Simultaneous determination of relative humidity and ammonia in air employing an optical fibre sensor and artificial neural network

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Abstract

The simultaneous determination of ammonia and relative humidity (RH) in air employing an optical fibre chemical sensor based on a nafion-crystal violet composite and a multivariate calibration based on and artificial neural network (ANN) has been described. Each and every measurement was made with a new film of 5 μm thickness, prepared from a 1.0×10^{-3} mol l^{-1} crystal violet and 1.0×10^{-2} mol l^{-1} nafion (as sulphonate groups) solution. Studies were performed in the ranges of 30–70% relative humidity and 0–25 ppm ammonia. A feed-forward ANN, with error back propagation training algorithm, was employed for treatment of data. Input neurons corresponding to reflectance intensities measured at 562, 583, 605, 626 and 660 nm were employed. The optimised ANN provided standard errors of prediction (SEP) of 28.4 and 7.3% for NH_3 and RH, respectively, when fed with spectral data recorded after 2 min of exposure (5 input neurons). The generalisation capability of the ANN was improved when it was fed with spectra data recorded after time intervals of 30, 60, 90 and 120 s (20 input neurons), providing SEPs equal to 9.9 and 4.5% for NH_3 and RH, respectively. This improvement can be explained considering that water vapour reacts faster than NH_3 with the film (a time interval <30 s is enough for the reaction to reach the equilibrium state) while the reaction rate for NH_3 is dependent on the RH (higher RH inhibits ammonia reaction). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Optical gas sensor; Ammonia; Relative humidity; Artificial neural network

1. Introduction

In the last decade, due to the development of signal processing using powerful microcomputers, the drawbacks concerning the selectivity of the analytical methods have been overcome by employing multivariate calibration chemometric methods, such as principal component regression (PCR), multiple linear regression (MLR), partial least square (PLS), which are among the most utilised linear mathematical models, and artificial neural networks (ANN), that are frequently employed to model non-linear data [1,2].

The ANNs can be classified, in a first approximation, as non-linear and non-parametric regression methods [2], providing to ANNs good flexibility, since, a priori, they do not need a rigid mathematical model and the calibration parameters can be determined using data, through a training (or learning) step. After training, the neural network is able to generalise its knowledge and making predictions for an unknown example [2,3].

Neural networks can be idealised based on different architectures and trained by employing different algorithms. The multi-layer perceptron (MLP), also called multi-layer feed-forward, trained by the error back propagation algorithm, is the most popular neural networks in chemistry [1–4]. The MLP network is constituted by an input layer of neurons, one or more hidden layers and one output layer. The number of neurons in the input and hidden layers must be optimised while the neurons in the output layer is determined by the number of dependent variables of the system (for example, three output neurons are employed in a simultaneous determination of iron, chromium and nickel in the metallic alloy). The neurons in a specific layer are connected to all neurons of the previous layer and each connection is characterised by a weight, which reflects its importance in the overall network.

Training a network is an optimisation process, in which the minimum value of a multidimensional error surface should be found. This surface, which is determined by the adjustable parameters of the model, shows many local

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minimum [2]. In the feed forward network, trained by employing the error back-propagation algorithm, data are sent from the input layer to the output layer, while the weight correction is made in the opposite direction, in an iterative process. Each whole cycle of this process is called epoch. The weights are corrected in order to minimise the difference between the expected value and the predicted value. The root-mean-square error (RMS) is usually employed to represent this difference, according to the following equation:

$$\text{RMS} = \sqrt{\frac{\sum_{s=1}^{n_i}\sum_{i=1}^{n}(y_{si} - \text{out}_{si})^2}{n_i \times n}} \tag{1}$$

where y_{si} and out_{si} are the expected and the predicted values for the ith component of the sth standard of the training set, n_i the number of standards employed to feed the network and n the number of output variables [5].

