



SPECTROMETRIC DETERMINATION OF SOME HEAVY METALS IN COSMETIC PRODUCTS FOUND BY PRINCIPAL COMPONENT REGRESSION AND PARTIAL LEAST SQUARES METHODS

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ABSTRACT

Two multivariate calibration-prediction techniques, principal component regression (PCR) and partial least squares (PLS) were applied to the spectrometric multicomponent analysis of the cosmetic products containing lead, copper and cadmium without any separation step. The selection of variables was studied. A series of synthetic solution containing different concentrations of lead, copper and cadmium were used to check the prediction ability of the PCR and PLS. The results obtained in this investigation strongly encourage us to apply these techniques for a routine analysis and quality control of the cosmetics.

Keywords: lead, copper, cadmium, spectrometry, multivariate calibration

1. Introduction

Throughout human history it has been the pursuit of beauty is indispensable to the society. Therefore, a variety of herbal and chemical content of cosmetic products are used. Doubts about the adverse effects of chemicals on health in the cosmetics is increasing in recent years. In this sense, most accused substances are heavy metals.

Lead ; sunscreens, foundation, nail polish, lipstick and is used in many products such as tooth whitening pastes. because of the neurotoxic effects of toxicity; speech can lead to learning difficulties and behavior problems. Cadmium; DNA can cause malignancy by inhibiting the correction of mismatch can lead to affect the metabolism of calcium by bone damage and kidney damage. Copper; soaps, hair creams and medical / non-medical are included in creams and

makeup products. Although the metal amounts in cosmetic products usually at very low levels (0.793 ppm maximum) should be considered long-term exposure in the event of an increased risk of repetitive use [1].

Lead, cadmium and copper, are metals that appear together in many real samples. Several techniques such as X-ray fluorescence [2], atomic fluorescence spectrometry [3], atomic absorption spectrometry [4] , etc. have been used for the simultaneous determination of these ions in different samples. 4-(2-pyridylazo) resorcinol (PAR) [5] is an excellent complexometric indicator and potentiometric reagent for determination of many metal ions. PAR is a classical example (but not the only one) of a pH dependent non-specific, non-selective color reagent. Among the most widely used analytical methods are those based on the UV-Vis spectrophotometry techniques [6,7], due to the resulting experimental rapidity, simplicity and the wide application. However, the simultaneous determination of these ions by the use of the traditional spectrophotometry techniques is difficult because, generally, the absorption spectra overlap in a bright region and them superimposed curves are not suitable for quantitative evaluation. Nowadays quantitative spectrophotometry has been greatly improved by the use of a variety of multivariate statistical method; particularly principle component regression (PCR) and partial least squares regression (PLS).

Partial least squares (PLS) are the widely used regression method in chemometrics [8]. On the contrary to what occurs with principal component regression (PCR) calibration for a PLS calibration it is known that information from the concentration values is introduced into the calculation of the so-called latent variables; thus, it is may be that the eliminating wavelengths after variable selection, change the structure and/or the order of the latent variables of the PLS model. The basic concept of PLS regression was originally developed by Wold [9] and application of PLS in spectrophotometric data have been discussed in several studies [10-14].

The multivariate calibration techniques use full spectrum, full automation, multivariate data analysis and the reduction of noise and the advantages of the selection calibration model. In addition these multivariate calibrations do not need any separation procedure, they are very cheap, very easy to apply and very sensitive. For these reasons these multivariate techniques are popular today.

This paper aims to develop simple, fast and sensitive methods for the simultaneous determination lead, copper and cadmium in cosmetic products by Uv-Vis spectroscopy with the

help of principle component regression and partial least squares multivariate calibration techniques.

2. Experimental

2.1.Apparatus

A Shimadzu (Model UV-1700) UV-Visible spectrometer (Shimadzu, Kyoto, Japan), equipped with 1cm matched quartz cells was used for spectrometric measurements.

