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Simultaneous kinetic spectrophotometric determination of Cu(II), Co(II) and Ni(II) using partial least squares (PLS) regression

Research Article

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Abstract: A partial least squares (PLS-1) calibration model based on kinetic--spectrophotometric measurement, for the simultaneous determination of Cu(II), Ni(II) and Co(II) ions is described. The method was based on the difference in the rate of the reaction between Co(II), Ni(II) and Cu(II) ions with 1-(2-pyridylazo)2-naphthol in a pH 5.8 buffer solution and in micellar media at 25°C. The absorption kinetic profiles of the solutions were monitored by measuring the absorbance at 570 nm at 2 s intervals during the time range of 0 – 10 min after initiation of the reaction. The experimental calibration matrix for the partial least squares (PLS-1) model was designed with 30 samples. The cross-validation method was used for selecting the number of factors. The results showed that simultaneous determination could be performed in the range 0.1-2 μg mL^{-1} for each cation. The proposed method was successfully applied to the simultaneous determination of Cu(II), Ni(II) and Co(II) ions in water and in synthetic alloy samples.

Keywords: *Partial least squares • Simultaneous kinetic determination • Cu(II) • Co(II) • Ni(II)*

1. Introduction

Heavy metals are grouped within the category of environmental toxins. Many organisms require trace amounts of metals to survive. Cobalt, nickel and copper are metals that appear together in many environmental samples. Therefore, their simultaneous analysis is important. Concomitant determination of metal cations by ultraviolet-visible (UV-Vis) spectrophotometry requires a non-selective chromogenic reagent. Different chelating agents have been proposed, such as 4-(2-pyridilazo) resorcinol (PAR), 1-(2-pyridylazo)2-naphthol (PAN) and diethyldithiocarbamate [1-5]. Melgarejo *et al*. [6] proposed a derivative spectrophotometric method based on the use of second-derivative absorption spectra for the simultaneous determination of microgram quantities of nickel, zinc and copper in an aqueous ethanol medium. The peak-to-baseline measurement technique was used with good results. Using the proposed method, nickel (0.3 – 2.0 ppm), zinc (0.5 – 3.0 ppm) and copper (0.5 – 3.0 ppm), in various ratios, were determined [6]. Additionally, Zarei *et al*. [7] applied a direct orthogonal signal correction-partial least squares method for simultaneous spectrophotometric determination of iron, nickel and cobalt in micellar media. In this method, the linear range was 0.30 – 4.50 μg mL^{-1} for Co(II), 0.20 – 3.00 μg mL^{-1} for Ni(II) and 0.30 – 5.00 μg mL^{-1} for Fe(II).

Reaction rate methods are becoming increasingly important in analytical chemistry. Recent breakthroughs in instrumental design and, especially, the incorporation of microcomputers into analytical chemical configurations

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are responsible for their present degree of development [8]. A number of differential kinetic methods were developed for resolving mixtures of analytes with similar or identical spectra that could not be resolved by equilibrium-based methods [9–17]. The simultaneous kinetic determination of such analytes is usually based on the difference in their reaction rate constants. The difference between the rate constants must be large enough for differential kinetic methods to discriminate the rate constants and for successful handling of univariate data [18]. However, in cases in which the sample matrix is complex or the analytes are present at low concentration levels, their reaction rates may be close to each other, and their similar chemical properties result in mutual interference, selectivity of the univariate approach is low and prediction is poor. Different chemometric methods, such as partial least squares (PLS) and artificial neural networks (ANN), can resolve multi-component kinetic systems by exploiting differences in kinetic behavior with respect to a common reagent [19-23] without requiring prior separation. PLS regression allows simultaneous spectrophotometric determination of several analytes and improves the data handling process of complex chemical systems [21]. The theory and applications of PLS in spectrometry have been discussed by several authors [22–26]. PLS is capable of being a full-spectrum method, and therefore, benefits from signal averaging of other full-spectrum methods, such as principal component regression (PCR) and classical least squares (CLS). PLS calibration of a multi-component system can be performed in two ways denoted PLS1 and PLS2. Several advantages of PLS2 are recognized. Firstly, a single common set of PLS factors exists for all analytes. This simplifies the procedure and interpretation and allows for simultaneous graphical inspection. Secondly, if analyte concentrations are strongly correlated, the PLS2 model is more robust than separate PLS1 models. Finally, when the number of analytes is large, the development of a single PLS2 model is performed more quickly than that of multiple individual PLS1 models. Practical experience, however, indicates that PLS1 calibration usually performs equally well or better in terms of predictive accuracy. Therefore, when the ultimate requirement of the calibration study is to permit the best possible prediction, a separate PLS1 regression for each analyte is advised [27]. In this research, the simultaneous kinetic-spectrophotometric determination of Cu(II), Co(II) and Ni(II) ions, using partial least squares (PLS) regression, is described. The method is based on the difference in the rate of the reaction between Cu(II), Co(II) and Ni(II) ions with PAN in micellar media.