The error back-propagation learning algorithm can employ the generalised delta rule and the gradient descent method for correction of the weights, which can be expressed as

$$\Delta w_{ji}^{l} = \eta \delta_j^l \ \text{out}_i^{l-1} + \mu \Delta w_{ji}^{l(\text{previous})} \tag{2}$$

where Δw_{ji}^{l} is the weight correction of the neuron j in the layer l, connected to the neuron i in the previous layer; δ_j^l the error of the neuron j in the layer l; out_i^{l-1} the output signal of the ith neuron in the layer $l-1$ and $\Delta w_{ji}^{l(\text{previous})}$ the correction of the weight w_{ji}^l in the previous step of the iterative process. The first term of this equation makes the network to converge quickly through the steepest descent gradient of the error surface. The learning rate constant, η, determines the speed of the weight correction. Low values allow very slight changes in weights, and the calculation is very slow while high values cause rapid changes in weights, decreasing the training time but increasing the possibility of the calculation ending in a local minimum instead a global minimum. The second term of the equation plays an opposite role of the first one, preventing sudden changes in the direction of successive iteration steps. High values for the momentum constant, μ, allow the network to change direction slowly, even if significant changes have been occurred in the gradient of the error, decreasing the probability of reaching a local minimum.

The neural network training, considering that the number of neurons in the input layer has been previously defined, consists basically the optimisation of (a) the number of hidden layers, (b) the number of neurons in each hidden layer and (c) the values of learning rate and of momentum constants. Although initial values have been suggested for these parameters [2,5], their values are determined by trial and error [3,6].

The ANNs have been applied frequently in different branches of Analytical Chemistry [2], chiefly in the field of sensors including areas such as electronic noses [7,8], electrochemical sensors [9–11,19], biosensors [12], optical sensors [6,13–18] and relative humidity [16]. As far as the determination of gaseous species is concerned, Yang et al. [10] have quantified H_2S and NO_2 in binary mixtures, by employing a sensor array of tin oxide. Huyberechts et al. [11] have also described the use of a sensor array for quantitative determination of CH_4 (0–0.5%) and CO (0–1000 ppm) in mixtures of different humidity, with a relative error <5%. Hongmei et al. [19] have applied ANNs to determine simultaneously SO_2 (10–50 ppm) and relative humidity (20–90%), employing a piezoelectric quartz crystal sensor covered with triethanolamine, with relative error of 10%.

Despite the present use of ANNs, it can be noted that in the recent literature attention has been paid to demonstrate clearly the potential of ANNs. As a consequence, the neural network performance has been frequently compared to well-established chemometric methods, such as PCR and PLS [20–29]. Results obtained by using ANN are better than [20,22,23,25,26,28,29] or similar to [21,24,27] those obtained with other chemometric methods, which assess the usefulness of ANNs in determinations based on multivariate calibration.

The ANNs have been frequently applied to simultaneous spectrophotometric determinations based on spectral differences between analytes or between the products of the reaction of the analytes with a non-selective reagent. However, recently, ANNs have been also employed in determinations based on kinetic methods [20–22,28,30–33]. In these cases, spectral differences between the monitored products, although desired, are not usually essential for the analytical resolution [22]. The multicomponent kinetic determinations are usually based on the assumption that (a) reactions occur according to a first-order or pseudo-first order kinetics, (b) the product formation rates are additives (that is, there are no interactions between analytes), and (c) the rate constants do not change in the experimental conditions [31]. However, rate constants can be altered in every measurement (by slight variations in the experimental conditions), and from standard to sample measurements (due to matrix effects) [31]. In addition, due to synergetic effects, product formation rates may not be additive, introducing non-linearity in the responses [28,31]. Considering these aspects, the ANNs seems to be a suitable tool for such kinetic determinations, since they can be applied to a non-linear systems, even when the reaction kinetics are not known.

