Cu. Only B7 sample consists of P and Bi in its composition (Figure 3). Analyses from Ag tube allowed better identification of bismuth element, because it detected three emission lines of this element, while the analysis performed with the Au tube pointed only the line Mα, the other lines were overlap with the spreading lines of the Au.

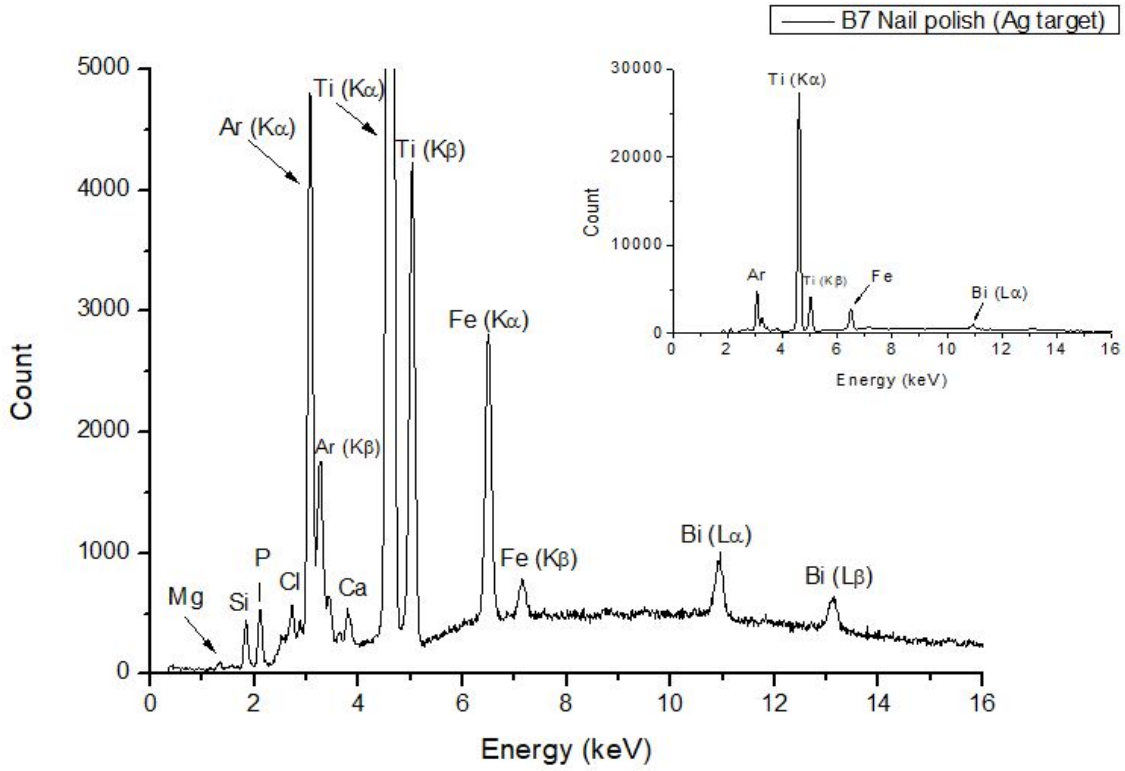

Figure 3: EDXRF spectra from pink nail polishes
Source: Own authorship

Brown nail polishes are composed of Mg, Al, Si, Cl, Ca, Ti and Fe (Figure 4). Only sample C10 does not contain phosphorus. Manganese is present in B10 and G10 samples. The F10 sample does not have Ni and K in its composition. The elements Cu and Zn are present in B10, C10 and D10 samples. The Ba element was found in B10 and C10 nail polishes and the Mn element in only one sample (B10).

