

SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF Pb(II) AND Cd(II) USING ARTIFICIAL NEURAL NETWORKS

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Abstract: A method for simultaneous analysis of Pb(II) and Cd(II) has been developed by using artificial neural network (ANN). This method is based on the difference concentration of Pb(II) and Cd(II) with 4-(2-pyridylazo)-resorcinol (PAR). A feed forward neural network using back-propagation (BP) algorithm has been employed in this study. The input layer consists of seven neurons, six neurons of hidden layer and two output neurons was found appropriate for the simultaneous determination of Pb(II) and Cd(II). The network was trained up to 20 epochs with 0.0001% learning rate. This reagent also provided good analytical performance with reproducibility characters of the method yield relative standard deviation (RSD) of 0.44% and 0.94% for Pb(II) and Cd(II), respectively. The limit of detection of the method for Pb(II) and Cd(II) was calculated to be 1.9 and 0.4 mg/l, respectively.

Keywords: Pb(II), Cd(II), simultaneous determination, artificial neural networks, spectrophotometry, PAR

1. INTRODUCTION

More recently, the application of artificial intelligence or expert systems in analytical chemistry and chemical engineering has emerged rapidly. ANN is a computing system made up of a number of simple and highly interconnected processing elements, which processes information by its dynamic state response to external inputs.¹

Pb(II) and Cd(II) are metals that appear together in many real samples. Several techniques such as flame atomic absorption,² voltammetric³ and spectrophotometric^{4,5} methods have been used for the determination of these ions in different samples. Among this, uv-visible spectrophotometry is the most commonly used techniques for Pb(II) and Cd(II).

It is more favorable because of its simplicity, acceptable precision and accuracy, low cost and it has a good sensitivity,⁶ but the simultaneous determination of these ions by the used of traditional spectrophotometry is difficult. Generally, the overlap of the absorption spectra and the superimpose

curves are not suitable for quantitative evaluation. Quantitative spectrophotometry has been improved by the use of multivariate statistical method, particularly principal component regression and artificial neural network (ANN).⁷

ANN has been widely used in chemical application such as interpretation of spectra, calibration, process control, molecular dynamics, optimization of the linear signal range, signal processing and modeling structure of protein.⁸⁻¹⁰ Rezaie et al.⁷ has studied the simultaneous determination of cobalt(II) and nickel(II) based on formation of their complexes with pyrrolidine and carbon disulfide. They found that, 42 neurons in the input layer and 60 neurons in the hidden layer was successfully applied in simultaneous determination of Co(II) and Ni(II).⁷

The aim in this study was the simultaneous determination of Pb(II) and Cd(II) by uv-visible spectrophotometry in some complex mixture using 4-(2-pyridylazo)-resorcinol (PAR), which is a popular reagent in spectrophotometric determination of different metal ion such as Pb(II) and Cd(II) using ANN.

2. EXPERIMENTAL

All chemicals were of analytical reagent grade and deionized water was used throughout the experiment. Stock standard solution (1000 mg/l) of Pb(II) and Cd(II) was prepared by dissolving 1.1261 g of $\text{Pb}(\text{NO}_3)_2$ (Fluka AG) and 1.0271 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Hamburg) in 1000 ml volumetric flasks and diluted to the mark with deionized water. PAR (BDH Chemical Ltd.) was used as a reagent. 0.001 M PAR stock solution was prepared by dissolving 0.2152 g of PAR powder in 1000 ml ethanol (95%) (Prochem). A series of standard solution were prepared by appropriate dilution of stock solution.

2.1 Instrumentation

Spectral measurements were made with a uv-visible spectrophotometer (Varian-Cary Win UV 100). For each concentration, the spectrum was scanned in the wavelength of 350–750 nm. A total of 18 spectral reading were obtained. Three of these spectra were used for testing the trained network whilst the remaining spectra were used for the training of the network.

2.2 Procedure

Sample solutions were prepared in 25 ml volumetric flask by taking a required volume of the solution to be analyzed to obtain Pb(II) and Cd(II) concentrations over this respective determination ranges 1–15 mg/l for Pb(II) and 2–16 mg/l for Cd(II). Then 0.6 ml buffer solution (boric acid and borax (0.2 M)) and 1.5 ml PAR were added. The solution was then diluted to the mark. The absorbance spectra of the complex solution were recorded from 350 to 700 nm.