Recently, Raimundo and Narayanaswamy described the use of a nafion-crystal violet composite film for determination of relative humidity [34] and ammonia [35] in air. The film reacts with these species at different reaction rates and the products also show different spectral characteristics. This paper, which stems from these studies, is aimed to determine simultaneously relative humidity (RH) and ammonia in air, by employing an optical sensor based on a nafion-crystal violet film and ANN to perform multivariate calibration. In addition, a kinetic approach is proposed in order to improve the ANN performance.

2. Experimental

The construction of the sensor probe and the apparatus employed in this work have been described elsewhere [34]. In order to improve the mixing between humidity and ammonia, an empty bubbling flask (50 ml) and a PTFE tubing (2 m × 1.6 mm i.d.) were connected at the outlet of the gas blender. A total flow rate of 1000 ml min^{-1} was always employed.

Sensing films of 5 μm thickness were prepared from a 1.0×10^{-3} mol l^{-1} crystal violet and 1.0×10^{-2} mol l^{-1} nafion (as sulphonate groups), according to the procedure described previously [34]. Each and every measurement was made using a freshly prepared film.

The calibration set was composed by 30 standard solutions, containing RH in the range of 30–70% (in steps of 10%) and NH$_3$ in the range of 0–25 ppmv (in steps of 5 ppmv), obtained by mixing these species in all possible combinations. The verification (or monitoring) and test sets were composed of 6 and 10 samples, respectively, as listed in Table 1.

3. Procedure

The film was initially exposed to dry air for 2 min and a reference reflectance spectrum was recorded in the 400–800 nm region. Then, the film was exposed to the gas mixture and reflectance spectra were recorded at 30 s interval, up to a period of 2 min. Measurements were carried out in triplicate.

4. Neural network architecture and optimisation

A feed-forward neural network with error back propagation training algorithm was employed for treatment of data.

Table 1
Composition of the gaseous mixtures of the monitoring and test sets, employed in the simultaneous determination of relative humidity and ammonia in air

Set	NH$_3$ (ppm)	RH (%)
Monitoring	7	38
Monitoring	11	63
Monitoring	17	42
Monitoring	19	59
Monitoring	21	37
Monitoring	23	52
Test	3	32
Test	9	65
Test	12	43
Test	16	35
Test	16	52
Test	16	65
Test	19	47
Test	20	60
Test	22	36
Test	23	68

Input neurons (5), corresponding to reflectance intensities measured at 562, 583, 605, 626 and 660 nm and two output neurons, for RH and NH$_3$ concentrations, were employed. One hidden layer was always used. Reflectance intensities at these wavelengths, normalised by taking the reflectance intensities in dry air as reference, were employed to feed the ANN. These normalised signals were initially scaled in the range of 0–1, by employing the min–max function. A linear transfer function was used in the input layer, while a sigmoid transfer function was employed in the hidden and output layers. The ANN was optimised with respect to the number of hidden neurons, momentum and learning rate constants, employing the Trajan Neural Network Simulator 4.0 software (Trajan Software Ltd., Chester-le-Street, UK).

5. Results and discussion

Nafion-crystal violet composite responds to humidity [34] and ammonia [35] at different reaction rates, resulting in products with dissimilar spectral characteristics. Maximum reflectance variations at 630 or 580 nm were found when the film was exposed to humidity or ammonia, respectively. The reaction with moisture is fast and an equilibrium state is reached after a period <30 s [34]. The ammonia reaction is inhibited in the presence of humidity, occurring at a slower rate with increase in the humidity [35].

Ammonia reacts continuously with the film, and the response cannot be totally reversed, which allows a signal recovery lower than 100% [35]. Therefore, every measurement in the present work was carried out using a new film. Although films could be stored in desiccator for a period of at least 1 month, without losing their spectral characteristics, they were always freshly prepared.

