Evaluation of Nafion–Crystal Violet films for the construction of an optical relative humidity sensor

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The composition of Nafion–Crystal Violet films and casting processes were studied in order to optimise the performance of an optical relative humidity sensor. The films were immobilised on a glass disc support, by placing a 5.0 μL drop of a methanolic solution of a mixture of various compositions (molar ratio) of Nafion and Crystal Violet. The homogeneity of the films, and also their reversibility to humidity, increased when the molar ratio of Nafion to Crystal Violet was increased. The homogeneity was even further improved when these films were treated with a 5.0 μL drop of methanol, leading to films of higher durability. The durability of films decreased with decrease in the film thickness. A methanol-treated, 5 μm thickness film with a Nafion : Crystal Violet molar ratio of 10.1 showed a linear response range from 30 to 70% relative humidity ($r^2 > 0.99$), with good stability and reversibility.

Introduction

Optical fibre chemical sensors (optodes) have attracted increasing interest in recent years owing to their inherent characteristics such as immunity to electrical noise, ease of miniaturisation and the possibility of real time monitoring and remote sensing.[1] These features make optodes a powerful tool for environmental and industrial process monitoring.

The relative humidity (RH) of air is an important parameter that needs to be measured or monitored in various chemical processes, such as in the food, electronics, textile, chemicals and pharmaceutical industries, and in the ambient environment. In these respects, different humidity sensors based on measurements of electrical[2–7] and optical[8–11] properties have been described. Conductometric humidity sensors based on poly(vinyl alcohol) and graphitised carbon black were studied by Barkauskas.[2] The optimised sensor showed a response time of *ca.* 45 s and a detection limit of 0.17%. Humidity sensors based on organic polymeric films have also been constructed.[3,4] Pérez and Freyre[3] employed the change in relative permittivity of poly(ethylene terephthalate) to measure RH in the range 10–97%. The sensor showed an accuracy of ±2% RH, good stability and a response time (63% of the final response value) of 1.2 min. Capacitive-type sensors using cross-linked polyimide films were employed by Matsuguch *et al.* to measure RH in the range 10–90%, with hysteresis lower than 1%.[4] Humidity sensors based on ceramic materials have also been frequently described.[5–7] Feng *et al.*[5] studied the impedance response to RH of Nafion, sol–gel derived SiO_2 and SiO_2–Nafion thin films, showing that the SiO_2–Nafion composite exhibits the best performance. Qu and Meyer[6] employed the semiconducting metal oxide $MnWO_4$ to fabricate a thick-film based sensor, which showed an operating range from 25 to 95% RH, a response time of 10 s and a hysteresis $< 0.5\%$. Pelino *et al.*[7] studied the influence of silica doping and coating on the response of a humidity sensor based on α-haematite, showing that its electrical response to RH can be optimised by the proper selection of silica concentration and sintering temperature. Several sensors involving spectrophotometric detection have also been described.[8–12] Kharaz and Jones[8] constructed a distributed sensing system by immobilising cobalt chloride on the surface of the core of an optical fibre. The system was investigated in the working ranges 20–80% RH and at 25–50 °C, with a time constant of 1 s and a resolution better than 4%. Films of cobalt oxide (Co_3O_4) showed absorbance changes in the visible wavelength region when exposed to different RH at room temperature.[9] The absorbance change of the film was reversible in the range 10–90% RH and the response time was about 5 min. Otsuki *et al.*[10] employed an extremely curved optical fibre covered with a sensing film composed of Rhodamine B and hydroxypropylcellulose to determine RH in the range 0–95%, with a response time of 2.3 min. A fluorimetric sensor based on the entrapment of ethylene glycol and Rhodamine 6G in gelatin was described by Choi and Tse.[11] The optode showed a stable response over an interval of time of 8 h, a working range from 10 to 100% RH and a response time of 1 min. Serious interferences from ethanol, chloroform, acetic acid and sulfur dioxide were observed.

Nafion (E. I. du Pont Nemours, Wilmington, DE, USA) is a perfluorosulfonate ion-exchange polymer that is highly hygroscopic and commercially available in a 5 wt.% solution in low aliphatic alcohols and 10% water. The special interest in Nafion arises from the fact that its films show very good chemical and thermal stability due to the fluorocarbon backbone and ion-exchange properties due to sulfonate groups.[12] It has been widely employed for the development of both electrochemical and optical sensors. Electrochemical sensors employing Nafion and based on different principles of operation have been described for the determination of many different species, such as CO,[13] NO,[14] glutamate,[15] hydrazines,[16] uric acid[17] and methyl viologen.[18] Nafion has also been used as a support membrane to study the photochemical and photophysical behaviour of incorporated organic dyes and metal complexes,[12,19] and several optical sensors for metal ions,[20–23] hydrogen ion[24,25] and RH[26−31] have also been developed.

