

Dew Point Effects in the Response of Polyaniline to Ammonia-Water Vapour Mixtures

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Increases in polyaniline (PAN) DC resistance are observed of up to 40% $\Delta R/R$ (percentage fractional change in resistance) for 10 ppm ammonia in high humidity nitrogen. For any given relative humidity (RH) value of gas mixture presented, decreasing the sensor temperature increases the sensitivity to ammonia, until a critical temperature is reached below which equilibrium resistance values cannot be obtained. It is found that these “critical temperatures” corresponded closely with the dewpoint temperatures expected for the gas mixture RH - temperature combinations used. The temperature of the sensor itself affects not only the energy of the PAN surface directly but also causes more or less water to form on or within the layer of chemi-resistor, thereby creating a more or less favourable environment for ammonia to partition into. More generally, for sensors possessing hydrophilic layers operating under a range of atmospheric conditions, proper consideration of sensor temperature is essential, particularly if water is involved in the absorption of the target gas.

1. Introduction

In recent years there has been considerable discussion about the susceptibility of some odour detection devices to variations in atmospheric humidity. In the present work polyaniline (PAN) chemi-resistive sensors are employed to measure ammonia at low concentrations and at different values of relative humidity (RH).

The many interesting properties of (PAN) have been matched by a large number of promising applications.^(1–3) One of the applications suggested is for the measurement of ammonia^(4–8) and where the interaction of ammonia with the PAN polymer backbone is usually described in terms of protonation/deprotonation processes causing changes to its

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electrical resistance.^(5,9)

Several investigations have addressed the interaction of PAN with water vapour.⁽¹⁰⁻¹⁵⁾ Chinn *et al.*⁽¹⁶⁾ suggested that the surface component of the PAN work function is rapidly affected by water but that overall, the resistance is dominated by bulk behaviour. Kukla *et al.*⁽⁵⁾ showed that water absorption is easily reversible.

Matveeva⁽¹²⁾ has suggested that the effects of water on PAN resistance are of two kinds: one involves a simple swelling/deswelling of the polymer matrix causing polymer islands to lose/gain contact with each other; in some circumstances a second effect could also arise from direct protonation of the water molecules at the PAN imine centres. The first effect is minimised by avoiding PAN films prepared as composites in a host matrix, particularly if the matrix is hydrophilic, and by using pure PAN films formed *in situ* electrochemically or deposited from solution.

In practical applications such as gas sensing and artificial nose devices inadequate control or understanding of water responses easily leads to spurious analytical results.⁽¹⁷⁾ From the work reported here a better practical understanding is gained of the part played by water in the absorption of ammonia by PAN.

2. Materials and Methods

Individual sensors were fabricated using PAN emeraldine salt (Aldrich Chemical Co.) as a saturated solution in *m*-cresol. The solution was painted across exposed screen printed silver tracks (separation 5 mm) on a ceramic substrate, approximately 10 mm×50 mm. Solvent was removed by vacuum and sensor resistances checked to ensure they came within the range 5–50 k Ω . The conducting layer was a tightly adhering pale green transparent film. Lead-out pins from the sensor were connected to a data logger controlled by purpose-written software. DC resistance measurements were logged at 0.25 s intervals.

To carry out gas phase measurements the sensor was installed within an aluminium block and thermostated using a small Peltier unit which fitted flat against the back of the sensor substrate. The sensor face was sealed into a cavity of approximately 0.2 mL through which a stream of analyte gas ("feed gas") was drawn at 100 mL/min using a small diaphragm pump. Known concentrations of ammonia gas were prepared by bubbling nitrogen at controlled rates through dilute solutions of ammonia. Gas concentrations generated in this way were based on the headspace values at particular temperatures.⁽¹⁸⁾ Where necessary, an extra mass flow controller was used to add dry nitrogen to the analyte gas stream to vary the final RH. The analyte gas stream was vented to atmosphere, with the sensor drawing in a fraction of the gas vented, via a nozzle inserted into the open end of the flow vent. In this way the flow of feed gas over the sensor was continuous and there were no pressure fluctuations in analyte gas supply. A controlled climate cabinet was used to house gas feed lines, bubblers and the sensor block. Within this environment the sensor block was capable of being controlled to a set temperature that differed from the cabinet set temperature by up to 20°C. The basic temperature dependence of the sensor was determined by changing the sensor block temperature while exposing it to a blank gas stream (dry or 100% RH nitrogen).

