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Chemometric evaluation of Cd, Co, Cr, Cu, Ni (inductively coupled plasma optical emission spectrometry) and Pb (graphite furnace atomic absorption spectrometry) concentrations in lipstick samples intended to be used by adults and children

Érica Ferreira Batista, Amanda dos Santos Augusto, Edenir Rodrigues Pereira-Filho *

Federal University of São Carlos, Chemistry Department, Group of Applied Instrumental Analysis, P.O. Box 676, Zip Code 13565-905 São Carlos, São Paulo State, Brazil

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ABSTRACT

A method was developed for determining the concentrations of Cd, Co, Cr, Cu, Ni and Pb in lipstick samples intended to be used by adults and children using inductively coupled plasma optical emission spectrometry (ICP OES) and graphite furnace atomic absorption spectrometry (GF AAS) after treatment with dilute HNO_3 and hot block. The combination of fractional factorial design and Desirability function was used to evaluate the ICP OES operational parameters and the regression models using Central Composite and Doehlert designs were calculated to stablish the best working condition for all analytes. Seventeen lipstick samples manufactured in different countries with different colors and brands were analyzed. Some samples contained high concentrations of toxic elements, such as Cr and Pb, which are carcinogenic and cause allergic and eczematous dermatitis. The maximum concentration detected was higher than the permissible safe limits for human use, and the samples containing these high metal concentrations were intended for use by children. Principal component analysis (PCA) was used as a chemometrics tool for exploratory analysis to observe the similarities between samples relative to the metal concentrations (a correlation between Cd and Pb was observed).

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1. Introduction

The first registry documenting the use of products to adorn lips originates from the Sumerians in 7000 BC, and the application of these products has been transmitted to civilizations until the present day. The first lipsticks consisted of beeswax, fat and pigment, and their 'stick' form has been used since the mid-1920s [1]. Since then, the global use of these products has been increasing due to the pursuit of individual beautification and product advertisements [2].

Lipsticks are composed of several constituents, such as oils, antioxidant materials, emollients, colorants and others, including silica, mica and titanium dioxide (TiO_2), that create different colors, properties and appearance in the final product. One of the features of these products is the wide variety of colors, that are produced by the addition of pigments, which may be mineral or organic and may contain metals, such as Cd, Co, Cr, Cu, Ni and Pb, as impurities in the pigment formulation [3–5].

These cosmetic products are applied directly to human skin, and because of the components, their use can present risks to human health, causing possible reactions, such as hypersensitivity and irritant reactions [6].

Among the elements mentioned, Ni, Co and Cr [7] are considered major causes of allergies and Cd, Cr and Pb are carcinogenic when present in the body in high concentrations. Eventually, these impurities could be absorbed by the users' skin and could cause diseases [8].

Special attention must be paid to the use of these products by children because of the increasingly earlier use of cosmetics. Children's skin is characterized as being sensitive, fragile, thin and has a greater percutaneous absorption, which can result in systemic toxicity [9]. In addition to the inconvenience of skin irritation, chronic contamination can occur with the accidental ingestion of cosmetics. Thus, the control and monitoring of toxic elements in cosmetics are required for consumer protection and sanitary control of these products [10].

Several countries specifies different regulations for cosmetics raw materials:

– United States [11]: Specify that the metal concentration limits

* Corresponding author.
E-mail address: erpf@ufscar.br (E.R. Pereira-Filho).

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depend on each additive and its color;
- Brazil [12,13]: As, Cd, Cr and Pb cannot be used to manufacture of cosmetic products, and the maximum impurity allowed for elements in organic colorants is 500 ppm for Ba, 3 ppm for As, 20 ppm for Pb and 100 ppm for other elements. Furthermore, the cosmetics formulated for children must be easily and safely removed to avoid the possibility of accidental ingestion;

On the other hand, Canada and Germany have regulations for the final products:

- Canada [14]: The maximum acceptable limit for Pb, As, Cd, Hg and Sb is 10, 3, 3, 3 and 5 mg kg^{-1}, respectively.
- Germany [15]: The maximal concentrations should be 20, 5, 5, 10 and 1 ppm for Pb, Cd, As, Sb and Hg, respectively.

Given the importance of determining the concentration of these metals in cosmetic samples, which are used daily by millions of people, including children, the goal of this study was to develop a simple analytical method for the determination of Cd, Co, Cr, Cu, Ni and Pb in lipsticks. In this way, inductively coupled plasma optical emission spectrometry (ICP OES) and graphite furnace atomic absorption spectrometry (GF AAS) were used in the determinations. Chemometric tools like factorial design were applied to optimize the analytical strategy, equipment working conditions and exploratory analysis was employed for data visualization and interpretation.

