



Spectrophotometric Simultaneous Determination of Cobalt and Nickel using 4-(5-Br-2 pyridylazo)-1,3-diaminobenzene (5-Br-PADAB) in Alloys by Partial Least Squares

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ABSTRACT

In this paper, a spectrophotometric method for simultaneous determination of Co (II) and Ni (II) using 4-(5-Br-2 pyridylazo)-1,3-diaminobenzene (5-Br-PADAB) as a chelating agent is introduced. During the study, the parameters controlling behavior of the system were examined and optimum conditions were selected. The impact of pH on the sensitivity and selectivity was investigated according to net analyte signal. A partial least squares multivariate calibration procedure was used for the analysis of binary mixtures of Co (II) and Ni (II) between 200 and 700 nm over the range of 85 – 1300 and 100 -1010 ng ml⁻¹ respectively. Applying the introduced method in several synthetic alloy solutions produced reliable results.

Key words: Nickel; Cobalt; 5-Br-PADAB; Simultaneous determination; PLS.

INTRODUCTION

Nickel and cobalt are metals existing together in many real and synthetic samples. Several techniques have been suggested and examined for the simultaneous quantification of cobalt and nickel in different media. Some of these methods include X-ray fluorescence, atomic fluorescence spectrometry, electrochemistry, chromatography and atomic absorption spectrometry¹⁻⁵. Using the UV-visible spectrometry techniques and conventional metallochromic

indicators in aqueous solution for the simultaneous determination of these ions is difficult because, generally, the absorption spectra overlap in this region and the superimposed curves are not suitable for quantitative evaluation. Then multivariate calibration methods are playing a very important role in the multicomponent analysis of mixture by UV-visible spectrophotometry and fluorimetry⁶⁻¹⁴. One of the recent applications of multivariate methods, including partial least squares (PLS) is to classify and quantify the results obtained from an array solutions of unspecific fluorescent indicators

which are exposed to these ions¹⁵⁻¹⁷. 4-(2-pyridylazo)-1, 3-diaminobenzene (PADAB) and its derivatives such as 5-Cl-PADAB, 5-Br-PADAB, 5-I-PADAB, 3,5-diBr-PADAB, and 3,5-diCl-PADAB are used as chromogens for the spectrophotometric determination of traces of Co(II). These reagents show high color stabilities and extreme sensitivities in their reactions in strongly acidic medium. 5-Br-PADAB has been applied to the determination of Co(II) in silicate rocks and meteorites and wine with good precision and accuracy¹⁸⁻¹⁹.

In this paper, using partial least-squares multivariate calibration, a UV-vis spectrophotometric method is proposed for simultaneous determination of cobalt and nickel in real samples. The method is based on the reaction between Co(II), Ni(II) and 5-Br-PADAB at pH 6. This multivariate calibration produced the accurate predictions as it was successfully applied to simultaneous determination of Co(II) and Ni(II) in several synthetic alloy solutions. As our knowledge indicates, this is the first report for the simultaneous spectrophotometric determination of metal ions by this reagent.

EXPERIMENTAL

Reagents

All chemicals applied in this study were of analytical-reagent grade and were used directly without further purification. Doubled distilled water was used to prepare buffer and reagent solutions. Stock solutions of Co(II) and Ni(II) were prepared by dissolving 1.4 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.29 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, respectively, in distilled water and diluting to 100 ml. 5-Br-PADAB solution ($3.3204 \times 10^{-4}\text{M}$) was prepared by dissolving appropriate amount of the powder in ethanol and diluting with water to 5 ml, and a buffer (pH 6, 0.2 M of KH_2PO_4) was prepared.

Apparatus

Using a varian carry 100 spectrophotometer, 1 cm quartz cell, scan rate of 600 nm min^{-1} and a slit width of 2 nm, UV-vis absorbance digitized spectra were collected. Having the blank solution as a reference, all spectral measurements were performed. The recorded spectra were digitized with one data point per nanometer and arranged in data matrix for calibration and prediction. Measurements

of pH were made with Metrohm 827 pH-meter using a combined glass electrode. The computations were made with a Pentium IV, 2.0 GHz computer. All the programs in the computing process were written in MATLAB (Mathworks, version 7.6) for windows.