2.2.Standard solutions

All materials used were of analytical grade. Stock solutions of 1000 ppm lead, copper and cadmium were prepared in 1.10^{-3} M HCl. The solutions were stable for the least two weeks if they had been stored in a cool ($< 25^{\circ}\text{C}$) and dark place. A buffer solution, pH 3.0 - 4.0 were prepared by mixing 0.4 M potassium chloride and 0.1 M hydrochloric acid, pH 5.0 - 6.0 were prepared by mixing 0.4 M sodium borate and 0.1 M potassium hydrogen phosphate, and pH 8.0 and 10.0 were prepared 0.1 M o-phosphoric acid and 2.0 M sodium hydroxide in a 250 mL volumetric flask and diluting to the mark with redistilled water.

3. Chemometrics Methods

3.1. PCR and PLS

PCR and PLS are factor analysis multivariate statistical tools which have many of the full spectrum advantages and have been successfully applied to spectrophotometric analyses of multicomponent mixtures. PCR and PLS need a calibration step where the models for the spectra and the component concentrations of the unknown are estimated from the sample spectrum. Both of these methods involve spectral decomposition. The PCR decomposition is based entirely on spectral variations without regard for the component concentrations. In PLS, the spectral decomposition is weighted to the concentration. The major difference in the predictive abilities of these two methods is that PLS seems to predict better than PCR when there are random linear baselines or independently varying major spectral components which overlap with the spectral features of the analysis. The optimal of calibration method depend on the particular experimental conditions. However, PLS seems to a reasonable choice over a wide range of conditions.

4. Results and discussion

Figure 1 shows the absorption spectra for lead, copper and cadmium and their mixture in 0.1 M HCl. In order to build the three chemometric calibration, a training set was randomly prepared by

using the standard mixture solution containing 0.1-0.5 $\mu\text{g/mL}$ lead, 0.1-0.5 $\mu\text{g/mL}$ copper and 0.1-0.9 $\mu\text{g/mL}$ cadmium in the variable proportions as shown in Table 1. The absorbance data matrix were obtained by measuring at the 27 wavelengths with the intervals $\Delta\lambda = 5 \text{ nm}$ in the 385 – 515 nm spectral region. The prepared calibrations of three techniques using the absorbance data sets were used to predict concentration of the unknown values of lead, copper and cadmium in their mixture. Linearity range was 0.1-0.5 $\mu\text{g/mL}$ for lead and copper, and 0.1-0.9 $\mu\text{g/mL}$ for cadmium in the multivariate calibration proposed.

