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Determination of Cd, Co, Cr, Cu, Ni and Pb in cosmetics samples using a simple method for sample preparation

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Abstract

In this study, a method has been used to prepare and evaluate the content of some metals in samples of eye shadow. The samples were manufactured in different countries (Brazil, China and USA). The sample preparation was performed using dilute nitric acid and hot block. The Pb content was measured using a graphite furnace atomic absorption spectrometer (GFAAS), and the quantification of Cd, Co, Cr, Cu and Ni was performed using inductively coupled plasma optical emission spectrometry (ICP OES). Chemometric tools were used for multivariate optimisation and to perform an exploratory analysis according to the metal concentration levels. Some samples presented metal concentrations above the values indicated by the FDA (USA) and ANVISA (Brazil).

Keywords: Cosmetics, toxic metals, cosmetic for child, sample preparation with dilute HNO$_3$. 
1 Introduction

Cosmetics are one of the most important products for the world economy. The cosmetic world market in 2012, for example, was around US$40 billion. The first archaeological evidence of the use of cosmetics was found in ancient Egypt, where men, women and children used green and black paints as makeup. According to the Brazilian Health Surveillance Agency (ANVISA) and the U.S. Food and Drug Administration (FDA), cosmetics are products made of natural or synthetic substances and used with the purpose of cleaning, perfuming or changing the appearance of parts of the human body.

Cosmetics are divided into several categories, such as makeup for children and adults, and include eye shadow, corrective facials, lipstick, blush and others. Most of these products have some metals in their pigmentation formulation that are used to provide a wide variety of colors. These metals are partially soluble in water and sweat and could be absorbed through the skin, causing an allergic reaction.

The U.S. and Brazilian legislative branches do not specify limits for the metal concentrations in makeup; however, the FDA and ANVISA established a threshold limit for metal content in raw materials. For the FDA regulations, the metal concentration limits depend on each additive and its color. For the Brazilian regulations, the limits of some metals in organic artificial colourants are 3 mg kg\(^{-1}\) for As, 20 mg kg\(^{-1}\) for Pb and 100 mg kg\(^{-1}\) for other elements.

Canada has a guide on heavy metals found as impurities in cosmetic products. The country follows the European legislation, however, by testing its own samples, cosmetics limits for some metals were established in the final product. The maximum tolerable limit for Pb, As, Cd and Hg are 10, 3, 3 and 5 mg kg\(^{-1}\), respectively.

Metals such as Ni, Co and Cr as mentioned before are considered major causes of allergies, but this risk awareness can be reduced if the level of these metals remain below 5 µg g\(^{-1}\).

The sample preparation, in the scope of the analytical sequence, is the process most likely to introduce errors; it is time consuming and has high costs. Usually, during the sample preparation, concentrated HNO\(_3\) and HF are used...
to completely digest the cosmetic samples (e.g., lipstick and eye shadow)\textsuperscript{6, 12, 13}. In this context, sample preparation using dilute HNO\textsubscript{3} is an interesting alternative and environmental friendly. This sample preparation is easier, safer and according with green chemistry due to the low consumption of reagents and the consequent reduction of laboratory residues\textsuperscript{14}. Furthermore there is a reduction of the blank signal and avoids dilution before determination\textsuperscript{15}. Although the use of diluted nitric acid was extremely evaluate for different types of samples, however there are no studies employing diluted acids for metal extraction in eye shadows\textsuperscript{16, 17}.

The efficiency of using diluted acids is a result of the temperature gradient inside the reaction vessel during the initial steps of sample digestion and due to the presence of a rich oxygen atmosphere inside the closed-vessel. The nitric acid is regenerated by nitrogen oxide species with the hydrogen peroxide as shown below\textsuperscript{18}:\[2\text{NO} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{HNO}_3 + 2\text{H}_2\text{O}\]

In some case strong treatments (concentrated acids) may not be feasible, following this thought some authors have proposed to employ a partial digestion of cosmetics\textsuperscript{19, 10}. Some parameters can be studied to optimize the process of sample preparation such as acid concentration, the sample mass, the heating time and the use of other reagents employed for digestion of the samples\textsuperscript{20}.