PLS calibration

Procedure

Having a series of 5 ml volumetric flasks, the researchers added 1.5ml of 5-Br-PADAB ($3.3204 \times 10^{-4}\text{M}$) to obtain a final concentration of $9.9 \times 10^{-5}\text{M}$, 1ml KCl (0.2 M), an appropriate amount of each metal ion containing Co(II) 0.42-6.35 μg , and of Ni(II) 0.5-5.05 μg to each of them and the solutions were made up to the mark with buffer (pH 6). To ensure quantitative formation of the complexes in the whole range of calibration, an excess concentration of 5-Br-PADAB has been applied. The concentration ranges were chosen in order that the absorbances obtained for all standard solutions were not greater than 2.5.

RESULTS AND DISCUSSION

The influences of the pH of the medium on the absorption spectra of metal complexes were studied over the pH range 1.0-11.0. To calculate sensitivity (SEN) and selectivity (SEL) for each analyte at different pH values, net analyte signal (NAS) was applied (Fig. 1).

The NAS is defined as:

$$\text{NAS} = (I - R_n R_n^+) r_n \quad \dots(1)$$

where I is the identity matrix, R_n the matrix of pure spectra of all constituent except the n th analyte, R_n^+ the pseudoinverse or general inverse of R_n and r_n the spectrum of the analyte. Therefore, pH 6 was selected as the optimum value, to compromise the sensitivity and selectivity of two metal ions. The NAS is a vector and is related to the regression vector as depicted in the following equations:

$$c = Rb + e \quad \dots(2)$$

$$b = \frac{\text{NAS}}{\| \text{NAS} \|_2} \quad \dots(3)$$

where $\|NAS\|_2$ designates the square root of the sum of squares of each element in the vector b , c the analyte concentration and e the error vector. Sensitivity (SEN) and selectivity (SEL) were calculated using following equations:

$$SEN = \frac{1}{\|b\|_2} = \|NAS\|_2 \quad \dots(4)$$

$$SEL = \frac{1}{\|b\|_2 \|r_x\|_2} = \frac{\|NAS\|_2}{\|r_x\|_2} \quad \dots(5)$$

To examine the stoichiometry of the reactions, mole ratio (mole of metal ion/mole of ligand) method was applied for each complex at a constant concentration of the ligand (5-Br-PADAB 4×10^{-5} M) and varying concentration of each metal

Table 1: Composition of synthetic samples, their predictions by PLS model and statistical parameters for the system

Sample	Synthetic ($\mu\text{g ml}^{-1}$)		prediction ($\mu\text{g ml}^{-1}$)		Recovery (%)	
	Ni ²⁺	Co ²⁺	Ni ²⁺	Co ²⁺	Ni ²⁺	Co ²⁺
1	0.75	0.28	0.76	0.28	100.61	101.72
2	1.00	0.28	0.99	0.27	98.20	98.27
3	0.25	0.56	0.25	0.55	99.52	98.40
4	0.88	0.56	0.90	0.56	101.63	99.81
5	0.75	0.70	0.76	0.70	101.48	100.03
6	0.88	0.70	0.88	0.70	100.00	99.25
7	0.88	0.84	0.87	0.85	98.83	100.29
8	0.50	0.99	0.51	0.99	101.55	100.45
9	0.75	0.99	0.77	0.99	101.77	100.17
10	0.63	1.13	0.62	1.13	99.21	100.32
11	1.00	1.13	0.99	1.11	98.12	98.27
12	0.38	1.27	0.37	1.26	99.78	99.59
13	0.63	1.27	0.64	1.26	100.97	99.60
14	0.75	1.27	0.76	1.27	101.12	99.91
15	0.88	1.27	0.87	1.26	98.79	99.73
Mean recovery	-	-	-	-	100.11	99.72
Single RSE/%	-	-	-	-	1.48	0.76
Total RSE/%	-	-	-	-		1.10