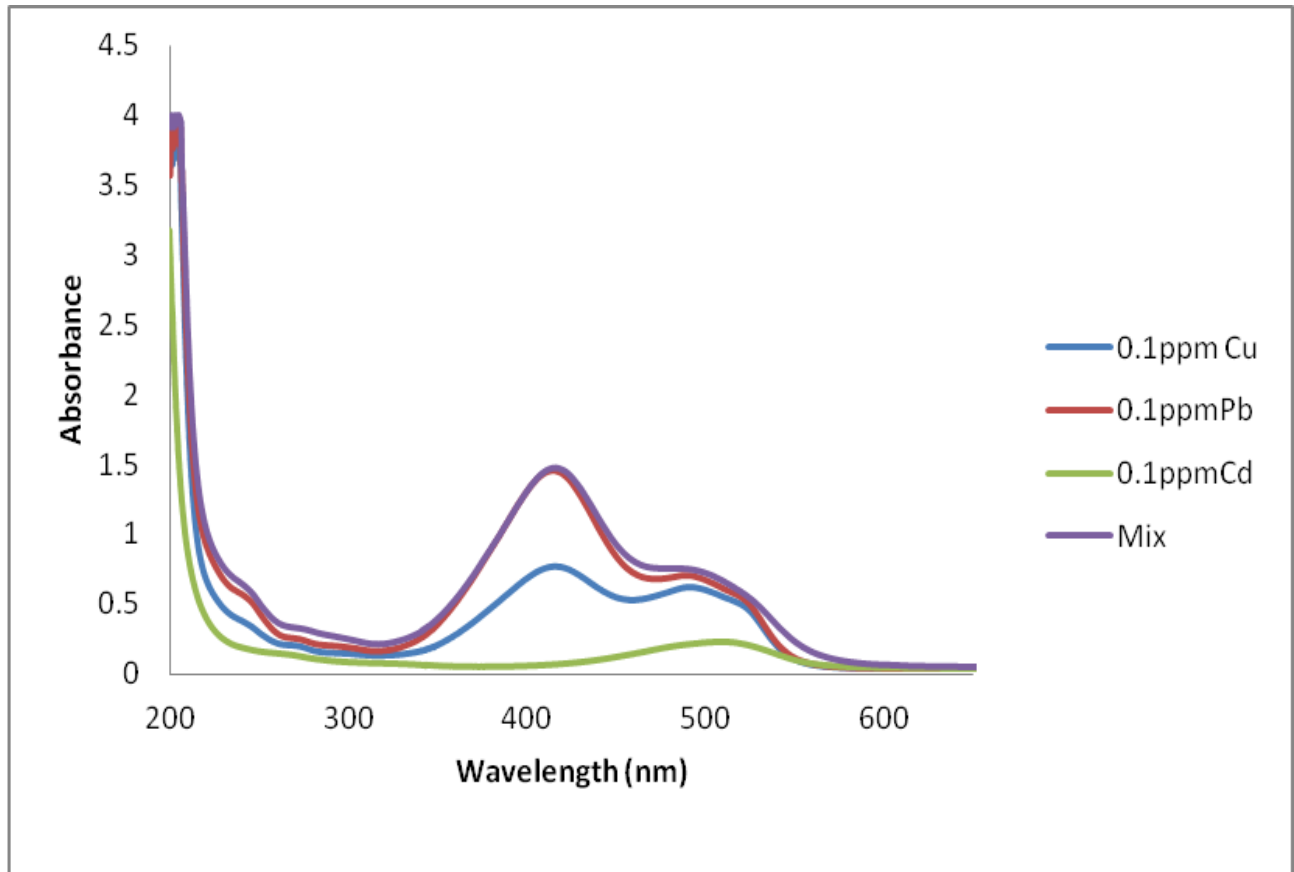


Fig.1. Original absorption spectra of 1.0 ppm Cu, 1.0 ppm Pb, 1.0 ppm Cd and their mixture in 0.1M HCl

Table 1. Concentration of Cu^{2+} , Pb^{2+} and Cd^{2+} in the calibration set. Concentration values are expressed as ppm.

Sample No	Cu^{2+}	Pb^{2+}	Cd^{2+}	Sample No	Cu^{2+}	Pb^{2+}	Cd^{2+}
1	0.10	0.10	0.10	17	0.20	0.20	0.30
2	0.10	0.40	0.10	18	0.20	0.20	0.70
3	0.10	0.10	0.30	19	0.20	0.30	0.30
4	0.10	0.40	0.30	20	0.20	0.30	0.70
5	0.20	0.10	0.10	21	0.40	0.20	0.30
6	0.20	0.10	0.30	22	0.40	0.20	0.70
7	0.20	0.40	0.10	23	0.40	0.30	0.30
8	0.20	0.40	0.30	24	0.40	0.30	0.70
9	0.20	0.10	0.10	25	0.10	0.20	0.30
10	0.20	0.10	0.50	26	0.10	0.20	0.50
11	0.20	0.30	0.10	27	0.10	0.40	0.30
12	0.20	0.30	0.50	28	0.10	0.40	0.50
13	0.30	0.10	0.10	29	0.30	0.20	0.30
14	0.30	0.10	0.50	30	0.30	0.20	0.50
15	0.30	0.30	0.10	31	0.30	0.40	0.30
16	0.30	0.30	0.50	32	0.30	0.40	0.50