2. Experimental

2.1. Samples and reagents

Lipstick samples manufactured in Brazil, China and USA were purchased at a local market and were analyzed. Two sample groups were selected: lipstick for adults and those intended to be used by children. The unitary price of these samples ranged from US$1.00 to US$10.00.

All of the multi-element standard solutions were prepared daily from 1000 mg L^{-1} Cd, Co, Cr, Cu, Ni and Pb stock solutions (Qhemis, Jundiaí, SP, Brazil). Deionized water (18.2 Ω M cm^{-1} resistivity) was generated using a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA) and was used to prepare all solutions. Prior to use, all glassware and polypropylene flasks were washed with soap, soaked in 10% v v^{-1} HNO_3 for 24 h, rinsed with deionized water and dried to ensure that no contamination had occurred. For mineralization of the samples, a mixture of H_2O_2 (30% w w^{-1}) (Synth, Diadema, SP, Brazil), HNO_3 (Synth) and Triton X-100 (5% and 25% v m^{-1}) (Sigma Aldrich, St. Louis, MO, USA) was used. HNO_3 was previously purified by sub-boiling distillation using Distillacid™ BSB-939-IR (Berghof, Eningen, Germany).

2.2. Instrumentation

A hot block (Tecnal, Brazil) designed to fit 30 PFA (perfluoroalkoxy, Savillex, Minnetonka, USA) tubes of 50 mL was used for sample preparation. An ICP OES instrument (iCAP 6000, Thermo Scientific, Waltham, MA, USA) was used for Cd, Co, Cr, Cu and Ni determination. This instrument allows sequential analytical signal collection using axial and radial viewings. Argon (99.996%, White Martins-Praxair, Sertãozinho, SP, Brazil) was used for all ICP OES measurements.

A GF AAS instrument (iCE 3000 Series, Thermo Scientific, Waltham, MA, USA) was used for Pb determination in which the heating program (Table S1) was used according to the manufacturer's recommendations. Magnesium nitrate (0.03 w v^{-1}) and ammonium dihydrogen phosphate (0.5% w v^{-1}) solutions were used as chemical modifiers in the Pb determination.

For each measurement, 15 μL of the sample or reference solution was used with 5 μL of the modifier solution (magnesium nitrate and ammonium dihydrogen phosphate). All measurements of integrated absorbance were obtained in triplicate.

2.3. Sample preparation

For the sample mineralization employing a hot block with PFA tubes, 250 mg of the lipstick sample was weighed using an analytical balance (model AY 220, max. 220 g, 0.1 mg resolution, Shimadzu, Kyoto, Japan). Five mL of HNO_3 (7 mol L^{-1}), 2 mL of H_2O_2 (30% w w^{-1}) and 1 mL of Triton X-100 (25% w v^{-1}) were added to the lipstick sample. The tubes were closed with PFA lids and the mixture was heated at 100 °C for 180 min, and the solutions were quantitatively transferred to polypropylene flasks and diluted with water to 25 mL, resulting in a final acidity of 1.4 mol L^{-1}. The mineralization was performed in triplicate with and without the addition of a standard to verify the accuracy of the analytical method and to detect possible loss of analytes during sample preparation. The final concentrations added for the standards were 24, 24, 420, 420, 120 and 48 μg L^{-1} for Cd, Co, Cr, Cu, Ni and Pb, respectively. This strategy was used because there is no cosmetic certified material available in our laboratory.

2.4. ICP OES operational optimization conditions

Six elements (Cd, Co, Cr, Cu, Ni and Pb) were studied, and two or three emission lines were used for each one. Table 1 shows the analytes and the emission lines selected (atomic, I or ionic, II).

During the optimization of operational parameters in an ICP OES spectrometer, several adjusts must be made in order to identify a commitment condition that allows the simultaneous determination of various elements.

Nine variables were studied: integration time for low (V1) and high (V2) emission lines, sample introduction flow rate (V3), sample flow rate during the analyses (V4), pump stabilization time (V5), radio frequency applied power (V6), and gas flow rate of auxiliary (V7), nebulization (V8) and cooling gas (V9). Table 2 shows more details of the levels studied. In this case, a fractional factorial design (2_{IV}^{9-5}) was performed with only 16 experiments. The variables selected were studied in two different levels (normalized in -1 and $+1$), and the goal is to identify among them (screening) the most important ones. These variables were chosen according to parameters available in the control software. Two types of response were monitored: (1) the analytical signals height after background correction in axial and radial viewings, and (2) relative standard deviations (RSD, $n=3$).

The fractional factorial design with 16 experiments was performed and a multielement solution containing 1 mg L^{-1} of each analyte was prepared. Analytical signals in axial and radial

Table 1
Analytes and seventeen emission lines used for determination of elements in ICP OES.

