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Applications of artificial neural network on signal processing of optical fibre pH sensor based on bromophenol blue doped with sol–gel film

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Abstract

In this paper, the applications 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 (BPB) 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 (BP) algorithm. Spectra generated from the pH sensor at several selected wavelengths are used as the input data 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 with low calibration error after training with ANN. The enhanced ANN could be used to predict the new measurement spectra from unknown buffer solution with an average error of 0.06 pH units. Changes of ionic strength showed minor effect on the dynamic range of the sensor. The sensor also demonstrated good analytical performance with repeatability and reproducibility characters of the sensor yield relative standard deviation (R.S.D.) of 3.6 and 5.4%, respectively. Meanwhile the R.S.D. value for this photostability test is 2.4% and it demonstrated no hysteresis when the sensor was cycled from pH 2.00–12.00–2.00 (acid–base–acid region) of different pH. Performance tests demonstrated a response time of 15–150 s, depending on the pH and quantity of the immobilized indicator.

Keywords: Artificial neural network; Optical fibre pH sensor; Signal processing; Sol–gel; pH indicator; Bromophenol blue

1. Introduction

There are several kinds of pH sensors such as electrochemical sensor, salt dependent sensor and lately optical fibre sensor [1]. 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 [2]. 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 [3].

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 [4]. A number of signal processing techniques, for instance polynomial curve-fitting [5] has also been applied for modelling the sensor response. Over the last several years, the number of studies on application of artificial neural network (ANN) for solving modelling problems in analytical chemistry and especially in optical fibre chemical sensor (OFCS) technology, has increased substantially.

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 [6]. It is composed of many simple processing elements that usually do little more than take a weighted sum of all their inputs.

The range of scope of applications of ANN comes from their capability to estimate complex functions that make them compatible for modelling non-linear relationships. 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 [7–9]. Meanwhile in OFCS technology, ANN is used in signal processing, data reduction and optimisation, interpretation and prediction of spectra and calibration [10].

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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 constructed sensor was evaluated with respect to prediction error of the ANN, reproducibility, repeatability, photostability, hysterisis effect, response time and effects of ionic strength of the buffer solution on the sensor response.

2. Experimental

2.1. 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 using deionised water (Barnstead E-Pure). All the buffer solutions range from pH 1.00–14.00 (0.01 mol l^{-1}) were prepared according to Dean [11] and were 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). A microscope slide glass was used to provide a support to a sol–gel film. The support material was used after washing with ethanol.

2.2. 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 were poured into a 100 ml beaker. The solution was briskly agitated using the magnetic stir bar (Stuart Sci. SM 22). The sol–gel solution was left stirred for 2 h. 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 a 1:1 ratio. The spinning process took place for 3 min with speed of 1500 rpm. Then, the thin film was allowed to dry for 1 week. After the drying process, the film is then washed under flowing water to remove any weakly bound or unbound molecules on the surface of the film.

2.3. Instrumentation and measurement of the absorbance spectra

Spectral measurements were made with an Ultraviolet-Visible Spectrophotometer (Varian-Cary win UV 100) using fibre optic accessories. For the measurement of the spectra, the optical fibre sensor was immersed in buffer solutions of varying pH values. For each pH, the spectrum was scanned in the wavelength range of 320–1000 nm. A total of 30 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 remaining spectra (pH 2.00, 2.50, 3.00, 3.50, 4.00, 4.50, 5.00, 5.50, 6.00, 6.50, 7.00, 7.50, 8.00, 8.50, 9.00, 9.50, 10.00, 10.50, 11.00, 11.50 and 12.00) were used for the training of the network. These spectra were selected to represent the data from the 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 capability of the trained ANN to predict the pH of unknown buffer solution.

2.4. Data treatment and 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 eight neurons which represent the absorbance intensities measured at eight different wavelengths from each spectrum. The output layer consists a single neuron which represents the pH values. Network having up to 19 neurons in hidden layer have been considered in this study.

The network training and data treatment were realised by using Matlab program [12] under a Pentium (II) processor having 64 MB of RAM. The sigmoidal function was employed for hidden neuron activation [13,14] and the training parameters used were set to the recommended values [15,16]. The training and optimisation processes carried out in this study 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. Finally, a new set of input data was introduced to the networks to check for its prediction capability and precision.

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 pH values employed by the Matlab program and simulation.