Spectra from a set of sodium acetate–acetic acid buffer solutions with pH values in the range of 4.0–10.0 were sampled at the reaction time of 300 s (see Fig. 2, 3 and 4). It can be seen that the different pH conditions did not affect significantly the spectral absorbance of the Pb^{2+} -PAR, Cu^{2+} -PAR and Cd^{2+} -PAR complexes. The absorbance versus pH of the Pb^{2+} -PAR, Cu^{2+} -PAR and Cd^{2+} -PAR reactions with the PAR ligand were also studied at different times with the measurements being recorded at λ_{max} ($\text{Pb(II)}) = 414.4\text{nm}$, and λ_{max} ($\text{Cu(II)}) = 506.0\text{ nm}$ and λ_{max} ($\text{Cd(II)}) = 412.8\text{ nm}$. The kinetic curves for iron(III)/ligand aluminum(III)/ligand and copper(II)/ligand reactions were not change with different pH. Thus, considering all the factors for the pH effects described above, a pH of 10.0 was selected for this work.

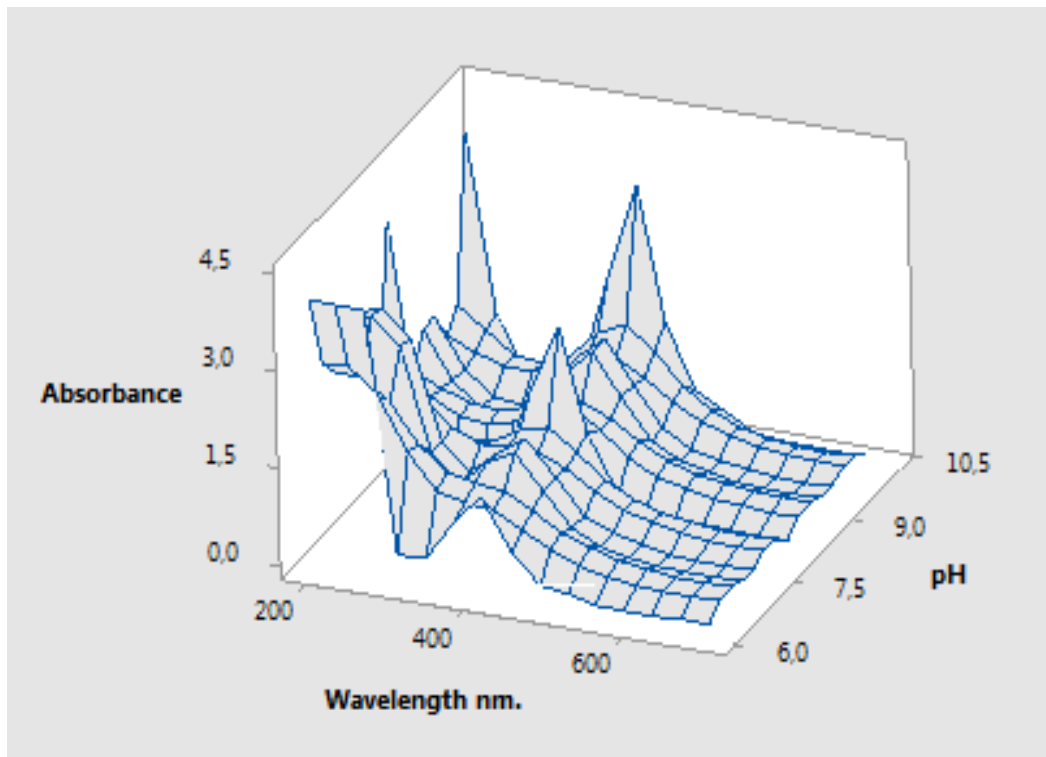


Fig.2. Spectra of Pb²⁺-PAR complexes at different pH

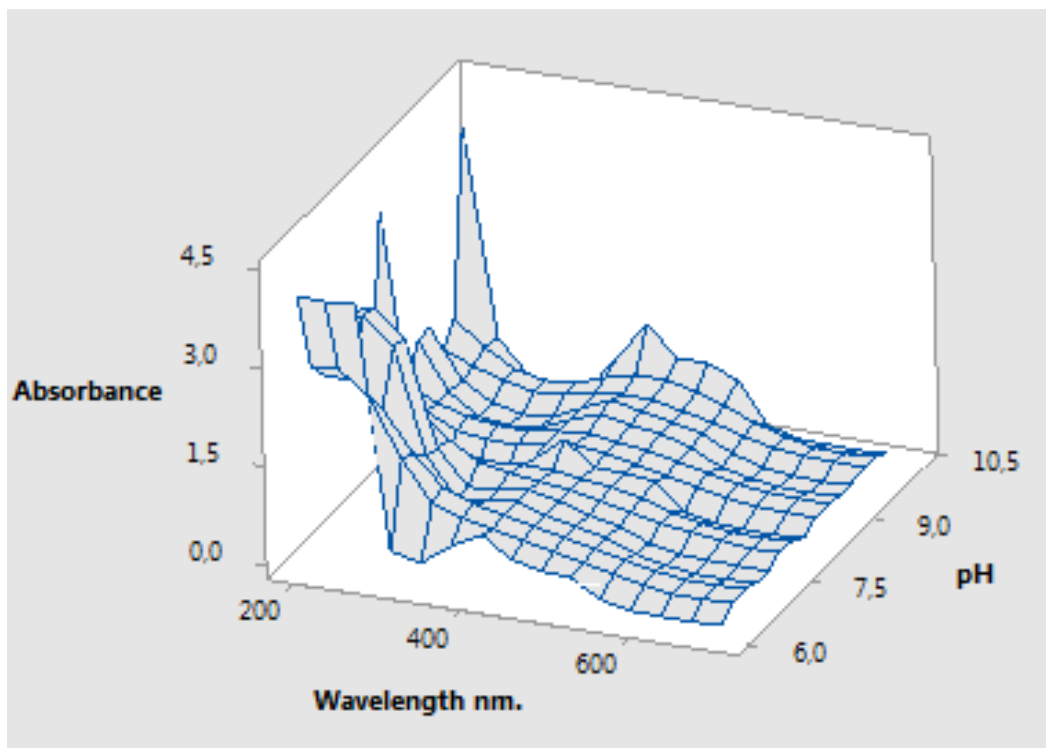


Fig.3. Spectra of Cu²⁺-PAR complexes at different pH

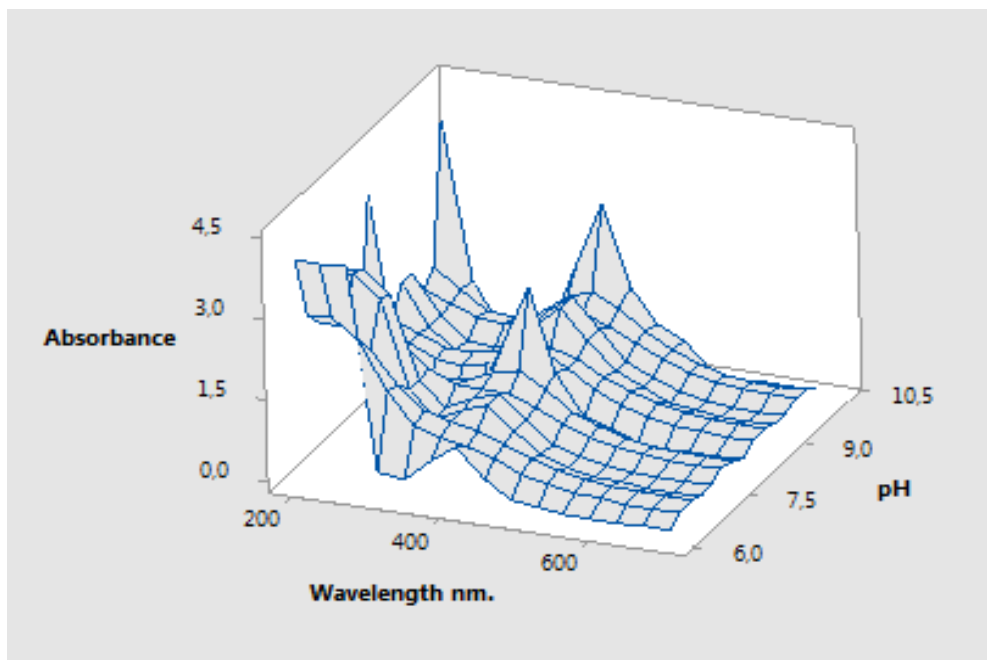


Fig.4. Spectra of Cd²⁺-PAR complexes at different pH

Pb²⁺-PAR, Cu²⁺-PAR and Cd²⁺-PAR ligand complex formation the amount of PAR in order to have the most appropriate, Pb²⁺, Cd²⁺ and Cd²⁺ solution pH by adding various volumes of metal solutions PAR ambient pH = 10 was adjusted with buffer. Passing to the results obtained with the graphs ligand 5 times more highest absorbance values is reached. According to these results, the most appropriate amount of ligand in the formation of the complex was selected 5 times.

