Extending the response range of bromophenol blue pH indicator using an artificial neural network

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Abstract : An artificial neural network (ANN) has been applied for the analysis of response of bromophenol blue pH indicator. A three layer feed-forward artificial neural network has been utilised to model the input-output data of a bromophenol blue pH indicator and network training was performed using the back-propagation algorithm. Responses from two wavelengths of UV-Visible spectrum are used as the input data for the neural network. It was found that an optimised network with 17 hidden neurons and 2000 epochs was highly accurate in predicting the response range of the pH indicator. The application of ANN enabled the broadening of the useful pH response range of the indicator from its limited linear range (pH 3.0-4.6) to the extensive calibration response (pH 5.0-9.5).

***Abstrak** : Rangkaian Neural Tiruan* (ANN) telah digunakan dalam menganalisis rangsangan penunjuk pH bromofenol biru. ANN dengan tiga lapisan suapan-hadapan telah digunakan sebagai model data masuk-keluar bagi penunjuk pH bromofenol biru dan latihan rangkaian dilakukan dengan menggunakan algoritma perambatan balik. Rangsangan daripada dua panjang gelombang spektrum UL-Nampak telah digunakan sebagai data masukan kepada rangkaian neural. Hasil kajian menunjukkan rangkaian dengan 17 neuron tersembunyi dan 2000 *epochs* adalah sangat sesuai dalam menentukan rangsangan julat penunjuk pH. Penggunaan ANN membolehkan julat rangsangan linear penunjuk pH yang sempit (pH 3.0-4.6) diluaskan kepada julat rangsangan yang lebih besar (pH 3.0-9.5).

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Introduction

Bromophenol blue is a pH indicator, a kind of chemical that changes colour when the pH goes up or down. Actually each indicator changes gradually from one colour to another over a range called “visual transition interval” [1]. Bromophenol blue indicator changes colour in a narrow interval of 3.0 - 4.6 pH units. Most of the pH indicators determine the pH changes indirectly in limited linear dynamic range, often 2-4 pH units only. It is very important to have a linear response because it leads to a simple calibration of the pH sensors, and more importantly a constant sensitivity and precision in pH measurement over the entire linear range. Therefore a good approach must be taken to extend the response range of pH indicators. Several approaches have been employed in order to extend the pH range especially in optical fiber pH sensor field [2] by using multiple pH indicators or one indicator with multiple steps of acid dissociation and artificial neural network (ANN) technique. The analysis for the response of a bromothymol blue pH indicator using ANN has been reported by Suah *et. al.* [3] and the extensive calibration response of the indicator have been extended.

Actually the original work on neural network was published more than 50 years ago by McCulloh and Pitts [4,5] and Hebb [6]. Recently, ANN has become the focus of interest in many disciplines including chemistry [7]. Over the last several years an increasing number of studies have examined ANN for solving modeling problems in chemistry. This has resulted in numerous applications including spectral identification, multivariate calibration, pattern recognition and control chemical processes as described by Taib *et. al.* [2]. ANN was inspired by theories of the brain in the 1940s; computer experts devised neural networks, mathematical models that rely on varying the strength of connections between internal processing elements to interpret data [8].

The structure of a neural network

The ANN is a computational simulation of biological parallel signal processing. They are usually built from several layers of neurons as depicted in Fig. 1. The first layer consists of neurons that simply take the input values of a pattern and is called the *input* layer. The last layer is called the *output* and produces the pattern output. The layer in between is called the *hidden* layers. Each neuron in the network is a simple computational device which receives a number of input signals, derives a total input signal *net* and from this produces an output signal using an output or squashing function, *f(net)*. Each input to a neuron is associated with a *weight* represented by a number, which represent the stimulating or inhibiting influence of an input signal.

Given a certain topology, i.e. a number of

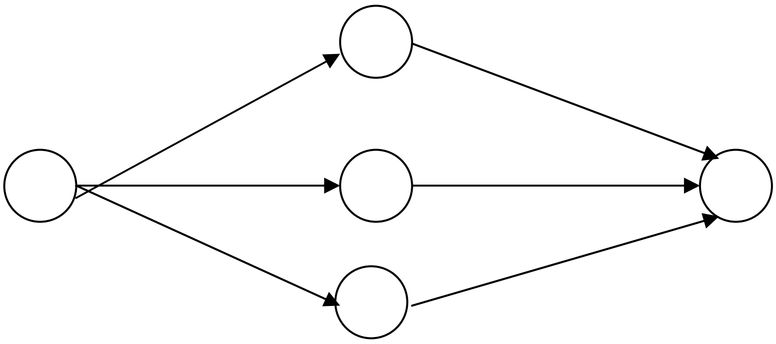


Fig. 1. Representation of an ANN in a 3-layer structure.

