J. Iranian Chem. Res.
5 (4) (**2012**) 213-221
ISSN 2008-1030

Simultaneous spectrophotometric determination of lead, copper and nickel using xylenol orange by partial least squares

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Received 02 August 2011
Received in revised form 05 October 2012
Accepted 20 October 2012

A partial least squares (PLS) calibration model was developed for the simultaneous spectrophotometric determination of Pb (II), Cu (II) and Ni (II) using xylenol orange as a chromogenic reagent. The parameters controlling behavior of the system were investigated and optimum conditions were selected. The calibration graphs were linear in the ranges of 0.0–9.091, 0.0–2.719 and 0.0–2.381 ppm for lead, copper and nickel, respectively. The experimental calibration matrix was designed with 21 mixtures of these chemicals. Absorbance data were taken between 350-650 nm and absorbance data were autoscaled. A set of synthetic sample mixtures were used to validate the proposed method. The root mean square errors of predictions (RMSEPs) and percent of relative prediction errors (RSEPs) are 0.2164, 0.0744, 0.0735 ppm and ±7.1855, ± 6.3193, ± 7.0806% for lead, copper and nickel, respectively.

Keywords: PLS; lead; copper; nickel; Simultaneous determination

1. INTRODUCTION

Lead and copper are metals of prime environmental concern. Nickel is among the toxic metals of significance for environmental surveillance, food control and occupational medicine, toxicology and hygiene. For studying environmental problems and environmental control, simple and sufficiently sensitive methods for the determination of these and other metals are necessary.

Several techniques such as polarography [1], flame atomic absorption spectrometry [2], voltametry and chromatographic methods such as reversed-phase liquid chromatography [3] and ion chromatography [4], inductively coupled plasma mass spectrometry (ICP-MS) [5] ect, have been used for the simultaneous determination of these ions in different samples.

Among the most widely used analytical methods are those based on the UV-visible spectrophotometry techniques, due to both the resulting experimental rapidity and simplicity and the wide application. The critical points against the use of spectrophotometric procedures for the determination of metal ions in solution are the potential problems associated with chemical interferences and the color development process itself, both closely related to the chemical condition of the reaction medium. This means that separation and/or masking steps always have to be considered and included in these analytical procedures, making them slower and more sensitive to operational errors which ultimately may reflect on the precision and accuracy of the method [6]. Also, the simultaneous determination of these ions by the use of the UV- visible spectrometry techniques and conventional metallochromic indicators in aqueous solution is difficult because, generally, the absorption spectra overlap in this region and the superimposed curves are not suitable for quantitative evaluation. Therefore, multivariate calibration methods are playing a very important role in the multicomponent analysis of mixture by UV-visible spectrophotometry.

Nowadays, multivariate calibration has become an indispensable part of modern analytical chemistry. The advantage of multicomponent analysis using multivariate calibration is the speed of the method of determination for components of interest in a mixture, as a separation step can be avoided.

Recently, the ability of PLS multivariate calibration method has been successfully employed in simultaneous determination of binary, ternary and quaternary mixtures [7-9]. The theory and application of PLS in spectrometry have been discussed by several workers [10- 16].

In this paper, a UV- visible spectrophotometric method using partial least squares (PLS), is proposed for simultaneous determination of lead, nickel and copper in synthesis solutions at low concentrations (ppm levels) without any priory step of separation. It was successfully applied to simultaneous determination of Pb (II), Cu (II) and Ni (II) in natural, tap waters solutions.

2. EXPERIMENTAL

2.1. Reagent

All chemicals were of analytical-reagent grade and used directly without further purification. Doubly distilled water was used to prepare buffer and reagent solutions.

The color development and the spectrophotometric measurements were performed at an ambient temperature of 25 ±0.5 ºC. Stock solutions of lead (II), copper (II) and nickel (II) were prepared from their commercial salts (nitrate) and standardized titrimetrically. A stock Xylenol orange solution (10^{-4} M) was prepared by dissolving reagent. A buffer solution (pH = 5) was prepared using acetate buffer solution.

2.2. Instrumentation and software

All spectra were recorded on an Agilent 8453 UV-visible diode array spectrophotometer using the Agilent UV-visible ChemStation Software for data acquisition. All spectra were recorded from 350 to 650 nm using quartz cuvettes with 1.00 cm light paths. Measurements of pH were made with a Metrohm 692 pH meter using a combined electrode.

