Available online at www.sciencedirect.com

SCIENCE DIRECT

Talanta 69 (2006) 631–636

Talanta

www.elsevier.com/locate/talanta

Highly sensitive optical humidity probe

H. Dacres, R. Narayanaswamy*

School of Chemical Engineering and Analytical Science, The University of Manchester, Faraday Tower,
P.O. Box 88, Sackville Street, Manchester M60 1QD, UK

Received 11 July 2005; received in revised form 28 September 2005; accepted 25 October 2005
Available online 2 December 2005

Abstract

A highly sensitive optical humidity probe based on reflectance measurements has been developed using Nafion®-crystal violet (CV) films. This sensor can be used to calibrate relative humidity (RH) in the range 0–0.25% with a detection limit (blank signal + $3\sigma_b$, where σ_b = the standard deviation (S.D.) of the blank signal) of 0.018% RH (~4.37 ppm) and exhibited low hysteresis. The sensor films were fully reversible in dry nitrogen and reversal times were shown to be dependent on exposure time and % RH. The response to 1% RH was highly reproducible (S.D. = 1.67%, number of samples (n) = 5). Hydrogen chloride gas did not interfere with the response of the sensor to RH but did reduce sensor reversal times. This sensor displayed sufficient sensitivity that it could be used to detect ppm levels of moisture in process gases such as nitrogen and HCl.

Keywords: Relative humidity sensor; Moisture detection; Reflectance probe; Optical fibre sensor

1. Introduction

The ability to monitor low levels of moisture has become even more critical in the semiconductor-manufacturing process since the demand for process gases with more stringent moisture specifications has continued to grow. Commonly used process gases include both nitrogen (N_2) and hydrogen chloride (HCl) [1]. Moisture is a particularly problematic contaminant in gas supplied from a cylinder as it can adsorb strongly onto metallic surfaces and cannot be easily removed by purging with dry inert gases. Humidity is often referred to as relative humidity (RH) and is defined as the ratio (%) of the concentration of water vapour in the gas to the saturated concentration at the same temperature and pressure. Humidity can also be expressed as volume concentration (ppm). In this paper, both units of concentration will be referred to intermittently.

Recent research in optical humidity sensing has been described in the literature [2–5]. Cobalt (II) chloride ($CoCl_2$) was one of the earlier reagent schemes investigated for this purpose [2]. Immobilised in gelatine it could be used to determine the RH of air between 40% and 80% [2] and, when immobilised on acetylated cellulose substrates, it could determine RH down to 4% [3]. Recently an evanescent wave sensor has been fabricated using PVA doped with $CoCl_2$ coated on the surface of a U-bend core of a plastic clad silica (PCS) fibre and this sensor responded to RH in the range 10–90% with a detection limit of 15% (~3660 ppm) and it displayed fast response and reversal times <1 s [4]. Using the same U-bend sensing principle phenol red was incorporated into a polymethylmethacrylate (PMMA) film and the resulting sensor was shown to respond to RH in the range 20–80% with a response time of 5 s [5].

In the identification of a suitable reagent scheme for the determination of moisture in process gases crystal violet in Nafion® is of considerable interest. It is well known that the colour of CV is very sensitive to the acidity of protons [6] and this property has been exploited in the development of an optical humidity sensor. Nafion® is a perfluorosulfonate resin in which hydrophilic perfluorinated ether side chains terminate with sulfate groups, which are periodically attached to hydrophobic perfluoroethy-

---

Abbreviations: ANN, artificial neural networks; a.u., arbitrary units; CO_2, carbon dioxide; $CoCl_2$, cobalt (II) chloride; CV, crystal violet; H, hydrogen; HCl, hydrogen chloride; HPC, hydroxypropylcellulose; kHz, kilohertz; LiCl, lithium chloride; N_2, nitrogen; NH_3, ammonia; NIR, near-infrared; nm, nanometres; NO_2, nitrogen dioxide; PCS, plastic clad silica; PMMA, polymethylmethacrylate; ppm, parts per million (v/v); PVA, poly(vinyl alcohol); r, correlation coefficient; RH, relative humidity; S.D., standard deviation; s/n, signal/noise ratio; wt, weight