2. Experimental Procedures

2.1. Apparatus

A Perkin-Elmer Lambda 45 UV–Vis spectrometer was used for recording and storage of UV–Vis absorbance spectra and kinetic curves using 10 mm quartz cells. A Metrohm model 713 pH-meter with a combined glass electrode was used for pH measurements. All calculations in the computing process were performed in Matlab7 and Microsoft Excel for Windows. The PLS_Toolbox 3.5 for MATLAB was used in this research.

2.2. Reagents

All chemicals were of analytical reagent grade and triply distilled water was used in all experiments. Stock Co(II), Cu(II) and Ni(II) solutions (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of $Co(NO_3)_6{\bullet}6H_2O$, $CuSO_4{\bullet}6H_2O$ and $NiSO_4{\bullet}6H_2O$ in water. A 5.0×10^{-3} mol L^{-1} PAN solution was prepared by dissolving 128 mg of PAN in 100 mL of ethanol (> 60°C). Citrate buffer solution (1 mol L^{-1}) of pH 5.8 was prepared from sodium citrate salt and sulfuric acid. Triton X-100 stock solution (14%, v/v) was prepared by dissolving 14 mL of concentrate solution (Merck) in distilled water (> 80°C).

2.3. Procedure

All solutions were equilibrated at 25 ± 0.1°C before initiating the reactions. An aliquot of the solution containing 1–20 μg each of Co(II), Cu(II) and Ni(II) cations was transferred into a 10 mL volumetric flask containing 1 mL of pH 5.8 citrate buffer solution. 1 mL of 14% Triton X-100 solution was added followed by 2 mL of 5.0×10^{-3} mol L^{-1} PAN solution. Immediately, the solution was diluted to the mark with triply distilled water and a portion was transferred into a quartz cell to monitor the increase in the absorbance at 570 nm over time. The absorption kinetic profiles of the standard solutions of Co(II), Cu(II) and Ni(II) with different concentrations, and their ternary mixtures, were recorded at 570 nm at 2 s intervals for 0 – 10 min after initiation of the reaction.

3. Results and discussion

3.1. Preliminary study of system

The chromogenic reagent, PAN, is a versatile reagent for the determination of trace amounts of numerous metals. PAN forms colored complexes with Zn(II), Cu(II), Fe(III), Cd(II), Co(II) and Ni(II). As Fig. 1 illustrates, the spectra for PAN and its complexes with Co(II), Cu(II) and Ni(II) cations overlap. Therefore, each compound interferes in the spectrophotometric determination

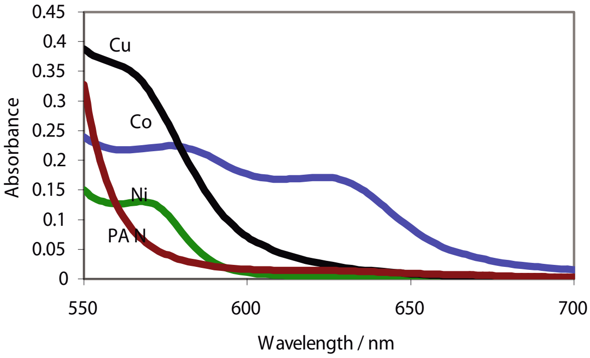

Figure 1. Absorbtion spectra of a 1.0°—10^{-3} mol L^{-1} of PAN solution and its complexes with 1.5 μg mL^{-1} each of of Co(II), Cu(II) and Ni(II).

