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# An Intelligent Optical Fibre pH Sensor Based on Sol-Gel Advanced Material and Artificial Neural Network

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**ABSTRACT**

*The application of artificial neural network (ANN) in signal processing of optical fibre pH sensor is presented. The pH sensor is developed based on the use of bromophenol blue indicator immobilized in a sol-gel thin film as a sensing material. A three layer feed-forward network was used and the network training was performed using the back-propagation algorithm. Spectra generated from the pH sensor at several selected wavelengths are used as the input for the ANN. The bromophenol blue indicator, which has a limited dynamic range of 3.00-5.50 pH units, was found to show higher pH dynamic range of 2.00-12.00 and low calibration error after training with ANN. The trained ANN was successfully employed to predict several spectra from unknown buffer solution with an average error of 0.06 pH units.*

**Keywords:** *Artificial neural network; Optical fibre pH sensor; Signal processing; Sol-gel; pH indicator; bromophenol blue*

## Introduction

Progress and application of optical fibre chemical sensor (OFCS) and biochemical sensor have been one of the fastest growing fields over the

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last two decades. The key step in developing a sensor is the immobilization of sensing agents [1]. A good immobilization method should meet the requirements such as simple and fast, produce immobilized reagents that retain their chemical and biochemical activities, non-specific, *i.e.* the method can be used for the immobilization of various sensing agents, produce immobilized reagents that are stable and do not leach from the substrate.

There are three most widely used methods for immobilization for example adsorption of sensing agents onto a solid substrate, covalent binding which involves the formation of permanent chemical bonds between sensing agents and a support and the last one is encapsulation or entrapment of sensing agents within a polymeric matrix. In 1990, Zusman *et al*. [2] reported that by trapping suitable analytical reagents, porous sol-gel glasses could be used for the preparation of a wide variety of chemical-sensing materials. Since that, sol-gel has been increasingly used as a solid matrix for entrapment of chemical and biochemical agents in OFCS and biochemical sensor development and applications especially the pH sensor.

The sol-gel process is a liquid-phase method of preparing glasses and ceramic at ambient temperature [3]. The process, which may be used to produce bulk glasses as well as film and fibres, generally involves the use of metal alkoxides which undergo hydrolysis and polymerisation reactions to give gels. The rates of the various reactions and properties of the final material depend on, among others, the precursor used, the pH of the precursor solution, the water concentration and temperature [3]. The sol-gel process has received considerable attention as a method for fabricating materials employed in chemical and biochemical sensors. Generally in such applications, sensor molecules are incorporated in the sol-gel derived cage-like microstructure, through which smaller analyte molecules can diffuse to interact with them. The principal advantages of this process are the ease with which the microstructure of the material can be modified by varying the process parameters and the low temperature involved.

The advantage of using doped sol-gel glasses for sensing material preparation is because they are chemically, thermally and photochemically stable. They are also transparent well into the ultraviolet region, allowing a whole array of photochemistry, photophysical and optical applications. The encapsulated molecules are well protected and their photodegradation rate is smaller, compared to solution and the trapped molecules are either non-leachable or in some cases leachable over a very long period [3].

There are several kinds of pH sensors such as electrochemical sensor, salt dependent sensor and lately optical fibre sensor [4]. However, the major disadvantage of an optical fibre pH sensor is that they determine pH indirectly by measuring the colour of the dissociated and undissociated forms of the indicators and their response is sigmoidal [5]. Regardless of the sigmoidal response showed by these sensors, a narrow linear range of the curve can be taken as linear (often 2-4 pH units only), in order to determine the pH by interpolation method [6].

Numerous attempts have been proposed in order to extend the pH range of these sensors by employing for example multiple pH indicators or one indicator with multiple steps of acid dissociation, fluorescent indicators and multiplexing several optical pH probes [1]. A number of signal processing techniques, for instance polynomial curve-fitting [7], have been applied for modelling the sensor response. Over the last several years, an increasing number of studies have observed artificial neural network (ANN) for solving modelling problems in analytical chemistry and especially in OFCS technology.

Actually 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 [8]. It is composed of many simple processing elements that usually do little more than take a weighted sum of all their inputs. The simple three layers feed-forward ANN is shown in Figure 1.