neurons with their interconnections, the network can collect "knowledge" by modifying its sets of *weights*. These weights are determined by starting with random values and applying a *learning* rule to train it with the help of experimental data. Despite the simple nature of the neurons, the network as a whole has impressive capabilities. Zupan and Gasteiger [9] have presented a thorough explanation of neural network theory. The networks described here are all of the feed forward type, i.e. each neuron in a layer only receives input from the neurons in the preceding layer. This is a requirement for the applied Back-Propagation (BP) rule.

The back-propagation (BP) rule

A description of the BP algorithm was given by Zupan and Gasteiger [9] and more extensive description can be found elsewhere [10]. Only a brief summary of specific details will be given here.

A neural network is first initialized by giving each weight a small random value, typically between –0.1 and +0.1. Then each pattern of the training set is sequentially presented to the network and the activation is propagated through the network to the final outputs using the input and output functions of the neurons. The outputs of the neurons in the output layer are compared with the required outputs for that pattern and for each an error term δ_j is derived:

$$\delta_j = (\text{target}_j - \text{output}_j)\, f'\,(\text{net}_j) \qquad (1)$$

The error are propagated backwards through the network starting from the layer preceding the output layer. For each neuron i in the preceding layer $l - 1$ the term δ_i is calculated using the δ_js from the succeeding layer i and the weight connecting the neuron i in layer $l - 1$ to the neuron j in the layer l:

$$\delta_i = f'\,(\text{net}_i) \sum w_{ij}\, \delta_j \qquad (2)$$

Using these error terms, adoptions of the weight factors (of the inputs of neuron i) are calculated according to the back-propagation rule:

$$\Delta w_{ji} = -\, \delta_i\, (\delta \text{net}_i \,/\, \delta\, w_{ji}) \qquad (3)$$

After each of the patterns has been processed in this way, the summed adaptions of the weights are added to the weights. Each processing of the entire training set in this fashion is referred to as an epoch in this work.

Objectives of the study

The main objective of this study is to extend the pH response range without using multiple indicators that has been used before [11]. The work presented in this paper is part of our on going research on the development of optical fibre pH sensor based on ANN. All the results presented in this paper were based on our preliminary work on the solution studies which involve the use of bromophenol blue solution for pH determination. Actually the ultimate goal for this research is to develop a portable instrument which contains ANN as the expert system for pH sensing.

Experimental

Apparatus

All absorption spectra were measured by using a Shimadzu UV-260 UV/VIS spectrophotometer interfaced with a microcomputer. The pH of the buffer solutions was measured with an Ecomet pH/mV/Temp P25 meter.

Reagents

All reagents were used as received without further purification. All solutions were prepared by using deionized water (Water Deionized E – Pure (Barnstead)). The pH buffers (ionic strength of 0.01 M) range from 2-12 pH units with alternate 0.5 unit were prepared according to Dean [12] and were stored in 100 ml polyethylene bottles. An amount of 0.20 g of bromophenol blue (BDH) was diluted in 20% ethanol (Spectrosol) in 100 ml volumetric flask. This solution was filtered with filter paper size 4 (Whatman) and was referred as a stock solution.

Bromophenol blue solutions at different pH were prepared by simply diluting 3.0 ml of the stock solution with an appropriate buffer solution in 25 ml volumetric flask.

Procedure

The pH value of each buffer solution was measured by using an Ecomet pH meter and standard potentiometric procedure [12]. All the absorption measurements of the bromophenol blue at different pH level were conducted by using the UV-VIS spectrophotometer at wavelength range between 250 nm and 700 nm. A total of 21 absorption data of bromophenol blue (pH 2.0 – 12.0), at absorption wavelength of 591.0 nm were used for the ANN training.

Artificial neural network structure and training

The network architecture adopted for this study was the feed forward network using back-propagation (BP) algorithm. The input layer consists of one neuron which corresponding to the absorption values measured at selected wavelength of 591.0 nm.