Crystal Violet is a cationic dye that contains three *N*-phenyl terminal groups. It is usually found in the form of the chloride salt and, therefore, has two free *N*-phenyl terminal groups that can act as basic sites. In water, Crystal Violet is frequently used as an acid–base indicator, undergoing a colour change from

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yellow to purple in the pH 0.1–2.0 region. When a solution of Crystal Violet and Nafion in a polar solvent is left to dry, a phase inversion occurs with the Nafion polymer and the dye remains entrapped in an ionic cluster.[19] Since the Nafion sulfonate groups are highly acidic, the Crystal Violet is in that acid environment. The acidity of the proton bound to the sulfonate group depends on the water content in the film. In a dry Crystal Violet–Nafion film, the acidity of the Nafion is very strong and, as a consequence, Crystal Violet is found in the diprotonated form[19] and the film remains yellow. With increasing water content in the film, the sulfonate groups become less acidic and the diprotonated Crystal Violet loses protons, converting to the monoprotonated and non-protonated forms, and consequently the colour of the film changes to green.

The behaviour of the sulfonate groups in Nafion films described above makes this polymer suitable as a matrix in the casting of films doped with different dyes. The spectrophotometric properties of films doped with Malachite Green,[19,28,29] Methylene Blue,[12] Ethyl Violet,[28,29] tri-phenylcarbinol[31] and Cresyl Violet[32] have been described. Nafion–Crystal Violet films for the determination of humidity in air have also been described.[26–30] Sadaoka *et al.*[28,30] showed that the sensitivity to humidity of a Nafion–Crystal Violet film decreases with an increase in the annealing temperature. Brook *et al.*[26] employed an artificial neural network to extend the response range to humidity of a Nafion–Crystal Violet optical fibre sensor from 40–55 to 40–82%. Otsuki and Adachi[19] described the changes that occur in the spectrum of a Nafion–Crystal Violet film with respect to humidity, but studied influence of Nafion concentration on the Crystal Violet absorption spectrum only in ethanol–water solutions.

This paper describes the optical properties of Nafion–Crystal Violet films with respect to their compositions and casting processes, in order to improve the analytical performance of an RH optical sensor based on this film. The influences of these factors on the homogeneity, linear response ranges, stability, durability and reversibility of the films were verified. The interference of gaseous species is also discussed and a timed-approach measurement is proposed as a means of overcoming this drawback.

Experimental

Reagents and solutions

A 5 wt.% Nafion solution (in low alcohols and 10% water) and Crystal Violet (98%) were purchased from Aldrich (Milwaukee, WI, USA) and used as received. A 0.010 mol L^{-1} Crystal Violet stock standard solution was prepared in methanol (BDH, Poole, Dorset, UK). Air was supplied by BOC (London, UK).

Sensor probe

Fig. 1 shows a schematic diagram of the optical sensor probe. A tube end fitting 1/16 in (Omnifit 002109 Cambridge, UK) was used as support for a 1.0 mm high × 4.5 mm diameter glass disc (Edmund Scientific, Watford, Herts, UK, optical window 30648). A reflective tape (3M) was placed between the support and glass, in order to improve the intensity of the reflected signal. A randomised 32 optical fibre bifurcated bundle (Toray Europe, London, UK) was constructed to guide the light. The common end of the bundle was sealed into a 10 mL syringe body (Becton Dickinson, NJ, USA), in which a two-way polypropylene coupling (Omnift 002301) was adapted. This coupling allows the glass disc to be held at different distances from the fibre optical tip. Two windows were open in the coupling support to permit the diffusion of air into the sensor film.

Apparatus

A gas blender composed of three mass flow controllers (Brooks Instruments, Veenendhal, Holland 5850TR) was used. Two controllers, with a flow rate range from 0 to 1000 mL min^{-1}, were employed to deliver dry and wet air. A 100% RH air was obtained by bubbling dry air into a series of bubbling flasks filled with de-ionised water. The third controller (flow rate range 0–70 mL min^{-1}) was employed to mix gaseous species, such as CO_2, NH_3 and NO_2, with the air. Proper mixing of the dry and 100% RH air produced air samples of different RH. The accuracy of the gas blender was verified with a commercial humidity meter (Kane–May Welwyn Garden City, Herts, UK KM8006). The gas blender was controlled by a microcomputer through an electronic interface. Software was written in Microsoft QuickBasic 4.5, allowing the user to set the analysis parameters, such as RH of the air, time of exposure, time of flushing, total flow rate, number of samples and number of replicates of each sample.