Analyte	Emission line (nm)		
Cd	214.438 (I)	226.502 (II)	228.802 (I)
Co	228.616 (II)	230.786 (II)	237.862 (II)
Cr	283.563 (II)	357.869 (I)	
Cu	221.810 (II)	224.700 (II)	324.754 (I)
Ni	221.647 (II)	231.604 (II)	341.476 (I)
Pb	182.205 (II)	216.999 (I)	220.353 (II)

I: atomic line.
II: ionic line.

Table 2
Variables studied and its levels employed in the fractional factorial design 2^{9-5}.

Variable	Lower level (−1)	Higher level (+1)
V1: Integration time for low emission line (s)	5	15
V2: Integration time for high emission line (s)	5	15
V3: Sample introduction flow rate (mL min^{-1})	2.1	4.2
V4: Sample flow rate during the analyses (mL min^{-1})	2.1	4.2
V5: Pump stabilization time (s)	25	250
V6: Radio frequency applied power (W)	750	1150
V7: Auxiliary gas flow rate (L min^{-1})	0.25	0.5
V8: Nebulization gas flow rate (L min^{-1})	0.325	0.65
V9: Cooling gas flow rate (L min^{-1})	10	16

viewings were sequentially recorded for each analyte in the seventeen emission lines described (see Table 1). A total of 68 responses were obtained: 34 signals (17 for axial and 17 for radial) and 34 RSD (17 for axial and 17 for radial) values.

The important aspect is how to comprise these data. In this case, Desirability function [16] was used, and the signals were normalized between 0 (lower signals) and 1 (higher signals). Eq. (1) shows how this transformation was performed:

$$\begin{cases} 0 \text{ if } y < L \\ \left(\dfrac{y-L}{T-L}\right)^{s} \text{ if } L \le y \le T \\ 1 \text{ if } y > T \end{cases} \quad (1)$$

where y, L and T are the analytical signals for a given analyte, the lowest and the highest signals for this element, respectively. It is possible to attribute weight(s) to each signal. In the specific case of this study, the weight was 1 for all analytes.

In the case of RSD, the goal was to obtain lower RSD's values (more precise results). Eq. (2) was used in this calculation:

$$\begin{cases} 1 \text{ if } y < T \\ \left(\dfrac{U-y}{U-T}\right)^{t} \text{ if } T \le y \le U \\ 0 \text{ if } y > U \end{cases} \quad (2)$$

where y, U and T are the RSD values for a given analyte in a specific emission line, the highest and the lowest values for the RSD's, respectively. It is also possible to attribute weight (t) to each RSD. In the specific case of this study the weight was also 1 for all analytes.

After the calculation of 68 individual desirabilities (di) values it is possible to combine the results using global desirability (D) calculated using geometric mean:

$$D = \sqrt[m]{d1 \times d2 \times \ldots dm} \quad (3)$$

After identification of the most important variables using an aqueous multielementar standard solution, two factorial designs were done: Central Composite Design (CCD) and Doehlert Design (DD) [17], but now using a mineralized sample. These two designs were performed in order to cover a wide range of variables range. This paper is related to a project were eye shadow and sunscreen were also analyzed. In this case, an eye shadow sample was used, as target sample for metals determination and the response observed was the signal intensity for each analyte. The results for eye shadow were previously published [18]. The regression models were calculated to stablish the best working condition for all analytes.

3. Results and discussion

3.1. ICP OES factorial design

Table 3 shows the Global desirability (D, see Eq. (3)) calculated for each experiment when the 2^{9-5} fractional design (Table 2) was performed.

As can be seen in Table 3 the variables from V5 to V9 were obtained from the combination of variables V1, V2, V3 and V4: for V5 (combination of variables V1, V2, V3 and V4), V6 (V1, V2 and V3), V7 (V1, V2 and V4), V8 (V1, V3 and V4), and for V9 (V2, V3 and V4). In this case, the calculated primary contrasts will be confounded with secondary, tertiary, and quaternary effects. The contrast for variable 1, for example, is the difference between the mean of D when V1 is in the higher level ($\bar{Y}_+$) and in the lower level ($\bar{Y}_-$):

$$\text{Contrast} = \bar{Y}_+ - \bar{Y}_- \quad (4)$$

Fig. 1 shows a pictorial description of the contrasts calculated. As can be observed, the highest contrasts (more sloping arrows) were obtained for variables 4 (sample flow rate during the analyses), V6 (RF power) and V8 (nebulization gas flow rate) in this order. The first one (V4) presented a negative contrast (−0.16), and the indication is use this variable in the lower level (2.1 mL min^{-1}, see Table 2). Variables 6 and V8 presented positive contrasts (0.20 and 0.29, respectively) and then, they must to be

Table 3
Global desirability (D, see Eq. (3)) calculated for each experiment performed.