The output layer involves a single neuron representing the variable pH. ANN with one hidden layer containing one to 30 neurons has been considered for modeling. The training and simulations algorithms were implemented using a Matlab [13] program, under an Intel Pentium II Processor having 32 MB of RAM. Typical training time for the 2000 epochs took at least 10 minutes. In one epoch, the algorithm cycles through the following tasks: presentation training data sets, calculation of the error index, assignment of elements, calculating of massive matrix manipulation and update of the network weights and data storage of all the necessary training variables as reported by Taib et. al. [2]. The general settings of the training parameters for the network are given in Table 1.

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

Specific Parameters	Values
Frequency of progress display (in epochs)	10
Maximum number of epochs to train	2000
Sum-squared error goal	0.02
Learning rate	0.01
Limits for weight randomization	-0.1; +0.1

Results and discussion

Figure 2 shows a three-dimensional (3D) spectra of the bromophenol blue pH indicator measured at different pH values ranging from pH 2.0 to 12.0 by using UV/VIS spectrophotometer. From the 3D spectra, it can be clearly seen that the maximum absorbance only occurred at two different wavelengths i.e. 437.0 nm and 591.0 nm. These absorption correspond to the colour changes of the bromophenol blue from yellow to purple between pH range 3.0 – 4.6. At these wavelengths the absorption readings varied with pH in characteristic sigmoid pattern as shown in Figure 3. As shown in Figure 3, the useful linear range line of this indicator is limited at around pH 3.0 – 4.5 for for both wavelengths. This pH range value agreed well with the working pH range for the same pH indicator, which has been reported [12] i.e. pH 3.0 – 4.6. However, the changes

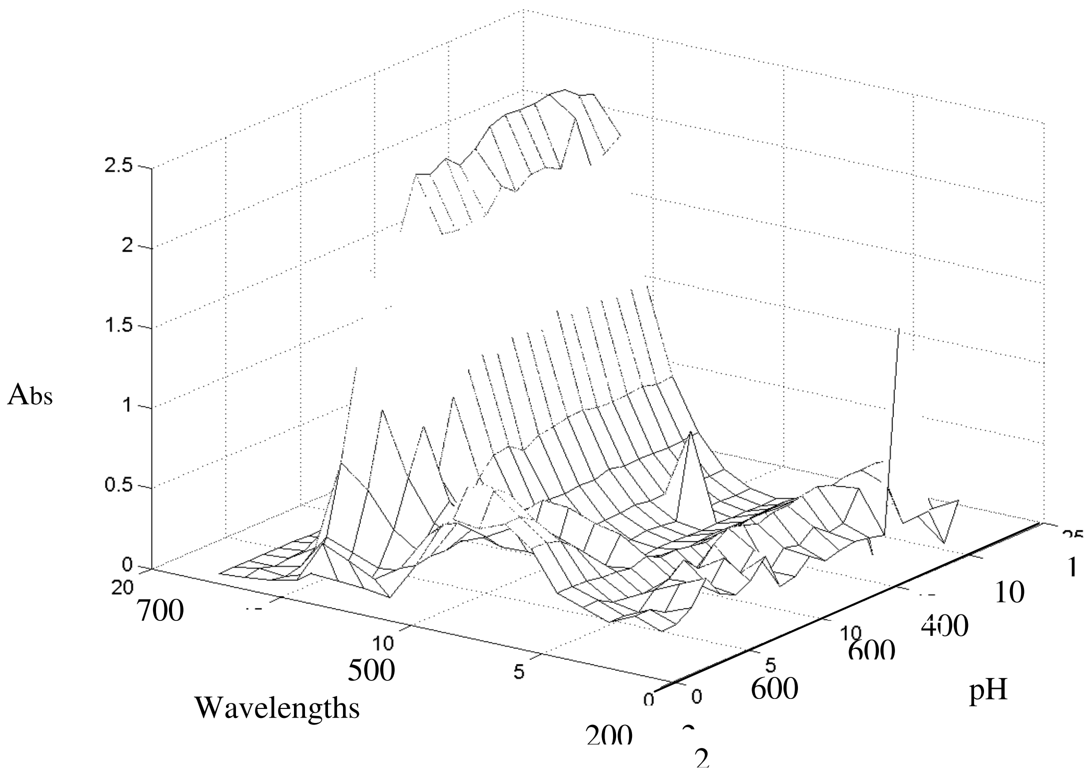


Fig. 2. Three-dimensional absorption spectra of the bromophenol blue at different pH values.