The data pretreatment was done with MATLAB for windows (Mathworks, Version 7.2). PLS program for calibration–prediction and experimental design was written in MATLAB according to the algorithm described by Martens and Naes [17] and PLS routine of PLS Toolbox (Eigenvector Company, Version (2.1).

2.3. Procedure

Known amounts of the standard solutions of each cation, 1.0 ml of buffer solution were placed in a 5 ml volumetric flask and completed to final volume with deionized water (final pH was 5.0). The final concentration of these solutions varied between 0.0–9.091, 0.0–2.719 and 0.0–2.381 ppm for lead, copper and nickel, respectively. Finally the spectra of all prepared solutions were recorded on spectrophotometer. The concentration ranges were chosen so that the absorbances obtained for all standard solutions were not greater than 1.5.

3. RESULTS AND DISCUSSION

3.1. Selection of the optimum chemical conditions

For finding the optimum conditions, the influence of pH values on the spectrum of each complex at a constant concentration of each ion was studied. The formed complexes with cited ions were affected with pH. In order to select the optimum pH value at which the minimum overlap occurs, influences of the pH of the medium on the absorption spectra of lead, cooper and nickel complexes were studied over the pH range 2.0-9.0. Therefore, pH of 5.0 was chosen as the optimum pH for this work because minimum overlap occurs at this pH. Fig. 1 shows the absorption spectra for the individual metal complexes at pH=5.

The effect of XO concentration on the accuracy of the determination was also investigated. A reagent concentration of 5×10^{-5} M was chosen because it ensures a sufficient reagent excess with respect to the all metal ions concentrations.

To ensure of linear behavior of each metal complex and to obtain the linear dynamic range for each metal ion an individual calibration curve was constructed with several points at λ_{max} of each complex (579.0 for lead, 574.0 for copper and 584.0 for nickel) as absorbance value versus metal ion concentration. The linear ranges, are 0-9.091, 0-2.719, 0-2.381 ppm for lead, copper and nickel, respectively.

Linear regression results; line equations and R^2 are:

Abs. = $0.1026C_{Pb}+0.031$ ($R^2=0.9975$),

Abs. = $0.1658C_{Cu}+0.0547$ ($R^2=0.9975$) and

Abs. = $0.3556C_{Ni}-0.0068$ ($R^2=09931$) for lead, copper and nickel respectively.

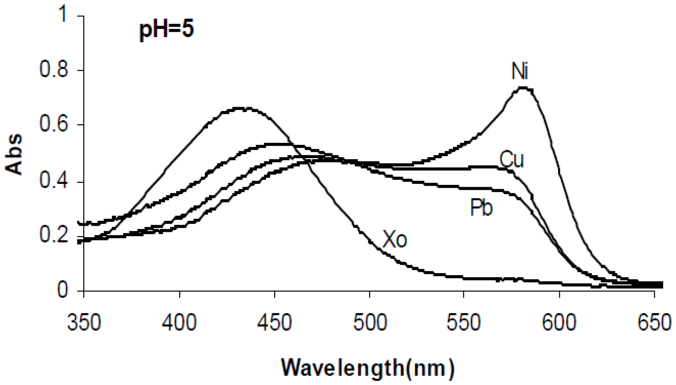

Fig. 1. The effect pH on the absorption spectra of the XO and lead, copper and nickel complexes in pH=5. Concentration of XO is 5×10^{-5} M and each ion is 2 ppm.

3.2. Calibration and prediction data sets

Multivariate calibration methods are suitable for the analysis of large number of samples. However, they are not advisable for the determination of large numbers of analytes because of the complexity of the calibration matrix. Moreover, the preparation and analysis of the standards belong to the calibration set are the most expensive step in the multivariate calibration procedure. A mixture design was used to maximize statistically the information content in the spectra [18]. The determination of the lead, copper and nickel in mixtures by spectrophotometric mean using multivariate calibration involved constructing a calibration and prediction set.

A training set of 21 samples was taken (Table 1). The concentrations of lead, copper, nickel 0-9.091, 0-2.719, 0-2.381 ppm varied, respectively. Each standard, prediction and synthetic mixture was prepared according to procedures explained in the procedure section. The absorption spectra were recorded between 350 and 650 nm against a blank. The spectral region between 350 and 650 nm, which implies working with 300 experimental points per spectra (as the spectra are digitized each 1.0 nm), was selected for the analysis, because this is the zone with the maximum spectral information from the mixture components of interest.