2.3 Data Treatment and Data Analysis

A feed-forward ANN having a single hidden neuron layer with back-propagation (BP) training algorithm was employed for treatment of the data. The structure of BP algorithm comprised of three layers, input, output and hidden layer. Figure 1 shows the architecture of the ANN. The input layer consists of seven neurons, which represent the absorbance intensities measured at seven different wavelengths from each spectrum. The output layer consists of two neurons which represent the concentration value of Pb(II) and Cd(II).

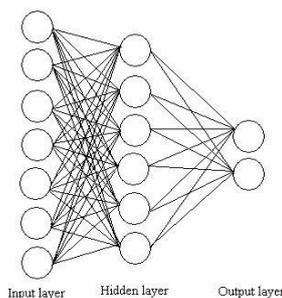


Figure 1: Schematic representation of a three layer artificial neural network

The network training and data treatment were realized by using MATLAB program¹¹ under an Intel Celeron processor having 256 MB of RAM. The training and optimization process carried out in this study is shown in Table 1. Network optimization was performed by changing the number of neuron in the hidden layer, the number of cycles during training and the percentage of learning rate. Network having from 5 up to 17 neurons in hidden layer has been considered in this study. Network trained with 20 epochs were used to predict the response of the concentration of Pb(II) and Cd(II). The mean-squared error (MSE) for training was measured at the end of the epochs by the MATLAB program to show the goal of the training achieved. Finally, a new set of input

data i.e., other absorbance intensities were introduced to the networks to check for its prediction capability and precision.

Table 1: The general setting of the BP specific parameters during network training

Specific parameters	Values
Maximum number of epochs to train	20
Sum-squared error (SSE) goal	0.02
Learning rate	0.0005

The preference of the best network was based on several tests using the trained network that incorporates the inspection for training data fitting errors and prediction test of errors. The selected network was then applied for computer-generated application where new measurement were taken, processed and converted to concentration values employed by the MATLAB program simulation.

3. RESULTS AND DISCUSSION

Pb(II) and Cd(II) reacted with PAR to form a complex. Figure 2 shows the spectra of these complexes. The absorption maximum for Pb(II)-PAR and Cd(II)-PAR is 518 and 409 nm, respectively. Figure 3 shows the 3D absorbance spectra of mixture of Pb(II) and Cd(II) after reaction with PAR at different concentration of Pb(II) and Cd(II).

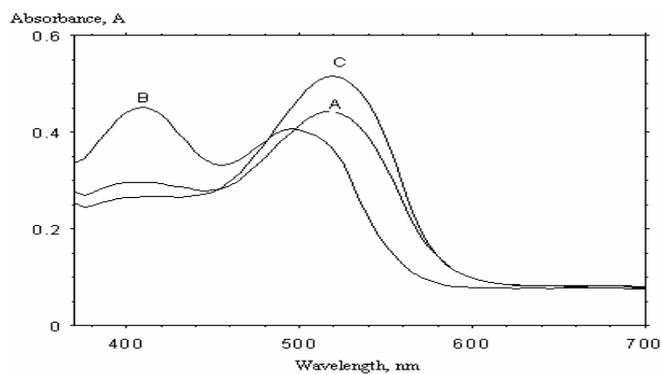


Figure 2: Absorption spectra for (a) Pb(II)-PAR complex, (b) Cd(II)-PAR complex, and (c) mixture of Pb(II) and Cd(II)

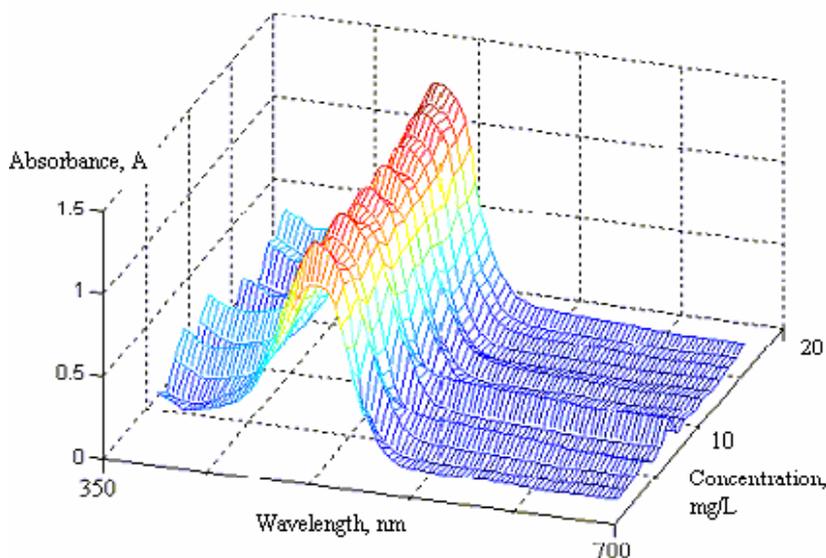


Figure 3: Generated 3D absorbance spectra for mixture of Pb(II) and Cd(II) after reaction with PAR at different analyte concentration