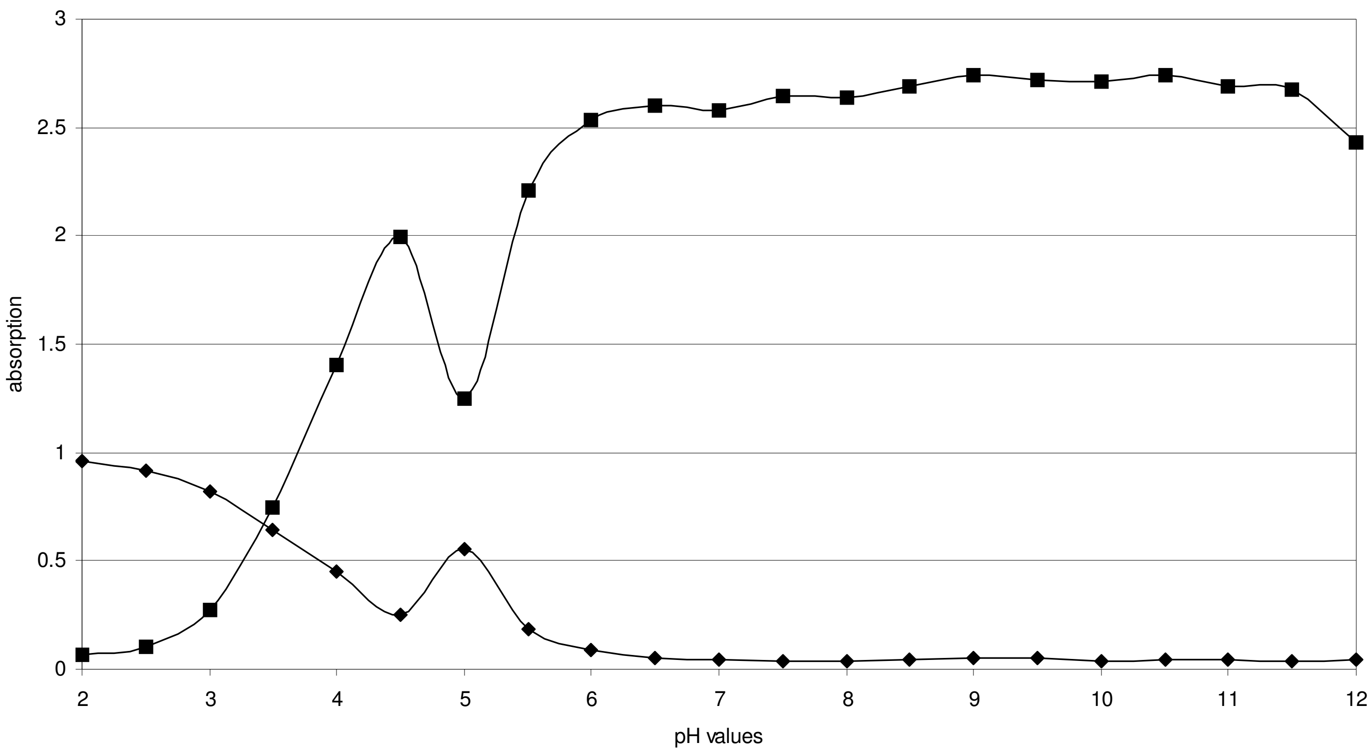


Fig.3. The absorption of the bromophenol blue at different pH values as measured at wavelengths of 437.0nm (A) and 591.0nm (B).

in the absorption reading with pH at 591.0 nm are much higher than absorption at 437.0 nm. For this reason, the absorption reading at wavelength of 591.0 nm was used in this study to train the network. ANN was applied in this study to optimize the response of the bromophenol blue pH indicator. For this purpose, the spectrum response at each pH values at wavelength of 591.0 nm was used as the input to the network. These points were chosen since they represent the wavelengths where significant variations in the absorbance spectra can be obtained.

A total of 21 spectra were used for the training of the ANN. The training parameters utilised in this study were the same as those recommended by Taib *et al.* [2] with the weights and biases were assigned with randomised initial values within the range ± 1. The training was carried out on several networks having varying number of neurons in the hidden layer. The sum-squared error, which was taken as the sum of all errors over each training spectrum was measured at the end of each epoch. Figure 4 and Figure 5 show the progress in the networks with 5 and 10 neurons respectively over 2000 epochs in the hidden layer. As shown, the index errors produced by utilising 5 and 10 neurons are quite high. Figure 6, on the other hand show that an optimised network with smaller index error was achieved by using 17 neurons in hidden layer.