Exp.	V1	V2	V3	V4	V5=1234	V6=123	V7=124	V8=134	V9=234	D
1	−1	−1	−1	−1	1	−1	−1	−1	−1	0.02
2	1	−1	−1	−1	−1	1	1	1	−1	0.54
3	−1	1	−1	−1	−1	1	1	−1	1	0.07
4	1	1	−1	−1	1	−1	−1	1	1	0.42
5	−1	−1	1	−1	−1	1	−1	1	1	0.81
6	1	−1	1	−1	1	−1	1	−1	1	0.01
7	−1	1	1	−1	1	−1	1	1	−1	0.26
8	1	1	1	−1	−1	1	−1	−1	−1	0.44
9	−1	−1	−1	1	−1	−1	1	1	1	0.26
10	1	−1	−1	1	1	1	−1	−1	1	0.03
11	−1	1	−1	1	1	1	−1	1	−1	0.68
12	1	1	−1	1	−1	−1	1	−1	−1	0.09
13	−1	−1	1	1	1	1	1	−1	−1	0.07
14	1	−1	1	1	−1	−1	−1	1	−1	0.01
15	−1	1	1	1	−1	−1	−1	−1	1	0.03
16	1	1	1	1	1	1	1	1	1	0.11

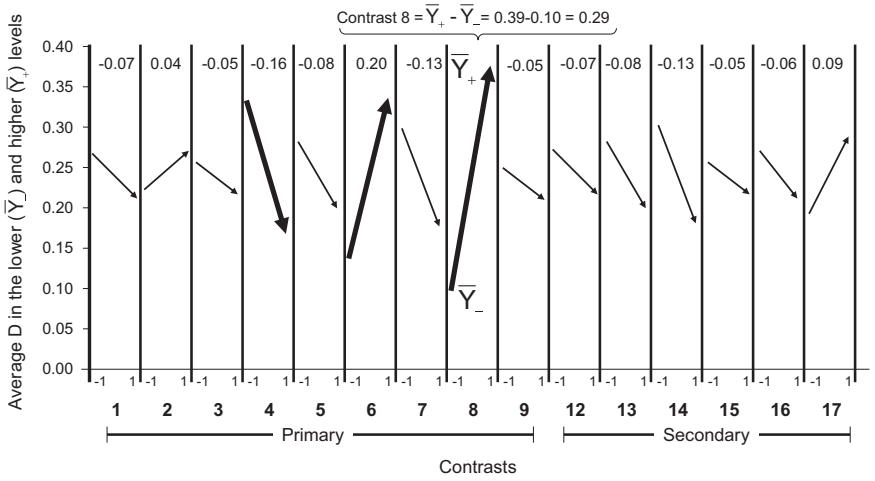

Fig. 1. Pictorial description of the contrasts calculated for primary (1–9) and secondary contrasts (12, 13, 14, 15, 16 and 17).

Table 4
Central Composite Design, CCD (exp 1–11), Doehlert Design, DD (exp 12–20) and global desirability (*D*, see Eq. (3)) results for axial and radial viewings.

	Experiment	V6		V8		*D* axial	*D* radial
		Coded	Real	Coded	Real		
CCD	1	−1	1175	−1	0.73	0.53	0.57
	2	+1	1250	−1	0.73	0.71	0.70
	3	−1	1175	+1	0.95	0	0
	4	+1	1250	+1	0.95	0.65	0
	5	0	1200	0	0.83	0.65	0.78
	6	0	1200	0	0.83	0.85	0.97
	7	0	1200	0	0.83	0.69	0.71
	8	−1.33	1150	0	0.83	0	0
	9	+2	1275	0	0.83	0.65	0.44
	10	0	1200	−1.41	0.65	0.82	0.60
	11	0	1200	+1.41	1	0	0
DD	12	0	1200	0	0.83	0.72	0.81
	13	0	1200	0	0.83	0.85	0.97
	14	0	1200	0	0.83	0.72	0.76
	15	0	1200	+1	1	0	0
	16	+1.2	1275	+0.5	0.91	0	0.56
	17	0	1200	−1	0.65	0.76	0
	18	−0.8	1150	−0.5	0.73	0.70	0.77
	19	−0.8	1150	+0.5	0.91	0.55	0.59
	20	+1.2	1275	−0.5	0.73	0.88	0.70

used in the highest levels (1150 W and 0.65 L min^{-1}, respectively). The other variables (V1–V3, V5, V7 and V9) presented negligible contrasts (see the low inclination of the arrows), and can be used in the lower level, for example. Six secondary contrasts were also calculated and the values are also low.

Through this screening study, it was possible to select the variables with a greater influence on the ICP OES response, in the range studied, using an aqueous multielementar solution. However, a new study was performed to identify the best operational conditions for the ICP OES instrument, considering the more important variables and the sample matrix (cosmetics) [19].

