

SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) AND COBALT(II) USING PARTIAL LEAST-SQUARES REGRESSION

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ABSTRACT

The simultaneous spectrophotometric determination of copper(II) and cobalt(II) is based on the formation of their complexes with diethyldithiocarbamate (DDTC) in the presence of polysorbate 20 (Tween 20) as a micellar media using partial least squares modeling. The absorption spectra were recorded from 290 to 500 nm. The calibration graph was linear in the range of 0.5-4.0 $\mu\text{g.mL}^{-1}$ for Cu(II) ($R^2 = 0.9979$) and 0.5-3.0 $\mu\text{g.mL}^{-1}$ for Co(II) ($R^2 = 0.9976$); The root mean squared error of prediction (RMSEP) was 0.160 and correlation coefficient (R^2) for copper and cobalt by PLS method were 0.988; 0.954 respectively. The results indicate the probability of the method in the simultaneous determination of copper(II) and cobalt(II).

Keywords: PLS, chemometric, UV-Vis.

1. INTRODUCTION

Metal ions accumulate in soil and are then absorbed by plants and animals, causing these metal ions to bioaccumulate and biomagnify as a result of the food chain. Because of the significant impact on human health, metal contamination is a serious concern. Metal pollution requires appropriate techniques for quantifying ion metal contaminants. There are numerous methods for determining metal content, including inductively coupled plasma mass spectrometry, atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). These methods provide high sensitivity and selectivity at a high analytical cost. Therefore, due to its low analysis cost, UV-Vis photometric method is used to determine metal content. Furthermore, this method produces a very simple and quick result [1].

In practice, metal ions frequently exist in a mixed state, making metal content quantification difficult because the absorption spectrum is resonant or overlapping. Furthermore, the factor affects the shifts in the absorption bands of UV vis, such as temperature, concentration, pH, and component... making it difficult to determine the metal content. Chemometrics is a set of mathematical tools and statistical methods that allows us to analyze multivariable data to solve linear problems, and it has been used to determine the function of spectroscopy [2-9]. Deng Xua and Wei Fana [5] determined the complexing of cadmium, zinc, and cobalt with 2- (5-bromo-2-pyridylazo)-5-(diethylamino) phenol (Br-PADAP) in surfactant medium using UV-Vis spectra combined Partial least squares regression (PLS) for quantification of ion metals.

This study aimed to combine UV-Vis spectroscopy with chemometrics techniques for analyzing Cobalt and Copper simultaneously. Multivariate calibration of partial least squares (PLS) regression was generated for the simultaneous prediction of the content of Cobalt and Copper in the binary mixture. The analysis was carried out in a Tween 20 aqueous micelle solution with sodium diethyldithiocarbamate (Na-DDTC) acting as a chromogenic complexing agent. Organic solvents are frequently used for extraction because DDTC-metal ion complexes are less soluble in water. To avoid environmental pollution and shorten the extraction time, we complexed in Tween 20 surfactant medium.

2. EXPERIMENTAL METHOD

2.1. Materials

All of the reagents were analytical grade. The water used was doubly distilled water. Stock solutions of 1000 ppm of cobalt and copper were prepared from their nitrate salt (Merck). The stock sodium diethyldithiocarbamate (Na-DDTC) (Merck) was prepared by dissolving a solid reagent in doubly distilled water. The pH values required for metal ions complexation were obtained by using buffer solution ammonium citrate and ammonia solution. 3% Tween 20 (Merck) solution was used. Spectrophotometric measurements were performed with Spectrophotometer Jasco V-730, in 1.0 cm Silica Quartz cells, at room temperature.

2.2. Procedure

In a 10 mL calibrated flask, a series of mixed standard solutions containing various ratios of each metal ion and 3.00 mL of buffer solution (pH = 8), 0.40 mL of DDTC-Na (0.05 g.L^{-1}) were placed and diluted to the mark with appropriate 3% Tween 20 solution. A blank solution that has the same composition but without metal ions. The final concentration of cobalt and copper varied between 0.5-3.0 and 0.5-4.0 $\mu\text{g.mL}^{-1}$, respectively. The binary mixtures of cobalt and copper were obtained randomly from the calibration and validation set solutions. Spectra were measured in 1 cm cuvettes between 290 and 500 nm concerning a reagent blank on spectroscopy. All the spectra measured were the means of 3 replicates and used for subsequent analysis. The concentrations of the cations were chosen in the range of the calibration set.

