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Using Artificial Neural Network for Simultaneous Spectrophotometric Determination of Cobalt and Nickel

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Simultaneous spectrophotometric determination of cobalt(II) and nickel(II) based on formation of their complexes with ethylenediamine tetraacetic acid (EDTA) has been studied. An artificial neural network (ANN) model has been used to analyze the mixture spectra. A series of standard solutions of Co-EDTA and Ni-EDTA as calibration set and testing set were prepared and the absorbance spectra in the wavelength between 530-690 nm have been recorded. Calibration set for training and optimization parameters of ANN such as learning rate, number of neurons in the hidden layer and iteration have been used. The performance of ANN has been evaluated with testing set and then in all steps the root mean square errors (RMSE) were measured. The RMSE for cobalt and nickel are 0.017 and 0.024, respectively.

Key Words: Simultaneous Spectrophotometry, Cobalt, Nickel, Artificial neural network.

INTRODUCTION

Cobalt and nickel are metals that appear together in many real samples. Several techniques such as voltammetric, atomic absorption, X-ray fluorescence, spectrophotometric and derivative spectrophotometric methods have been used for the simultaneous determination of these ions in different samples[1–6]. The simultaneous determination of Co(II) and Ni(II) by the use of the traditional spectrophotometry is difficult because, generally, the absorption spectra overlap and the superimposed curves are not suitable for quantitative evaluation. Quantitative spectrophotometry has been greatly improved by the use of chemometrics methods. Chemometrics is a discipline which is using mathematics statistical methods. In recent years, chemometrics methods based on artificial intelligence such as ANN have proved to be very successful in modelling complex systems for multi-component determinations[7–10]. This paper reports on the simultaneous determination of Co(II) and Ni(II) complexes with EDTA by spectrophotometric method and ANN.

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The basic concepts of ANN are processing elements (Pes) and weighted connections. The collection of processing elements defined as a layer consists of input layer, hidden layer and output layer (Fig. 1). Each processing element

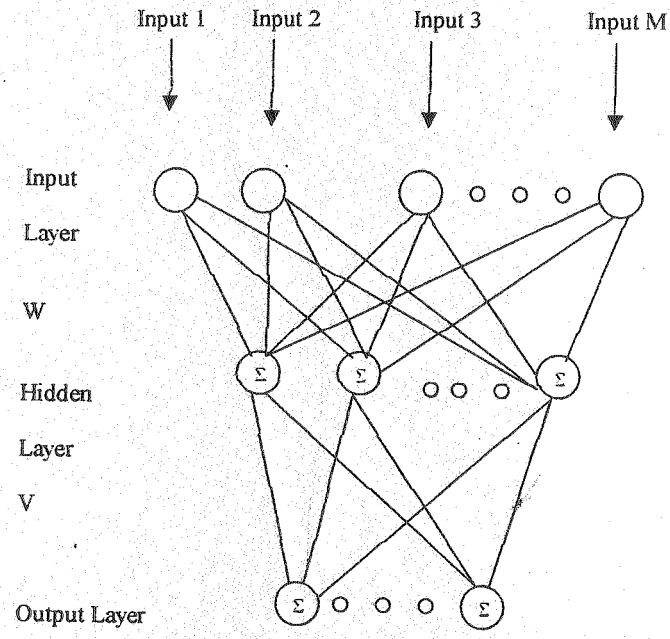

Fig. 1. Schematic diagram demonstrating the topology of three layered neural network

collects values from all its input connections, operations and produces a single output value. The process of changing the weight of the connections to achieve some desired result is called learning or adaptation. Neural network learning procedure determines the value of the connection weights, such as, algorithm and back-propagation. Therefore, the neural network model requires a calibration or training step in order to minimize the error of the model. A way to define this error is sum square error (SSE) which is given by eqn. (1).

$$SSE = \sum_{k=1}^{M} \sum_{j=1}^{N} (T_{jk} - O_{jk})^2 \quad (1)$$

where M is the number of test cases, N is the number of output units, (O_{jk}) is the sum of the squares of the differences between the output of the network and (T_{jk}) is its corresponding target summed over all test cases. A back-propagation network learns by calculating an error between desired and actual output and propagating this error information back to each node in the network. This back-propagation error is then used to derive and also to adjust the value for the weighted matrix elements. The basic concepts for ANN and its applications to chemical problems are given in literature[11-15].