* Corresponding author. Tel.: +44 161 306 4891; fax: +44 161 306 4911.
E-mail address: Ramaier.Narayanaswamy@manchester.ac.uk (R. Narayanaswamy).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.10.037

lene backbone molecules. Nafion® is commercially available as a 5 wt.% solution in low aliphatic alcohols and 10% water. The fluorocarbon backbone provides exceptional chemical and thermal stability while the sulfonate groups are responsible for ion exchange [7]. The acidity of the proton bound to the sulfonate group depends on the water content in the film. When a solution of Nafion® and CV in a polar solvent is left to dry a phase inversion occurs with the Nafion® polymer and the dye remaining entrapped in an ionic cluster [8]. Nafion® is very strongly acidic and CV exists in the diprotonated form; dried Nafion®–CV films appear to be yellow in colour. In response to an increase in the water content within the film the sulfonate groups become less acidic and CV is converted to its mono - and non-protonated forms which is accompanied by a colour change from yellow to green [9,10]. The degree of deprotonation is accelerated with increasing water content. This colour change can be monitored using both absorbance [9,11] and reflectance measurements [9,12–15] at 630 nm. This allows the use of cheap plastic optical fibres in the development of an optical fibre sensor for humidity. This method exhibits low hysteresis and fast response times (1 min and 10 s, respectively) [9,10]. The response range using this system was extended from 40–55 to 40–82% using artificial neural networks (ANNs) [12] and a later paper written by the same authors described the detection limit for RH to be <2% [13], which shows promise for detection of low ppm levels of humidity. The linear response range was further extended to 30–70% RH by using an optimum Nafion®:CV molar ratio of 10:1 and the homogeneity was improved by treating the Nafion®–CV films with methanol [10]. Nafion®–CV films can also be used to simultaneously detect ammonia (NH_3) and RH [14,15] and although NH_3, HCl and nitrogen dioxide (NO_2) react with the films, only humidity caused a decrease in reflectance at 630 nm [14].

This paper describes investigations into the sensitivity and reversibility of an optical fibre sensor for the detection of humidity at low ppm levels in gases such as N_2 and HCl gases.

2. Experimental

2.1. Apparatus

Experiments were carried out using a commercially available miniature fibre-optic based spectrometer (Ocean Optics PC 1000) which utilises a small tungsten halogen lamp (Ocean Optics) as the light source and a CCD based detector for both absorbance and reflectance measurements. A combination of Ocean Optics PC 1000 data sampling rate of 25 kHz and averaging of 70 scans was used to obtain the highest signal/noise (s/n) ratio of the blank signal. A gas blender comprising of three mass flow controllers (Brooks 5850 TR) was used. Two controllers, with flow rates ranging from 0 to 1000 ml/min, were employed to deliver dry nitrogen or dry HCl gas. The third controller (flow rate 0–100 ml/min) was employed to deliver humid nitrogen. All measurements were made using an optimum total flow rate of 1000 ml/min [10,14,15]. One hundred percent RH nitrogen was obtained by bubbling dry air into a series of bubbling flasks filled with de-ionised water and mixing of dried gases with 100% RH produced samples of different RH. The accuracy of the gas blender was verified with a commercial humidity meter (Kane-May, KM8006). Initial studies used the spectrometer in conjunction with purpose built flow cells designed for absorbance [16] and reflectance measurements (Fig. 1). Temperature was maintained at 20 °C throughout the study by conducting experiments in a Thermotron environmental chamber. Films were stored in a desiccator until use.