3. Results and discussion

3.1. Spectral properties

At acidic pH region, only a single absorption peak was obtained from the sensor in the wavelength range of 450–650 nm and pH range of 2.00–5.50, which corresponds to the yellow form of the immobilised indicator. When the pH increase, the single peak shifted into two peaks in the wavelength range of 450–650 nm and pH range of 6.00–12.00 that matches up to the bluish purple form of the immobilized indicator. The absorption spectra at pH lower

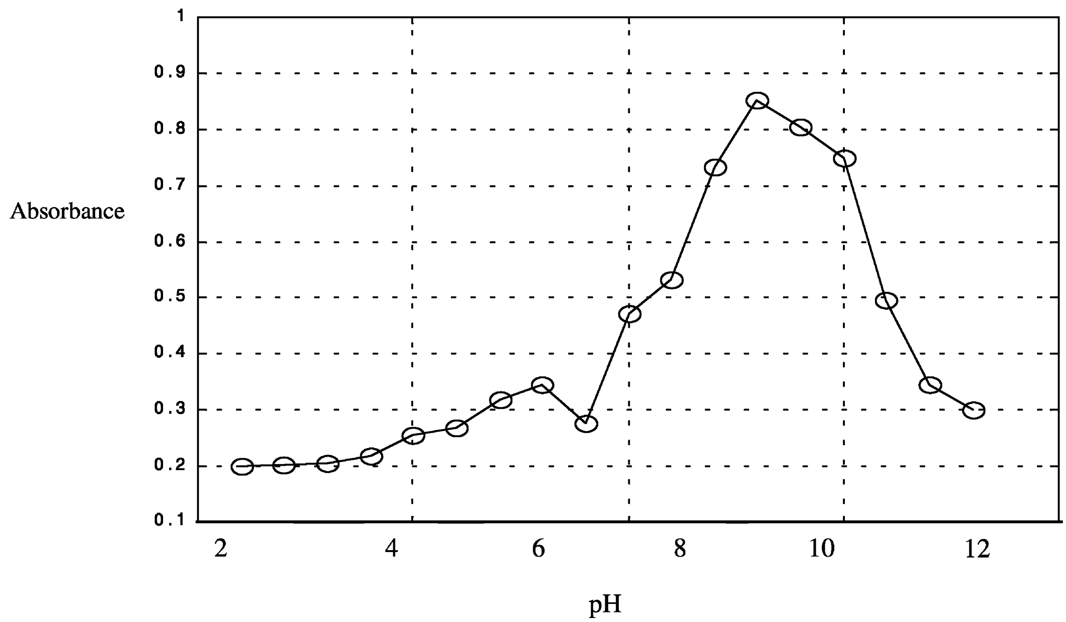

Fig. 1. The optical fibre pH sensor's response at different pH values before training with ANN. The absorbance was measured at wavelength 600 nm.

than 2.00 and higher than 12.00 were not included due to leaching problem, which rendered the sensor useless for pH measurement in these ranges. The spectra also displayed the non-linear characteristics lie beneath the sensor's response. These kinds of data are very suitable for non-linear modelling purposes using ANN. This result agreed well with the preliminary study on the BPB solution, which has been carried out earlier [16]. The maximum absorbance intensity was observed at 600 nm. At this wavelength, the absorbance readings varied with pH and the beneficial linear range is limited only in the pH range of 3.00–5.50 (Fig. 1).

3.2. Multivariate calibration using ANN

Subsequently ANN was operated to process the signal of the pH sensor. Signal from each pH was used as the input to the network. To avoid several problems during network training such as a long training period, a large number of matrices for the network connections and tendency to be locked into a local minima [17,18], only several wavelengths points were selected. For that reason, only eight wavelengths points (350, 400, 450, 500, 550, 600, 625 and 650 nm) from each spectrum were chosen to represent the input data for the ANN. All of these points were selected due to their significant variations in the sensor signal.

Twenty-one spectra were employed for the training of the ANN. The network training or optimisation was performed on several networks having different number of neurons in the hidden layer. The SSE for each training was measured at the end of each epoch. Table 1 shows the SSE values of the networks with 3, 6, 7, 10, 11, 13, 17 and 19 hidden neurons after completing the 40,000 epochs. For the network with three neurons, the convergence of SSE was observed to be very slow. The fastest convergence was achieved using seven neurons in hidden layer. This result agreed well with the results reported by Taib and Narayanaswamy [13] which reported that an optimised and suitable network can be attained with network size of 6–17 neurons in hidden layer. The number of hidden neurons when arranged in declining SSE order was 3, 13, 19, 6, 10, 17, 11 and 7.