Preliminary experiments indicated that the reproducibility of the reflectance spectra become worse if the film was exposed to the ammonia/humidity mixture for long periods of time. Fig. 1 shows the normalised spectra obtained by placing the optical fibre bundle tip at a distance of 1 mm from the film and exposing it to a mixture of 60% RH and 15 ppmv NH$_3$, for 0.5 and 4.0 min. As can be noted, the signals are less reproducible as the exposing time is increased. Under these conditions, the film becomes blue in colour after a long period of exposure, indicating it has been degraded. In fact, the colour change to blue from the edge of the film to its centre, through a process that is not reproducible, because the film is not completely homogeneous. As the film and the optical fibre bundle diameters were 4.5 and 1.5 mm, respectively, the light reflected at the blue region could enter into the optical fibre and influence the reproducibility of the measurements.

In order to evaluate the influence of the exposure time and the distance between the film and the optical fibre tip on the reproducibility of the measurements, a series of experiments were performed, employing two different mixtures containing 15 ppmv NH$_3$ and 30 or 60% RH. Experiments were
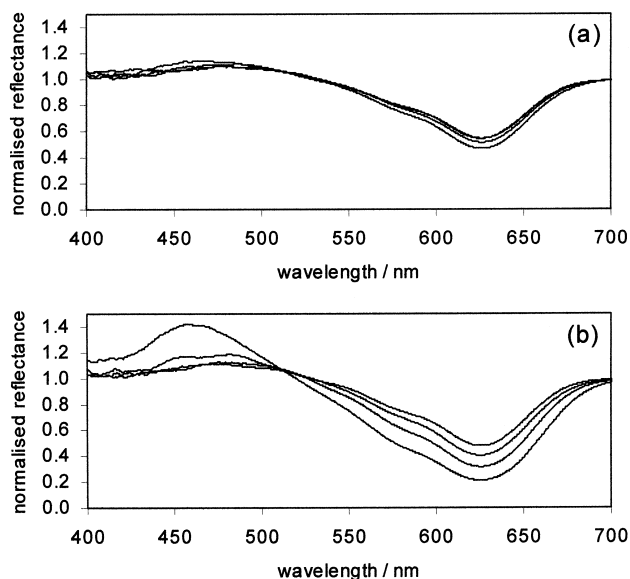
Fig. 1. Normalised spectra (four replicates) obtained by exposing the film to 15 ppmv NH_3 and 60% RH for (a) 0.5 min and (b) 4 min (distance between the film and the optical fibre tip = 1 mm).

carried out by placing the optical fibre tip at distances of 1, 2 and 3 mm from the film and measuring reflectance intensities at 580 and 630 nm, after 0.5, 1.0 and 2.0 min of exposure of the film to the mixture. Table 2 shows the relative standard deviations obtained in these measurements, after normalisation the signals, taken the reflectance intensity in dry air as reference. It can be noted, as a general rule, that precision is decreased as the exposure time is increased, while the distance between the film and the fibre tip remains the same. A similar behaviour is observed when the distance between the film and the fibre tip is increased and the exposure time is kept constant. These results agree with those showed in Fig. 1, showing the necessity of taking measurements before the degradation of the film occurs. It is also important to emphasise that the signal normalisation is very efficient in order to minimise the reflectance intensity differences that arise when the film is placed at different distances from the optical fibre tip. As expected, the reflected signal intensity decreases when the distance is

increased, but normalisation can compensate the oscillation of the signal. Considering the results obtained in these experiments, a distance of 1 mm between the film and the tip was employed, and spectra were scanned at 30 s interval, up to a period of 2 min.

Fig. 2 shows the normalised signals measured at 580 nm (higher sensitivity to ammonia) and 630 nm (higher sensitivity to humidity), obtained after exposure times of 30 s and 2 min. When the film is exposed only to humidity, signal intensities after an exposure time of 30 s are very similar to those obtained after 2 min, showing that an equilibrium state is rapidly achieved. However, when the film is exposed to the mixture of ammonia and moisture, signals obtained after an exposure time of 2 min are less intense than those obtained after 30 s, indicating that ammonia has reacted with the film after reaction with the moisture.