In prediction step, 8 mixtures prepared that these are not included in the previous set and were employed as an independent test (Table2). Prediction solutions were chosen according to their situation on the graph, inside the range of calibration solutions (i.e. lies in the calibration range).

Table 1. The 21 designed experimental.

Solution Number	Concentration (ppm)		
	Ni	Cu	Pb
1	0	0	9.091
2	0.476	0	7.172
3	0.952	0	5.454
4	1.428	0	3.636
5	1.910	0	1.818
6	2.381	0	0
7	1.910	0.544	0
8	1.428	1.088	0
9	0.952	1.632	0
10	0.476	2.176	0
11	0	2.719	0
12	0	2.176	1.818
13	0	1.632	3.636
14	0	1.088	5.454
15	0	0.544	7.172
16	0.476	0.544	5.454
17	0.476	1.088	3.636
18	0.476	1.632	1.818
19	0.952	0.544	3.636
20	0.952	1.088	1.818
21	1.428	0.544	1.818

Table 2. Prediction set composition, predicted values and relative error.

No.	Actual value (ppm)			Prediction value (ppm)			Relative error (%)		
	Pb	Cu	Ni	Pb	Cu	Ni	Pb	Cu	Ni
1	0.46	2.25	0.38	0.50	2.17	0.35	8.64	-3.48	-8.16
2	5.84	0.08	0.95	5.41	0.07	0.90	-7.28	-9.38	-5.04
3	3.74	1.20	0.47	3.64	1.13	0.44	-2.63	-6.24	-5.85
4	2.44	0.82	1.20	2.24	0.75	1.14	-8.02	-8.37	-4.94
5	2.00	0.83	1.23	1.95	0.77	1.20	-2.75	-7.22	-2.56
6	3.00	0.45	1.40	2.82	0.39	1.30	-5.88	-12.81	-7.18
7	1.93	1.45	0.70	2.18	1.37	0.61	12.64	-5.27	-12.86
8	1.26	0.95	1.30	1.49	0.83	1.27	17.81	-12.90	-2.30

3.3. Number of significant factors

The selection of the number of factors used in the calibration with PLS is very important for achieving the best prediction. In order to determine the optimum number of factors (latent variables) for the partial least squares calibration model, we applied the cross validation procedure. There are several cross validation routines and "leave one sample out" was used in our experiments. As the calibration set was performed with 21 spectra, the calibration was performed on 20 of them and the concentration of the sample left out was predicted. The process was repeated 21 times until each calibration sample had been left out once. The prediction residual sum of squares (PRESS) for each number of factors was calculated by comparing the predicted concentration of compounds in each sample with known concentration of compounds in standard solutions. PRESS is defined as follows, equation 1,:

$$\textbf{PRESS}= \sum_{i=1}^{n}(\hat{C}i - Ci)^2 \qquad \text{(eq.1)}$$

Where C_i is the reference concentration for the ith sample and $\hat{C}_i$ represents the estimated concentration. One reasonable choice for the optimum number of factors would be the number which yielded the minimum PRESS. In our case, 11 factors (half the standards + 1) were used as the maximum number of initial factors. However, using the number of factors (h*) that yields a minimum PRESS usually leads to some overfitting. A better criterion for selecting the optimum number of factors involves the comparison of PRESS from models with fewer than (h*) factors. Fig. 2 shows a plot of PRESS versus the number of factors. For finding the smallest model (fewest number of factors), the F-statistic was used to carry out the significance determination [19].

In this work, 8 synthetic test samples were analyzed with the proposed method. The prediction results are given in Table 2. The plots of these predicted concentrations versus actual concentrations using the optimum model are shown in Fig. 3.