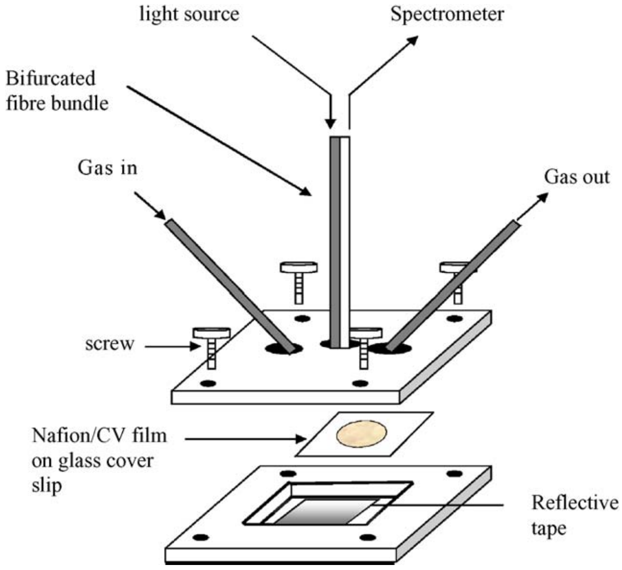

Fig. 1. Flow cell for reflectance measurements.

2.2. Probe design

The reflectance probe design employed in this work has been described elsewhere [10,15] and uses a randomized 32 bifurcated optical fibre bundle to transmit source and detected light.

2.3. Reagents and solutions

A 5 wt.% Nafion® solution (in low aliphatic alcohols and 10% water) and crystal violet were purchased from Aldrich and used without further purification. A 0.1 M crystal violet stock solution was prepared in methanol and was prepared on the day it was required for use. Nitrogen (100%) and HCl gas (1000 ppm) were supplied by BOC.

2.4. Procedure

2.4.1. Film preparation

Nafion®–CV films of ∼5 μm thickness were either prepared by pipetting 5 μl of solution onto clean glass cover slips (22 mm^2, BDH) for use in the flow cells or onto a glass disc (1.0 mm high × 4.5 mm diameter, UQG Optics Ltd.) for use in conjunction with the reflectance probe. 5 μl of Nafion®–CV solution was pipetted onto the chosen glass substrate and allowed to dry for 30 min in the environmental chamber kept at 20 ± 1 °C.

Following this the films were treated by dropping 5 μl of methanol onto the cast film and allowed to dry for a further 30 min at 22 ± 1 °C. This has been shown to improve homogeneity and durability of these films [10]. A number of solutions of varying molar ratios of Nafion®:CV ranging from 100:1 to 10:1 were used to prepare the films.

2.4.2. *Optical measurements*

As an equilibrium response to 1% RH was not achieved following 30 min exposure a kinetic method was employed which entailed exposing the Nafion® films to the analyte gas for a short period of time (5 or 2 min) followed by reversal in dry nitrogen. This method has previously been employed successfully to overcome the lack of stability exhibited by a fluorescent porphyrinic sensor for hydrogen chloride gas detection [17]. The change in optical intensity was measured by recording the intensity before and after exposure to RH.

3. Results and discussion

Both absorbance and reflectance measurements were initially taken to enable the two different types of measurements to be compared for their usefulness for monitoring low levels of RH.

3.1. *Absorbance measurements*

3.1.1. *Absorbance spectrum*

Fig. 2 shows the absorbance spectra of crystal violet immobilised in Nafion® before and after exposure to 100% RH.

The largest change in absorbance intensity was observed as an increase at a wavelength of 630 nm. This change in absorbance was accompanied by a colour change of the film from yellow to green. The absorbance maxima previously reported in aqueous solutions are 590 nm for CV^+, 635 and 420 nm for CVH^{2+}, and 434 nm for $CVH_2{}^{3+}$ [8]. Films used to produce Fig. 2 were prepared from solutions consisting of a 10:1 Nafion®:CV molar ratio.