A calibration for each technique was computed in the MAPLE 7.0 and PLS Toolbox 4.0 software by using set consisting of cosmetic products and their absorbance data. The multivariate calibrations of two techniques were used to predict the unknown concentrations of lead, copper and cadmium in the samples.

Some statistical parameters were given for the validation of the constructed calibrations for the training set and synthetic triple mixtures of cosmetic products.

The application competence of a calibration model can be explained in several ways. We can also examine these results numerically. One of the best ways to do this by examining the predicted residual error sum-of-squares or PRESS. To calculate PRESS we compute the errors between the expected and predicted values for all the samples, square them, and sum them together.

$$\text{PRESS} = \sum_{i=1}^n (C_i^{\text{added}} - C_i^{\text{found}})^2$$

Strikingly speaking, this is not a correct way to normalize the PRESS values when not all of the data sets contain the same number of samples. If we want correctly compare PRESS values for data sets that contain differing numbers of samples, we should convert to standard error of prediction (SEP), which is given by following formula.

$$\text{SEP} = \sqrt{\frac{\sum_{i=1}^n (C_i^{\text{added}} - C_i^{\text{found}})^2}{n-1}}$$

Where C_i^{added} the added concentration of analyte is, C_i^{found} is the found concentration of analyte and n is the total number of the synthetic mixtures. The SEP can provide a good measure of how well, on average, the calibration model performs. Often, however, the performance of the calibration model varies depending on the analyte level.

In the application of two chemometric techniques to the synthetic mixtures containing cosmetic products in variable compositions, the mean recoveries and relative standard deviations for PCR and PLS were found to be 99.99% , 0.002; 99.91% , 6.620 for lead and 99.96%, 0.014; 98.92%, 5.63 for copper and 100.00%, 0.002; 100.57%, 4.764 respectively for cadmium (Table 2).

Table 2. Composition of test set and predicted values for Cu^{2+} , Pb^{2+} and Cd^{2+} by PCR and PLS regression. Concentration values are expressed as ppm.

Cu^{2+}			Pb^{2+}			Cd^{2+}		
Actual	PCR	PLS	Actual	PCR	PLS	Actual	PCR	PLS
0.30	0.29	0.29	0.10	0.09	0.10	0.10	0.10	0.09
0.30	0.29	0.31	0.10	0.09	0.11	0.70	0.70	0.67
0.30	0.29	0.32	0.20	0.19	0.17	0.10	0.10	0.11
0.30	0.29	0.28	0.20	0.20	0.19	0.70	0.70	0.72
0.40	0.39	0.39	0.10	0.09	0.11	0.10	0.10	0.10
0.40	0.39	0.38	0.10	0.09	0.09	0.70	0.70	0.72
0.40	0.39	0.37	0.20	0.09	0.19	0.10	0.10	0.10
0.40	0.39	0.42	0.20	0.19	0.20	0.70	0.69	0.69
0.10	0.09	0.08	0.30	0.29	0.31	0.50	0.50	0.54