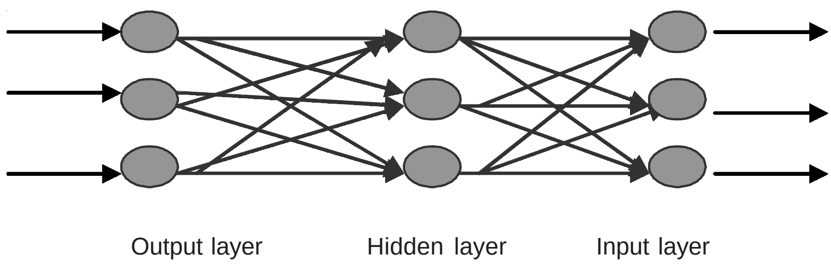


Figure 1: A Three Layer Feed-forward Artificial Neural Network

The extent of applications of ANN comes from their capability to estimate complex functions that make them compatible for modelling non-linear relationship. The range of chemical applications of ANN is very large and it includes fields as diverse as modelling structure of protein, molecular dynamics, process control, interpretation of spectra, calibration, pattern recognition, optimisation of the linear signal range and signal processing have been reviewed [9-11]. Meanwhile in OFCS technology, ANN is used in signal processing, data reduction and optimisation, interpretation and prediction of spectra and calibration [12].

This study describes the preparation and the development of optical fibre pH sensor system based on immobilised bromophenol blue (BPB) into sol-gel film. The main objective of this study is to extend the linearity of the sensor's response while at the same time maintaining the prediction error at an acceptable level.

## Experimental

The experiment reported here may be divided into three major parts, *i.e.* chemicals and solution preparation, instrumentation and data treatment.

### Chemicals and Solutions

BPB (Aldrich) was used in this study for the pH sensing material preparation. The pH indicator solution were prepared by dissolving 0.050 g of the indicator powder in ethanol 20 % (BDH) and the solution were made to 50.00 mL volume in volumetric flask. All the buffer solutions, range from pH 1.00–14.00 (0.01 M), was prepared according to Dean [13] and stored in 100 ml polyethylene bottle.

The chemicals used to prepare a sol-gel matrix include tetraetylorthosilicate (TEOS) (Aldrich), ethanol, distilled deionised water (Barnstead), hydrochloric acid (BDH) and triton x-100 (Fluka). Microscope slide glass is used to provide a support to a sol-gel film. All these support materials are used after washing with ethanol.

### Procedure

A mixture of 30.00 ml TEOS, 30.00 ml distilled deionised water, 31.00 ml ethanol, 0.50 ml hydrochloric acid and an appropriate amount of triton x-100 is poured into a 100 ml beaker. The solution is briskly agitated using the magnetic stir bar (Stuart Sci. SM 22). The sol-gel solution is left stirred for two hours. The sol-gel films were deposited on the support materials by spin coating method. The spin coating technique was carried out by using vacuum spin coater (Chemat KW 4A) with an adjustable speed. An amount of 1.0 mL sol-gel solution and 1.0 mL of BPB solution were placed onto the support (microscope slide glass) to give 1:1 ratio. The stirring process took place for three minutes with speed of 1500 rpm. Then, the thin film is allowed to dry for 24 hours in ambient temperature. Then the film is left to dry for 1 week. After the drying process, the film is then washed under flowing water to clean any molecule adsorpted on the surface of the film.

### Instrumentation

In this study, all the absorption of the sol-gel film is measured by using Ultraviolet - Visible Spectrophotometer (Varian-Cary win UV 100) were used for all measurements using fibre optic accessories.

### Measurement of the Absorbance Spectra

For the measurement of the spectra, the optical fibre probe was immersed in buffer solutions of varying pH values. For each pH, the spectrum was scanned in the wavelength range 320-1000 nm. A total of thirty spectral reading were obtained. Five of these spectra (pH 2.05, 4.05, 6.05, 8.05 and 10.05) were used for testing the trained network whilst the rest spectra were used for the training of the network. These selected spectra are corresponding to linear region (pH 4.05) and non-linear regions (pH 2.05, 6.05, 8.05 and 10.05) of the pH sensor. Finally, a set of four buffer solutions (pH 3.60, 7.25, 9.60 and 11.90) was also employed to test the selected network whether it is suitable for the final purpose, which is to predict the pH of unknown buffer solution.