3.1.2. *Molar ratio of Nafion®:CV solutions*

Films produced from solutions of different Nafion®:CV molar ratios (100:1–10:1 range) were exposed to nitrogen gas of different humidity in the range 0–100%. Films prepared from solutions consisting of a 10:1 molar ratio of Nafion®:CV responded the most sensitively to changing RH at the lower RH range (0–20% RH). It was previously found that a 10:1 ratio of Nafion®:CV produced films with the greatest sensitivity to changing RH [10]. The rapid response and reversibility times to 100% RH (90% signal) were also illustrated in this study (∼25 and 71 s, respectively). This is consistent with previous observations using these films where response and reversal times recorded to 70% RH were 30 s and ∼2 min, respectively [10].

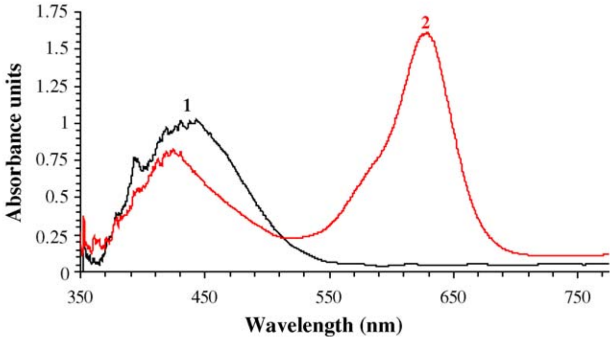

Fig. 2. Change in absorbance spectrum of Nafion®–CV films prepared from solutions consisting of 10:1 molar ratio of Nafion®:CV before (1) and after (2) exposure to 100% RH.

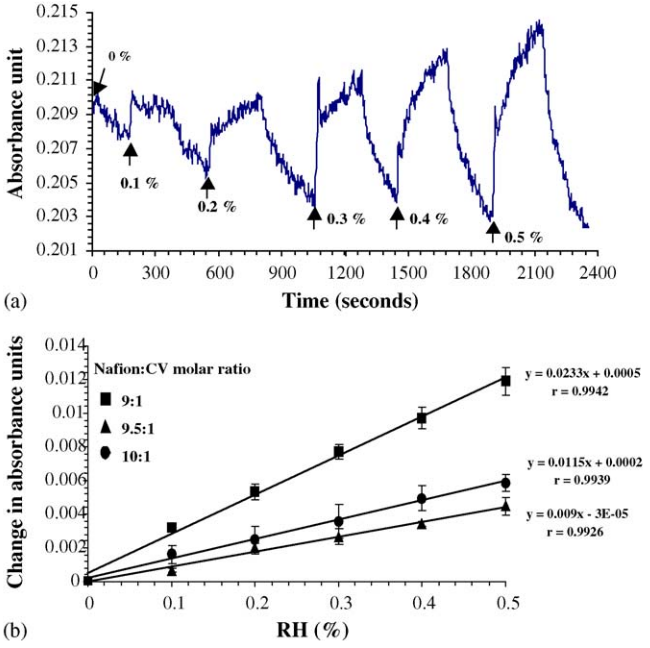

Fig. 3. (a) Change in absorbance (630 nm) of Nafion®–CV films prepared from solutions of 9:1 Nafion®:CV molar ratio in response to low RH (0–0.5%) as a function of time and reversal is in dry nitrogen and (b) calibration of RH (0–0.5%) using Nafion®–CV films prepared from solutions of differing Nafion®–CV molar ratio (mean ± S.D., $n = 3$).

Experiments were recorded to establish whether small changes in the molar ratio of Nafion®:CV (10:1) solution could enhance the sensitivity of the response of the films to low humidity concentrations. Films were additionally prepared from solutions containing Nafion®:CV at ratios of 9:1 and 9.5:1. Fig. 3(a), shows an example of the changes in absorbance (630 nm) in response to RH in the 0–0.5% range as a function of time, where the films were exposed to RH for 5 min followed by dry nitrogen for 5 min and Fig. 3(b) shows three sets of calibration plots of RH in the range 0–0.5% RH using films produced using these three solutions.