The variables used in this new study were: V6 and V8. Variable 4 had a lower influence when comparing with the others variables, and was fixed in 2.1 mL min^{-1}. Twenty experiments were performed (11 experiments of CCD and 9 experiments of DD) and Table 4 shows the experiments and results for axial and radial viewings. In the CCD values the 2 variables (V6 and V8) were tested in 5 levels. On the other hand for DD, the V6 was tested in 3 levels and V8 in 5 levels (this variable presented the highest contrast at 2^{9-5} fractional factorial design, see Fig. 1).

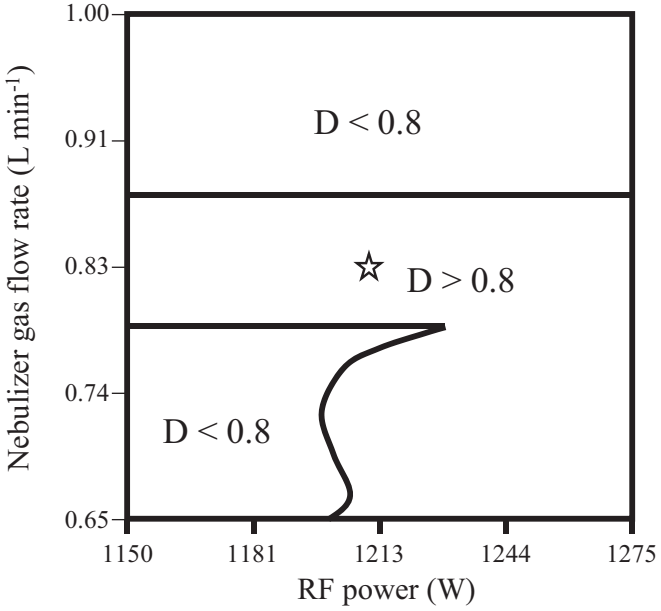

Fig. 2. Contour plot by superimposing the 4 generated models.

Table 5
Global desirability (*D*, see Eq. (3)) values.

Experiments	Values of *D*		
	Axial (*D*1)	Radial (*D*2)	Axial and radial (*D*)
1	0.1	0.3	0.2
2	0.9	0.7	0.8
3	0.0	0.0	0.0
4	0.2	0.3	0.3
5	0.2	0.5	0.3
6	1.0	0.8	0.9
7	0.0	0.6	0.0
8	0.1	0.0	0.0

The responses were evaluated in terms of recovery of analytes added and values of LOQ. For each experimental condition described at Table 4 an analytical curve for the analytes was performed and the global desirabilities (*D* values) were calculated for Axial and Radial modes taking into consideration LOQ and recovery. For the calculation of *di* values using the LOQ responses was used the Eq. (2) (minimize), while the *di* values using the

Table 6
Analytical performance parameters for analytes determination in ICP OES (Cd, Co, Cr, Cu and Ni) and GFAAS (Pb).

Parameters	Cd 228.8 nm		Co 228.6 nm		Cr 283.5 nm		Cu 324.7 nm		Ni 231.6 nm		Pb[a] 283.3 nm
	Axial	Radial	Axial	Radial	Axial	Radial	Axial	Radial	Axial	Radial	GF AAS
Regression coefficient (r)	1.00		1.00		1.00		1.00		1.00		0.99
Linear range ($\mu g\ L^{-1}$)	2.5–80		5–1500		5–1500		5–1500		5–1500		5–100
Limit of detection ($mg\ kg^{-1}$)	0.02	0.1	0.04	0.2	0.02	0.2	0.02	0.09	0.07	0.4	0.01
Limit of quantification ($mg\ kg^{-1}$)	0.07	0.4	0.14	0.5	0.07	0.6	0.08	0.3	0.3	1	0.04

[a] GF AAS.

Table 7
Cd, Co, Cr, Cu, Ni and Pb concentration ($mg\ kg^{-1}$) found in lipsticks intended to be used by adults and children.