After repeated for 3 times, the attained results for the training of the ANN were still remains the same with the index error for the network still within the range of 10^1 and 10^2 when 17 neurons in hidden layer and 2000 epochs were used. The index error is considered low and the chosen network is acceptable for the training purposes. The chosen network produced almost linear response between pH 3.0 –5.0 and 6.0 – 9.5 as shown in Figure 7.

By using Figure 7 as the calibration graph, the selected ANN architecture can now be applied for the pH determination of the unknown solution having pH values in the range of pH 3.0 – 9.5. It can be done by providing the ANN with the absorption data of the unknown solution at wavelength of 591.0 nm. The absorption data will be used as data input to the architecture. Based on the trained data, the ANN will be able to predict and determine the pH of the solution.

Conclusion

The application of ANN for pH optimisation of the bromophenol blue indicator has been demonstrated successfully in this study. The architecture of the network used for the pH optimisation consists of 1 input neuron, 17 neurons in single hidden layer and 1 output neuron. The finding from this study also indicates that the number of epochs that was found suitable for the pH optimisation was 2000. By using ANN, the response of bromophenol blue pH indicator could be optimised from its limited linear response of pH 3.0 – 4.6 to pH

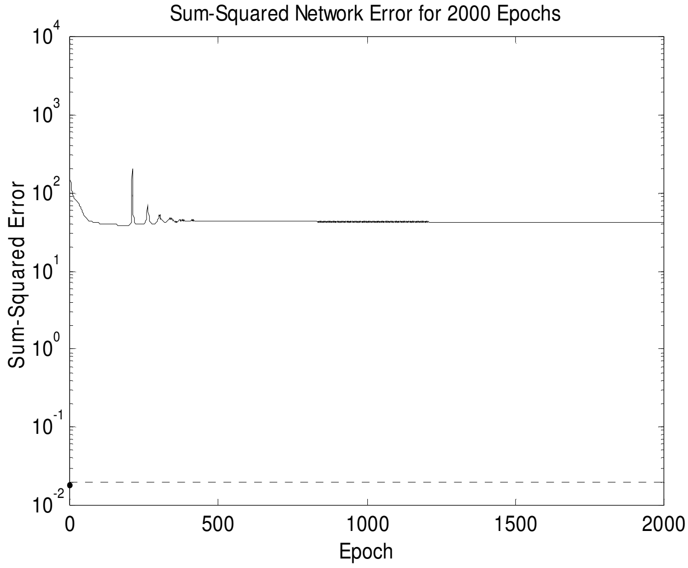
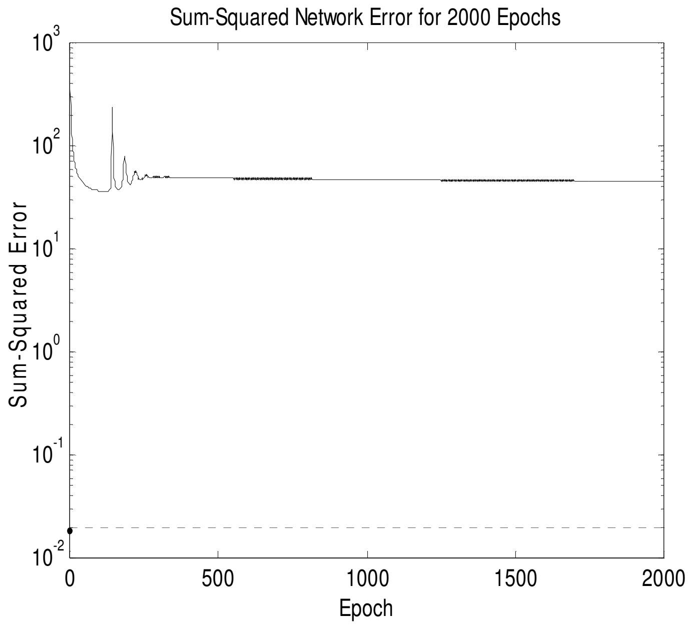


Fig. 4. Progress in training error index of network with 5 neurons in hidden layer and 2000 epochs.