EXPERIMENTAL

A double beam spectrophotometer UV-ICON 922 was used for recording absorbance spectra. The ANN algorithm was written in MATLAB[16] and the program was run using a Pentium III, IBM personal computer.

All chemicals were of analytical reagent grade (Merck) and doubly distilled water was used throughout. Stock standard solutions (5.047 g L^{-1} of cobalt and 10.012 g L^{-1} of nickel) were prepared from their chloride salts, $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$, respectively. These salts were then dissolved in 1% (v/v) sulfuric acid. A buffer of pH 4.0 was prepared from sodium acetate and acetic acid. The standard EDTA solution (0.1 mol L^{-1} was prepared by distilled water and stored in a standard flask.

Procedure: Suitable aliquots of stock solutions of Ca(II) and Ni(II) were transferred to 25 mL volumetric flasks followed by the addition of 5.0 mL acetic acid/sodium acetate buffer and 8 mL of EDTA solution. Each solution was thoroughly mixed and diluted up to the mark with distilled water and mixed thoroughly. The absorbance spectra of each solution was measured from 530–690 nm against a blank containing EDTA, buffer solution and water.

RESULTS AND DISCUSSION

Absorption spectra: Cobalt(II) and nickel(II) react with EDTA to form stable complex solutions. Fig. 2 shows the absorption spectra of these complexes over the range 530–690 nm. As can be seen from Fig. 2, the absorption curves of these two metals show overlapping. Therefore, the quantitative determination cannot be carried out successfully using conventional calibration method. Thus, a calibration design was employed to resolve the spectrum of each complex in the mixture.

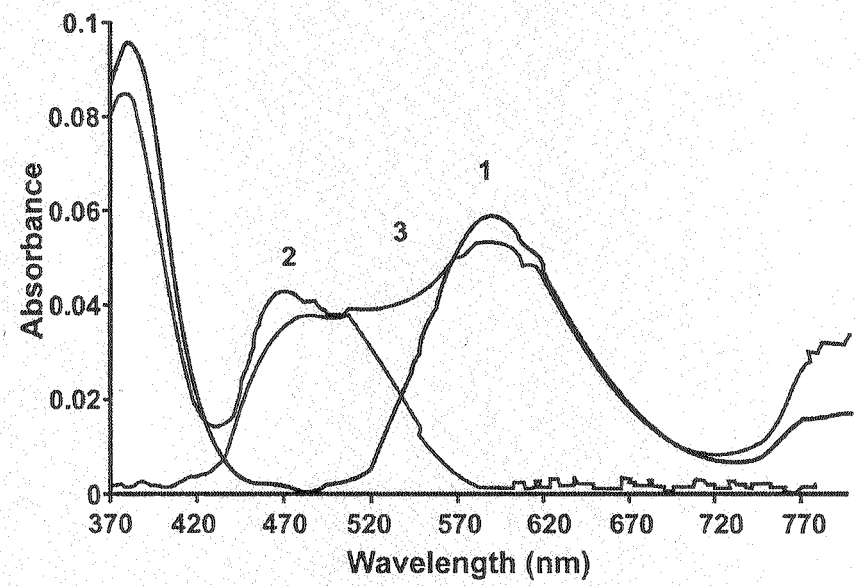

Fig. 2. Absorbance spectra of the metal ions in the presence of EDTA: (1) Ni(II), (2) Co(II) and (3) their mixture.

Calibration method: The first step in the simultaneous determination of different metals by ANN methodology involves constructing the calibration set for the binary mixtures of Co(II) and Ni(II). In this study, seventeen standard solutions of binary mixtures were selected as the calibration set (Table-1) and the concentrations of Co(II) and Ni(II) were between 0 and 0.2 g L^{-1} and 0 and 0.4 g L^{-1}, respectively. Then the absorbance spectra were recorded from 530 to 690

nm to carry out the analysis. Nine standard solutions were chosen randomly for the training set and eight solutions were selected for the testing set (Table-2).