Films prepared from solutions consisting of a 9:1 Nafion®:CV molar ratio responded the most sensitively to RH in this range and the calculated detection limits (blank signal + $3\sigma_b$) were 0.049%, 0.12% and 0.048% for films prepared from Nafion®:CV solutions of molar ratio 10:1, 9.5:1 and 9:1, respectively. Films prepared from Nafion®:CV solutions of a 9:1 molar ratio consistency respond the most sensitively to RH in the 0–0.5% and also exhibited the lowest detection limit. Further investigations were then carried out using films prepared using this solution composition.

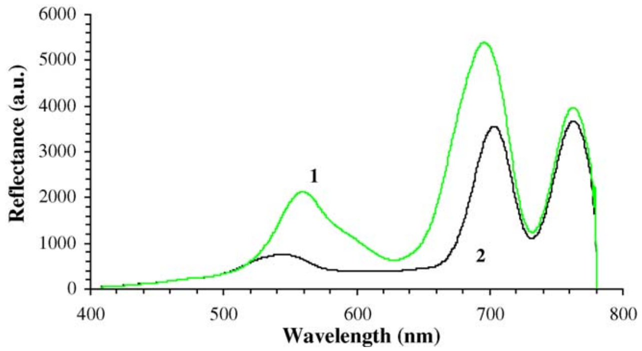

Fig. 4. Change in reflectance in response to (1) 0% RH and (2) 100% RH.

3.2. *Reflectance measurements*

3.2.1. *Reflectance spectrum*

The change in the reflectance spectra in response to 100% RH is shown in Fig. 4.

The dried films exhibit reflectance peaks at 560 and 698 nm and after exposure to 100% RH these shifted to 546 and 705 nm, respectively. The largest changes in reflectance intensity upon exposure to 100% RH were observed at 562 and 682 nm, and of these the intensity at the 682 nm wavelength will be monitored as a function of time for construction of calibration graphs and kinetic studies.

3.2.2. *Calibration of RH*

To compare the absorbance and reflectance techniques Nafion®–CV films were initially exposed to the same lower RH range as that used in absorbance measurements (0–0.5%). The calibration was linear over the 0–0.5% RH range ($y = -123.88x - 1.84$, $r = 0.9973$) with a calculated detection limit (blank signal + $3\sigma_b$) of 0.039% RH which was lower than that obtained in absorbance measurements. The results of the study established that further work should be carried out using reflectance measurements.

3.2.3. *Stability studies*

The storage stability of the films was investigated by measuring the reflectance intensity (682 nm) of the films on a daily basis for a period of one week. Films stored in a desiccator maintained a signal intensity 98.4% of the original and those left under the laboratory environment only maintained 61.5% of the original signal intensity. To complement this study a further stability study was carried out which involved exposing the Nafion®–CV films to 0.5% RH on a weekly basis over a period of 1 month to establish whether the sensitivity would be affected by film ageing. It appeared that the sensitivity decreased gradually over a 4-week period with the average response to 0.5% RH being 76.78% that of the original after this period. However, there is no significant difference between the original mean response to 0.5% RH (66.67 ± 3.15 a.u.) and that of the consecutive week (62.65 ± 6.55 a.u.) (probability $(P) = 0.05$) suggesting that statistically the films response to RH is stable over a 2-week period.

3.2.4. *Film conditioning*

It was found that the films needed to be conditioned using dry nitrogen prior to exposure to RH and the response to repeated exposure to 5% RH was reproducible (-178.40 ± 1.25, $n = 3$) with a standard deviation of less than 1% (0.70%) after approximately 70 min pre-conditioning with dry nitrogen.

3.2.5. *Reproducibility of film preparation*

The reproducibility of the film preparation was verified by casting five different solutions (9:1 Nafion®:CV solution) onto five different slides and the intensity of the films was measured at 682 nm and the standard deviation was calculated to be 6.79% ($n = 5$) which is of a similar magnitude as previously observed for such films [10]. Although the treatment of Nafion® films with methanol has previously been shown to improve homogeneity of the films [10] the use of spin-coating technique could also be used to produce better quality thin films in terms of homogeneity and reproducibility. This technique has previously been shown to improve the quality of silicone rubber thin films for gas sensing purposes [18].

