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Application of Artificial Neural Network to Simultaneous Spectrophotometric Determination of Lead(II) and Mercury(II) Based on 2-(5-Bromo-2-Piridylazo)-5-Diethylaminophenol

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Abstract : A method for simultaneous analysis of Pb(II) and Hg(II) has been developed by using artificial neural network (ANN). This method is based on spectrophotometric determination of Pb(II) and Hg(II) with 2-(5-bromo-2-piridylazo)-5-diethylaminophenol (Br-PADAP). A feed forward neural network using back-propagation (BP) algorithm has been employed in this study. The input layer consisting of 13 neurons, 10 neurons in the hidden layer and 2 output neurons were found appropriate for the simultaneous determination of Pb(II) and Hg(II). The network was trained up to 40 epochs with 0.006% learning rate. This reagent also provide good analytical performance where reproducibility characters of the method yield relative standard deviation (RSD) of 0.4% and 0.4% for Pb(II) and Hg(II), respectively. The limit of detection of the method was calculated to be 0.2 mg/L and 0.4 mg/L, respectively.

Keyword: Pb(II); Hg(II); Simultaneous determination; Artificial neural networks; Spectrophotometry; Br-PADAP.

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Introduction

An artificial neural network (ANN) is a system loosely modeled on the human brain. The field goes by many names, such as connectionism, parallel distributed processing, neuron computing, natural intelligent system, machine learning algorithms and artificial neural networks [1]. The ANN is able to acquire information and provide models even when the information and data are complex, noise contaminated, nonlinear and incomplete [2-5].

Nowadays, the ANN modeling method has found extensive application in the field of simultaneous determination of several species in a given sample. This method makes it possible to eliminate or reduce the effect of the analyte–analyte interaction, the multi-step process and any other unknown non-linearity in systems [6]. The better advantage of ANN is its anti-jamming, anti-noise and robust nonlinear transfer ability. In a proper model, ANN results in lower calibration errors and prediction errors [7].

Pb(II) and Hg(II) are metals that appear together in many real samples. Several techniques such as flame atomic absorption [8] and voltammetric [9] methods have been used for the determination of these ions in different samples. The cross-interferences among different metal species often cause problem using these methods, which in turn raise the uncertainty level in the analytical results. Further more, those techniques require expensive instrumentation and maintenance, which limit the application of the techniques in many laboratories. Among this, uv-visible spectrophotometry is the most commonly used techniques for Pb(II) and Hg(II) [10, 11]. It is more favorable because of its simplicity, acceptable precision and accuracy, low cost and it has a good sensitivity [12].

Simultaneous determination of trace amounts of metals in environmental samples is still a challenging analytical problem because of the sensitivity and specificity required in environmental monitoring and regulations. Recently, spectrophotometric methods based on ANNs have found increasing applications for multicomponent determination. This method is effective because they can improve the performance and application of the analytical method with the use of simultaneous analysis of several spectra. Rezaie et al. [13] has studied the simultaneous determination of cobalt(II) and nickel(II) based on formation of their complexes with pyrolidine and carbon disulfide. They found that, 42 neurons in the input layer and 60 neurons in the hidden layer can be successfully applied in the simultaneous determination of Co(II) and Ni(II). Kompany-Zareh et al. [14] has applied ANN in the simultaneous spectrophotometric determination of Fe and Ni with xylenol orange. An

ANN consisting of three layers of nodes, trained by applying a back-propagation learning rule was used in their studies.

The basic configuration used in this study consisted of a linear input layer, a hidden layer of neurons with tansigmoid transfer function, [Eq. (1)] and an output layer of two neurons with a linear transfer function:

$$f(x) = \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}} \quad (1)$$

The tansigmoidal hidden layer is critical as it allows the network to learn non-linear relationships between inputs and outputs [13]. The aim in this study is to determine simultaneously Pb(II) and Hg(II) in complex mixture using Br-PADAP. In this work, a three-layer ANN with back-propagation algorithm is employed.

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 Hg(II) were prepared by dissolving appropriate amounts of $Pb(NO_3)_2$ (Fluka AG) and $Hg(NO_3)_2.4H_2O$ (Hamburg), respectively in 1000 mL volumetric flasks and diluted to the mark with deionized water. 2-(5-bromo-2-piridylazo)-5-diethylaminophenol (Br-PADAP) (Fluka) was used as a reagent. 0.001 M Br-PADAP stock solution was prepared by dissolving appropriate amount of Br-PADAP powder in 1000 mL ethanol (95%) (Prochem). A series of standard solution were prepared by appropriate dilution of stock solution.