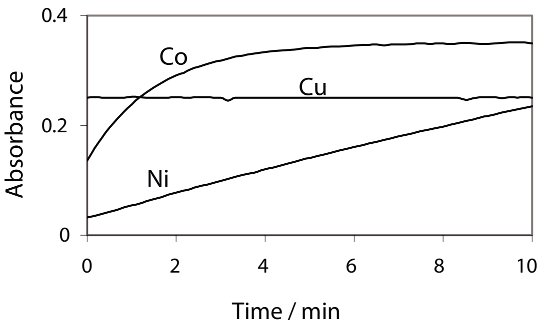

Figure 2. Kinetic profiles of complexation reaction of 0.5 μg mL^{-1} each of Co(II), Ni(II) and Cu(II) with PAN (1°—10^{-3} mol L^{-1}) in micellar media, buffer citrate (0.1 mol L^{-1}, pH 5.8) at 570 nm.

of the others. The kinetic profiles of complexation reactions of Co(II), Cu(II) and Ni(II) with PAN in micellar media (at 570 nm and 25°C) are presented in Fig. 2. As Fig. 2 shows, the complexation reaction of Cu(II) with PAN at pH 5.4 occurred immediately after mixing the reagents, whereas the complexation reactions of Co(II) and Ni(II) proceeded at different rates. Because the kinetic profiles for the complexation reactions of the cations investigated are different, the system was used for their simultaneous determination. PAN, and its metal complexes, are insoluble in water. Therefore, 1.4% (v/v) of Triton X-100 was applied to provide a micellar medium in order to prevent the necessity for extraction or mixed solvent systems. The effect of Triton X-100 concentration on the absorbance of the system was investigated previously [1,27].

3.2 Optimization of the system

In order to determine the optimum pH, the effect of pH and different buffer solutions on the spectra of the complexes formed, and on the rate of the complexation reaction, was investigated using a constant concentration of each ion with PAN. Although no significant changes in the spectra of Co(II), Cu(II) and Ni(II) complexes with PAN were observed in the pH range 3 – 10, the rates of the complex formation reactions were affected by the pH of the solution and the type of the buffer. For example, in acetate buffer at pH 4.5, the complexation reaction of nickel was completed in approximately 60 min, whereas in an ammonium/ammonia buffer at pH 9.2, the reaction was completed in less than 10 min. Various buffer solutions and pH values were tested. A citrate buffer solution at pH 5.8 was determined to provide the optimum results. A 1 × 10^{-3} mol L^{-1} solution of PAN (a 30-fold excess over the maximum concentration of metal ions) was applied to obtain a pseudo-first order reaction with respect to each analyte ion.

3.3 Univariate Calibration

In the proposed method, Beer's law was obeyed in the concentration range of 0.1 – 2 μg mL^{-1} for Co(II), Cu(II) and Ni(II). Table 1 itemizes the linear regression parameters for calibration data for determination of Co(II), Cu(II) and Ni(II) individually. The limits of detection (LOD) of the method for determination of Co(II), Cu(II) and Ni(II) individually-defined as the concentration equivalent to three times the standard deviation of five replicate measurements of the blank-are also shown in Table 1.

3.4 Partial Least Squares (PLS) Method

The first step in simultaneous determination of different metal ions by PLS methodology involves construction the calibration set for ternary mixtures of Co–Ni–Cu. The concentration ranges for analytes were chosen such that the absorbences obtained for all standard samples were less than 2. Thirty ternary mixtures were selected as the calibration set (Table 2). Their composition was

Table 1. Analytical characteristics for analysis of Co(II), Cu(II) and Ni(II) in ternary mixtures by PLS regression.