To evaluate the effect of increasing number of the training epoch on the fitting capability of the network, the networks were retrained by using 100,000 epochs. As shown in Table 1, the results indicates that increasing the training epochs to 100,000, it did not showed much influent on SSE values. Therefore, networks trained with 40,000 epochs were sufficient to be used in predicting the response of the pH sensor. ANN training by using much higher number of epochs will usually caused problems such as over training and over fitting problems [8].

To improve the process in choosing the best network's architecture, the trained networks with different number of hidden neurons were presented with five calibration spectra

Table 1
SSE values obtained from the networks consists of different number of hidden neurons after being trained with 40,000 and 100,000 epochs

Number of hidden neurons	Sum-square error (SSE) with 40,000 epoch	Sum-square error (SSE) with 100,000 epoch
3	4.213	4.186
6	0.944	0.901
7	0.513	0.508
10	0.874	0.890
11	0.712	0.728
13	3.144	3.125
17	0.736	0.738
19	1.978	1.954

Table 2
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[a]
	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	0.184
6	2.18	0.13	4.10	0.05	5.94	0.11	7.95	0.10	10.23	0.18	0.114
7	2.11	0.06	4.08	0.03	6.00	0.05	8.10	0.05	10.11	0.06	0.050
10	2.14	0.09	3.99	0.06	6.12	0.07	8.13	0.08	9.93	0.12	0.084
11	2.13	0.08	4.09	0.04	6.11	0.06	7.97	0.08	9.96	0.09	0.087
13	2.18	0.13	3.99	0.06	5.97	0.08	8.15	0.10	10.16	0.11	0.096
17	2.21	0.16	3.96	0.09	5.92	0.13	7.95	0.10	10.22	0.17	0.130
19	2.24	0.19	3.91	0.14	6.18	0.13	8.21	0.16	9.83	0.22	0.168

[a] Average calibration error = |predicted pH − measured pH|/5.

(pH 2.05, 4.05, 6.05, 8.05 and 10.05) to establish their prediction capability [13,18]. Table 2 displays the predicted pH values against the expected pH values as measured by glass electrode pH meter. As shown, the network with 7 and 11 neurons in hidden layer produced the best predictions results with average calibration errors of 0.05 and 0.07 each. The prediction capability of the network was carried out both within the linear (pH 4.05) and non-linear (pH 2.05, 6.05, 8.05 and 10.05) response range of the sensor. The average calibration errors for the trained networks were in the range of 0.050–0.184 pH unit.

From this study, it was found that the network with seven neurons in hidden layer gave the best architecture for generating accurate prediction of pH. This network also extends the useful response range of the sensor from 2.00 to 5.00 pH to full calibration range of 2.00–12.00 pH (Fig. 2). In addition, this network proved its ability to predict the response of the sensor with minimum error (Table 3). Shaffer et al. [19] reported it would be difficult to predict the non-linear response of the sensor by using conventional chemometrics methods.

3.3. Prediction of unknown pH solution using trained network

The network with seven neurons in hidden layer was applied in this study to predict the pH of unknown buffer solution. A new of spectra obtained from four different 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 3. The network was found to be able to effectively predict the pH values with the worst prediction error of only 0.09 pH unit for buffer solution with pH 11.90. This result also shows minimum prediction error for buffer solution with pH within the training range (pH 2.00–12.00). An error of only 0.04 pH unit was recorded for prediction in the linear