The method developed produced a linear response when the Pb(II) concentration is within the range of 1–10 mg/l, then almost constant in the range of 40–60 mg/l. The limit of detection of the method was calculated to be 1.9 mg/l.

The method developed produced a linear response when the Cd(II) concentration is within the range of 1–10 ppm. The limit of detection was calculated to be 0.4 mg/l.

Data obtained from uv-visible spectrophotometer were used as the input to the ANN. Only seven wavelengths points (370, 405, 430, 450, 500, 519 and 550 nm) from each spectrum were chosen to represent the input data for the ANN to avoid several problem during network training period.

Fifteen spectra were used for the training of the ANN and three spectra were used for prediction. Network optimization was performed by changing the number of neuron in the hidden layer, the number of cycle during training and the percentage of learning rate.

Table 2 shows the MSE values of the network with 5–17 hidden neurons after completing the 20 epochs. The number of hidden neurons when arranged in declining MSE order was 8, 10, 14, 7, 17, 5 and 6. Figure 4 shows the MSE

versus the number of neurons in the hidden layer, required to get fixed (2%) error. The results show that, by increasing the number of neuron from 6 to 8, the MSE value increased and then, decreased. Six neurons of hidden layer performed the lowest MSE value. This result agreed well with the results reported by Taib and Narayanaswamy which reported that an optimized and suitable network can be attained with network size of 6–17 neurons in hidden layer.¹³

Table 2: MSE values of the networks with 5–17 hidden neurons

Number of neuron in the hidden layer	MSE
5	0.01223
6	0.01175
7	0.01521
8	0.01836
10	0.01645
14	0.01545
17	0.01233

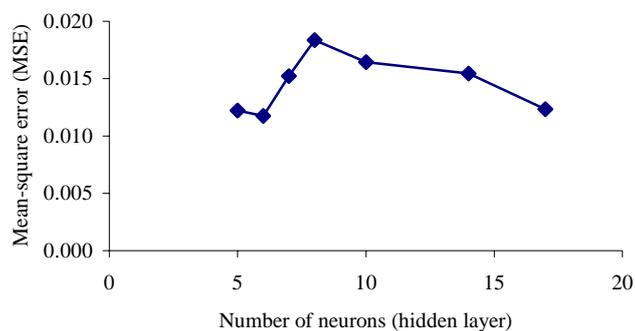


Figure 4: The relationship between numbers of neuron in hidden layer versus MSE

Table 3: The network of Pb(II) and Cd(II) concentration using calibration data

Hidden layer size	Pb(II)						Cd(II)						Average calibration error ^a
	Expected 4.0		Expected 9.0		Expected 14.0		Expected 5.0		Expected 10.0		Expected 15.0		
	Predicted	Error	Predicted	Error	Predicted	Error	Predicted	Error	Predicted	Error	Predicted	Error	
5	1.2	2.8	12.7	3.7	14.0	0	3.2	1.8	11.0	1.0	15.1	0.1	1.567
6	3.0	1.0	8.3	0.7	15.0	1.0	4.6	0.4	9.2	0.8	15.7	0.7	0.767
7	4.8	0.8	8.4	0.6	13.6	0.4	5.4	0.4	12.2	2.2	14.6	0.4	0.800
8	6.4	2.4	14.2	5.2	14.2	0.2	4.2	0.8	13.3	3.3	14.5	0.5	2.067
10	4.1	0.1	6.5	2.5	14.1	0.1	5.7	0.7	13.9	3.9	14.7	0.3	1.267
14	8.9	4.9	9.0	0	8.8	5.2	6.2	1.2	6.5	3.5	16.0	1.0	2.633
17	6.1	2.1	10.2	1.2	17.7	3.7	7.0	2.0	8.2	1.8	14.9	0.1	1.816

Note: ^aAverage calibration error = |predicted V(V) concentration – expected V(V) concentration| / 3