TABLE-1
COMPOSITIONS OF THE CALIBRATION SAMPLES

Samples	Concentrations ($g\ L^{-1}$)	
	Co(II)	Ni(II)
1	0.00	0.0
2	0.05	0.1
3	0.05	0.2
4	0.05	0.3
5	0.05	0.4
6	0.10	0.1
7	0.10	0.2
8	0.10	0.3
9	0.10	0.4
10	0.15	0.1
11	0.15	0.2
12	0.15	0.3
13	0.15	0.4
14	0.20	0.1
15	0.20	0.2
16	0.20	0.3
17	0.20	0.4

TABLE-2
COMPOSITIONS OF THE SYNTHETIC SAMPLES AS TESTING SET

Samples	Concentrations ($g\ L^{-1}$)			
	Co(II)		Ni(II)	
	Found	Actual	Found	Actual
1	0.054	0.050	0.339	0.30
2	0.054	0.050	0.439	0.40
3	0.075	0.10	0.084	0.10
4	0.079	0.10	0.164	0.20
5	0.0119	0.15	0.084	0.10
6	0.0163	0.15	0.388	0.40
7	0.0197	0.20	0.217	0.20
8	0.0200	0.20	0.283	0.30

The training set was used for construction and optimization of ANN model, and the testing set was used to evaluate the performance of the model. The root mean square errors (RMSE) of the model were measured by using eqn. (2).

$$RMSE = \left(\frac{\sum_{i=1}^{n} (T_i - O_i)^2}{n} \right)^{1/2} \quad (2)$$

where n is the number of samples, T_i is the target (actual) value and O_t is the output of neural networks. The aim of any training set is to reach the smallest RMSE value possible in the shortest possible time.

Construction of ANN model: In order to investigate the best optimized structure for the neural network, several topologies of neural networks were surveyed by varying the number of hidden nodes, number of iterations and learning rates. The construction of these ANN models is shown in Table-3.

TABLE-3
OPTIMIZED PARAMETERS USED FOR CONSTRUCTION OF ANN MODELS

Paramters	Co(II)	Ni(II)
Input nodes	29	29
Output nodes	1	1
Hidden nodes	6	5
Learning rate	0.6	0.6
Momentum	0.9	0.9
Number of iterations	538	6096

In all steps the sum square error (SSE) was used as an index of the learning efficiency of the network during the training process. The optimum learning rate, which adjusts the weight matrices for both layers, is G (Fig. 3). The momentum coefficient, which enhances the stability of the network and reduces the training time is 0.9. The best numbers of iteration for Co(II) and Ni(II) are 538 and 6096