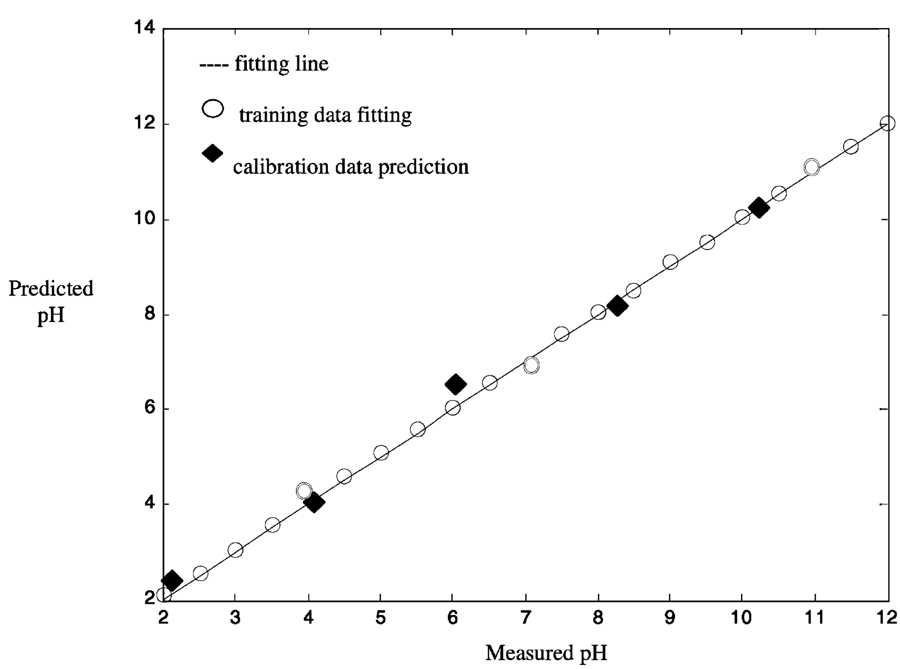

Fig. 2. Training data fitting and calibration by the network with seven neurons in hidden layer.

Table 3
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.

Table 4
The effect of ionic strength on the capability of optimised ANN with 8:7:1 neurons architecture to predict the pH of four different buffer solutions

Measured pH	Ionic strength at 0.01 mol l^{-1}		Ionic strength at 0.30 mol l^{-1}	
	Predicted pH	Error (%)	Predicted pH	Error (%)
3.60	3.56	1.1	3.57	0.8
7.25	7.19	0.8	7.30	0.6
9.60	9.65	0.5	9.75	1.5
11.50	11.81	0.8	11.42	0.7

region (pH 3.60). For non-linear region, the prediction for buffer solution with pH 7.25 and pH 9.60, yield error of 0.06 and 0.05 pH unit, respectively. Overall, the average prediction error for the unknown buffer solution is quite low and acceptable, with an average error of only 0.06 pH.

3.4. Ionic strength effect

The effect of an ionic strength on the sensor response was studied by using ANN with an architecture of 8:7:1 neurons. A series of buffer solutions at different ionic strength of 0.01, 0.15 and 0.30 mol l^{-1} was used. As shown in Fig. 3, it was found that ionic strength had insignificant influence on the sensor response. Table 4 summarised the effect of ionic strength on the capability of optimised ANN with 8:7:1 neurons architecture to predict the pH of four different buffer solutions at two different ionic strength. Statistically, it was found that the ionic strength used in this study has insignificant influence on the trained network. Sotomayor et. al. [3] have pointed out that the pH error caused by ionic strength depends on the type of indicator used and on the concentration of all ionic species in solution. However, further studies such as replacing the sodium ions by potassium ions and chloride by perchlorate, effects from the sample matrix and effects from variations of pK_a values are essential and need to be done to investigate the effect of the ionic strength to the sensor response.

3.5. Repeatability and reproducibility

The repeatability and reproducibility of the sensor were studied in this work at pH 6.00. The sensor repeatability refers to the successive runs made using a single sensor to evaluate discrepancies in its response. The sensor reproducibility on the other hand refers to the sensor discrepancies in response between individual members of a batch of similarly constructed sensors. The repeatability of the sensor was studied by using the same sensor to repeatedly measure eight different buffer solutions with the same pH (pH 6.00). In the meantime, the reproducibility of the sensor was studied by using eight various similarly constructed sensor to measure the same buffer solution of pH 6.00. The relative standard deviation (R.S.D.) for repeatability and reproducibility of the