It should be noted in Fig. 2 that response is highly non-linear. For example, considering the signals obtained with 25 ppmv NH_3, the reflectance intensity at 60% RH is higher than those at 50% RH, probably because the reaction with ammonia is inhibited due to higher humidity content. This fact means that the generalisation ability of the ANN, that is, its capability of prediction, can be improved by increasing the number of standards in the training set, since the response surface can be better defined. Furthermore, the leave-k-out cross-validation as means of estimating the generalisation capability of the ANN is not recommended [2]. For example, if the 60% RH and 25 ppmv NH_3 standard is transferred from training set to the monitoring set (as would be done in a leave-k-out cross-validation), the generalisation ability of the ANN would be worsened, as the information about non-linearity is omitted.

Many wavelengths would be employed as input neurons in the ANN. However, data reduction is important in order to avoid irrelevant information such as noise and/or redundancies, to decrease the training time, providing neural network with better performance. Although methods for variable selection, such as PCA and PLS have been proposed [2,4,8], the choice of the wavelengths employed as input neurons was done by considering the film response to the species and the availability of commercial LEDs. This strategy was adopted in order to evaluate the possibility

Table 2
Repeatability of the normalised signals, expressed as relative standard deviation of four measurements, as a function of the distance between the film and the optical fibre tip and of the exposure time to the gaseous mixture

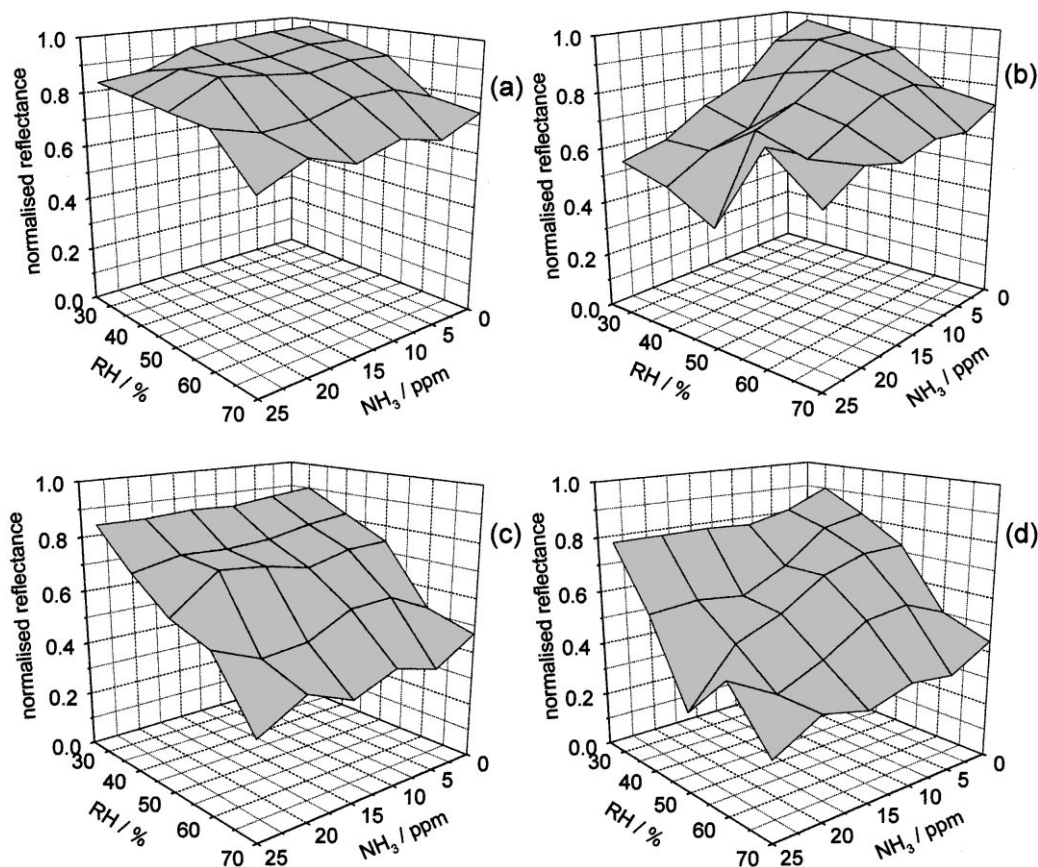| Exposure time (min)	Reflectance intensities (nm)	NH_3 (15 ppmv), RH (30%)			NH_3 (15 ppmv), RH (60%)		
		1 mm	2 mm	3 mm	1 mm	2 mm	3 mm
0.5	580	1.7	1.9	3.7	1.6	1.3	1.0
	630	2.5	3.2	4.1	8.1	5.7	7.0
1.0	580	2.5	2.6	5.2	1.6	2.0	7.3
	630	2.7	3.4	4.3	8.0	8.2	23.3
2.0	580	3.5	3.6	6.8	2.9	6.5	19.1
	630	2.9	3.6	4.6	12.1	18.1	32.4