3.3. *Probe measurements*

Initial studies demonstrated that reflectance measurements responded more sensitively to RH compared to the absorbance response, therefore, a reflectance probe was designed and applied to the detection of ppm levels of moisture.

It was determined that the smaller the distance between the probe and the tip of the optical fibre bundle the greater the reflectance intensity and also the more sensitive the response to changing RH. It was previously established that the optimum distance was 1 mm and this was again adopted for this study [10].

3.3.1. *Probe reproducibility*

To determine if the film could be replaced reproducibly within the probe head, the intensity of the same film (682 nm) was monitored after repeatedly removing and replacing the film. The standard deviation in this study was calculated to be 2.64% ($n = 5$). Reproducibility of the films response to 1% RH showed a standard deviation of 1.67% ($n = 5$) using 5 min exposure times and 10 min reversal times. The standard deviation increased to 4.63% ($n = 5$) if only a 5 min reversal time was used. When a 2 min exposure time and a 7.5 min reversal time was used the same value of standard deviation of 1.67% ($n = 5$) was obtained. A discussion regarding response and reversal times is presented below.

3.3.2. *Response and reversal times*

As the % RH exposure increased the reversal time increased from 2.5 min (0.2% RH) to 9 min (1% RH). If the exposure time was reduced to 2 min then the reversal times ranged from 1 min (0.2% RH) to 7.5 min (1% RH). This demonstrates that reducing exposure times reduces the reversal times. Reversal times referred to in this section is the time taken for obtaining the original intensity when exposed to dry nitrogen following RH exposure.

3.3.3. Calibration of RH with probe

The average ($n = 3$) calibration of RH (0–1%) was obtained by exposing the films to increasing, decreasing and random orders of RH for 5 min. The linear equations of three calibration graphs obtained with increasing, decreasing and randomly ordered humidity concentration ranges gave the average linear equation of $-44.34\ (\pm 1.99) + 3.91\ (\pm 0.85)$, $r = 0.9984$. This demonstrated that this sensor showed very little hysteresis.

Changing the exposure times has a large effect on the sensitivity of the sensor's response to RH. Exposure time of 5 and 2 min result in sensitivities of 44.34 a.u./% RH and 29.10 a.u./% RH, respectively, demonstrating that decreasing the exposure time decreased the sensitivity of the sensor response to RH. However, there was very little difference between the detection limits (blank signal + $3\sigma_b$) of 0.081% RH and 0.094% RH obtained with 5 and 2 min exposure times, respectively. A further calibration was carried out in the 0–0.25% RH range using a 5 min exposure time due to the superior sensitivity observed here and the detection limit (blank signal + $3\sigma_b$) was calculated to be 0.018% RH (∼4.37 ppm). This compared well with the other optical techniques for humidity measurements presented in the literature; the detection limits presented here being much lower than those obtained using either $CoCl_2$ [2–4] or phenol red [5]. The lowest detection limit reported in the literature was 0.11% RH and this was obtained by monitoring the phosphorescence of mercurochrome immobilised in sol–gel matrices [19], which is still approximately six times greater than the figure obtained in this work. Therefore, the method presented here is more suitable for detecting ppm levels of humidity than phosphorescence techniques.

3.4. Interference by HCl

The first part of the study involved assessing the reaction of HCl gas with Nafion®–CV films (Fig. 5(a)). Conditioned films were exposed to either 1000 ppm HCl gas or 100% dry nitrogen for periods of 5 min (both at flow rates of 1000 ml/min).