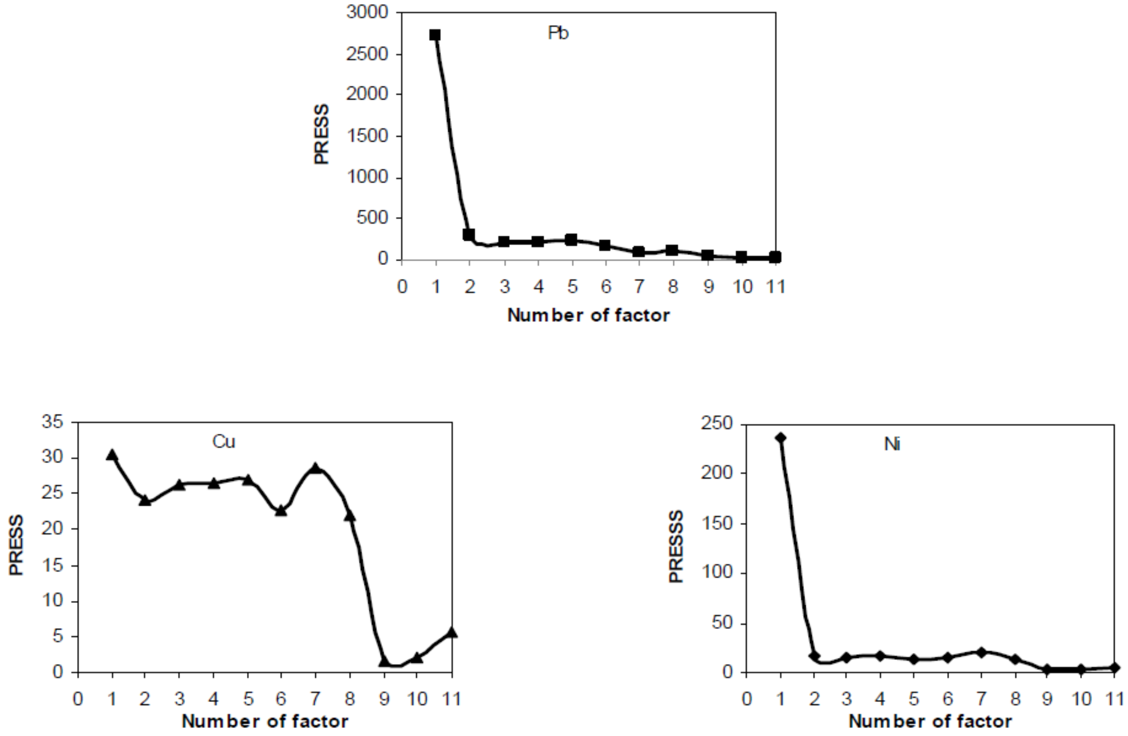

Fig. 2. The PRESS values as a function of number of factors.

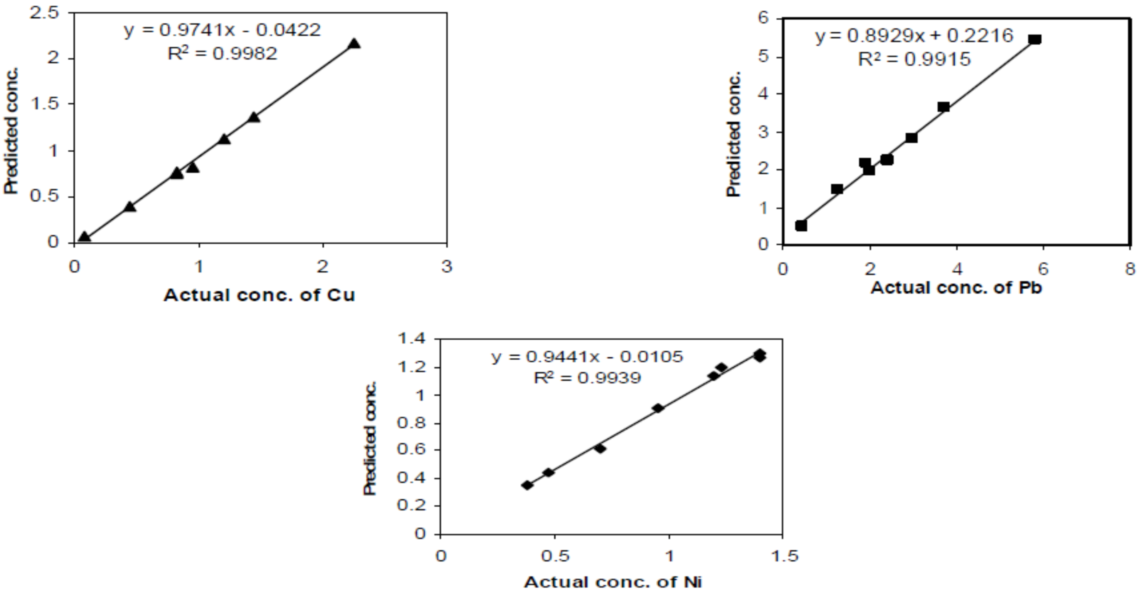

Fig. 3. Plots of predicted concentration vs. actual concentration for three cations in the prediction set.