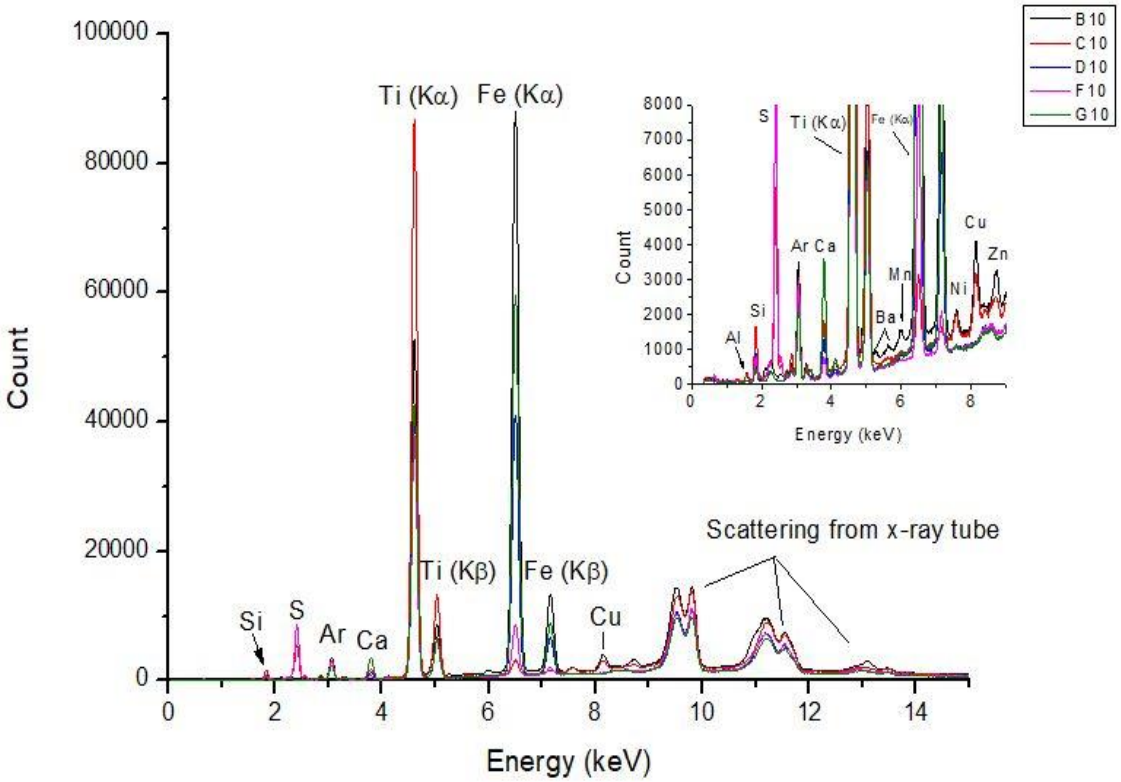

Figure 4: EDXRF spectra from brown nail polishes
Source: Own authorship

All red nail polishes contain Mg, Al, Si, S, Cl, Fe and Ni (Figure 5). As opposed to the other analyzed colors, the red nail polishes were characterized by having the element Ba in its constitution. Only barium was not identified in two samples. The Sr element is present with low counts in four samples.