A tungsten–halogen lamp (Ocean Optics Dunedin, FL, USA) was used as the light source and a CCD based multi-channel spectrophotometer (Ocean Optics PC1000) was employed to measure the reflected light in the 400–800 nm region. A 20 mL glass vial was employed as the flow cell.

Procedure

Nafion–Crystal Violet films were prepared by two different methods, using the solutions shown in Table 1. In the first method, a 5.0 μL solution drop was placed on the glass disc and allowed to dry for 30 min in a chamber at 22 ± 1 °C. In the second method, the film was treated with methanol, that is, a 5.0 μL drop of methanol was pipetted on to the film already cast as described above and allowed to dry for 30 min at 22 ± 1 °C. The glass disc was screwed in the coupling and placed at a distance of 1.0 mm from the optical fibre bundle tip, which was placed in the flow cell. All measurements were made using a total flow rate of 1000 mL min^{-1} and at 22 ± 1 °C.

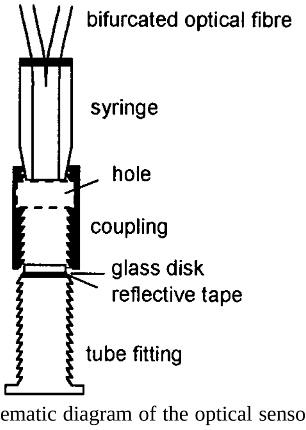

Fig. 1 Schematic diagram of the optical sensor probe.

Table 1 Solutions of Crystal Volet and Nafion in methanol employed in the preparation of the films

Solution	Crystal violet/ mol L^{-1}	Nafion-SO_3^-/ mol L^{-1}	Nafion: Crystal Violet molar ratio
A	0.00490	0.01985	4.1
B	0.00392	0.01985	5.1
C	0.00294	0.01985	6.8
D	0.00245	0.01985	8.1
E	0.00196	0.01985	10.1
F	0.00098	0.01985	20.4

Results and discussion

Preliminary experiments were carried out by placing the Nafion–Crystal Violet film at different distances from the optical fibre bundle tip. With decreasing distance between the film and the bundle, the signal intensities increased and more precise measurements were obtained. A distance of 1 mm was adopted, since it provided intense signals, good precision and no interference from the ambient light. This result indicates that the probe design is suitable to be used in continuous monitoring, without the necessity for any special cell or a modulated light source and in conjunction with photomultiplier tube or photodiode detectors.

The homogeneity of the films, produced from the solutions listed in Table 1, increases from film A through to film F. As expected, the films become transparent in the same sequence, because more dilute Crystal Violet solutions are employed. For example, in the case of the untreated films and in ambient air (relative humidity *ca.* 35%), film B showed a lime colour at the centre, with a blue–greenish edge, whereas film D was also lime in colour, but almost completely homogeneous, with only a small green edge. On the other hand, the methanol-treated films were homogeneous, with the exception of the dark blue film A. For example, film B was dark green and film D was yellow, with a very small and light green edge.

Figs. 2(a) and (b) show the reflectance spectra in dry air of the untreated and methanol-treated films, respectively. As a general rule, the reflectance intensities increase with dilution of the Crystal Violet dye. Fig. 2(c) shows the spectra of the glass support with and without a Nafion film of 10 μm thickness. No detectable change occurs in the Nafion film spectrum when the humidity is changed from 0 to 100%, indicating that any swelling of the polymer with water does not affect the analytical signal.