	Samples	Color	Origin	Concentration ($mg\ kg^{-1}$)						Recovery (%)					
				Cd	Co	Cr	Cu	Ni	Pb[a]	Cd	Co	Cr	Cu	Ni	Pb[a]
Adult sample (1–9)	1	Red	China	< LOQ	< LOQ	< LOQ	< LOQ	1.2 ± 0.1	< LOQ	87	87	88	91	85	96
	2	Red	Brazil	< LOQ	1.8 ± 0.3	< LOQ	< LOQ	< LOQ	0.11 ± 0.01	96	94	90	100	95	86
	3	Red	USA	< LOQ	0.16 ± 0.03	< LOQ	< LOQ	< LOQ	< LOQ	92	83	95	101	84	109
	4	Pink	China	< LOQ	< LOQ	0.3 ± 0.1	< LOQ	< LOQ	0.55 ± 0.05	89	80	91	92	86	96
	5	Pink	Brazil	< LOQ	2.7 ± 0.3	1.2 ± 0.2	0.6 ± 0.2	1.4 ± 0.3	0.43 ± 0.03	94	85	90	92	83	84
	6	Pink	USA	< LOQ	< LOQ	< LOQ	0.6 ± 0.2	< LOQ	< LOQ	94	85	93	93	83	101
	7	Orange	China	< LOQ	< LOQ	0.20 ± 0.03	< LOQ	< LOQ	0.3 ± 0.1	86	85	87	84	86	103
	8	Orange	Brazil	< LOQ	< LOQ	0.7 ± 0.2	0.95 ± 0.03	0.9 ± 0.1	0.50 ± 0.07	91	84	88	88	81	89
	9	Orange	USA	< LOQ	0.13 ± 0.03	3.8 ± 0.2	0.6 ± 0.2	< LOQ	0.22 ± 0.02	91	83	88	89	84	110
Child sample (10–17)	10	Red	China	< LOQ	< LOQ	1.48 ± 0.03	< LOQ	< LOQ	0.09 ± 0.02	103	92	88	104	90	102
	11	Lilac	China	< LOQ	0.242 ± 0.009	0.171 ± 0.004	0.16 ± 0.03	< LOQ	0.33 ± 0.05	94	86	89	98	86	103
	12	Brown	China	< LOQ	< LOQ	3.4 ± 0.5	3.8 ± 0.3	0.57 ± 0.09	0.27 ± 0.06	88	87	87	102	86	85
	13	Pink	China	0.022 ± 0.006	0.36 ± 0.02	0.23 ± 0.02	0.30 ± 0.09	< LOQ	0.38 ± 0.07	92	81	88	101	83	94
	14	Pink	China	< LOQ	0.6 ± 0.1	3.9 ± 0.2	1.3 ± 0.1	0.10 ± 0.04	11.7 ± 0.7	98	90	99	107	92	84
	15	Red	China	< LOQ	1.22 ± 0.03	5.0 ± 0.7	1.2 ± 0.2	1.3 ± 0.2	1.09 ± 0.02	101	93	96	111	92	90
	16	Pink	China	0.12 ± 0.03	< LOQ	12.2 ± 0.6	3.2 ± 0.2	0.27 ± 0.04	37 ± 7	93	81	92	88	84	85
	17	Golden	China	< LOQ	0.80 ± 0.02	12 ± 1	3.5 ± 0.1	3.0 ± 0.1	0.96 ± 0.03	94	89	92	102	89	90

[a] GF AAS.

recovery response were calculated using Eqs. (1) and (2): recovery below 50% and above 150% were considered $di=0$ (not desirable), and the range between 80% and 120% were considered $di=1$. Finally, recovery in the range of 50% and 80% and between 120% and 150%, the Eqs. (1) and (2) were used to calculate the di, respectively.

After processing the data, it was calculated the values of D (Eq. (3)) for each response obtained in the two viewings (axial and radial) in two factorial design (Central Composite and Doehlert), and the results can be observed in Table 4.

Using the values of D for each viewing mode, 4 models were generated. In this case, only the significant coefficients at a confidence level of 95% were considered. The proposed models were:

Model 1, CCD (exp 1–11, see Table 4) – axial viewing:

$D=0.494+0.185$ [power, V8] -0.217 [flow rate, V6]

Model 2, CCD – radial viewing (CCD):

$D=0.43$ (the other coefficients were not significant)

Model 3, DD (exp 12–20, see Table 4) – axial viewing:

$D=0.691-0.40$[flow rate, V6] -0.347 [flow rate, V6]^2 -0.370 [power, V8][flow rate, V6] (There is an interaction between power and flow rate)

Model 4, DD – radial viewing:

$D=0.858-0.853$ [flow rate, V6]^2

To verify the quality of the generated models, the calculated and tabulated F values were compared (95% of confidence) and all models were statistically significant.

Model 2 was not considered because only b0 was significant ($b0=0.43$).

Through these calculations, it was possible to obtain contour plots and Fig. 2 shows the result when they were superimposed.

In the Fig. 2, it is possible to observe a region ($D>0.8$) with good results for all analytes. In this case, the final working conditions selected were that in the central point (see star: exp. 5–7 and 12–14, Table 4): radiofrequency power of 1200 W and nebulizer gas flow rate of 0.83 L min^{-1} (see star in Fig. 2). This combination provides a compromise between all analytes in both determination modes (axial and radial). In addition, from Table 4 is possible to observe that the D values (for axial and radial viewings) varied from 0.65 to 0.97.

3.2. Lipstick preparation optimization

The parameters studied to optimize the process of sample preparation included acid concentration, Triton X-100 concentration, the sample weight and the heating time. The solution of Triton X-100 was used as a stabilizing agent and as an additive to reduce the surface tension of water.