## Data Treatment and Analysis

A feed-forward neural network having a single hidden neuron layer with back-propagation (BP) training algorithm was employed for treatment of the data. The input layer consisted of eight neurons corresponding to the absorbance intensities measured at eight different wavelengths from each spectrum. The output layer consists a single neuron corresponds to variable pH values. Network, with hidden layer size up to 19, have been considered.

The network training and data treatment were realised using Matlab [14] running on a Pentium (II) processor having 64 MB of RAM. The sigmoidal function was employed for hidden neuron activation [15-16];

the training parameters used was set to the recommended values [17-18]. The training and optimisation processes include the following: the networks were trained up to 40,000 epochs and the progress of sum-squared error (SSE) between the calculated and the measured output was recorded. The SSE will be used to check for the convergence of network training. After that, the networks prediction will be measured. Finally, a new set of input data will be operated to the networks to check for its forecast capability and precision.

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

## Results and Discussion

The results are first analysed based on their spectral responses. Subsets of these responses were employed for ANN training and optimisation. Finally, the prediction capability of the trained ANN to measure unknown pH was examined.

### Spectral Properties

The three dimensional (3D) absorption spectra of the optical fibre pH sensor based on immobilised BPB, measured at different pH values are shown in Figure 2. The absorption spectra at pH lower than 2.00 and higher than 12.00 were not included due to leaching problem, which render the sensor useless for pH measurement in this range. As shown, Figure 2 also displayed the non-linear characteristics lie beneath the sensor’s data. These kinds of data are very suitable for non-linear modelling purposes using ANN. At acidic pH region, only one single peak was obtained from the sensor in the wavelength range 450-650 nm and pH range 2.00-5.50, which corresponds to the yellow form of the immobilised indicator. After the pH increase, the single peak shifted into two different major peaks in the wavelength range 450-650 nm and pH range 6.00-12.00 that matches up to the bluish purple form of the immobilised indicator. This result agreed well with the preliminary study on the BPB solution, which has been carried out earlier [18].

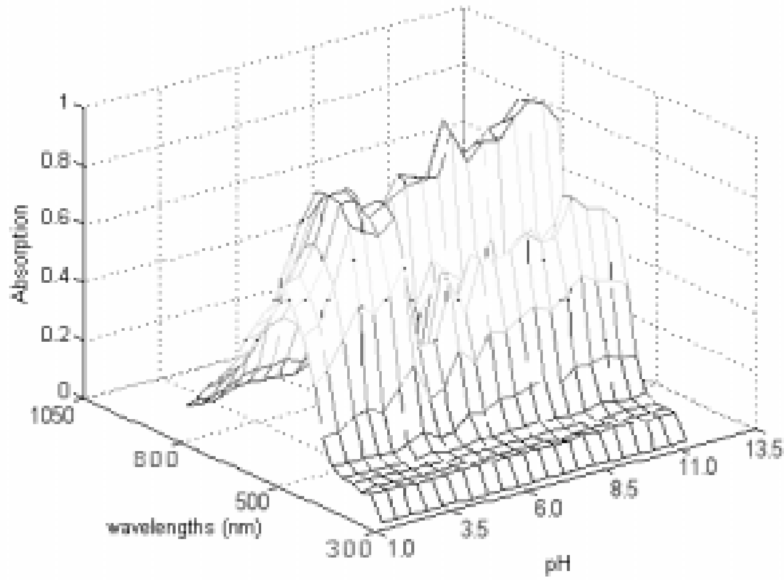


Figure 2: Generated pH Spectra of the Optical Fibre pH Sensor Response Measured at Different pH Values

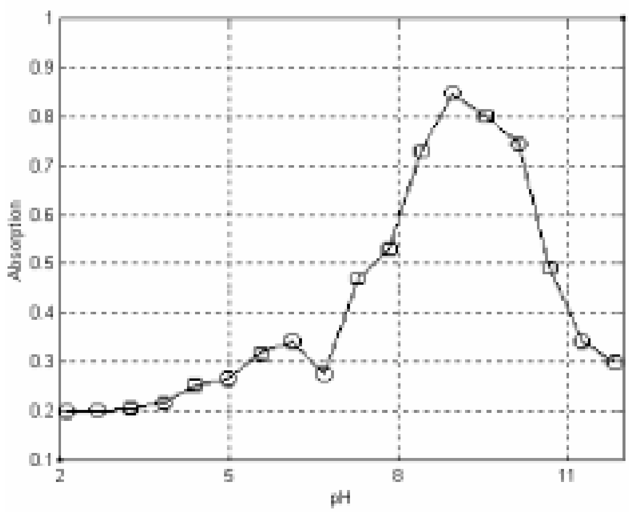


Figure 3: The Optical Fibre pH Sensor's Response at Different pH Values before Training with ANN. The Reflectance Signal was Measured at Wavelength 600 nm