Analytes	Calibration equation[a]	(R^2)[b]	linear range (μg mL^{-1})	LOD[c] (μg mL^{-1})
Co(II)	Y = 0.6922C − 0.0035	0.9987 (n = 7)	0.1 – 2.0	0.030
Ni(II)	Y =1.0427C + 0.008	0.9996 (n = 7)	0.1 – 2.0	0.020
Cu(II)	Y=0.612C - 0.010	0.9865 (n = 6)	0.1 – 2.0	0.033

[a] *C is the concentration of metal ion in μg mL^{-1}.*
[b] *Squared correlation coefficient.*
[c] *LOD.*

randomly designed for obtaining more information from the calibration procedure. Under these conditions, the calibration models were obtained.

Table 2. Values of the Cu(II), Co(II) and Ni(II) concentrations (μg mL^{-1}) used as calibration solutions (randomly designed)

Sample	Concentration (μg mL^{-1}) Ni	Co	Cu
1	1.0	0.4	0.2
2	0.9	0.7	0.9
3	0.4	0.7	0.6
4	0.5	0.5	0.8
5	0.3	0.7	0.0
6	0.8	0.5	0.0
5	0.0	0.9	1.2
8	0.8	1.0	0.7
9	0.5	0.5	0.7
10	0.8	0.9	0.2
11	1.2	0.8	0.2
12	0.7	0.3	0.0
13	0.1	0.7	0.6
14	0.8	1.0	0.6
15	0.8	1.0	0.4
16	0.9	0.3	0.2
17	0.1	0.5	0.7
18	0.2	0.2	0.4
19	0.5	0.7	0.4
20	0.5	0.3	0.5
21	0.2	1.3	0.2
22	0.6	0.4	0.8
23	0.3	0.4	0.8
24	0.1	0.7	2.0
25	0.3	0.5	0.6
26	0.8	1.0	0.5
27	0.4	0.6	0.4
28	0.2	0.2	0.1
29	0.3	0.7	0.8
30	0.1	0.9	1.0

The resulting model was validated with a synthetic 13-mixture set containing the metal ions of interest in different proportions that were randomly selected. To select the number of factors in the PLS algorithm, a cross-validation method, leaving out one sample at a time, was employed [27-28]. For the data set of 30 calibration kinetic profiles, PLS-1 calibration on 29 of the calibration kinetic profiles was performed, and, using this calibration, the concentration of the single sample omitted during the calibration process was obtained. This process was repeated 30 times-each sample having been left out only once. Thereby, the concentration of each sample was predicted and compared with the known concentration of the reference sample to calculate the prediction residual error sum of squares (PRESS). Fig. 3 illustrates a plot of the PRESS versus the number of factors for each individual component. For finding the smallest number of factors, the F-statistic test was used to perform significant determination. The optimal number of factors for Cu(II), Co(II) and Ni(II) was 3, 4 and 3, respectively. In this work, 13 synthetic test samples were analyzed with the proposed method. The results obtained are listed in Table 3. The prediction error of a single component in the mixtures was calculated as the relative standard error (RSE) of the predicted concentration [27-28]:

$$\mathrm{R.S.E.}(\%) = \left(\frac{\Sigma_{j=1}^{N} (\hat{C}_j - C_j)^2}{\Sigma_{J=1}^{N} (C_j)^2} \right)^{1/2} \times 100 \qquad (1)$$

where N is the number of samples, C_j is the concentration of the component in the jth mixture and is the estimated concentration. The total prediction error of N samples is calculated as follows:

$$\mathrm{R.S.E.}_{\cdot t}(\%) = \left(\frac{\Sigma_{i=1}^{M} \Sigma_{j=1}^{N} (\hat{C}_{ij} - C_{ij})^2}{\Sigma_{i=1}^{M} \Sigma_{J=1}^{N} (C_{ij})^2} \right)^{1/2} \times 100 \qquad (2)$$

where C_{ij} is the concentration of the ith component in the jth sample and $\hat{C}_{ij}$ is its estimation. Table 3 also shows the reasonable single and total relative errors for such a system. In addition, the plots of predicted concentrations versus true concentrations for the validation data set (Fig. 4) show that the residual values are significantly low. Therefore, the PLS-1-based method is a valuable predictive tool for real sample analysis.