3.4. Statistical parameters

There are several functions to evaluate and assess the correctness and also the validity of the calibration model the effects of the preprocessing methods. In this study we have applied several objective functions to check the efficiency of the calibration and preprocessing methods. The root mean square error of prediction (RMSEP), equation 2, is:

$$\textbf{RMSEP}=\sqrt{\frac{\sum_{i=1}^{n}(\hat{C}_i - C_i)^2}{n}} \qquad \text{(eq. 2)}$$

And the relative standard error of prediction (RSEP), equation 3:

$$\textbf{RSEP (\%)} = 100\times\sqrt{\frac{\sum_{i=1}^{n}(\hat{C}_i - C_i)^2}{\sum (C_i)^2}} \qquad \text{(eq. 3)}$$

where C_i is the true concentration of the analyte in the sample i, $\hat{C}_i$ represents the estimated concentration of the analyte in the sample i, C is the mean of the true concentration in the prediction set, and n is the total number of samples used in the prediction sets, that were calculated. The concentration data of the prediction set and the values of RMSEP, RSEP, and PRESS are summarized in Table 3.

Table 3. Statistical parameter of the test matrix using the PLS model.

cations	NPC	PRESS	RSEP (%)	RMSEP
Pb	9	0.3747	7.1855	0.2134
Cu	9	0.0441	6.3193	0.0744
Ni	9	0.0433	7.0806	0.0735

3. 5. Interference study

One of the striking points of any new method is its interfering limit of the potential interferences. So to check and evaluate the tolerance limit of different interferes for the proposed method, the interferences due to several cations and anions were studied

in detail. The influence of various species on the absorbance of a solution mixture containing 5.454 ppm of Pb (II), 0.544 ppm of Cu (II) and 0.476 ppm of Ni (II) was investigated. The starting point was 1200 ppm of interference metal ions in the presence of lead, copper and nickel; an ion was considered as interference when its presence produced a variation in the absorbance of the sample greater than 5%. This increment of absorbance was evaluated at λ_{max} for every metal ion, in order to establish the different effects of the interfering ions on each analyte. The cations and anions tested and their interfering limits are listed in Table 4.

3.6. Analysis of test samples

In order to test the applicability in the presence of matrix interference, the proposed method was applied in a variety of situations. Real matrix samples were analyzed as described under the experimental section. The results of the prediction are summarized in Table 5. The results in Table 5 show that PLS model is able to predict the concentrations of lead, copper and nickel in alloy samples.

Table 4. Effect of various ions on the simultaneous determination of three metals**.**

Foreign ions	Tolerance limit (ppm)
Na^+, Br^-, F^-, Cl^-, No^{2-}, No^{3-}	1200[a]
Ti^+	800
K^+, Mg^{2+}	500
Cu^{2+}	400
Sr^{2+}	60
Cd^{2+}	8
Hg^{2+}, Zn^{2+}	<2
La^{3+}	<1

[a] Maximum concentration studied.

Table 5. PLS results applied on the real matrix samples (ppm)

Type of water	Added (ppm)			Found (ppm)			Recovery %		
	Pb	Cu	Ni	Pb	Cu	Ni	Pb	Cu	Ni
Tap water	2.40	1.40	0.53	2.34	1.45	0.51	97.5	103.6	96.2
Taq-e-bostan(Frontal)	3.75	1.20	0.37	3.70	1.22	0.36	98.7	101.6	97.3
	3.45	0.97	0.61	3.60	0.96	0.60	104.3	99.0	98.3

4. CONCLUSION

Multivariate method PLS by use of spectrophotometric data have proved to be valid analytical tools even when applied to complex mixtures characterized by a severe overlapping and high ratios in analytes concentration. This technique is simple, fast, precise and affordable. Also it requires no complex pretreatment or chromatographic separations of the samples containing analytes. The results confirm that the model can be used for the simultaneous determination of lead, copper and nickel in synthetic and alloy samples at a wide range of metal ion concentration ratios to each other.

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