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).

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$_2$O$_2$ (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$_2$O$_2$ (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.