The variables studied were the HNO_3 concentration (2 or 7 mol L^{-1}), Triton X-100 concentration (25% or 50% wv^{-1}) and heating time (1 or 3 h). The hot block temperature was fixed at 100 °C; 2 mL of H_2O_2 was used in all experiments, and the sample weight was 250 mg. In all experiments, a red lipstick sample from China was used. Eight experiments (2^3) were performed with two replicates and Table 5 (global desirability) shows the obtained results when signals of the analytes were monitored.

Analysis of the data revealed that experiments 2 and 6 showed the highest values of D and these experiments had the following variables in common: Triton X-100 concentration (25% m v^{-1}) and HNO_3 concentration (7 mol L^{-1}). The heating time was fixed at 3 h because this time was qualitatively more efficient in the mineralization process, with a distinct loss of pigmentation of samples.

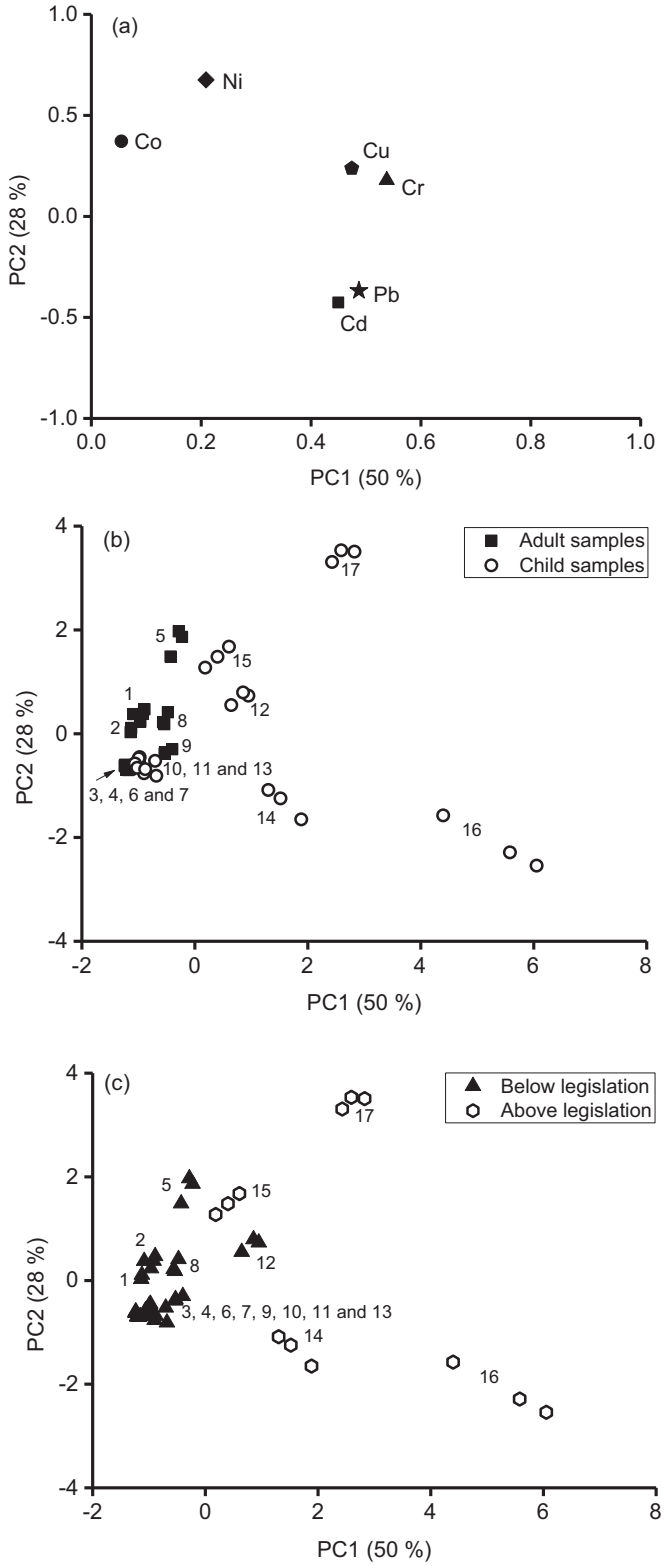

Fig. 3. Graphical representation of the (a) Loadings of PC1 × PC2 relative to the elements; (b) Score of PC1 × PC2 relative to the public category; and (c) Score of PC1 × PC2 relative to the legislation category.

3.3. Analytical performance

After selecting the conditions for ICP OES and sample preparation, analytical parameters were obtained for the Cd, Co, Cr, Cu, Ni and Pb determinations. The determinations were performed using ICP OES for Cd, Co, Cr, Cu and Ni, and GFAAS was used for Pb because it was not possible to select an ICP OES emission line without spectral interferences. The working conditions used for GFAAS were according to the manufacturer's recommendations (Table S1). Table 6 shows the parameters obtained to evaluate the analytical performance.