Table 2: Determination of Co(II) and Ni(II) in synthetic samples by PLS (concentration in $\mu\text{g ml}^{-1}$)

Sample	Composition of synthetic mixture	Found ^a	
		Ni ²⁺	Co ²⁺
Nilo	Co(0.50),Ni(0.87),Fe(1.56)	0.85±0.02	0.49±0.04
Permivax	Co(0.55),Ni(1.00),Fe(0.66)	0.99±0.02	0.55±0.03
Low expansion	Ni(1.05),Fe(1.27)	1.04±0.03	-

a) Mean ± S.D. (four replicates)

ion. The results showed that Co(II) and Ni(II) react with 5-Br-PADAB in 1:2 mole ratio. To ensure quantitative formation of the complexes in 1:2 mole ratio, an excess concentration of 5-Br-PADAB has been chosen. In order to ensure linear behavior of each metal complex and to obtain the linear dynamic range for each metal ion, an individual

calibration curve was drawn with several points at λ_{max} of each complex (508 for cobalt, and 497 for nickel) as absorbance value versus metal ion concentration. The linear ranges are 0.1–1.3 ppm for cobalt and 0.1–1 ppm for nickel. Linear regression results, line equations and R^2 are $Abs = 0.9515 C_{Co} + 0.4735$ ($R^2 = 0.9993$) for cobalt and

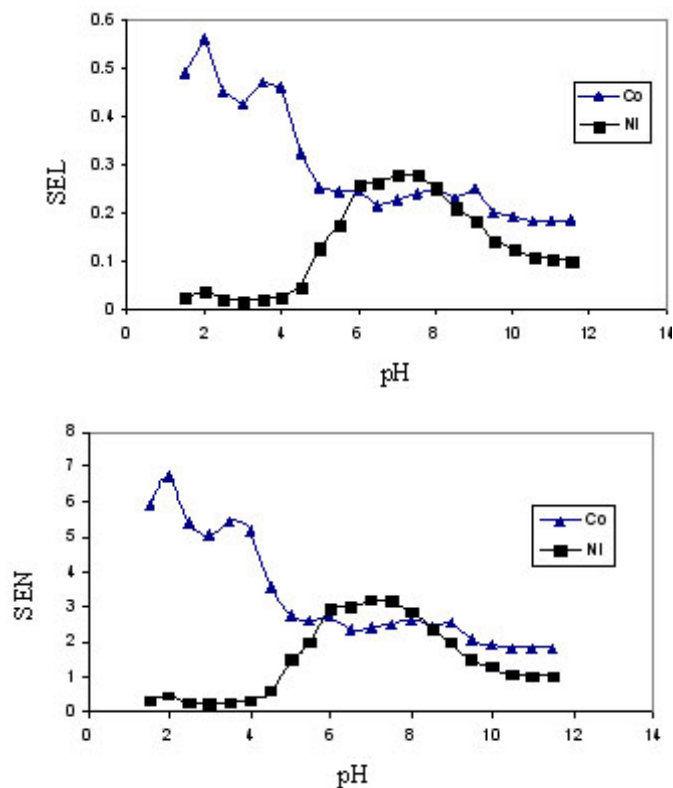


Fig. 1: Plot of sensitivity (SEN) and selectivity (SEL) for Co(II) (\blacktriangle) and Ni(II) (\blacksquare) at different pH values

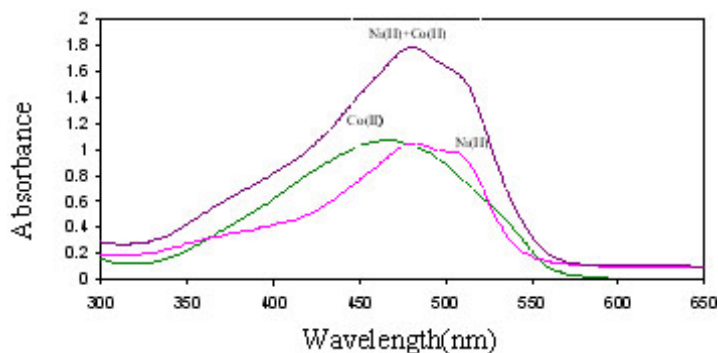


Fig. 2: Absorption spectra of Co(II) and Ni(II) complexes and their mixture complexes with 5-Br-PADAB. Curves for $0.849 \mu\text{g ml}^{-1}$ of Co(II) and $0.845 \mu\text{g ml}^{-1}$ of Ni(II)