Fig. 2. Response of the nafion-crystal violet film to mixtures of NH_3 and RH, measured at 580 nm after a exposure time of (a) 30 s and (b) 2 min and at 630 nm after a exposure time of (c) 30 s and (d) 2 min (signals are average of three measurements).

of constructing a portable solid-state instrument [36] for the simultaneous determination of these species. In this regard, five wavelengths (562, 583, 605, 626 and 600 nm) were chosen for input neurons since there are commercial LEDs available with these wavelengths.[2]

In the optimisation process, the input data were scaled between 0–1 through the function min–max [2] and a sigmoid transfer function was used in the hidden and output layer. Only one hidden layer was employed, as it has been recommended to solve many analytical problems [3,10]. The training step was performed by employing the incremental learning method [2], in which the weights are corrected after estimating the error of the predicted response. The learning rate and the momentum constants are usually determined by trial and error, and different values have been employed [6,11,12,17]. In the present work, values of 0.1 and 0.9 were fixed for these constants, respectively, since they seemed to be reasonable and have also been used by others [17]. Furthermore, attempts of using different values were not successful.

The ANN optimisation was carried out by checking the RMS error of the monitoring set after every epoch. The training was always stopped as soon as this error started to increase, in order to prevent the over-fitting of the network

[2,3]. Each training was performed by altering the number of neurons in the hidden layer and the network which provided the lowest RMS error for the monitoring set was considered as the best one. Afterwards, the generalisation ability of the ANN was assessed with the test set.

Initially, the network was fed with spectral data obtained after an exposure time of 2 min, that is, 5 input neurons were used. The network with 7 neurons in the hidden layer, trained with 3000 iterations, presented the best performance, with RMS errors equal to 5.00 and 4.39 for the training and monitoring sets, respectively. Considering the test set, relative standard errors of prediction (SEP) of 28.4 and 7.3% for NH_3 and RH were obtained, respectively. Fig. 3 shows the correlation between the expected and predicted values obtained in this training and Table 3 lists the results obtained for the test set, expressed as mean of three measurements. Although the results for RH can be accepted as reasonable, those for NH_3 lack in accuracy. This fact can be explained considering that the nafion-crystal violet film is more sensitive to humidity, which also inhibits the ammonia reaction. This initial strategy employed for the simultaneous determination of ammonia and relative humidity in air was based on the spectral differences showed by the film in the presence of these species. Furthermore, taking into account that water vapour reacts faster than ammonia with the film [34]