3.5 Interference study

The effects of different ions on the simultaneous determination of 0.5 mg L^{-1} of the Co(II), Cu(II) and Ni(II) ions by PLS regression was studied. An ion was considered to be an interferent, when it caused a variation in the recovery of analytes greater than ± 5%. As the results (Table 4) demonstrate, most of the cations and anions did not interfere in the determination of Co(II), Cu(II) and Ni(II) even when present in a 500 – 1000-fold excess greater than the concentrations of Co(II), Cu(II) and Ni(II). However, Hg(II) interfered strongly in the determination of Cu(II). The reaction of Hg(II) with PAN, as with Cu(II), occurred immediately and produced a constant signal at 570 nm during the entire time range of the experiment. In the presence of ethylenediaminetetraacetic acid (EDTA) and cyanate the complexation between metals (II) and PAN is completely masked and they have serious interference effect in this system.

Table 3. Composition of prediction data set (randomly designed), validation by the PLS model and statistical parameters for the system

Sample	Synthetic samples (μg mL⁻¹)			Prediction (μg mL⁻¹)			Recovery (%)		
	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
1	0.2	1.5	0.0	0.2	1.44	0	100.0	96.0	-
2	0.5	0.7	0.3	0.48	0.7	0.29	96.0	100.0	96.7
3	0.3	0.3	0.7	0.28	0.29	0.67	93.3	96.7	95.7
4	0.5	1.1	0.3	0.48	1.08	0.3	96.0	98.2	100.0
5	0.8	0.3	0.8	0.83	0.32	0.78	103.8	106.7	97.5
6	0.6	1.0	0.6	0.58	1	0.61	96.7	100.0	101.7
7	0.4	0.8	0.7	0.39	0.79	0.66	97.5	98.8	94.3
8	0.1	0.2	0.1	0.1	0.21	0.09	100.0	105.0	90.0
9	0.4	1.7	0.2	0.4	1.78	0.2	100.0	104.7	100.0
10	0.4	0.7	0.9	0.38	0.65	0.88	95.0	92.9	97.8
11	0.7	0.7	0.1	0.69	0.64	0.1	98.6	91.4	100.0
12	0.7	0.6	0.3	0.71	0.65	0.29	101.4	108.3	96.7
13	1.5	0.3	0.7	1.49	0.31	0.67	99.3	103.3	95.7
Mean Recoveries							98.3	100.1	97.2
RSE_{single} (%)^a							2.48	4.42	3.61
RSE_{total} (%)^b									3.80

[a, b] *Calculated using Eqs. 1 and 2.*

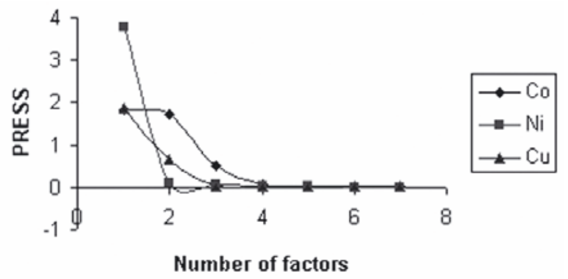

Figure 3. Plot of PRESS against the number of factors for Cu(II), Ni(II) and Co(II)

Table 4. Tolerance ratio of diverse ions on the determination of a mixture of 0.5 μg mL⁻¹ Co(II), Cu(II) and Ni(II) ions.