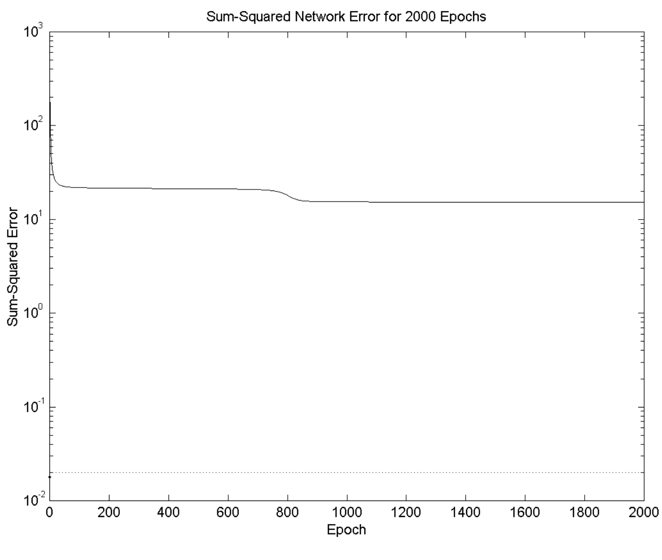


Fig. 6. The training error index for networks with 17 neurons and 2000 epochs.

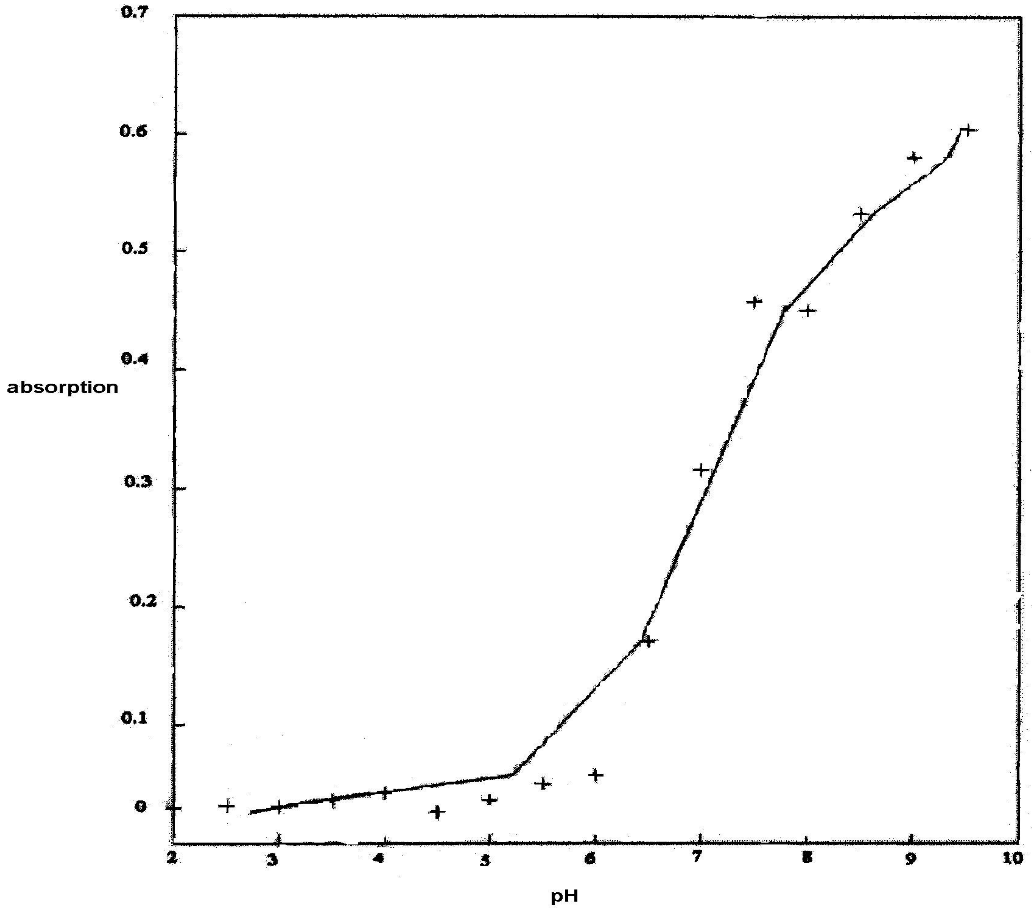


Fig. 7. Training data fitting by the networks with 17 neurons in hidden layer.

5.0 – 9.5. Better consequence and accuracy may be achieved by providing more training data to the network and a proper procedure should be introduced to certify the parameter drift.

Acknowledgements

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