Instrumentation

Spectral measurements were made with an ultraviolet-visible spectrophotometer (Varian-Cary Win UV 100). For each concentration, the spectrum was scanned in the wavelength of 350 – 700 nm. A total of 24 spectra reading were obtained. Five of these spectra were used to test the network whilst the remaining spectra were used for the training of the network.

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 Hg(II) concentrations over this respective determination ranges 0.5 – 12.0 mg/L for Pb(II) and 1.0 – 12.5 mg/L for Hg(II). Then 0.6 mL buffer solution (boric acid and borax (0.2 M)) and 1.5 mL Br-PADAP were added. The solution was then diluted to the mark. The absorbance spectra of the complex solution were recorded from 350 to 700 nm.

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 input layer consists of 13 neurons, which represent the absorbance intensities measured at 13 different wavelengths (350, 380, 410, 440, 470, 500, 529, 550, 580, 610, 640, 670 and 700 nm) from each spectrum. The output layer consists two neurons which represent the concentration value of Pb(II) and Hg(II). Networks having up to 6 to 17 neurons in the hidden layer have been considered in this study.

The network training and data treatment were realized by using Matlab program [15] 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. The network was trained up to 40 epochs and the progress of mean-squared error (MSE) between the calculated and the measured output was recorded. Finally, a new set of input data (testing set) was introduced to the networks to check for its prediction capability and precision.

Table 1: The general setting of the back-propagation specific parameters during network training

Parameters	Simulated data
Input neuron	13
Output neuron	2
Hidden layer	1
Number of neurons in hidden layer	Variable
Maximum number of epochs to train	40
Mean-squared error (MSE) goal	0.02
Learning rate	0.006
Number of iteration (in epochs)	5

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 measurements were taken, processed and converted to concentration values employed by the Matlab program simulation.

Results and Discussion

Pb(II) and Hg(II) reacted with Br-PADAP to form a complex. Figure 1 shows the spectra of these complexes. The absorption maximum for Pb(II)-Br-PADAP and Hg(II)-Br-PADAP both occurred at 560nm. Figure 2 shows the 3D absorbance spectra of mixture of Pb(II) and Hg(II) after reaction with Br-PADAP.

The method developed produced a linear response when the Pb(II) concentration is within the range of 1 – 8 mg/L. The limit of detection of the method, defined as the concentration equivalent to a signal of blank plus three times the standard deviation of the blank, was calculated to be 0.1 mg/L.

In the determination of Hg(II), a linear response was produced when the Hg(II) concentration is within the range of 1 – 8 mg/. The limit of detection was calculated to be 0.4 mg/L.

The reproducibility study was carried out by measuring the absorbance of ten different batches of similar proportions of mixed solutions. The relative standard deviations (RSD) were calculated to be 0.4% for both determination of Pb(II) and Hg(II) using Br-PADAP. Small RSD values observed for these methods indicate a good precision of the method being used.

Data obtained from uv-visible spectrophotometer were used as the input to the ANN. Only 13 wavelengths points (350, 380, 410, 440, 470, 500, 529, 550, 580, 610, 640, 670 and 700 nm) from each spectrum were chosen to represent the input data for the ANN. To avoid several problems during network training periods, a large number of matrices for the network connections and tendency to be locked into a local minima [16, 17].