Initially, PAN sensors as prepared above were used to take measurements in aqueous solutions but it was found that they quickly deteriorated and gave unstable readings. However, when the PAN layer and surrounding area were lightly coated with a spray-on silicone water-repellent, the performance in solution was greatly improved although at the cost of some sensitivity. Measurements of sensor resistance in 0.1 M KCl solutions were made with a silicone coated PAN sensor immersed below the liquid surface while ammonium hydroxide was added with stirring to the solution. A glass electrode and pH meter (Model 220, Denver Instrument Co.) was used to measure associated changes in solution pH. Rapid return of sensor resistance to its base value could be achieved by brief exposure to the headspace above a concentrated HCl solution.

3. Results

The temperature dependence of the PAN sensors in dry nitrogen in the range 15–30°C was zero within the limits of system noise ($\leq \pm 0.5\%$), and estimated to be 0.1% per °C between 30–45°C with a minimum in the vicinity of 20°C. These observations relate well to more detailed temperature-conductivity studies.^(13,19)

The response to water vapour alone is shown in Fig. 1. The temperature of the feed gas throughout the run was held at 22°C. Initially the sensor temperature was set at 22°C. At $t = 50$ s the gas stream is changed from dry N₂ to 100% RH N₂ resulting, at $t = 150$ s, in a decrease in resistance of approximately 5% $\Delta R/R$ (percentage fractional change in resistance). Others similarly report negative changes in PAN resistance on exposure to water vapour^(14,20) and relate this to proton solvation processes in the polymer.⁽²¹⁾ The subsequent changes in sensor temperature, for $t = 150$ –400 s, cause the sensor resistance to fall until the

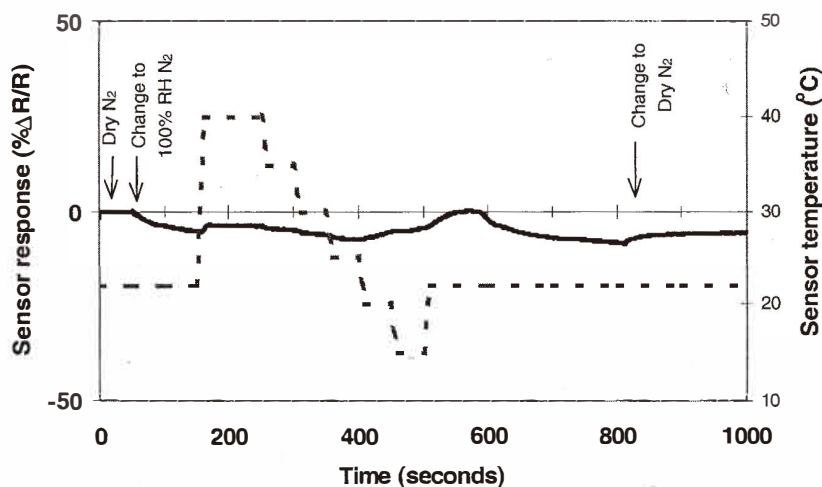


Fig. 1. Response of PAN sensor exposed to dry and 100% RH nitrogen feed gas. Sensor temperature (dotted line) has been changed as shown during the course of the run.

sensor temperature drops some 2°C below the temperature of the gas presented to the sensor (22°C). At this point ($t = 400$ s) the sensor resistance starts to increase and continues to do so until $t = 600$ s. The subsequent (delayed) decrease in sensor resistance is a consequence of the sensor temperature increase to 22°C at $t = 500$ s. The delay in the resistance change suggests that the water that has condensed on the sensor surface while it was below 22°C has required some 100 s for it to be lost and for the PAN at the sensor surface to equilibrate to conditions at 22°C . This behaviour parallels other responses observed in the presence of water vapour (see below).