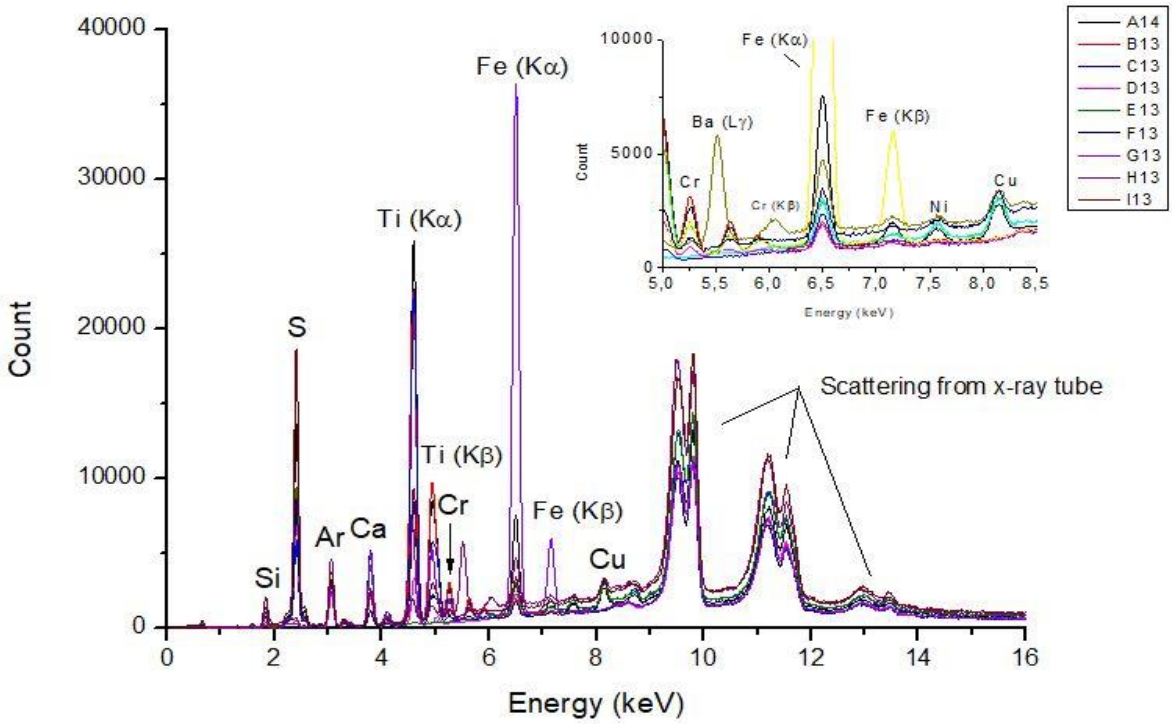

Figure 5: EDXRF spectra from red nail polishes
Source: Own authorship

All purple nail polishes contain Mg, Al, Si, S, Cl, K, Ca, Ti and Fe. Only two samples have Mn in their formulation. Nickel appeared on all samples except for B16, which also does not contain copper or zinc.

Therefore, it was observed that for most nail polish results, the elements Al, Ni, Cu and Zn were better detected with the Au target tube. According to regulations, some nail polishes are irregular because they contain P, Cl, Cr and Ni [11; 13].

Magnesium element was detected with low counting and this made interpreting the spectra difficult. The presence of sulfur in most samples may be related to TSFR resin (formaldehyde toluene sulfonamide). Two hypoallergenic nail polishes analyzed (C13 and C14) presented the sulfur element in their composition.

4. CONCLUSIONS

The qualitative analysis with the EDXRF method cannot be used as the only method of quality control of the cosmetic product. However, it proved to be very efficient and fast in detecting the chemical elements that are not allowed according to the resolutions present in the nail polish samples.

Nail polishes are widely used, but there are few studies about it. In this way, it is necessary to develop more work concerning the elementary analysis of this products for the purpose of contribute to the elucidation of the cosmetic legislations.

ACKNOWLEDGMENTS

The authors are very thankful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and the Graduate Course in Electrical Engineering and Industrial Informatics (CPGEI) for financial support.

REFERENCES

[1] BRASIL: ANVISA - Brazilian Health Regulatory Agency. Resolution RDC ANVISA 79 de 25 de agosto de 2000 - DOU de 31/08/2000. **Diário Oficial, República Federativa do Brasil**. Poder Executivo, Brasília, DF, 2000.

[2] ABIHPEPC. Anuário 2018. ABIHPEC – **Associação Brasileira da Indústria de Higiene Pessoal, Perfumaria e Cosméticos**. Available at: <https://abihpec.org.br/anuario-2018-en/> Last accessed: 10 Jun 2020.

[3] Bolognia, J., Schaffer, J. V., Jorizzo, J. L. **Dermatology**. v. 1. 3 ed., Elsevier. Rio de Janeiro, 2015. ISBN: 978-85-352-6326-8.