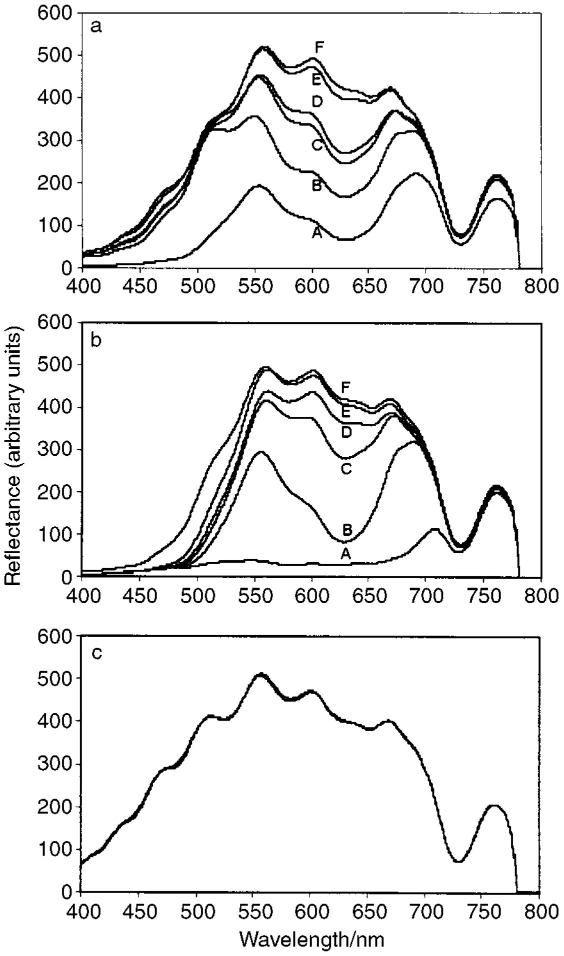

Fig. 2 Reflectance spectra of (a) untreated and (b) methanol-treated films in dry air (films A–F in Table 1) and (c) glass support uncovered and covered with a 10 μm thickness of Nafion polymer film.

Comparing of the spectra in Figs. 2(a) and (b) with that in Fig. 2(c), it can be seen that their shapes are similar (except for film A), differing mainly in intensities. However, the methanol-treated films absorb light in the 400–500 nm region whereas the untreated films do not absorb in this region, as depicted by the high reflectance signals measured. In addition, as shown in Figs. 3(a) and (b), the methanol-treated film (in this case, film E) also exhibit high absorption at around 600 nm when the relative humidity is high. These differences possibly arise, due to the uniformity of the films; as pointed out before, methanol-treated films are more homogeneous than the untreated films.

In order to verify the reversibility, that is, the recovery of the original signal measured at 630 nm, films were exposed to air with 100% RH for 10 min and then to dry air for 2 min. The untreated films are found to be reversible (except for film A), whereas in the case of the methanol-treated films the reversibility increases as the Crystal Violet dye concentration decreases (in fact, films E and F are completely reversible).

The stability of the films is improved with the treatment with methanol. For example, after 2 d in the laboratory environment, the reflectance of film D was measured in dry air at 630 nm. The untreated film showed an intensity of only 44% of the original signal whereas the methanol-treated film exhibited a signal equal to 93% of the original value.

Figs. 4(a) and (b) show the responses to humidity of the untreated and the methanol-treated films, respectively, measured at 630 nm. As can be seen, methanol-treated films show higher sensitivity, possibly owing to their greater homogeneity. These films show different behaviours, which can be explained on the basis of the molar ratio of Nafion to Crystal Violet and the acid strength of the sulfonate groups in the Nafion polymer. In dry conditions, Crystal Violet remains protonated because of the high acidity of the sulfonate.[19] When the humidity is increased, Crystal Violet is deprotonated, since the acidity of the sulfonate groups decreases. The methanol-treated films C and F are sensitive to low and high levels of humidity, respectively. The Crystal Violet is readily deprotonated in film C owing to the moisture, because the Nafion : Crystal Violet ratio is relatively low (*ca.* 6.8). In film F, Crystal Violet remains protonated at low humidity because the amount of Nafion in the

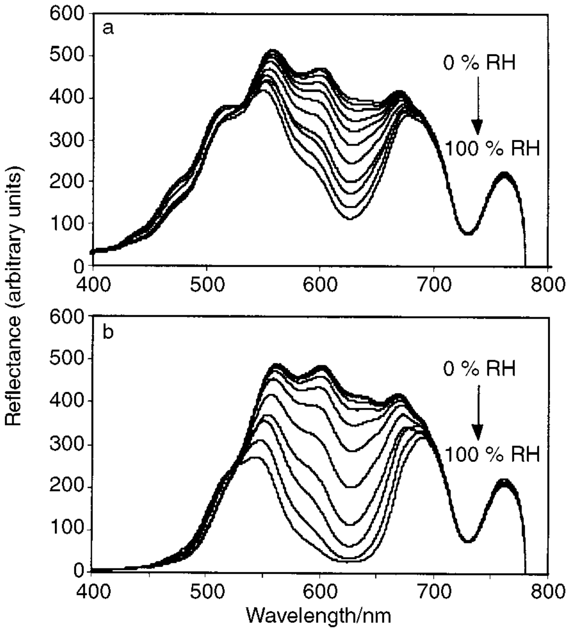

Fig. 3 Reflectance spectra of (a) untreated and (b) methanol-treated film E (RH increased from 0 to 100% in steps of 10%).