One of the strategy to optimise the process of sample preparation is multivariate analysis. This approach enables the collection of information about the effects of each evaluated variable and their interactions to find the possible best or most favourable conditions\textsuperscript{21}. One of the chemometric tools used for system optimisation is factorial design. Using this approach, a reduced number of experiments is performed, and the information is maximised\textsuperscript{21}. When factorial design and multielement analysis are combined, several responses can be obtained. In this case, the desirability function becomes an alternative method to normalise these responses and combine them in a single value named the overall desirability (D) and then come to a better working condition for all responses evaluated\textsuperscript{21}. Thus, the goal of this study was the development of a simple method of cosmetic samples preparation and determination of Cd,
Co, Cr, Cu and Ni using ICP OES and Pb using GFAAS in eye shadow. Several chemometric tools were used for multivariate optimisation and to perform an exploratory analysis categorising the samples according to the metal concentration levels.

2 Experimental

2.1 Reagents

All reagents were of analytical grade or higher purity. Deionised water (18.2 $\Omega \text{M cm}^{-1}$ resistivity) produced using a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA) 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 deionised water and dried to ensure that no contamination occurred. For sample mineralisation, a mixture of H$_2$O$_2$ (30 % w w$^{-1}$) (Synth, Diadema, SP, Brazil), HNO$_3$ (2 mol L$^{-1}$) (Synth) and Triton X-100 (5% v m$^{-1}$) (Sigma Aldrich, St. Louis, MO, USA) was used. The HNO$_3$ was previously purified using sub-boiling distillation Distillacid™ BSB-939-IR (Berghof, Eningen, Germany). To compare the method of sample preparation we used the mixture of H$_2$O$_2$ (30 % w w$^{-1}$), HF (40% v v$^{-1}$) (House of Chemistry, Diadema, SP, Brazil) and boric acid solution (4% w v$^{-1}$) (Mallinckrodt, Kentucky, USA).

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) via dilution in 0.67 mol L$^{-1}$ HNO$_3$. This acid solution was also used as the blank.

A mixture of magnesium nitrate solution (0.03 % w v$^{-1}$) and ammonium dihydrogen phosphate (0.5% w v$^{-1}$) solution was used as chemical modifier in the Pb determination using GFAAS.

2.2 Instrumentation

A hot block (Tecnal, Brazil), built to fit up to 30 units of PFA (Perfluoroalkoxy, Savillex, Minnetonka, USA) closed bottles of 50 mL was used for samples preparation. The HNO$_3$ concentration, sample mass, and heating...
time were studied using a $2^3$ full factorial design. An ICP OES (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 both axial and radial viewings. The ICP OES parameters were studied using a fractional factorial design $2^{9-5}$. Argon 99.996% (White Martins-Praxair, Sertãozinho, SP, Brazil) was used in all ICP OES measurements.

A GF AAS (iCE 3000 Series, Thermo Scientific, Waltham, MA, USA) was used for Pb determination. The heating program (Table 1) for Pb determination was used with the recommended conditions provided by the manufacturer. For each measurement the autosampler of the GF AAS collected 15 µL of the sample or reference solution along with 5 µL of the modifier solution (a mixture of magnesium nitrate and ammonium dihydrogen phosphate), so this mixture was introduced into the graphite tube. Preliminary tests in ICP OES demonstrate high values of recuperation indicating possible spectral interferences arising of the sample complexity. Graphite AAS and the mixture of chemical modifiers as magnesium nitrate and ammonium dihydrogen phosphate were applied to overcome this problems. All measurements of integrated absorbance were made in triplicate.

The samples were also digested using a microwave oven (Speedwave four, Berghof) furnished with 12 digestion vessels (TFM™-PTFE) with an internal volume of 100 mL (DAP-100+). An analytical balance (model AY 220, max. 220 g, 0.1 mg resolution, Shimadzu, Kyoto, Japan) was used for sample preparation.

2.3 Sample preparation

Samples of powdered eye shadows (made in Brazil, China and USA) were purchased in a local market and analysed. Two sample groups were selected: cosmetics for adult and children. The price of these samples ranged from US$ 3.00 to US$ 20.00.