The limits of detection (LOD) and quantification (LOQ) of the method were calculated using the concept of background equivalent concentration (BEC) [19], and the LOD and LOQ are adequate for the quality control of lipsticks.

Different volumes of standard were added to study the accuracy, and the final concentrations were 24, 24, 420, 420, 120 and 48 $\mu g\ L^{-1}$ for Cd, Co, Cr, Cu, Ni and Pb, respectively, in the sample and in the blank before the sample preparation. The recovery rates obtained were between 80% and 111%, as observed in Table 7. According to Taverniers et al. [20] these values are considered adequate for concentrations in the range of 10 $\mu g\ L^{-1}$.

The method developed was suitable for lipstick analysis, considering the legislation previously mentioned.

3.4. Determination of Cd, Co, Cr, Cu, Ni and Pb in lipstick samples

Nine and eight lipstick samples intended to be used by adults and by children, respectively, were analyzed and the concentrations (mg kg^{-1}) of each element are reported in Table 7. Table S2 at supplementary material shows the individual values for each replicate ($n=3$)

Most of the samples had concentrations of analytes below the maximum values allowed by the legislation and often below the limits of quantification of the method. Samples 16 and 17 (lipstick intended to be used by children) had concentrations higher than the concentrations allowed for Cr (5 ppm) [21]. Only sample 16 showed Pb concentrations above 20 ppm [11], while sample 14 showed a Pb concentration of 10 ppm by extrapolation of the data in this case, according to Canadian regulations [14].

All samples with concentrations above the legislation are aimed to be used by children. Metals accumulate in the body over time, and the repetitive application of products containing metals may lead to significant and dangerous exposure levels. In addition, children are exposed at an increasingly young age to cosmetic products, further prolonging the use of these products throughout life.

All of the lipstick samples intended to be used by children that were analyzed were from China. The large variation in the metal concentrations may be attributed to the quality of the raw materials used in the production of the lipsticks [22].

3.5. Exploratory analysis of lipstick samples

The concentrations of the analytes were used in a chemometric study. A matrix was generated with 51 rows (17 samples with triplicates) and 6 columns (analytes concentration). Principal component analysis (PCA) was used as a chemometrics tool for an exploratory evaluation to visualize the data structure, to find similarities between samples, to detect anomalous samples and to reduce the dimensionality of the data set.

Data were autoscaled, and a model was generated with 4 principal components, with 97% of the explained variance. Classes that were considered in the exploratory analysis included: country of production, target consumer, price, color and legislation. Fig. 3 represents the graphical illustration of the loadings (a) of PC1 × PC2 relative to the elements and the score of PC1 × PC2 relative to the public category (b) and legislation category (c). From Fig. 3a is observed a correlation between Cu and Cr, Co and Ni and Cd and Pb. Fig. 3-b shows the difference between public (adult and child) samples, except samples 10, 11 and 13,

which have a low concentration of the determine elements. The other samples for children are highly correlated with the concentrations of Cd, Cr, Cu and Pb, confirming the high concentrations of the analytes. Discrimination in PC1 between samples below and above the legislation is also observed (Fig. 3-c), and these samples are associated with the same elements. All samples were analyzed in triplicate, and through scores plot, it is possible to verify that all replicates are well clustered, which demonstrates a good repeatability of the proposed procedure.

4. Conclusions

The study of ICP OES operational conditions was feasible using a fractional factorial design. In order to identify a commitment condition that allows the determination of Cd, Co, Cr, Cu, Ni and Pb using ICP OES, the analytical signals recorded sequentially in axial and radial viewings and the relative standard deviations (RSD) were evaluated. Since too many data were analyzed simultaneously, the Desirability function was used to improve the identification of the commitment condition of the instrumental parameters.

After the identification the working conditions of the ICP OES, an interesting alternative and environmentally friendly procedure was studied for sample preparation using dilute HNO_3, whereas most of the proposed methods use a concentrated acid, such as HF.

The analyses were performed using ICP OES and GF AAS (Pb, due to spectral interferences at ICP OES), and three samples had concentrations higher than the concentrations allowed for Cr or Pb. All of the samples that were above the legislative limits are aimed to be used by children.

Principal component analysis was used to perform an exploratory analysis to determine the similar characteristics between samples (origin, color, legislation and intended public) relative to the metal concentrations, but the only classes that showed discrimination were legislation and intended public.

The results of this study demonstrate the deficiency in the supervision of these products and the importance of testing the quality of these cosmetics that reach the consumer market, especially for cosmetics intended to be used by children.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2015.12.011.

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