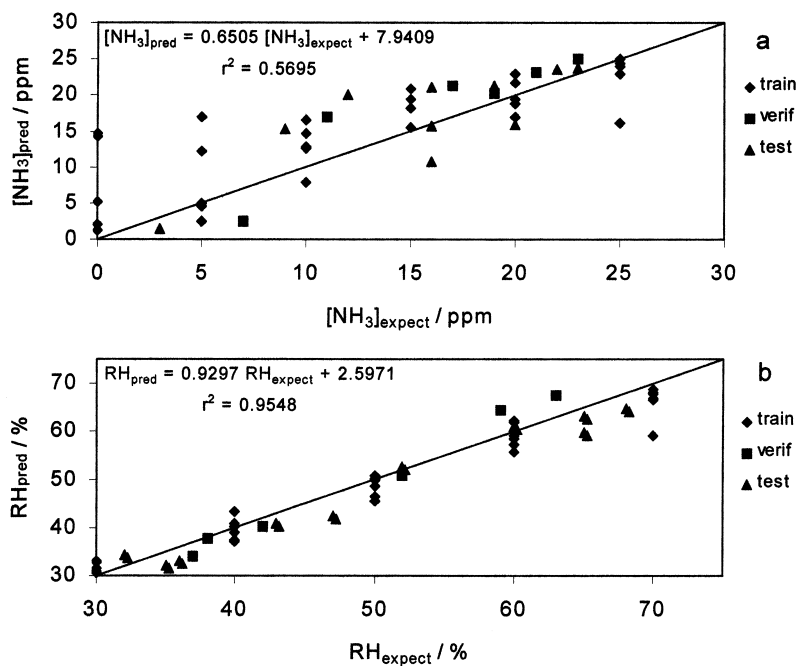
[2] RS catalogue, http://rswww.com.

Fig. 3. Correlation between the expected and predicted results, employing an optimised neural network with 5 neurons in the input layer and 7 neurons in the hidden layer (iterations = 3000).

and that the reaction rate for ammonia is dependent on the relative humidity [35], measurements were performed after an exposure time of 2 min. It was assumed that after this period of time ammonia would have reacted with the film in order to be detected, without causing significant degradation of the film.

As a means of improving the performance of the neural network, another training was carried out, employing 20 neurons in the input layer. These neurons were defined by the five wavelengths employed previously, whose reflectance intensities were measured at 30 s interval, up to a period of 2 min. The best network, with 7 neurons in the hidden layer and trained with 3000 iterations, provided RMS errors of 3.00 and 3.16 for the training and monitoring sets, respectively. Fig. 4 shows the correlation between the

expected and predicted values for training, monitoring and test sets, while Table 4 shows the results obtained for the test set, which presented SEPs of 9.9 and 4.5% for NH_3 and RH, respectively. These results indicate that better performance can be achieved when the ANN is fed with kinetic data, providing a more efficient discrimination for NH_3 and, as a consequence, its concentration can be determined with better precision and accuracy.

The improvement in the ANN performance can be explained based on the fact that moisture reacts with the film, reaching an equilibrium state in a time interval <30 s. Afterwards, variations in the reflectance intensities are caused by the reaction of ammonia, providing a response surface with more details. Finally, the SEP values obtained in this work for NH_3 and RH can be considered acceptable

Table 3
Results for the test set obtained by feeding the ANN with reflectance intensities measured after an exposure time of 2 min (input neurons = 5, neurons in the hidden layer = 7, average of three measurements)