The samples were accurately weighed and were mineralised in a block digester. In the mineralization, 100 mg of the eye shadow sample was weighed in PFA tubes, followed by the addition of 5 mL of HNO₃ (2 mol L⁻¹), 2 mL of
H₂O₂ (30% w w⁻¹) and 1 mL of Triton X-100 (5% w v⁻¹). The tubes were closed, the mixture was heated at 100 °C for 180 min and the solutions were quantitatively transferred to polypropylene flasks and diluted with water to 15 mL. The mineralization were made in triplicate with and without the addition of standard to verify the accuracy of the analytical method and to detect possible losses of analytes during sample preparation. The final concentrations added were of 40, 40, 700, 700, 200 and 80 µg L⁻¹ for Cd, Co, Cr, Cu, Ni and Pb, respectively.

A sample of black color was used for microwave digestion with HF. Two hundred mg of each eye shadow sample were weighed into a Teflon (DAP 100) vessel and added 6 mL of concentrated HNO₃, 2 mL of H₂O₂ (30%) and 2 mL of concentrated HF. After cooling, the samples were transferred to 50 mL volumetric flasks, were added 24 mL of H₃BO₃ (4%) and filled up to volume with deionized water. The microwave oven heating program performed was composed of two steps: (1) 5-minute ramp (800W), 5-minute holding time (800 W); (2) 5-minute ramp (1800W), 30-minute holding time (1800 W). The maximum temperature and pressure for steps 1 and 2 were 180°C and 70 bar and 210°C and 70 bar, respectively.

3 Results and Discussion

3.1 Optimisation of the sample preparation

The sample preparation was optimised with the help a full factorial design (2³ = 8 experiments). The variables studied were HNO₃ concentration (2 or 7 mol L⁻¹), sample mass (150 or 250 mg) and heating time (1 or 3 hours). Sample mass and HNO₃ variables were studied in order to identify the best compromise condition for low dilution factor and acidity. As the system (digester block) has no pressure control, we tried to achieve a suitable sample preparation controlling the heating time. In this case, this variable was also studied. The objective was to identify the best condition for sample mineralisation. In all of the experiments, 2 mL of 30% w w⁻¹ H₂O₂ and 1 mL of Triton X-100 (5% w v⁻¹) were added to the eye shadow.
Triton X-100 was used as a surfactant because it was observed that the eye shadows remained on the solution surfaces due to the small particle size and a high value of surface water tension, the surfactant helps with homogenization.

The analyses were performed in axial and radial modes and a total of 12 responses were obtained for each experiment.

As several responses were analysed simultaneously, an important aspect is how to combine these data. In this case, the desirability function was used, and the signals were normalised between 0 (lowest signals) and 1 (highest signals). Equation 1 shows how this transformation was performed:

$$
\begin{align*}
0 & \text{ if } y < L \\
\left( \frac{y - L}{T - L} \right)^{s} & \text{ if } L \leq y \leq T \\
1 & \text{ if } y > T
\end{align*}
$$

Equation 1

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

After the calculation of the individual desirability values ($d_i$), it is possible to combine the results and obtain the global desirability ($D$), calculated using the geometric mean (Equation 2):

$$
D = \sqrt[d_1\times d_2 \times \ldots \times d_m]{d_1\times d_2 \times \ldots \times d_m}
$$

Equation 2

The global desirability ($D$) values can be viewed in Table 2. As can be observed, the best working conditions (values near 1) for axial mode ($D_1$) were obtained in experiment 5 (0.95), while for radial mode ($D_2$), the best result was obtained in experiment 8 (0.96). However, the goal was to identify a commitment condition for both modes. Thus, a new calculation of the geometric mean was made using the global desirability values of the each mode ($D = \sqrt{D_1 \times D_2}$).