Dry HCl caused a greater increase in reflectance (∼18 a.u.) than dry nitrogen during the same period of time (∼3 a.u.) and rates of change in reflectance were 0.0668 and 0.0141 a.u./s for HCl and nitrogen, respectively (Fig. 4(a)). The interference of gaseous species such as CO_2, HCl, NO_2 and NH_3 on the film response has been described previously and it was shown that HCl gas caused a decrease in reflectance at around 580 nm [14]. It was thought that this was due to this acidic species reacting with the protonated cationic crystal violet by forming a charge-transfer complex. In this case, it appears that HCl displaces the water molecules from the Nafion® film at a faster rate than nitrogen. It has previously been reported that displacement of water molecules from a Nafion® membrane is a relatively slow process because of the strong hydrogen bond formed between the water molecule and Nafion® [20]. This suggests that HCl may also reverse the sensor's response to RH at a faster rate than dry nitrogen can and this may be useful in sensor reversal if HCl gas does not interfere with the reaction of water with crystal violet.

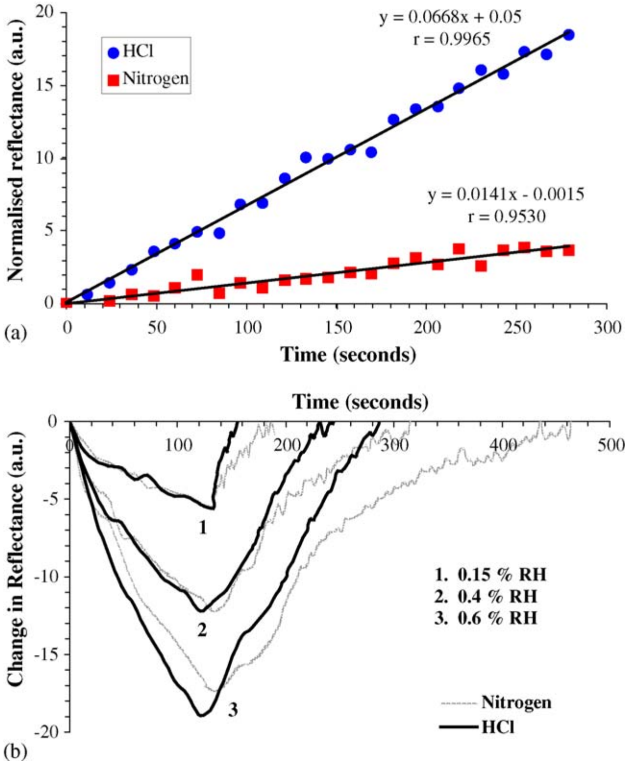

Fig. 5. Change in reflectance (682 nm) of Nafion®–CV films in response to (a) 1000 ppm HCl or 100% N_2 and (b) 0.15% RH (1), 0.4% RH (2) and 0.6% RH (3) (for 2 min) in either N_2 (100%) or HCl (1000 ppm) and the subsequent reversal.

It is clearly demonstrated that HCl gas does not interfere with the response Nafion®–CV films to RH (Fig. 5(b)). The rate of change of reflectance upon exposure to 0.15%, 0.4%, 0.6% and 5% RH in nitrogen and HCl were almost identical (Fig. 5(b)) and there was no significant difference ($P = 0.05$) between the mean amplitude of the response upon exposure to RH in this range for 2 min in nitrogen or HCl gas (Table 1). However, HCl

Table 1
Change in reflectance (682 nm) of Nafion®–CV films in response to 0.15%, 0.4%, 0.6% and 5% RH (2 min exposure time) in either N_2 (100%) or HCl (1000 ppm), and the calculated significance of changing the diluent (t) (critical value = 2.78, 4 d.f.)

RH (%)	Change in reflectance (682 nm) (mean ± S.D.) (a.u.)		t	Reversal times (s)	
	N_2	HCl		N_2	HCl
0.15	5.65 ± 0.25	5.57 ± 1.77	0.08	55	25
0.4	12.33 ± 0.17	12.71 ± 0.86	0.75	180	120
0.6	18.58 ± 0.25	19.23 ± 0.33	2.71	320	160
5	131.88 ± 6.65	137.0 ± 6.16	0.98	560	200

The reversal times in either N_2 (100%) or HCl (1000 ppm) are also presented.

gas reduced the sensor recovery time after exposure of the film for all of these RH values compared to dry nitrogen (Table 1).