film is relatively high (Nafion : Crystal Violet molar ratio = 20.4), meaning that under these conditions there are sufficient sulfonate groups fully dissociated to protonate the Crystal Violet. Considering these results, it can be stated that the Nafion : Crystal Violet ratio can be selected so as to construct humidity optical sensors with different sensitivities and the methanol-treated E film would be the most suitable film in such a sensor construction, owing to its high sensitivity. In addition, the sigmoidal response can be readily modelled using an artificial neural network,[26] leading to a sensor that can exhibit a response over the full range of RH (0–100%).

The thickness of the films was studied by preparing sensors employing solutions diluted from solution E. The same responses to humidity were obtained for films that are two, three and four times more dilute than solution E. Solutions that are four times more dilute than solution E produced very thin films, which are very difficult to cast. Although the thinner films show a rapid response, their stability is decreased, as described previously.[33] For example, films prepared from solutions that are two and four times more dilute than solution E were left for 24 h in the laboratory atmosphere. After this period of time, the film diluted twice provided an intensity of reflectance (measured at 630 nm in dry air) equal to 96% of the original signal, whereas for the film that is diluted fourfold only 79% of the original signal was recovered.

Films prepared from 9.8×10^{-4} mol L^{-1} Crystal Violet and 1.0×10^{-2} mol L^{-1} Nafion-SO_3^- (solution E diluted twice) and treated with methanol provide a thickness of *ca.* 5 μm and show good characteristics for an optical humidity sensor. Therefore, these films were employed in the subsequent experiments, unless specified otherwise. When it was exposed for 1 h in dry air, the reflectance intensity at 630 nm was equal to 96.9% of the original signal. Similarly, when it was exposed to air of 50% of RH for 1 h, the signal obtained was 102.6% of the original reflectance intensity after 30 s of exposure. Both of these results agree well, showing that the film shows good stability for humidity measurements. As pointed out in the above discussion, the Nafion–Crystal Violet film degrades when exposed to the ambient atmosphere and can last for a couple of days. However, when the film was stored in a desiccator for 1 month, a signal of 97.6% (measured at 630 nm in dry air) of the original reflectance intensity was obtained, showing that the characteristics of the film can be preserved if it is properly stored. The reproducibility of the sensor was verified by casting three different films on to three different supports. The analytical curves obtained, measured at 630 nm, showed a mean relative standard deviation of 5.8%, which attests to the good performance of the system, in addition to the ease of preparation of the film.

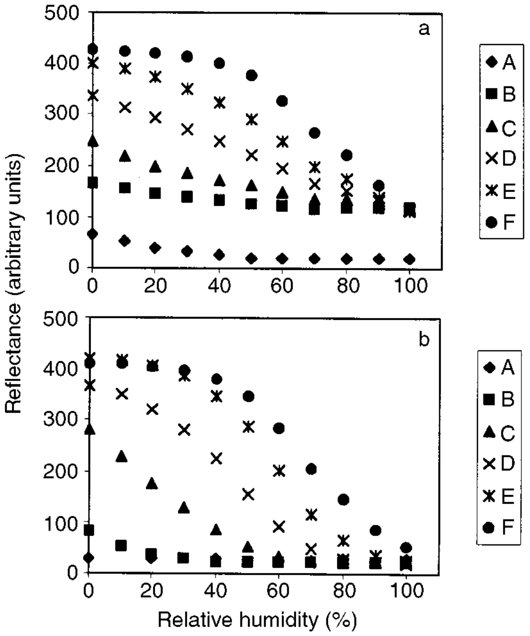

Fig. 4 Response to humidity of (a) untreated and (b) methanol-treated films (A–F), measured at 630 nm.