After performing the new global desirability calculation, it was observed that the experiments 5, 7 and 8 showed the best conditions with desirability.
values very similar (ranging from 0.92 to 0.93). The acid concentration used in the experiments 7 and 8 were 7 mol L\(^{-1}\), while in the experiment 5 was 2 mol L\(^{-1}\). Thus, the acid concentration influenced (2 mol L\(^{-1}\)) the choice of experiment 5 as the ideal, because used acid concentration 2 mol L\(^{-1}\), once it has been previously reported the advantages of the use of dilute acid, and require lower dilution for analysis by ICP OES. Table 3 shows the final conditions of the sample preparation.

3.2 Analytical Performance Parameters

The ICP OES parameters were studied using a fractional factorial design (2\(^{9-5}\)), requiring 16 experiments to study 9 variables simultaneously. A 1 mg L\(^{-1}\) aqueous multi-element solution was used. Table 4 shows the variables and the working conditions\(^{24}\). The determination of Pb was performed with GF AAS due an interference of Fe in the most intense emission lines and the lack of adequate sensitivity in the analysis with ICP OES.

After optimising the conditions of sample preparation and instrumental parameters of the ICP OES, the analytical performance parameters were evaluated. Table 5 shows the limits of detection and quantification, linearity, sensitivity and precision to axial and radial views ICP OES and GF AAS (Pb determination).

Particularly for calculation of limits of detection in ICP OES was used the concept of background equivalent concentration (BEC), defined as the concentration of the analyte that produces a signal equivalent to the emission intensity of the background at the spectral line measured. The incorporation of BEC values in the calculation of LOD allows the evaluation of any change in operational conditions\(^ {25}\). The LOD and LOQ for the GF AAS were calculated from 10 independent blank samples measured once each in accordance with IUPAC recommendations\(^ {26}\).

The precision was evaluated in terms of repeatability and was determined the relative standard deviation (RSD) of 10 measurements of a multielement solution with concentration of 40 µg L\(^{-1}\) for Cd, 50 µg L\(^{-1}\) for Pb and 250 µg L\(^{-1}\) for Co, Cr, Cu and Ni. The precision for each element is
adequate according to the standards of the acceptability criterion set by INMETRO (Instituto Nacional de Metrologia) which establishes an acceptable relative standard deviation of up to 10% for concentrations above 100 ng g$^{-1}$\textsuperscript{27}. The linearity was confirmed in the working range of each element, and the correlation coefficients found were equal or exceed 0.99.

The methods are with analytical performance parameters adequate to determine these elements in eye shadow and meet the limits required by legislations \textsuperscript{7,9}.

Certified reference materials similar to eye shadow were not available; thus, the validity of the proposed method was verified by addition-recovery studies and by comparing the proposed method with the conventional acid digestion procedure performed with microwave oven (closed vessel system) and HF.

The results, obtained from proposed method and the microwave-assisted digestion procedure, (Table 6) were compared using the Paired $t$ test. The sample used was the same employing in all optimisation study. The results obtained by both procedures for all elements were in concordance at the 95% confidence level. The values of Cd were lower than the LOQ (see details at Table 5).

Recovery rates between 80% and 120% were obtained (Table 7); these findings are considered according to FDA \textsuperscript{7} (which requires recoveries between 80% and 120% for concentrations above 1 µg g$^{-1}$). Thus, the results of the performance parameters studied confirmed quality assurance when using the proposed method for the determination of Cd, Co, Cr, Cu, Ni and Pd in eye shadow.

3.3 Determination of Cd, Co, Cr, Cu, Ni and Pb in the eye shadow samples

Table 7 shows the concentration values for the analytes in the samples. Among the 14 child eye shadow samples, 5 had concentrations above those permitted by the legislation. Samples 6 and 9 had higher concentrations than allowed for the Cd (ca. 5 mg kg$^{-1}$) and Pb (ca. 30 mg kg$^{-1}$). Sample number 10 presented concentrations near the allowed for Cd and Pb. Sample 11 showed
concentration above advisable (5 mg kg\(^{-1}\)) for Cr (44 mg kg\(^{-1}\)) and Ni (23.1 mg kg\(^{-1}\)) and the sample 14, the concentration exceeded the recommended concentration for the Cr (11.5 mg kg\(^{-1}\)). For adults’ eye shadow samples, 9 among 21 samples presented concentrations above tolerable value for Cr (samples 15, 17, 18, 19, 20, 24, 25, 26 and 30) and 6 samples for Ni (samples 15, 17, 18, 20, 25 and 30)\(^7\),\(^9\).