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

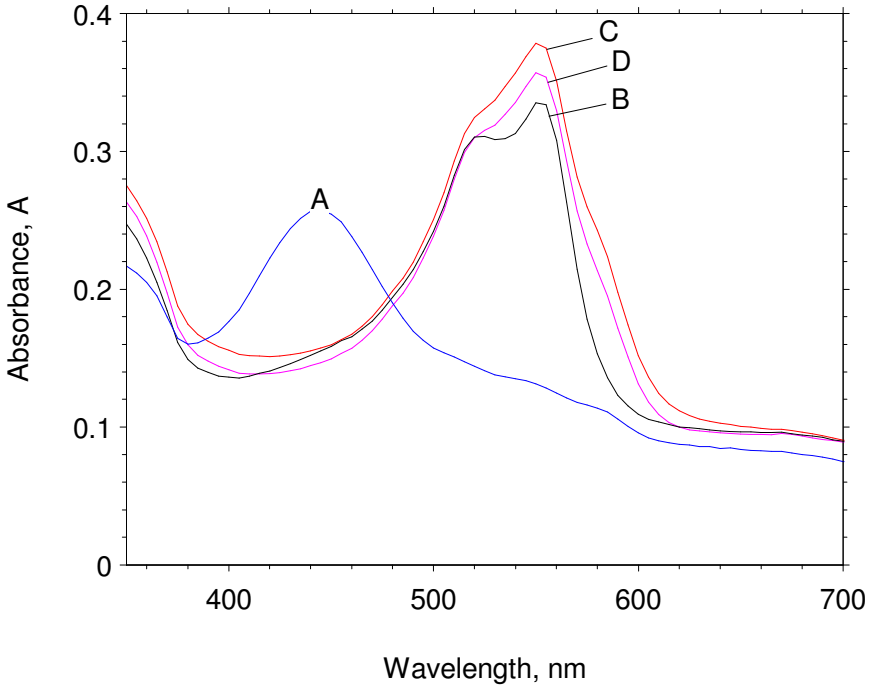

Figure 1: Absorption spectra for the (A) Br-PADAP, (B) Pb(II)-Br-PADAP complex, (C) Hg(II)-Br-PADAP complex and (D) mixture of Pb(II)-Hg(II)-Br-PADAP complex

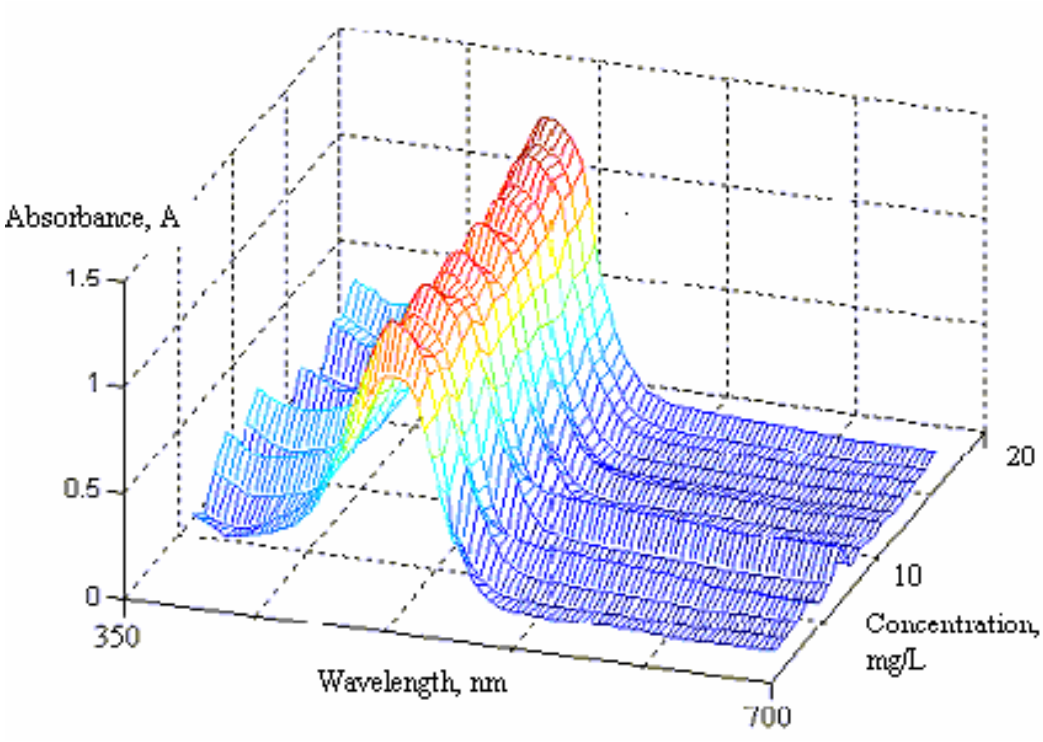

Figure 2 : Generated 3D absorbance spectra for mixture of Pb(II) and Hg(II) after reaction with Br-PADAP at different analyte concentration

Figure 3 shows the MSE values of the network with 6 to 17 hidden neurons after completing the 40 epochs. The number of hidden neurons arranged in declining MSE order was 15, 17, 6, 8 and 10. The results show that, by increasing the number of neurons from 6 to 10, the MSE value decreased and then increased rapidly. Ten neurons in the hidden layer gave the lowest MSE value. This result agrees well with the results reported by Taib and Narayanaswamy [18], which reported that an optimized and suitable network can be attained with network size of 6 to 17 neurons in the hidden layer [18].