The maximum absorbance intensity was occurred at 600 nm. At this wavelength, the absorbance readings varied with pH as shown in Figure 3. Still, the beneficial linear range is limited only from pH 3.00-5.50. This outcome also has the same opinion with the working pH of the BPB solution, which has been reported in the literature [13] *i.e.* 3.0-4.6.

## Multivariate Calibration using ANN

Subsequently ANN was operated to process the signal of the optical fibre pH sensor. Signal from each pH was used as the input to the network. To avoid several problems during network training such as long training period, entail a large matrices for the network connections and can be locked into a local minima [19-20], only several wavelengths points were selected, *i.e.* only eight wavelengths (350, 400, 450, 500, 550, 600, 625 and 650 nm) from each spectrum were chosen as the input for the ANN. These points also represent significant variations in the sensor signal, isobestic points and they also provide the general outline of the original spectra [5].

Twenty-one spectra were employed for the training of the ANN. The limit weights and biases were assigned and randomised initial values within the range ± 0.1. The network training or optimisation was performed on several networks having different hidden layer size. The SSE for each training was measured at the end of each epoch. The progress of SSE of the networks is shown in Figure 4 with 3, 6, 7, 10, 11, 13, 17 and 19 hidden neurons, trained through 40,000 epochs. For the network with three neurons, the convergence of SSE was very slow. The fastest convergence was obtained using seven neurons in hidden layer. This result discloses that an optimised and suitable network can be attained with hidden layer size of 6 to 17 neurons [15]. The number of hidden neurons when arranged in declining SSE order is 3, 19, 13, 6, 10, 17, 11 and 7 (Figure 5).

To evaluate the effect of increasing training epoch on the fitting capability of the network, all the networks were retrained by using 100,000 epochs. Results produced indicate that training over 100,000 epochs do not effect the SSE of these networks; hence networks trained with 40,000 epochs were sufficient to be used in predicting the response of the optical fibre pH sensor. This outcome also demonstrates that training over 100,000 epochs will only generate the trained network with over training and over fitting problems [10].

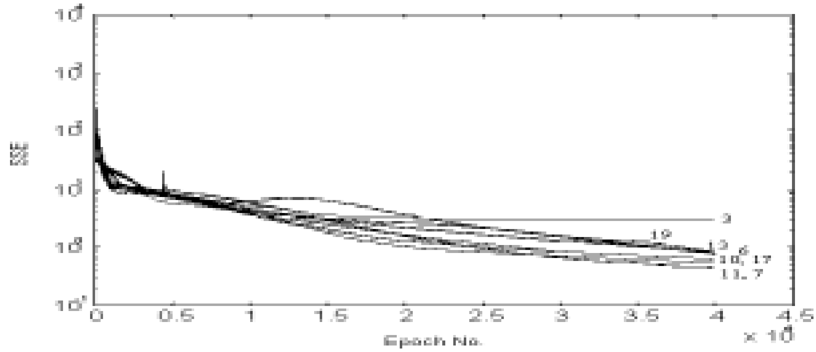


Figure 4: Convergence in the Training Error Indexes over 40,000 Epochs. Numbers Indicate the Hidden Neurons