To analyse the behaviour of the samples in relation to the levels of the elements, a PCA (Principal Component Analysis) was performed on a 104 x 11 data matrix that contained samples with three authentic replicates in the rows (except for the Sample 16, which contains two authentic replicates) and the analytes in the columns, which were determined in the axial and radial modes (except for Pb). The data was auto-scaled and Pirouette version 4.5 was used in the calculation (Infometrix, Bothell, USA).

A model with 4 principal components (PCs) was selected to evaluate the behaviour of the samples and explained 96% of the total variance. The results are shown in Figure 1 as graphical representations of the scores (related to samples, Figure 1a) and loadings (related to the analyte, Figure 1b).

The authentic replicates and data obtained from the radial and axial views are very close, showing the low standard deviation in the measurements, but it was not possible to see the separation between the child and adult samples in the figure.

If the scores (Figure 1a) are analysed with the graph of loadings (Figure 1b), it is possible see that some child sample have high values of Cd and Pb. These samples have the values which are above the legislation.

It is also possible to observe the separation of the samples with respect to the black color. The black color samples (see dotted line ellipses) have higher concentrations of Co, Cr, Cu and Ni.

### 4 Conclusions

A simple and fast analytical method for the determination of Cd, Co, Cr, Cu, Ni and Pb in eye shadow, using diluted HNO\(_3\) (2 mol L\(^{-1}\)) for the sample preparation, has been proposed. It was possible to optimise the mineralisation
procedure for samples of eye shadow using the experimental design and the results were compared with microwave-assisted digestion procedure. Despite what is proposed in the literature, that this type of sample is digested with concentrated acids, it was possible to obtain good results using an acid concentration of $2 \text{ mol L}^{-1}$.

Using the optimised conditions of the sample preparation and instrumental parameters of the ICP OES and GF AAS, it was possible to determine the Cd, Co, Cr, Cu, Ni and Pb concentrations in the eye shadow samples from different brands, consumers, colors and countries and, by employing chemometric tools, observing a separation of the samples according to the concentration levels of the elements.

The analyte concentrations found in some samples were above the values recommended for both, adult and child samples. These results confirm the importance of quality control in the production of cosmetics as well as the applicability of the proposed method.

Acknowledgments

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References


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Figure captions

Fig. 1 Graphical representation of the (a) Scores and (b) Loadings of PC1 x PC2 in relation to elements concentration presented at Table 7.
Figure 1a

- Adult Sample
- Child Sample

PC1 50%

PC2 27%

Black eye shadow
Figure 1b

Axial View
Radial View
GF ASS

PC1 50%

PC2 27%
Table 1 The heating program for Pb determination using GFAAS

<table>
<thead>
<tr>
<th>Step</th>
<th>Temp (°C)</th>
<th>Time (s)</th>
<th>Ramp (°C s⁻¹)</th>
<th>Gas Flow (L min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>2 (Pyrolysis)</td>
<td>800</td>
<td>20</td>
<td>150</td>
<td>0.2</td>
</tr>
<tr>
<td>3 (Atomisation)</td>
<td>1200</td>
<td>3</td>
<td>0</td>
<td>Off</td>
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<tr>
<td>4</td>
<td>2500</td>
<td>3</td>
<td>0</td>
<td>0.2</td>
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<td>Experiments</td>
<td>Axial (D1)</td>
<td>Radial (D2)</td>
<td>Axial and Radial (D)</td>
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<tr>
<td>-------------</td>
<td>------------</td>
<td>-------------</td>
<td>---------------------</td>
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</tr>
<tr>
<td>1</td>
<td>0.62</td>
<td>0.64</td>
<td>0.63</td>
<td></td>
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<tr>
<td>2</td>
<td>0.44</td>
<td>0.47</td>
<td>0.46</td>
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<td>3</td>
<td>0.88</td>
<td>0.83</td>
<td>0.85</td>
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</tr>
<tr>
<td>4</td>
<td>0.71</td>
<td>0.77</td>
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<tr>
<td>5</td>
<td>0.95</td>
<td>0.89</td>
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<td>6</td>
<td>0.85</td>
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<td>7</td>
<td>0.93</td>
<td>0.93</td>
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<td>8</td>
<td>0.90</td>
<td>0.96</td>
<td>0.93</td>
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<tr>
<td>Parameters</td>
<td>Conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>----------------------------------------</td>
<td></td>
<td></td>
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<tr>
<td>Heating time</td>
<td>3 hours</td>
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<tr>
<td>Temperature</td>
<td>100 °C</td>
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<tr>
<td>Volume de H$_2$O$_2$ (30% m/v)</td>
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<td>Sample mass</td>
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<td>5 mL (2 mol L$^{-1}$)</td>
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<tr>
<td>Volume of Triton X-100</td>
<td>1 mL (5 % m/v)</td>
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Table 4 Optimized operation parameters for ICP OES measurements