Abs = 0.7815C_{Ni} + 0.7427 (*R*² = 0.9889) for nickel. Fig. 2 shows the absorption spectra for the individual metal complexes and a binary mixture of them. The PLS multivariate calibration requires a careful experimental design of the standard composition of calibration set. In this work, a calibration set was produced by using 40 standards of binary mixtures to construct the model. In order to select the mixtures providing more information from calibration set, their compositions were randomly designed. The calibration covers concentrations between 85 and 1300 ng ml⁻¹ for Co(II) and 100 and 1010 ng ml⁻¹ for Ni (II). Absorbance data were recorded between 200 and 700 nm at 1 nm intervals. The calibration model was validated with 15 synthetic mixture sets containing the considered metal ions in different proportions. The obtained results are given in Table

1. The selection of the number of factors applied in the calibration with PLS is very vital for achieving the best prediction. The number of factors was estimated by cross-validation method, leaving out one sample at a time and plotting the prediction residual sum of squares (PRESS) versus the number of factors for each individual component. The prediction residual sum of squares 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. Fig. 3 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 determination²⁰. The optimal number of factors for Co(II) and Ni(II) was obtained as 2 and 4, respectively.

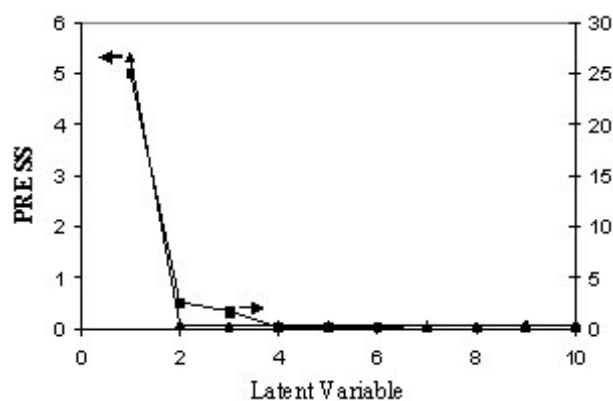


Fig. 3: Plot of PRESS against the numbers of factors for Co(II) (■) and Ni (II) (▲)

In this work 15 synthetic test samples were analyzed with the proposed method. The prediction results are given in Table 1. The prediction error of a single component in the mixture was calculated as the relative standard error (R.S.E.) of the prediction concentrations,

$$R.S.E.(\%) = 100 \times \left(\frac{\sum_{j=1}^N (\hat{C}_j - C_j)^2}{\sum_{j=1}^N (C_j)^2} \right)^{1/2} \quad \dots(6)$$

where N is the number of samples, C_j the concentration of the component in the jth mixture and \hat{C}_j is the estimated concentration. The total

prediction error of N samples is calculated as follows:

$$R.S.E.(\%) = 100 \times \left(\frac{\sum_{j=1}^M \sum_{i=1}^N (\hat{C}_{ij} - C_{ij})^2}{\sum_{j=1}^M \sum_{i=1}^N (C_{ij})^2} \right)^{1/2} \quad \dots(7)$$

where C_{ij} is the concentration of the ith component in the jth sample and \hat{C}_{ij} is its estimation. Table 1, also shows reasonable single and total relative standard error for such a system.

Effect of foreign ions

The impact of different cations and anions on the absorbance of a solution mixture containing

0.782 $\mu\text{g ml}^{-1}$ of Co(II), 0.785 $\mu\text{g ml}^{-1}$ of Ni(II) was studied. When an ion produced a variation in the absorbance of the sample greater than 5%, it was considered as interference.