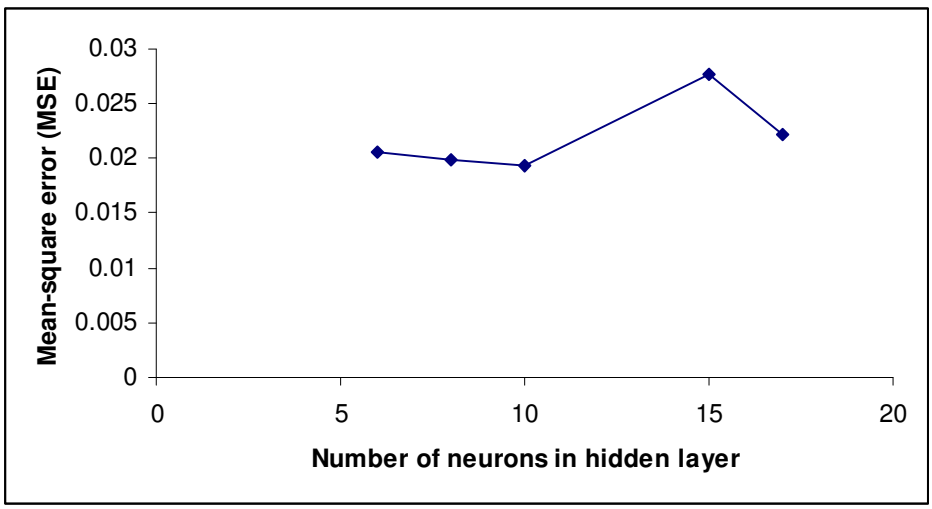

Figure 3 : The relationship between number of neurons in the hidden layer versus MSE

Table 2 : Mean-sum square error, MSE values of the networks with different values of percentage of learning rate at ten neurons in the hidden layer

Learning rate	Mean-squared error (MSE)
0.6	0.04278
0.06	0.04606
0.006	0.01938
0.0006	0.01984

Table 2 shows the MSE value of the percentage of learning rate when the number of neurons in hidden layer was fixed at ten. It shows that, the percentage of learning rate of 0.006 give the lowest MSE value.

A network trained with 30 epochs was suitable to be used in predicting the response of the concentration of Pb(II) and Hg(II) simultaneously since it showed a low MSE value. Zupan et al. [19] reported that, ANN training by using a much higher number of epochs usually caused problems such as over training and over fitting problems. Five calibration spectra of Pb(II) and Hg(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 [20].

Table 3 shows the predicted concentration values against the expected concentration values as measured by uv-visible spectrophotometer. As shown, the network with ten neurons in hidden layer produced good predictions results with average calibration errors of 0.597. Figure 4 and Figure 5 show the predicting data fitting by the network with ten neurons in hidden layer for Pb(II) and Hg(II), respectively. The results show the good regression between actual values and prediction values for Pb(II) and Hg(II) concentration. The regression equation of Pb(II) and Hg(II) were A = 0.975 + 0.891T (R = 0.995) and A = 0.529 + 1T (R = 0.969), respectively, where T is the prediction value and A is the actual value of the metal ions.

Conclusion

The most important aspect of this work is the possibility of simultaneous determination of Pb(II) and Hg(II). It has been successfully performed in this study. A network architecture consisting 13 input neurons, ten neurons of hidden layer and two output neuron after completing the 40 epochs with 0.006% learning rate was found appropriate for the simultaneous determination of Pb(II) and Hg(II). The average calibration error was found to be 0.597 for simultaneous determination of Pb(II) and Hg(II).

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

Expected		Predicted											
		N = 10		N = 12		N = 13		N = 14		N = 15		N =17	
Pb(II), mg/L	Hg(II), mg/L	Pb(II), mg/L	Hg(II), mg/L	Pb(II), mg/L	Hg(II), mg/L	Pb(II), mg/L	Hg(II), mg/L	Pb(II), mg/L	Hg(II), mg/L	Pb(II), mg/L	Hg(II), mg/L	Pb(II), mg/L	Hg(II), mg/L
2.00	2.50	1.03	0.77	0.36	1.87	1.27	0.85	1.13	2.34	1.90	1.95	0.68	1.06
4.50	5.00	5.48	4.62	7.05	8.58	9.57	11.90	4.85	8.10	6.13	4.81	5.71	7.74
7.00	7.50	13.94	8.04	11.50	8.68	9.05	9.51	8.65	6.65	10.73	11.32	8.61	9.37
9.50	10.00	14.30	12.06	13.43	10.80	11.57	11.00	9.42	9.54	10.67	10.91	8.94	9.68
12.00	12.50	8.70	10.71	10.32	11.48	10.46	8.91	12.69	11.99	12.29	12.84	12.23	11.67
[a]Average calibration error		2.40		2.04		2.66		0.87		1.27		1.21	