Figure 2 shows how a change in sensor temperature affects the response of the PAN sensor to ammonia. In this experiment ammonia at 80 mg/m^3 is present in a 100% RH feed gas. The observed responses are reversible. Equilibrium values in resistance are reached approximately 30 s following a decrease in sensor temperature, but after much longer (up to 10 min) following an increase in sensor temperature. Since the sensor begins to respond to temperature changes almost immediately, the resistance changes in Fig. 2 would seem to be due to PAN adjustments to more or less water. Chinn *et al.*⁽¹⁶⁾ have also noted the different rates of water uptake and release by PAN. The shape of the response curves in Fig. 2 suggests that when water is released (sensor temperature increases from 22°C to 30°C), two processes are operating—one fast, the other much slower.

Figure 3 exhibits further the responses to sensor temperature for gaseous ammonia-water vapour mixtures in nitrogen. It shows the response to ammonia at a concentration of 40 mg/m^3 in 80% RH feed gas at 26°C . The pattern of changes in resistance as the sensor temperature was lowered in steps is characteristic of all such similar runs, with the resistance achieving a more or less equilibrium value at each temperature until a critical temperature is reached; then it was found that resistance increased indefinitely, sometimes

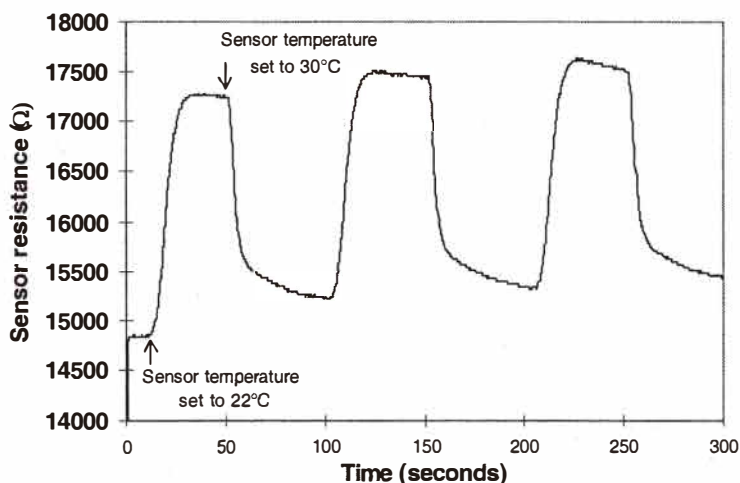


Fig. 2. Successive responses of PAN sensor to ammonia 80 mg/m^3 in 100% RH feed gas at 20°C . Peaks correspond to step changes in sensor temperature between 30°C and 22°C .

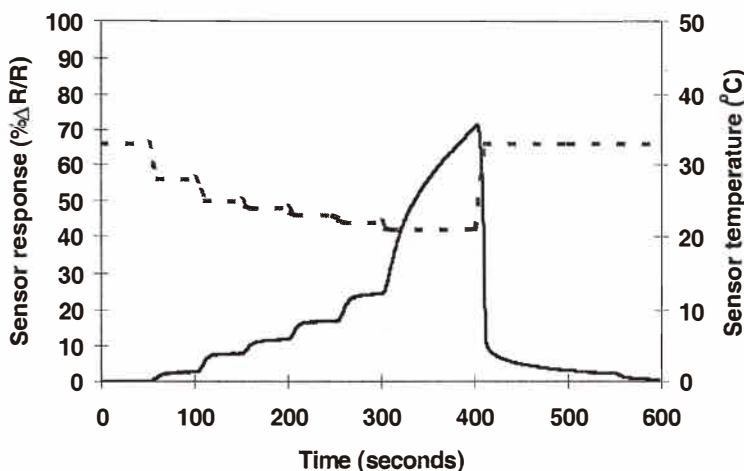


Fig. 3. Response of PAN sensor exposed to ammonia, 40 mg/m^3 in 80% RH feed gas at 26°C . Sensor temperature (dotted line) has been changed during the course of the run as shown. Equilibrium resistance values are obtained at each temperature until the dewpoint is reached (approximately 22°C). With the sensor held below the dewpoint, resistance increases indefinitely. Uncertainty in each temperature setting is approximately $\pm 0.5^\circ\text{C}$. Prior to commencement of the run the sensor was equilibrated at about 30°C .