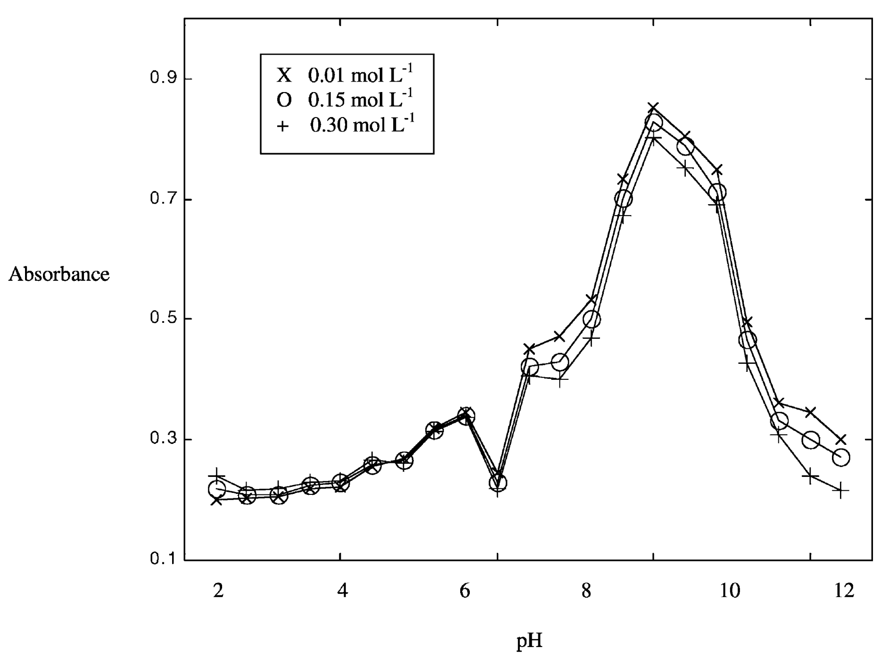

Fig. 3. The effect of ionic strength on the sensor response.

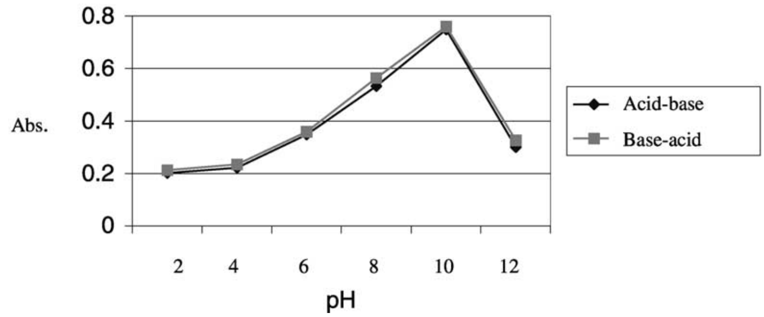

Fig. 4. The reversibility response of the sensor at pH 6.0.

sensor was evaluated to be 3.6 and 5.4%, respectively. The variation in the response of the pH sensor has been observed to appear from two main sources, which were construction variation and operational variation [20].

3.6. Hysterisis study

The reversibility of the constructed sensor was assessed by immersing the sensor into buffer solutions of pH 2.00–12.00 followed by solution of pH 12.00–2.00. As shown in Fig. 4, the response of the pH sensor demonstrated no hysteresis when the sensor was used to measure different pH in the cycled from pH 2.00–12.00–2.00 (acid–base–acid region). These results confirm the reversibility of the sensor.

Data obtained from hysterisis study could also be used to estimate the response time of the sensor. In general, the response time of the sensor was fast and the immobilised indicator changed its colour within 15–20 s after immersion in buffer solution. Alabbas et al. [20], reported that the response time of a sensor is governed by several factors such as quantity of the immobilized indicator, thickness of the membrane used and the indicator dynamic range.

3.7. Photostability

The sensor stability was evaluated by immersing the sensor into buffer solution of pH 7.00 for 8 h and the absorbance intensities were measured at 600 nm. The sensor was found to be very stable with R.S.D. value of 2.4%. The study on long-term stability and the effects of the storage conditions was not done.

4. Conclusion

The result 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 sensor with an average prediction error of 0.06 pH unit. The trained network also shown 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.

This study also shown that ionic strength has minor effect on the sensor response and the trained network was capable in predicting new measurement spectra from different ionic strength (0.30 mol l^{-1}) with an average prediction error of 0.11 pH. The repeatability and reproducibility of the sensor are good with R.S.D. of 3.6 and 5.4%, respectively. The sensor also demonstrates no hysteresis when the sensor was cycled through the acid–base–acid region and has a good photostability character (R.S.D. of 2.4%). Performance tests demonstrated a response time of 15–25 s. Further studies on the characteristics of the sensor especially its potential for use in on-line monitoring are currently in progress in order to develop an intelligent, small and portable optical fibre pH sensor.

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