Data was processed by Python software. Several statistical parameters were used to assess the performance of the multivariate calibration model, such as coefficient of determination for calibration (R^2), and root mean square error of prediction (RMSE).

3. RESULTS AND DISCUSSION

The colorimetric method's determination of Co(II) and Cu(II) was based on the formation of a colored complex between metal ion and DDTC as a chromogenic reagent. The absorption spectra of Co(II)-DDTC complex and Cu(II)-DDTC complex in the presence of Tween 20 showed the absorbance maxima at 320 nm and 426 nm, respectively (Figure 1).

Figure 1 shows the UV spectral profiles and calibration curves obtained in the case of spectrophotometric determination of Co(II) and Cu(II) with Na-DDTC. An individual calibration curve was constructed with several points at λ_{max} , which was identified from the UV spectra of each complex (320 and 436 nm for cobalt, and copper respectively) in response to metal ion concentrations. The linear ranges are 0.5-3.0, and 0.5-4.0 $\mu\text{g.mL}^{-1}$ for cobalt, and

copper respectively. The linear equations are $Abs. = 0.3345 C_{Co} + 0.0051$ ($R^2 = 0.9976$); and $Abs. = 0.1796 C_{Cu} + 0.0417$ ($R^2 = 0.9979$) for cobalt, and copper respectively. Both models gave $R^2 > 0.9$, suggesting a good linear relationship between the concentration of metal ions and the absorbance at their λ_{max} .

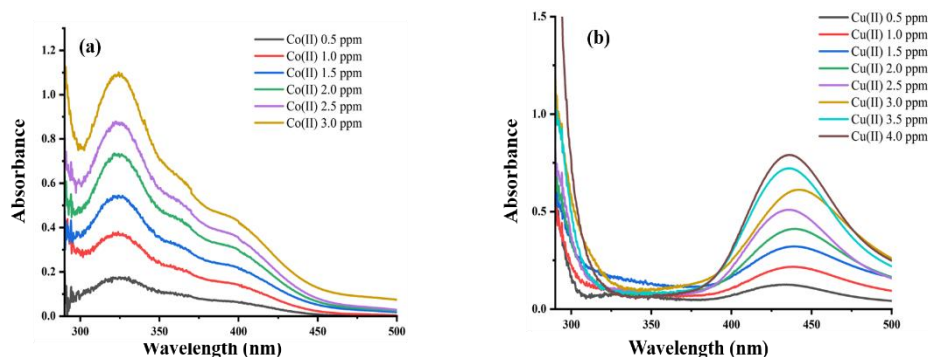


Figure 1. The absorption spectra of (a) Co(II), (b) Cu(II) with DDTC in Tween 20 solution

The main quantitative characteristics of Co(II) and Cu(II) spectrophotometric determination, such as linear dynamic range, detection limit, the calibration sensitivity (which is the slope of the calibration curve), etc., are summarized in Table 1.

Table 1. Quantitative Characteristics of Spectrophotometric Method

Statistical parameters	Co(II)	Cu(II)
Wavelength λ_{max} , [nm]	320	436
Linear range, $\mu\text{g.mL}^{-1}$	0.5-3.0	0.5-4.0
Regression coefficient	0.9976	0.9978
Calibration sensitivity, ppm	0.3345	0.1796
LOD	0.1588	0.1574
LOQ	0.4813	0.4770

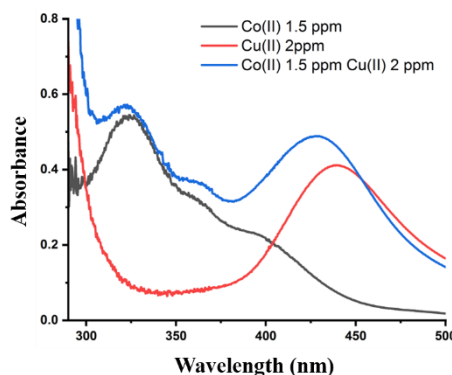


Figure 2. The absorption spectra of Co(II), Cu(II), and the mixture of Co(II) and Cu(II) with DDTC in Tween 20 solution.

Figure 2 shows the superimposed curves of absorption spectra of cobalt and copper, so we need to combine UV-Vis spectroscopy with chemometrics techniques for analyzing cobalt and copper simultaneously without any separation stages.