with eventual damage to the sensor, unless the temperature was raised or the feed gas removed. Similarly, excessive exposure to aqueous ammonia appeared to damage the sensor with an associated change in the appearance of the PAN layer. In Fig. 3 the last equilibrium resistance value was obtained with the sensor temperature at just over 22°C , representing an overall change in sensor resistance of about 25%. In other similar experiments the response to ammonia at the same concentration (40 mg/m^3) but at different RH values, was very similar (i.e., approximately 25%).

The possibility that this type of response is related to the concentration of water forming on the sensor surface as the dew point is approached is explored in Fig. 4. The data for this graph are taken from response curves of the kind shown in Fig. 3. For all such curves the ammonia concentration was the same (40 mg/m^3), but with different RH. For each, the lowest temperature at which an equilibrium resistance value could be obtained was noted. These values were plotted against the nominal dewpoint⁽²²⁾ for the three RH values at the cabinet temperature (26°C).

Figure 5 shows the response to different concentrations of ammonia in 100% RH feed gas at 20°C . At each concentration and with the sensor at 22°C the equilibrium resistance was recorded. Baseline resistance was taken to be that for water vapour alone under the same conditions. With the sensor temperature held 2°C above the feed gas dewpoint the indefinite increase in resistance already noted above was avoided, although at 50 s some of the resistance values were not at equilibrium. Concentrations of 5 mg/m^3 (approximately 10 times below odour threshold) are clearly measurable with this equipment.

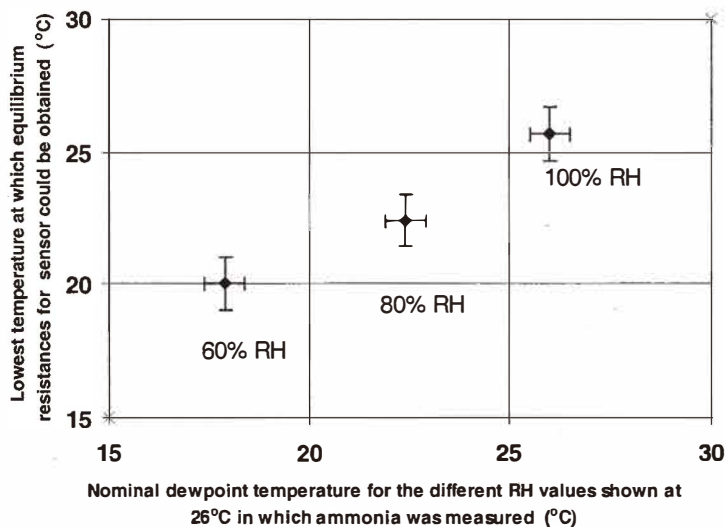


Fig. 4. Plot derived from measurements of ammonia in humid nitrogen using data derived from curves of the kind shown in Fig. 2. Nominal dewpoint temperatures for the different RH values at 26°C have been plotted against the lowest temperature at which an equilibrium sensor response could be obtained. Error bars represent the uncertainty in temperature settings of the environmental cabinet, sensor temperature settings and “lowest temperature” estimate.