Ion	Tolerance ratio (w/w)
SCN⁻, CH_3COO^-, $S_2O_3^{2-}$, tartrate, urea, thiourea, oxalate, F⁻, citrate, Cl⁻, I⁻, Br⁻, ascorbic acid	1000
Mg^{2+}, Bi^{3+}, Na^+, K^+, Mo(VI), Al^{3+}, Cr^{3+}, Fe^{3+}, Ag^+, Ca^{2+}, Mn^{2+}, As^{3+}, Fe^{2+}, Cd^{2+}	500
Hg^{2+}	1

3.6. Application

The PLS regression method was successfully applied to the simultaneous determination of Co(II), Cu(II) and Ni(II) in a synthetic sample that was prepared according to the composition of three alloys [29,30]. The results are shown in Table 5. Acceptable agreement between the results obtained and known values indicated the successful applicability of the PLS regression method for the simultaneous determination of Co(II), Cu(II) and Ni(II) in complex samples.

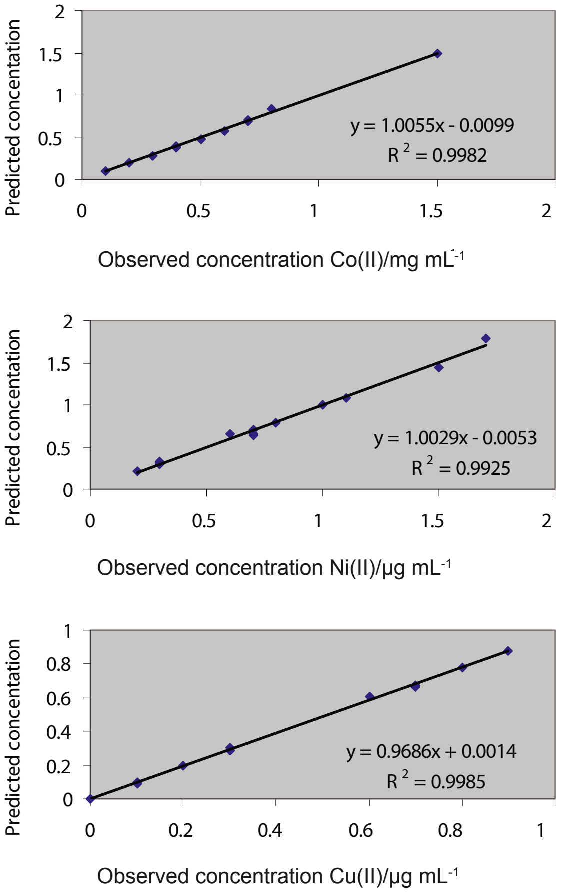

Figure 4. Predicted vs. true concentration of Co(II), Ni(II) and Cu(II) using PLS-1 by the proposed method.

Table 5. Results of analysis of Co(II), Cu(II) and Ni(II) in alloys by the proposed method.

Recovery(%)			Found [a]			Composition	Alloy
Co(II)	Ni(II)	Cu(II)	Cu(II)	Ni(II)	Co(II)		
100	98.05		-	51.2, 0.7	12.5, 0.3	Ni(52) Co(12.5) Mo(9) Cr(22) Al(1.2) / (%)	Ineonel 617
93.5	100		-	29.5, 0.45	15.9, 0.5	Ni(29.5) Fe(53) Co(17) / (%)	Nillo alloy K
111.2	99.1	106.5	7900, 46	2875, 55	1065, 72	Si(7800) Cu(7100) Mn(2000) Mg(4600) Cr(2700) Ni(2900) Zn(8000) Sn(2000) Pb(1000) V(1500) Ga(500) Co(1000) Sb(100) Ca(300) Ti(1500) Bi(600) / ng mL^{-1}	Coal (NBS, SRM-1632)

[a] *Average of four replicate measurements as (resulting value, standard deviation: (X, SD))*

4. Conclusion

The results presented indicate that PLS-1 is an excellent calibration method for the simultaneous determination of Co(II), Cu(II) and Ni(II) based on the differences in their reaction rates with PAN without requiring prior separation or masking. PLS regression is a powerful tool for the simultaneous determination of the analytes. Accuracy, precision, reproducibility, sensitivity and the linear range for the proposed method were satisfactory. This method is simpler and more rapid than some existing methods and provides lower LOD values.

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