Network trained with 20 epochs were suitable to be used in predicting the response of the concentration of Pb(II) and Cd(II) since it showed a low MSE value. Zupan and Gasteiger⁸ reported that, ANN training by using much higher number of epochs usually caused problems such as over training and over fitting problems. Three calibration spectra of Pb(II) and Cd(II) were employed to establish their prediction capability. The trained networks with different number of hidden neurons were present to improve the process in choosing the best network's architecture.¹³

Table 3 shows the predicted concentration values against the expected concentration values as measured by uv-visible spectrophotometer. As shown, the network with 6 neurons in hidden layer produced the good predictions results with average calibration errors of 0.767. Figures 5 and 6 show the training data fitting and calibration by the network with 6 neurons in hidden layer for Pb(II) and Cd(II), respectively.

4. CONCLUSION

The most important aspect of this work is the possibility of simultaneous determination of Pb(II) and Cd(II). A network architecture consisting 7 input neurons, 6 neurons of hidden layer and 2 output neuron after completing the 20 epochs with 0.0001% learning rate was found appropriate for the simultaneous determination of Pb(II) and Cd(II). The average calibration error was found to be 0.767 for simultaneous determination of Pb(II) and Cd(II). The proposed method has been applied successfully to the simultaneous determination of Pb(II) and Cd(II) in some complex mixture.

5. ACKNOWLEDGEMENTS

The author would like to acknowledge Ministry of Environmental and Science of Malaysia for funding this research through IRPA research grant IRPA 09-02-04-818-EA001.

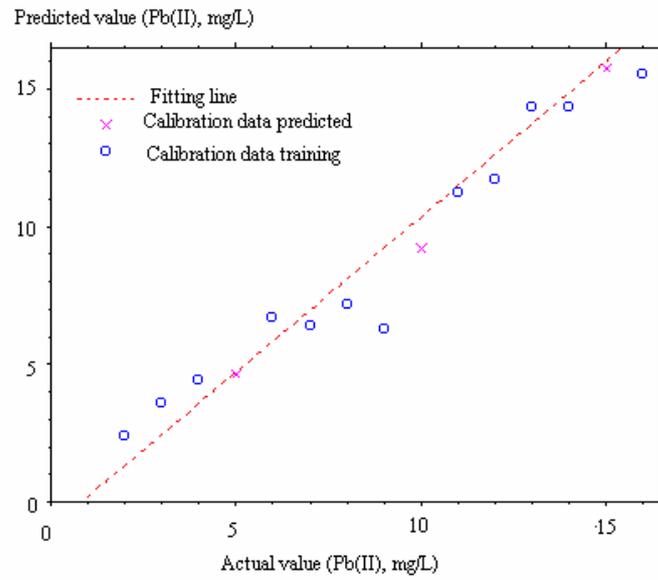


Figure 4: Training data fitting and calibration of Pb(II) concentration by the network with six neurons in hidden layer

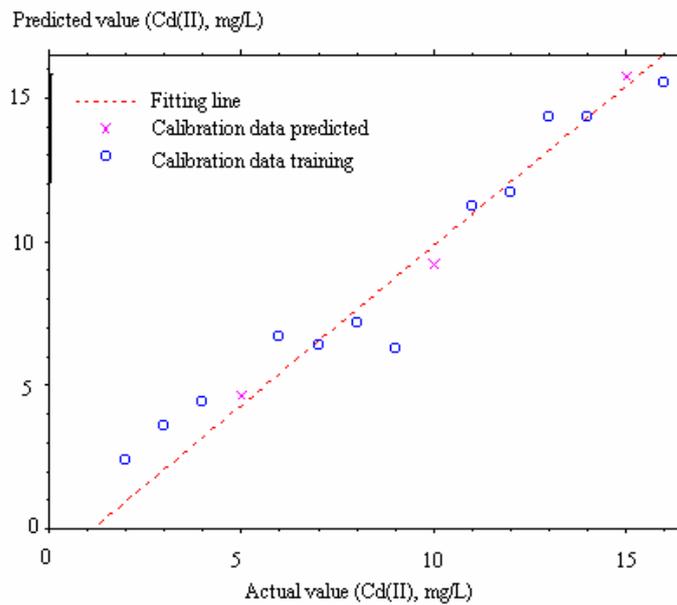


Figure 5: Training data fitting and calibration of Cd(II) concentration by the network with six neurons in hidden layer

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