Due to the overlap of the spectral signals of copper and cobalt, the derivative spectroscopy using continuous wavelet transform is an effective method to solve the problem. Due to the overlap of the spectral signals of copper and cobalt, the derivative spectroscopy using continuous wavelet transform is an effective method to solve the problem. PLS has two steps: calibration (training) and test (prediction). For getting the best results at the calibration step, all samples with ratio splitting randomly 75% were used to construct the calibration matrix and 25% as the external validation set to determine the predictive capability of the method. Under optimal conditions, absorbing the mixtures (Table 2) has been recorded at 290-500 nm wavelengths.

Table 2. Concentration data of the different mixtures used in the calibration and test set for the determination of copper and cobalt (ppm)

Mixture	Cu (II), μg.mL ⁻¹	Co (II), μg.mL ⁻¹	Mixture	Cu (II), μg.mL ⁻¹	Co (II), μg.mL ⁻¹	Mixture	Cu (II), μg.mL ⁻¹	Co (II), μg.mL ⁻¹
1	0.5	0	22	4	0.5	43	2.5	2
2	1	0	23	0.5	1	44	3	2
3	1.5	0	24	1	1	45	3.5	2
4	2	0	25	1.5	1	46	4	2
5	2.5	0	26	2	1	47	0.5	2.5
6	3	0	27	2.5	1	48	1	2.5
7	3.5	0	28	3	1	49	1.5	2.5
8	4	0	29	3.5	1	50	2	2.5
9	0	0.5	30	4	1	51	2.5	2.5
10	0	1	31	0.5	1.5	52	3	2.5
11	0	1.5	32	1	1.5	53	3.5	2.5
12	0	2	33	1.5	1.5	54	4	2.5
13	0	2.5	34	2	1.5	55	0.5	3
14	0	3	35	2.5	1.5	56	1	3
15	0.5	0.5	36	3	1.5	57	1.5	3
16	1	0.5	37	3.5	1.5	58	2	3
17	1.5	0.5	38	4	1.5	59	2.5	3
18	2	0.5	39	0.5	2	60	3	3
19	2.5	0.5	40	1	2	61	3.5	3
20	3	0.5	41	1.5	2	62	4	3
21	3.5	0.5	42	2	2			

The predictive ability of the method was determined using all samples with a ratio splitting randomly 25% of metal ions. The plots of the predicted concentration versus actual values are shown in Figure 3 for copper and cobalt.

For the constructed model, the root-mean-square errors of predictions (RSME) were selected to test the prediction ability of the model for the simultaneous determination of copper and cobalt.

$$RSME = \left[\frac{1}{n} \sum_{i=1}^n (\hat{x}_i - x_i)^2 \right]^{0.5}$$

Where x_i is the true concentration of the analyte in sample i , \hat{x} representing the estimated.

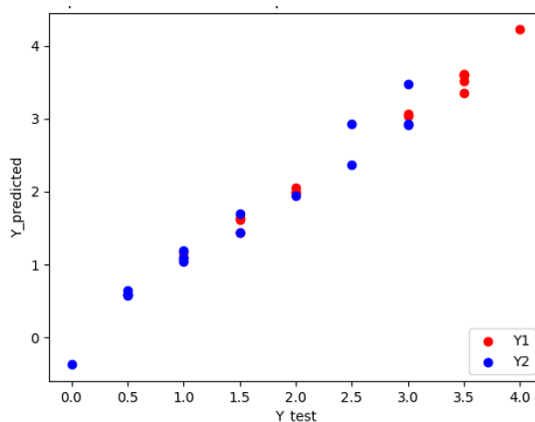


Figure 3. Plots of predicted concentration versus actual concentration for copper (Y1) and cobalt (Y2) from PLS method

The data is around the line of best fit. This indicates the successful application of the built model in the prediction of the test set. $R^2 > 0.9$; representing the smaller differences between the actual and predicted values. In addition, the root mean squared error (RMSE) is low, indicating that the high accuracy of the model predicts the response.

Good results were achieved in the PLS model. RMSE of prediction (RMSEP) was 0.160, and correlation coefficient (R^2) for copper and cobalt by PLS method were 0.988 and 0.954, respectively.