This increase of absorbance was evaluated at two wavelengths: 508 and 497 nm corresponding to the maximum absorption of Co(II) and Ni(II) complexes, respectively. Testing the interfering ions showed that Na^+ , NH_4^+ , K^+ , CH_3COO^- , NO_3^- and Br^- , Cl^- , F^- , I^- , CO_3^{2-} , SO_4^{2-} , SO_3^{2-} , SCN^- , IO_3^- did not interfere at concentrations 2000 times higher than those of the analytes and Mg^{2+} at concentrations 250 times higher than those of the analytes, Hg^{2+} , Fe^{2+} , Ca^{2+} 100 times higher than those of the analytes Mn^{2+} , Ba^{2+} , Zn^{2+} 50 times higher than those of the analytes. Cd^{2+} , Al^{3+} 30 times higher than those of the analytes and Cr^{3+} 5 times higher than those of the analytes.

Analysis of alloy samples

Preparing different synthetic alloy solutions

according to some known alloys(21-22) , the researchers analyzed the samples by the proposed method. The results shown in Table 2, prove good accuracy of the method.

CONCLUSION

On the Basis of the obtained results, application of UV-vis spectrophotometric method for the simultaneous determination of Co(II) and Ni(II) in real samples using Partial least-squares multivariate calibration is an effective and accurate way. This technique is simple, fast, precise and manageable. Besides, it does not need complex pretreatment or chromatographic separations of the samples containing analytes.

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REFERENCES

- Lau, O. W., Ho, S. Y *Anal. Chim. Acta*, **280**: 269-277 (1993).
- Rigin, V *Anal. Chim. Acta*, **283**: 895-901 (1993).
- Iliadou, E. N., Girusi, S.T., Dietze, U., Otto, M., Voulgaropoulos, A.N., Papadopoulos, C *Analyst*, **122**: 596-600 (1997).
- Ryan, N., Glennon, J. D., Muller, D *Anal. Chim. Acta*, **283**: 344-349 (1993).
- Brotheridge, R. M., Newton, K. E., Taggart, M. A., P.H, M *Analyst*, **123**: 69-72 (1998).
- O'Haver, T. C., Green, G. L *Anal. Chem.*, **48**: 312-318 (1976).
- O'Haver, T. C *Anal. Chem.*, **51**: 91A-99A (1979).
- Geladi, P., Kowalski, B. R *Anal. Chim. Acta*, **185**: 1-17(1986).
- Zarei, K., Atabati, M., Malekshabani, Z *Anal. Chim. Acta*, **556**: 247-254 (2006).
- Ghasemi, J., Ahmadi, S., Torkestani, K *Anal. Chim. Acta*, **487**: 181-188 (2003).
- Ghasemi, J., Shahabadi, N., Seraji, H. R *Anal. Chim. Acta*, **510**: 121-126 (2004).
- P-Kumar, A., R- Reddy, A. P., K-Reddy, V *J. Automat. Meth. Manag. Chem*, **2007**: 1-6 (2007).
- Safavi, A., Abdollahi, H *Anal. Lett*, **34**: 2817-2827 (2001).
- Kaur, V., K-Malik, A., Verma, N J. *Chin. Chem. Soc.*, **54**: 715-722 (2007).
- Ghasemi, J., Niazi, A *Microchem J.*, **68**: 1-11 (2001).
- Kaur, V., K-Malik, A., Verma, N *Annali di Chimica*, **97**: 237-249 (2007).
- Rezaei, B., Ensafi, A.-A., Shandizi, F *Microchem J.*, **70**: 35-40 (2001).
- Kiss, E *Anal. Chim. Acta*, **66**: 385-396 (1973).
- Baudino, O. M., de Pedernera, M. M., G-Calderon, C. E., Suero, E. A *Spanish J. Agr. Res*, **5**: 506-509 (2007).
- Haaland, D. M., Thomas, E. V *Anal. Chem.*, **60**: 1193-1202 (1988).
- Snell, F. D., Ettore, L. S *Encyclopedia of Industrial Chemical Analysis*, Vol. 10 and 16, Wiley Interscience, New York(1972).
- Davis, J. R., *Metals Handbook*, 9th ed., Machining, ASM International Handbook Committee (1989).