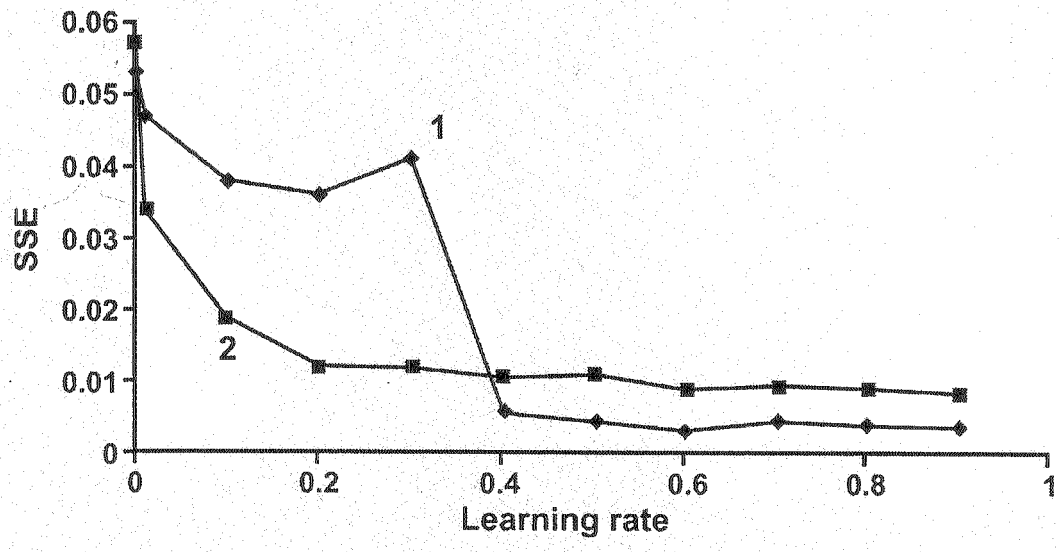

Fig. 3. Plot of SSE against learning rate for (1) Co(II) and (2) Ni(II) in the presence of EDTA

epochs, respectively. A minimum in error occurred when six and five nodes were used in the hidden layer for Co(II) and Ni(II), respectively (Fig. 4). The ability of optimized ANN model was evaluated by testing set and the RMSE measured for Co(II) and Ni(II) are 0.017 and 0.024, respectively.

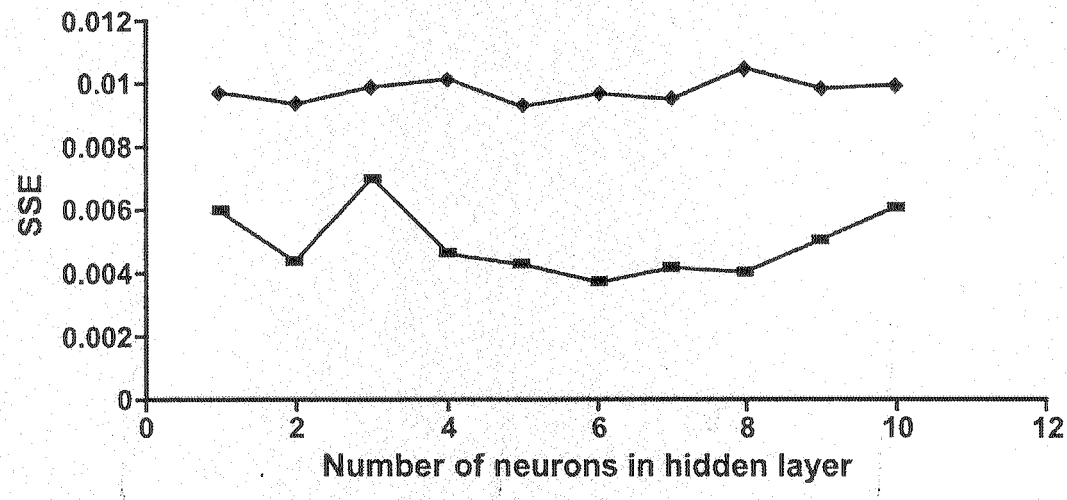

Fig. 4. Relationship of SSE and number of neurons in hidden layer for (1) Ni(II) and (2) Co(II)

Real sample analysis: The proposed method was also applied for the determination of nickel in electroplating solution. An electroplating solution of 0.1 mL was transferred to a 25 mL volumetric flask and then was treated as described in the procedure. Ultimately, the optimized neural network was applied to the analysis of electroplating solution to test the ability of the established network in real sample. The result obtained by the neural network was then compared with that obtained by atomic absorption spectrometry method (AAS). The results show good agreement between these two methods (Table-4).

TABLE-4
RESULTS OBTAINED BY ANN AND AAS IN REAL SAMPLE

Method	Concentrations ($g\ L^{-1}$)	
	Co(II)	Ni(II)
ASS	0	0.492
ANN	Not detected	0.496

Conclusions

In this study, Co(II) and Ni(II) were simultaneously determined with EDTA by spectrophotometric method and artificial neural network. The proposed method appears to be a rapid, simple and inexpensive method. The optimum values of learning rates and the number of hidden nodes show that they can affect artificial neural networks. The optimum parameters were applied to the analysis of Co(II) and Ni(II) synthetic mixture and also in real samples and the results obtained by neural network show good agreement and reliability of the method.

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