Table 3. The predicted concentrations of Cu and Co by PLS methods ($\mu\text{g mL}^{-1}$)

Sample	Actual [Cu(II)]	Predicted [Cu(II)]	%Error [Cu(II)]	Actual [Co(II)]	Predicted [Co(II)]	%Error [Co(II)]
1	2.0000	1.9966	-0.17	1.0000	1.0371	3.57
2	2.0000	1.9813	-0.94	3.0000	2.9167	-2.86
3	2.0000	2.0534	2.6	2.5000	2.3618	-5.85
4	1.0000	1.0782	7.25	2.5000	2.9331	14.77
5	3.0000	3.0689	2.25	0.5000	0.5955	16.04
6	1.5000	1.6476	8.96	0.5000	0.5748	13.01
7	3.5000	3.5205	0.58	2.0000	1.9456	-2.79
8	1.5000	1.6134	7.03	1.5000	1.4384	-4.28
9	1.5000	1.4396	-4.19	3.0000	2.9253	-2.55
10	3.5000	3.6034	2.87	0.0000	-0.3709	0
11	3.5000	3.6018	2.83	1.0000	1.1987	16.58
12	3.0000	3.0352	1.16	1.5000	1.7044	11.99
13	3.5000	3.3528	-4.39	3.0000	3.4805	13.8
14	4.0000	4.2204	5.22	1.0000	1.1018	9.24
15	3.5000	3.6103	3.06	0.5000	0.6402	21.9
16	1.0000	1.1637	14.07	0.5000	0.5926	15.62

In Table 3, synthetic samples have been prepared for assessing the developed calibration model. According to the presented results, we have probably tuned the PLS Regression model for the use case of predicting the concentration of copper and cobalt. In some cases, the percentage of error of predicted concentration of copper and cobalt by PLS method were high (more than 10%). Despite the good linear regression, predictions can be off because of the prediction error's bias and/or variance. In this study, our PLS predicted model had a prediction error (%) higher than R. Moradi [7] and M. Kompany-Zareh [10] (less than 5%). However, in the preparation of the solution of complex, various factors could cause the change of the absorbance such as pH, the concentration of surfactant, the temperature as well as the kinetics of the complex reaction. In other words, these factors could give rise to the addition of a model relationship resulting in the relevant out-of-sample error statistic. Therefore, for further study, a set of competing factors should be established before starting the set up the mixture to receive the balance between theory and predictive power, even in out-of-sample.

4. CONCLUSION

Combining UV-Vis spectroscopy with chemometrics techniques presents a new method for measuring copper and cobalt without any separation stages. The results showed the ability of the PLS model in the calibration. The findings of this study show that using PLS regression is a multivariate calibration method. The points of R^2 and RSME values indicate the probability of the method in the simultaneous determination of copper and cobalt. Because of some high % errors of predicted value, we should be considered the time kinetics of the complex reaction.

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TÓM TẮT

ĐỊNH LƯỢNG ĐỒNG THỜI COPPER(II) VÀ COBALT(II) BẰNG PHƯƠNG PHÁP TRẮC QUANG KẾT HỢP MÔ HÌNH HỒI QUY BÌNH PHƯƠNG CỰC TIỂU TỪNG PHẦN

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Nghiên cứu này sử dụng mô hình bình phương cực tiểu từng phần PLS (Partial Least Squares) để xác định đồng thời Cu (II) và Co (II) bằng phương pháp trắc quang, dựa trên sự hình thành phức của chúng với sodium diethyldithiocarbamate (Na-DDTC) trong môi trường mixen tạo bởi polysorbate 20 (Tween 20). Vùng quang phổ khảo sát trong khoảng bước sóng 290-500 nm. Khoảng nồng độ tuyến tính của Cu(II) là 0,5-4,0 $\mu\text{g}\cdot\text{mL}^{-1}$ ($R^2 = 0,9979$) và khoảng nồng độ tuyến tính của Co(II) là 0,5-0-3,0 $\mu\text{g}\cdot\text{mL}^{-1}$ ($R^2 = 0,9976$). Kết quả của mô hình PLS có sai số trung bình bình phương của các dự đoán (RSME) là 0,160 và R^2 đối với Cu(II) là 0,988, đối với Co(II) R^2 là 0,954. Phương pháp PLS có thể áp dụng để định lượng đồng thời Cu (II) và Co (II).

Từ khóa: PLS, hóa đặc, UV-Vis.