4. Conclusions

Initial absorbance studies leading to the development of an optical fibre sensor for detection of low levels of humidity demonstrated that films prepared from solutions containing a 9:1 molar ratio of Nafion®:CV would be the most suitable. Comparison of absorbance (630 nm) and reflectance measurements (682 nm) demonstrated that reflectance measurements produced a signal with a larger s/n ratio, responded more sensitively to changing RH and could detect lower levels of RH (0.039% RH) compared to absorbance measurements (0.048% RH). An optical fibre reflectance probe could detect down to 0.018% RH in N_2 and this compared favourably with other optical methods for humidity sensing including phosphorescence techniques.

The intensity of the sensing films was shown to be stable for up to a week with the response of the sensor stable for up to 2 weeks. The film preparation was reproducible (6.79%, $n = 5$) and the response to 1% RH was also highly reproducible (1.67%, $n = 5$). HCl did not interfere with the reaction of humidity with the CV films but did improve the recovery times. This study has identified the use of crystal violet immobilised in Nafion® as a highly sensitive sensor for RH and shows great potential for the determination of very low levels (ppm) of moisture in process gases.

References

[1] H.H. Funke, B.L. Grisson, C.E. McGrew, M.W. Raynor, Rev. Sci. Instrum. 74 (2003) 3909.
[2] A.P. Russell, K.S. Fletcher, Anal. Chim. Acta 170 (1985) 209.
[3] F. Boltinghouse, K. Abel, Anal. Chem. 60 (1989) 1863.
[4] S.K. Khijwania, K.L. Srinivasan, J.P. Singh, Sens. Actuators B 104 (2005) 217.
[5] B.D. Gupta, Ratnanjali, Sens. Actuators B 80 (2001) 132.
[6] E.Q. Adams, L. Rosenstein, J. Am. Chem. Soc. 30 (1914) 1452.
[7] S.A. John, R. Ramaraj, J. Appl. Polym. Sci. 65 (1997) 777.
[8] S. Otsuki, K. Adachi, J. Appl. Polym. Sci. 56 (1995) 697.
[9] Y. Sadaoka, M. Matsuguchi, Y. Sakai, Y.-U. Murata, Sens. Actuators B 7 (1992) 443.
[10] I.M. Raimundo Jr., R. Narayanaswamy, Analyst 124 (1999) 1623.
[11] J.C. Grunlan, A.R. Mehrabi, A.T. Chavira, A.B. Nugent, D.L. Saunders, J. Comb. Screen. 5 (2003) 362.
[12] T.E. Brook, M.N. Taib, R. Narayanaswamy, Sens. Actuators B 38/39 (1997) 272.
[13] T.E. Brook, R. Narayanaswamy, Sens. Actuators B 51 (1998) 77.
[14] I.M. Raimundo Jr., R. Narayanaswamy, Quimica Anal. 19 (2000) 127.
[15] I.M. Raimundo Jr., R. Narayanaswamy, Sens. Actuators B 74 (2001) 60.
[16] H. Dacres, R. Narayanaswamy, Sens. Actuators B 90 (2003) 222.
[17] M.G. Baron, R. Narayanaswamy, S.C. Thorpe, Sens. Actuators B 34 (1996) 511.
[18] M.G. Baron, R. Narayanaswamy, S.C. Thorpe, Sens. Actuators B 29 (1995) 358.
[19] J.M. Costa-Fernandez, A. Sanz-Medel, Anal. Chim. Acta 407 (2000) 61.
[20] H.-W. Chen, R.-J. Wu, K.-H. Chan, Y.-L. Sun, P.-G. Su, Sens. Actuators B 104 (2005) 80.