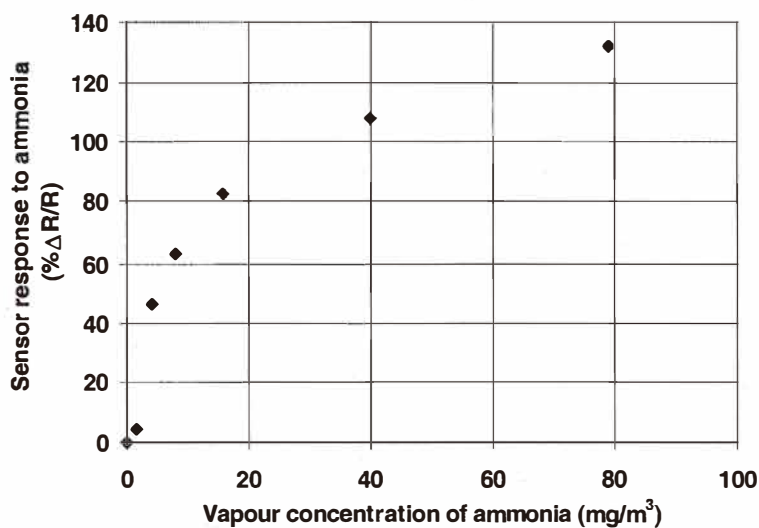


Fig. 5. PAN sensor responses to different concentrations of ammonia in 100% RH feed gas at 20°C. The baseline resistance was obtained from water vapour alone under the same conditions (same feed gas but without ammonia). Equilibrium values were recorded for the sensor set at 22°C—approximately 2°C above dewpoint.

Preliminary tests in aqueous solutions using bare PAN sensors showed that resistances quickly rose to many times their initial base values and were thus easily damaged. The technique of overspraying these sensors with silicone appeared to eliminate this problem, making them much more stable, although their sensitivity to ammonia was thereby reduced. Following its use in aqueous solutions the particular sensor employed in these tests consistently returned to within 5% of its base resistance of 8 k Ω .

Measurements of PAN sensor resistance in aqueous solutions revealed that equilibrium values could not be obtained. This effect appeared to be similar to that already noted when these sensors are operated in the gas phase below their dewpoint. Even in solutions carefully controlled at neutral pH, some drift in resistance was evident. The rate of change of resistance in mildly alkaline solutions was generally linear and these linear responses have been used here to demonstrate changes in PAN response to changes in pH (see Fig. 6).

4. Discussion

This work draws attention to the PAN response to ammonia with respect to three variables: sensor temperature, RH of gas mixture presented to the sensor and temperature of this gas mixture. The key finding is a dewpoint effect as demonstrated in Fig. 4. The most obvious explanation for these results is that when the sensor temperature is set below the dewpoint for a given water vapour concentration, liquid water forms on and/or in the sensor surface; in turn this creates a more favourable environment for ammonia to partition into and to affect the PAN conduction mechanism. As Fig. 3 shows, for sensor temperatures close to the dewpoint a change of only 1°C can produce a 10% change in $\Delta R/R$, making it extremely important to recognize this effect in any practical device.

The relatively small response to water alone, in the absence of ammonia, is evidence that the kind of responses seen in Fig. 3 involve both water and ammonia. The indefinite increases in resistance observed when the sensor temperature was set to values below the

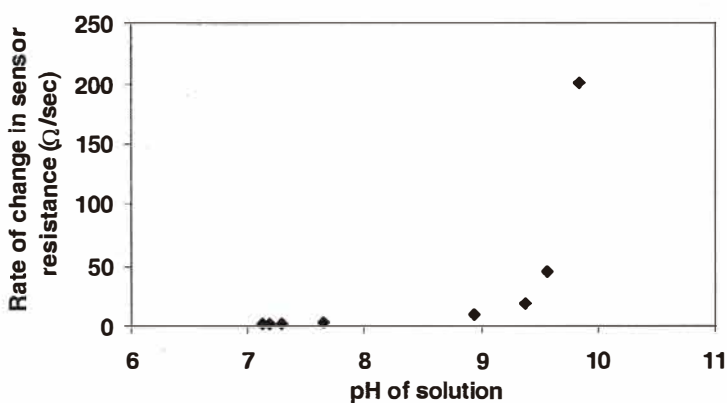


Fig. 6. Response of PAN sensor to pH changes in KCl solution made by adding NH_4OH . Relative sensitivity of PAN at each pH is indicated by the rate of change of resistance.

dewpoint relates to the extreme solubility of ammonia in water: as long as ammonia from the gas phase continues to accumulate in the water film covering the sensor, the resistance also continues to increase. In our experience, unless proper attention is paid to the sensor temperature, resistance values can become very erratic.