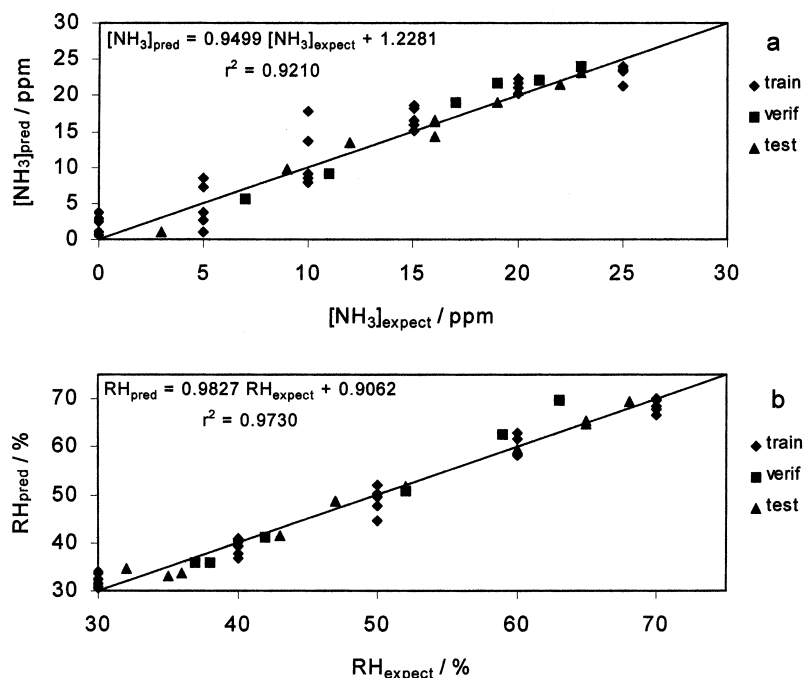| Sample	NH_3 expected (ppm)	NH_3 predicted (ppm)	S.D.	Deviation	RH expected (%)	RH predicted (%)	S.D.	Deviation
1	3.0	1.45	0.19	−1.55	32.0	34.45	1.24	2.45
2	9.0	15.30	1.42	6.30	65.0	59.83	2.16	−5.17
3	12.0	20.03	0.37	8.03	43.0	40.89	0.50	−2.11
4	16.0	21.10	0.32	5.10	35.0	32.05	0.74	−2.95
5	16.0	10.84	2.27	−5.16	52.0	52.69	0.35	0.69
6	16.0	15.62	1.24	−0.38	65.0	63.32	2.48	−1.68
7	19.0	21.33	0.04	2.33	47.0	42.44	0.32	−4.56
8	20.0	15.90	2.21	−4.10	60.0	60.97	2.70	0.97
9	22.0	23.58	0.31	1.58	36.0	33.04	0.26	−2.96
10	23.0	23.76	1.71	0.76	68.0	64.84	7.00	−3.16

Fig. 4. Correlation between the expected and predicted results, employing an optimised neural network with 20 neurons in the input layer and 7 neurons in the hidden layer (iterations = 3000).

Table 4
Results for the test set obtained by feeding the ANN with reflectance intensities measured every 30 s, up to 2 min (input neurons = 20, neurons in the hidden layer = 7, average of three measurements)

Sample	NH_3 expected (ppm)	NH_3 predicted (ppm)	S.D.	Deviation	RH expected (%)	RH predicted (%)	S.D.	Deviation
1	3.0	1.05	0.14	−1.95	32.0	34.77	0.46	2.77
2	9.0	9.64	1.10	0.64	65.0	65.31	1.16	0.31
3	12.0	13.50	0.65	1.50	43.0	41.60	1.30	−1.40
4	16.0	16.59	1.33	0.59	35.0	33.12	1.34	−1.88
5	16.0	14.20	1.51	−1.80	52.0	51.76	1.09	−0.24
6	16.0	16.24	0.96	0.24	65.0	64.65	2.96	−0.35
7	19.0	19.06	0.65	0.06	47.0	48.59	2.15	1.59
8	20.0	20.73	0.94	0.73	60.0	59.55	1.63	−0.45
9	22.0	21.49	0.85	−0.51	36.0	33.65	0.31	−2.35
10	23.0	23.17	0.37	0.17	68.0	69.26	0.68	1.26

for gas analysis at low concentrations, since they are better than those described in the literature [19].

6. Conclusions

Results obtained in this work show that a film of nafion-crystal violet composite is useful for the construction of an optical sensor for simultaneous determination of relative humidity and ammonia in air. In spite of the irreversible reaction of ammonia, which makes the procedure for obtaining data to train the ANN time consuming, the disposable film provides good results. Furthermore, once the ANN has been trained, satisfactory calibration is obtained if the film composition is not changed. Finally, it has been shown that the kinetic approach improved the generalisation ability of

the ANN, overcoming the drawbacks that arose from the difference of sensitivities of the film to humidity and ammonia.

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