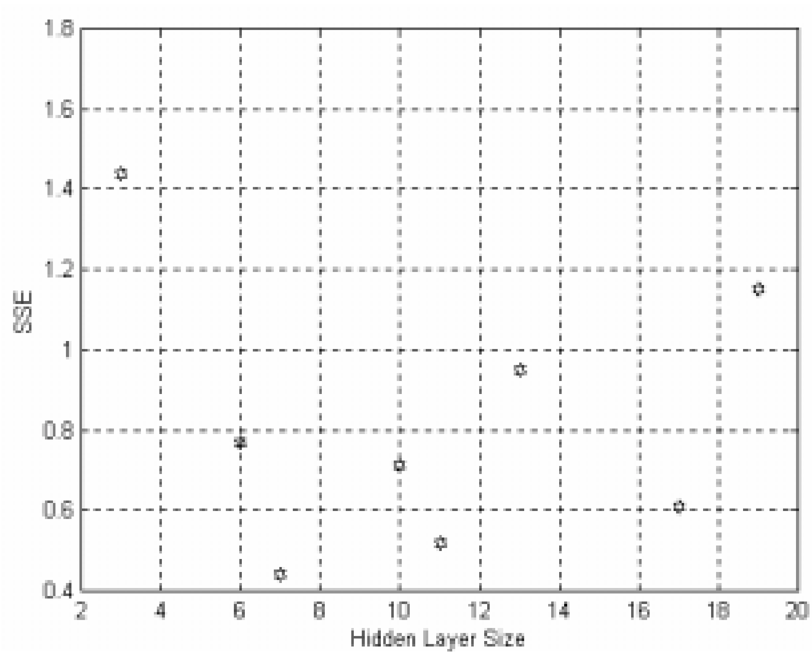


Figure 5: Plot of Error Index for Networks with Different Hidden Layer Sizes after Training over 40,000 Epochs

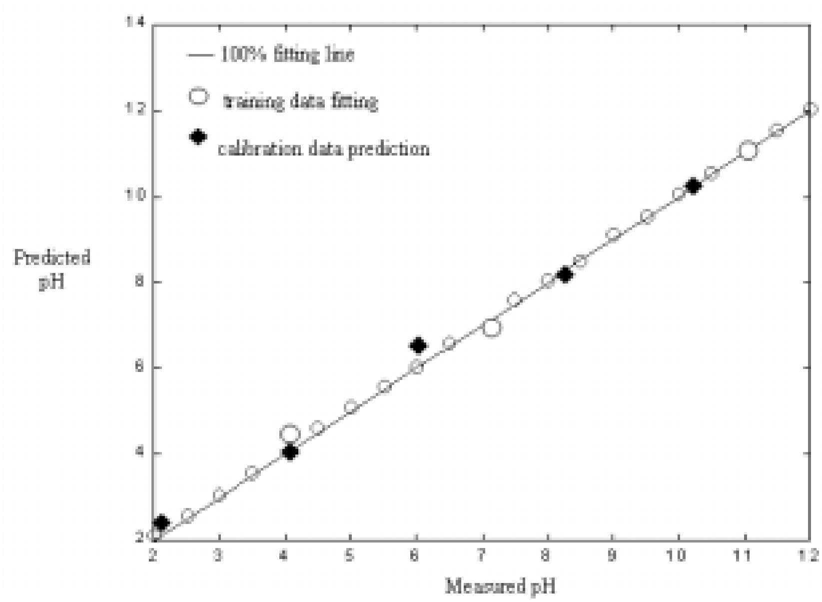


Figure 6: Training Data Fitting and Calibration by the Network with Seven Neurons in Hidden Layer

To test the network's prediction capability, all of the networks were presented with five new calibration spectra (pH 2.05, 4.05, 6.05, 8.05 and 10.05) as recommended before [15, 20]. Table 1 in the appendix, displays the predicted pH values given by these networks contrary to the expected pH (measured by glass electrode pH meter). As can be noticed in Table 1, the network with 7 and 11 neurons in hidden layer created the best predictions with average calibration errors of 0.05 and 0.07 each. The network prediction potential was done in two parts, which is within the linear response range of the sensor training data (pH 4.05) and outside its linear response range (pH 2.05, 6.05, 8.05 and 10.05). The average calibration error for the trained networks is very small, *i.e.* 0.11 pH.

From the outcome above, it is obvious that the network with seven neurons in hidden layer gives the best architecture for generating accurate prediction of pH. This network also extends the linear response range of the sensor from 2.00-5.00 pH to full calibration range of 2.00-12.00 pH (Figure 6). In addition, this network proved its ability to predict the response of the sensor with minimum error (Table 2). Otherwise, it would be difficult to predict the response of non-linear response data using the conventional chemometrics methods that have reported by Shaffer *et al.* [21].