Fig. 5 shows the response of the optimised film at 630 nm that was repeatedly exposed to 70% RH for 30 s and dry air for 2 min. There is a rapid response (< 30 s) when the humidity is changed from a low value (0%) to a high value (70%). However, the reversal of response is longer (> 2 min). The small gradient in the reflectance signals that appears in the peak corresponding to 70% RH is probably due to the homogenisation of the mixture between dry and humid air, but this does not seriously affect the precision of the measurements. The repeatability of the sensor response is about 2.5% as obtained from the reflectance intensities of the signals recorded in Fig. 5. Analytical curves were recorded from 0 to 100% RH, in steps of 10%, by measuring the reflectance intensity at 630 nm, after 1 min of exposure. The sensor exhibited a linear response range from 30 to 70%, which means a better linearity than for sensors that have been described previously.[26,27] Furthermore, the analytical curves obtained by increasing the relative humidity ($R = 557 - 6.72\text{RH}$, $r^2 = 0.993$, $n = 5$, where R is the reflectance intensity) and by decreasing it ($R = 506 - 6.00\text{RH}$, $r^2 = 0.995$, $n = 5$) indicate that the sensor shows very little hysteresis. These facts confirm the results shown in Fig. 5 and that a time interval of > 2 min is necessary to allow the sensor to equilibrate with the humidity present in the air, when measurements are taken from air that has a high moisture content to air that is low in moisture.

The interferences of gaseous species such as CO_2, HCl, NO_2 and NH_3 on the film response have been described recently.[34] It was shown that the film does not respond to carbon dioxide, but responds to hydrogen hydrochloride and to nitrogen dioxide in atmospheres with RH lower than 50%.[34] The response of the sensor to gaseous ammonia is dependent on the water content in the film. Table 2 shows the normalised reflectance intensities (the signal in dry air is taken as the reference), measured after a

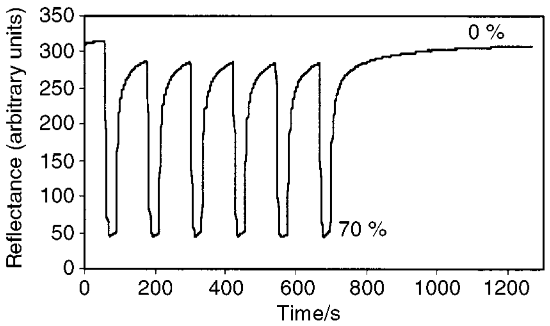

Fig. 5 Response of film E (diluted twice) to 70% RH at 630 nm.

Table 2 Normalised reflectance signals obtained by exposing the film to humidity and ammonia simultaneously for 30 s and 2 min

Exposure time	RH (%)	NH_3 (ppm) 0	5	10	15	20	25
30 s	30	0.902	0.884	0.865	0.871	0.859	0.859
	40	0.819	0.800	0.766	0.755	0.761	0.726
	50	0.741	0.736	0.696	0.730	0.745	0.616
	60	0.520	0.595	0.588	0.508	0.492	0.564
	70	0.468	0.380	0.427	0.366	0.434	0.344
2 min	30	0.901	0.831	0.793	0.802	0.799	0.800
	40	0.820	0.786	0.667	0.583	0.600	0.583
	50	0.725	0.720	0.667	0.561	0.490	0.292
	60	0.504	0.567	0.545	0.445	0.370	0.465
	70	0.438	0.357	0.375	0.330	0.370	0.278

period of 30 s and 2 min, when the film was exposed to different RH and different ammonia concentrations. As can be seen, the signal intensities obtained after 30 s show a smaller influence of the ammonia gas, indicating that its interference can be avoided by recording spectra after an exposure time of less than 30 s. This procedure does not affect the sensitivity of the method, since the response time of the sensor is much shorter than 30 s, as can be seen in Fig. 5. Considering that the response of the film to HCl and NO_2 is less significant than that to NH_3, the same procedure can be employed to overcome these interferences. Furthermore, chemometric methods, such as an artificial neural network, can also be employed to process the analytical signals and even to determine these species simultaneously in a mixture.

Conclusions

The composition of a Nafion–Crystal Violet film was optimised for use in an optical humidity sensor. The molar ratio of Crystal Violet to Nafion can be changed in order to obtain films that are sensitive to different humidity ranges. A methanol-treated film composed of 9.8×10^{-4} mol L^{-1} Crystal Violet and 1.0×10^{-2} mol L^{-1} Nafion-SO_3^- provides a linear response from 30 to 70% RH, with a fast response time and good reversibility and stability. The linear range can be readily altered by changing the film composition in order to satisfy specific applications. Furthermore, the sensor is easier to construct than those based on electrical measurements. The sensor exhibits a better linear response range than similar systems based on optical measurements described in the literature. The interference of species such as hydrogen chloride, nitrogen dioxide and mainly ammonia can be minimised or even eliminated by recording the spectra after a short exposure period of less than 30 s.

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