[4] Söğüt, Ö.; Reyhanlıoğlu, H.; Ezer, M.; Baltaş, H. Elemental compositions of some cosmetic products marketed in Turkey. **Fresenius Environmental Bulletin**. v. 25, No. 4, p. 1068-1077, 2016.

[5] Iwegbue, C.M.A. Safety evaluation of the metals in some brands of nail polish in Nigeria. **Journal of Consumer Protection and Food Safety**. v.11, p. 271–278, 2016. DOI 10.1007/s00003-016-1027-3

[6] Melquiades, F. L.; Silva, A. M. A. Identification of sulphur in nail polish by pattern recognition methods combined with portable energy dispersive X-ray fluorescence spectral data. The Royal Society of Chemistry. **Analitycal Methods**. v. 8, p. 3920-3926, 2016. DOI: 101039/c6ay00195e.

[7] Grosser Z, Davidowski L, Thompson L. The determination of metals in cosmetics. **PerkinElmer Application Note, ICPMass spectrometry, PerkinElmer**, Inc. Shelton, CT 06484, USA p. 1–6, 2011.

[8] Oga, S., Camargo, M. M. A., Batistuzzo, J. A. O.**Fundamentos de toxicologia**. 3 ed. Atheneu, São Paulo. Brasil, 2008. ISBN: 978-85-7454-098-6.

[9] Costa, A. **Tratado Internacional de Cosmecêuticos**. Rio de Janeiro: Guanabara Koogan, 2012. ISBN: 978-85277-2146-2.

[10] Brazil: ANVISA - Brazilian Health Regulatory Agency. Resolution RDC nº 79, de 28 de agosto de 2000 (D.O.U. 31/08/00) **Diário Oficial, República Federativa do Brasil.** 2000. Available at: <http://www.anvisa.gov.br/anvisalegis/resol/2000/79_2000.pdf >. Last accessed: 26 Jan. 2020 (in Portuguese)

[11] Brazil: ANVISA - Brazilian Health Regulatory Agency. Resolution RDC nº 83, de 20 de junho de 2016 (D.O.U. 116). **Diário Oficial, República Federativa do Brasil.** Poder Executivo,

Brasília, DF. 2016. Available at: <http://www.abc-cosmetologia.org.br/wp-content/uploads/2016/06/1RDC_83_2016.pdf >. Last accessed: 09 Jun 2020 (in Portuguese).

[12] Brazil: ANVISA - Brazilian Health Regulatory Agency. Resolution RDC/ANVISA 48 de 16 de março de 2006 - DOU de 17/03/2006 p.61 - seção 1, nº 53. **Diário Oficial, República Federativa do Brasil**. Poder Executivo, Brasília, DF, 2006.

[13] European Union. Regulation (EC) N1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products. **Official Journal of the European Union**, 2009.

[14] Health Canada – Government Canada. **Safety of Cosmetic Ingredients**. 2019. Available at: <https://www.canada.ca/en/health-canada/services/consumer-product-safety/cosmetics/labelling/safety-ingredients.html#a4.6>. Last accessed: 25 Jun. 2020.

[15] Verma, H. R. **Atomic and nuclear analytical methods**. New York: Springer, 2007. ISBN: 13-978-3-540-30277-3.

[16] Bocca B, Pino A, Alimonti A, Forte G. Toxic metals contained in cosmetics: a status report. **Regul Toxicol Pharmacol** v. 68, p. 447–467, 2014.

[17] Andrea C. McWilliams, Al A. Martin, Michael A. Levine, Keith E. Levine, Lauren Felder, Daniel J. Young, and James M. Harrington. Preparation of thin films for elemental analysis of nail polish by wavelength dispersive x-ray fluorescence spectroscopy. **Analytical Letters**, v.48, p. 2122–2135, 2015. Taylor & Francis Group. DOI: 10.1080/00032719.2015.1015072.