Table 1: The Networks pH Prediction using Calibration Data

| Hidden layer size | Expected pH 2.05 | | Expected pH 4.05 | | Expected pH 6.05 | | Expected pH 8.05 | | Expected pH 10.05 | | *Average calibration error |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | prediction | error | prediction | error | prediction | error | prediction | error | prediction | error | |
| 3 | 2.32 | 0.27 | 4.11 | 0.06 | 6.13 | 0.08 | 7.86 | 0.19 | 9.73 | 0.32 | 0.18 |
| 6 | 2.18 | 0.13 | 4.10 | 0.05 | 5.94 | 0.11 | 7.95 | 0.10 | 10.23 | 0.18 | 0.11 |
| 7 | 2.11 | 0.06 | 4.08 | 0.03 | 6.00 | 0.05 | 8.10 | 0.05 | 10.11 | 0.06 | 0.05 |
| 10 | 2.14 | 0.09 | 3.99 | 0.06 | 6.12 | 0.07 | 8.13 | 0.08 | 9.93 | 0.12 | 0.08 |
| 11 | 2.13 | 0.08 | 4.09 | 0.04 | 6.11 | 0.06 | 7.97 | 0.08 | 9.96 | 0.09 | 0.09 |
| 13 | 2.18 | 0.13 | 3.99 | 0.06 | 5.97 | 0.08 | 8.15 | 0.10 | 10.16 | 0.11 | 0.09 |
| 17 | 2.21 | 0.16 | 3.96 | 0.09 | 5.92 | 0.13 | 7.95 | 0.10 | 10.22 | 0.17 | 0.13 |
| 19 | 2.24 | 0.19 | 3.91 | 0.14 | 6.18 | 0.13 | 8.21 | 0.16 | 9.83 | 0.22 | 0.17 |

*Average calibration error = (%predicted pH – measured pH%) / 5

Table 2: Predictions of the Network with Seven Hidden Neurons using New pH Spectra

| Measured pH | Predicted pH | Error (pH) |
|---|---|---|
| 3.60 | 3.56 | 0.04 |
| 7.25 | 7.19 | 0.06 |
| 9.60 | 9.65 | 0.05 |
| 11.90 | 11.81 | 0.09 |

Average prediction error = 0.06 pH.

### Prediction of Unknown pH Solution Using Trained Network

Lastly, the network with seven neurons in hidden layer was applied to predict the pH of unknown buffer solution. New spectra from a set of four buffer solutions (pH 3.60, 7.25, 9.60 and 11.90) were fed to the network. The result of this application is shown in Table 2. The network was found to be able to effectively predict the pH values with the worst prediction error of only 0.09 pH unit. The highest recorded error of 0.09 pH unit for measurement of buffer solution with pH 11.90 is expected because the pH of this buffer is almost outside the network training range (pH 2.00-12.00). This result also shows minimum prediction error for the spectra within the training range, where there is only 0.04 pH error for prediction in the linear region (pH 3.60). Predictions for the measurements at 7.25 pH and 9.60 pH yield errors of 0.06 and 0.05 pH, respectively. This is due to non-linear region of sigmoidal response of the sensor for both measurement spectra (Figure 3). Overall, the average prediction error for the unknown new solution is quite low and acceptable, with error of only 0.06 pH.

## Conclusion

The results obtained in this study reveal that sol-gel film is a suitable solid support to immobilise BPB for the construction of optical fibre pH sensor. Successful application of an ANN trained with BP algorithm in processing the highly non-linear calibration of an optical fibre pH sensor has been performed. A network architecture consisting eight input neurons, seven hidden neurons and one output neuron was found appropriate for the multivariate calibration use. The trained network was highly accurate in predicting the response of the optode with an average prediction error of 0.06 pH unit. The trained network also demonstrated no generalisation and over fitting problems, although the network was trained up to 40,000 epochs.

The ultimate consequence of using ANN on the optical fibre pH sensor was the broadening of the limited linear range of the sensor (pH 3.00-5.50) to the full calibration range (pH 2.00-12.00) that cover almost of the pH range (pH 1.00-14.00). Only leaching of the immobilised reagent (BPB) at very acidic and basic region prevents the ultimate goal, which is to extend the linear range to full pH range. Further studies of the characteristics of the optode such as response time, optode lifetime and its on-line monitoring are in progress to develop an intelligent, small and portable optical fibre pH sensor.

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