[a]Average calibration error $= \sum_{i=1}^{5} |$predicted analyte concentration – expected analyte concentration$|/5$

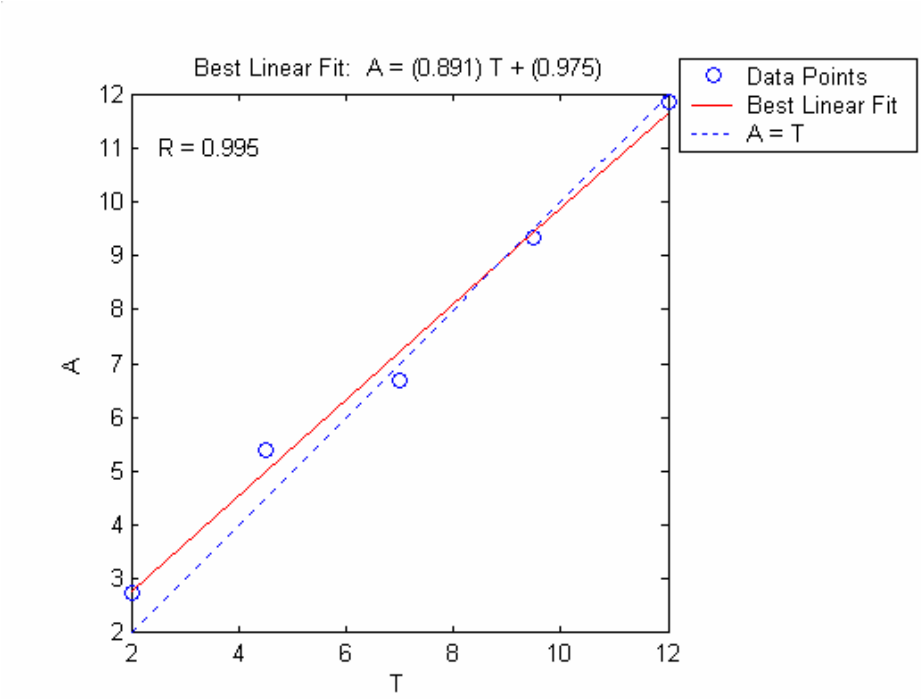

Figure 4 : The relationship between the predicted (T) and actual (A) values for Pb(II) by the network with ten neurons in the hidden layer.

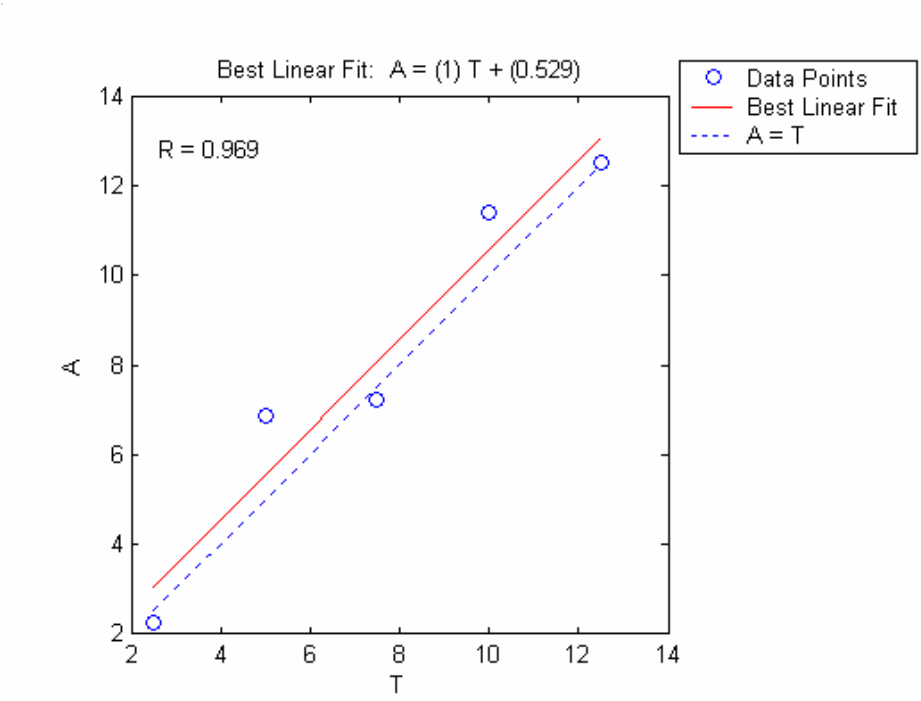

Figure 5 : The relationship between the predicted (T) and actual (A) values for Hg(II) by the network with ten neurons in the hidden layer.

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