<table>
<thead>
<tr>
<th>Variables</th>
<th>Conditions</th>
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<tbody>
<tr>
<td>V1: Integration time for low emission line (s)</td>
<td>5</td>
</tr>
<tr>
<td>V2: Integration time for high emission line (s)</td>
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</tr>
<tr>
<td>V3: Sample introduction flow rate (mL min$^{-1}$)</td>
<td>4.2</td>
</tr>
<tr>
<td>V4: Sample flow rate during the analyses (mL min$^{-1}$)</td>
<td>2.1</td>
</tr>
<tr>
<td>V5: Pump stabilisation time (s)</td>
<td>25</td>
</tr>
<tr>
<td>V6: Radio frequency applied power (W)</td>
<td>1200</td>
</tr>
<tr>
<td>V7: Auxiliary gas flow rate (L min$^{-1}$)</td>
<td>0.25</td>
</tr>
<tr>
<td>V8: Nebulisation gas flow rate (L min$^{-1}$)</td>
<td>0.83</td>
</tr>
<tr>
<td>V9: Cooling gas flow rate (L min$^{-1}$)</td>
<td>16</td>
</tr>
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</table>
Table 5 Analytical performance parameters

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<thead>
<tr>
<th>Parameters</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>**Pb</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>228.802</td>
<td>228.616</td>
<td>357.869</td>
<td>224.700</td>
<td>341.476</td>
<td>283.3</td>
</tr>
<tr>
<td>Calibration Curve</td>
<td>y=7.3x+10.4</td>
<td>y=5.03x+6.25</td>
<td>y=14.6x+5.9</td>
<td>y=2.7x+16.8</td>
<td>y=3.7x+2.6</td>
<td>y=0.004x+0.008</td>
</tr>
<tr>
<td>*y=1.03x+1.28</td>
<td>*y=0.7x+0.6</td>
<td>*y=0.9x+0.6</td>
<td>*y=0.3x+1.8</td>
<td>*y=0.3x+0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linearity (µgL⁻¹)</td>
<td>2.5 – 80</td>
<td>5 – 1500</td>
<td>5 - 1500</td>
<td>5 – 1500</td>
<td>5 - 1500</td>
<td>5 - 120</td>
</tr>
<tr>
<td>Regression Coefficient (r)</td>
<td>0.99</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>LOD (mg Kg⁻¹)</td>
<td>*0.2</td>
<td>*0.2</td>
<td>*0.8</td>
<td>*0.8</td>
<td>*0.9</td>
<td>0.02</td>
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<tr>
<td>LOQ (mg Kg⁻¹)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.9</td>
<td>0.06</td>
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<tr>
<td>*0.7</td>
<td>*0.7</td>
<td>*3</td>
<td>*3</td>
<td>*3</td>
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**GF AAS
*Radial View
Table 6 Mean and standard deviation values (n=3) for analytes content of black eye shadow sample obtained by method proposed and method comparative

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<th>Cu</th>
<th>Ni</th>
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Table 7 Cd, Co, Cr, Cu, Ni and Pb concentration (mg kg\(^{-1}\)) found in eye shadows for adult and child.

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Graphical Abstract

Eye shadow samples

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Adults

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