0.10	0.09	0.09	0.30	0.30	0.29	0.70	0.70	0.68
0.10	0.09	0.09	0.40	0.40	0.40	0.50	0.50	0.53
0.10	0.09	0.10	0.40	0.39	0.40	0.70	0.70	0.65
0.40	0.39	0.42	0.30	0.29	0.28	0.50	0.49	0.51
0.40	0.39	0.40	0.30	0.29	0.30	0.70	0.70	0.64
0.40	0.39	0.40	0.40	0.40	0.41	0.50	0.50	0.50
0.40	0.39	0.35	0.40	0.39	0.40	0.70	0.70	0.68

According to the added concentration and the concentration found in samples, the SEP and PRESS values of PCR and PLS techniques were calculated $2.95 \cdot 10^{-10}$, $4.29 \cdot 10^{-6}$ and 0.0017, 0.0105 for lead, $1.36 \cdot 10^{-7}$, $9.22 \cdot 10^{-5}$ and 0.0051, 0.0178 for copper and $6.47 \cdot 10^{-10}$, $2.52 \cdot 10^{-12}$ and 0.0107, 0.0295 respectively for cadmium (Table 3).

Table 3. Statistical parameters in the calibration-prediction

Parameter	Method	Cu ²⁺	Pb ²⁺	Cd ²⁺
PRESS	PCR	$1.36 \cdot 10^{-7}$	$2.95 \cdot 10^{-10}$	$6.47 \cdot 10^{-10}$
	PLS	0.0051	0.0017	0.0107
SEP	PCR	$9.22 \cdot 10^{-5}$	$4.29 \cdot 10^{-6}$	$2.52 \cdot 10^{-12}$
	PLS	0.0178	0.0105	0.2950
r	PCR	1.0000	1.0000	1.0000
	PLS	0.9793	0.9913	0.9891
Intercept	PCR	0.9999	1.0000	1.0000
	PLS	0.9999	1.0021	0.9716
Slope	PCR	$5 \cdot 10^{-5}$	$7 \cdot 10^{-6}$	$6 \cdot 10^{-6}$
	PLS	-0.0017	-0.0018	0.0128

The linear regression analysis of the added concentration and the concentration found in the synthetic mixtures were realized for each cosmetic products and for each calibration technique. In this regression analysis, the correlation coefficient (r), intercept, slope and relative standard deviation values were found satisfactory for the proposed chemometric techniques in Table 3. As can be seen, all the statistic values indicated that principle component regression techniques is convenient for the determination of cosmetic products in synthetic mixtures.

A summary of the assay results for the cosmetic products are given Table 4. The results of all methods were very to each other as well as to the label value of commercial cosmetic products formulation.

Table 4. Assay results for the commercial cosmetic products

Sample Name	PCR			PLS		
	Cu ²⁺	Pb ²⁺	Cd ²⁺	Cu ²⁺	Pb ²⁺	Cd ²⁺
Lipstick	150±1.02	122±0.80	Not found	148±1.18	118±2.02	Not found
Foundation cream	140±0.88	136±0.74	12±0.82	126±0.20	132±0.60	9±0.70
Eye shadow	168±1.54	112±1.12	48±0.30	154±0.74	108±0.80	41±1.30
Eyeliner	180±1.10	324±0.40	66±1.30	172±1.20	288±3.30	60±1.70

Results obtained are average of six experiments for each technique.

Conclusion

Two chemometric technique in spectrometric analysis, PCR and PLS, were proposed for the simultaneous determination of lead, copper and cadmium in their triple mixtures. These techniques were applied with great success to four commercial cosmetic products. The resolution of highly overlapping cosmetic mixtures was achieved by the use of PCR and PLS techniques. A selection of working wavelength having high correlation values with concentration due to interference coming from matrix sample or additional analytes outside the working range. The proposed chemometric techniques can be applied for the routine analysis of cosmetic products formulation without any a priori chemical separation and without time consuming.

Acknowledgement

This research work has been supported by research grants from Süleyman Demirel University Scientific Research Project 4424-YL1-15.

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