Jiakun and Hirata,⁽²³⁾ while not themselves recognizing any dewpoint effects, reported some results using PAN resistances to measure ammonia gas which supports the dewpoint idea: for ammonia in 50% RH (gas temperature not given) they reported the greatest sensitivity in one measurement series with sensor temperature at about 20°C—the lowest of the sensor temperatures tried, although well above the dewpoint for the gas mixture used (assuming it was presented at room temperature). In this work and in a later study⁽²⁴⁾ the sharp stepwise increases observed in PAN resistance as ammonia concentration was increased, and with attainment of equilibrium at each step, are what one would expect when the sensor temperature is held above the dewpoint.

However, we would wish to extend the explanation of Hirata and Sun⁽²⁴⁾ of PAN temperature sensitivity to ammonia as involving changes in surface potential, to include recognition of the part played by the increasing concentration of water which develops on or in the PAN surface as its temperature is decreased. In fact, the concentration of the water on or in the PAN surface may be the primary factor that determines the sensor response to ammonia.

Unfortunately, it is difficult to make reasonable comparisons with other work using PAN to measure ammonia in the gas phase since temperature control of the sensor element or of the gas presented to the sensor was either not implemented or not reported.^(6,11) However, our results appear to compare very favourably with others reported for PAN sensors measuring ammonia: 20–50 ppm threshold;⁽⁸⁾ and approximately 1.3% $\Delta R/R$ for 100 ppm at 27°C.⁽⁵⁾ The responses reported by Karakisla *et al.*⁽²⁵⁾ are several orders of magnitude less sensitive although this is probably largely due to the incorporation of PAN into poly(methyl methacrylate) films. Sotzing *et al.*⁽²⁶⁾ have reported very high sensitivities of PAN—carbon black blends to volatile amines and one assumes that ammonia would respond in a similar manner.

As a first approximation, Fig. 4 is good evidence of a dewpoint effect at work with the PAN sensors. It is also interesting to note the departure from theoretical linearity in this graph for the 60% RH system. Two effects can be expected to contribute to this: the interaction of PAN with both water and ammonia and the direct effect of ammonia on dewpoint. Wylie *et al.*⁽²⁷⁾ have pointed out that even very small amounts of a soluble material at the surface can raise the dewpoint (Raoult effect). For a given concentration of ammonia this effect will be more marked at lower RH values, as seen in Fig. 4.

As Fig. 5 shows, the system used in this work could detect ammonia, in the presence of 100% RH, at concentrations well below the 10 mg/m³ level (approximately 10 ppm) for which the percentage change in resistance ($\% \Delta R/R$) was approximately 40%. Ultimate threshold detection limits would probably be an order of magnitude lower (i.e., 1 ppm) particularly if more care were taken to reduce noise levels. Over the period of the experiment the PAN sensor exhibited good stability and consistently returned to the same base resistance when left to equilibrate under the same atmospheric conditions. The marked nonlinear response seen in Fig. 5 may indicate that a self-limiting effect is at work as exposure to increasing amounts of ammonia draws progressively more water into the

PAN film. If this is the case, one would expect that at lower RH the departure from linearity for graphs of the kind shown in Fig. 5 would be less marked. Experiments to test this point of view have yet to be undertaken. Clearly, further clarification of this matter will be important in applying PAN sensors to ammonia detection.

As already noted, equilibrium measurements in aqueous solutions could not be obtained although the rate-of-change data presented in Fig. 6 is helpful. The fact that when KOH was used to control the pH similar results were obtained to those for NH_4OH suggests that an important aspect of the mechanism involves the interaction of hydroxyl ions with the PAN polymer. It would appear that a hydroxide concentration of about 10^{-5} M is detectable with this system—similar to that reported by Laranjeira *et al.*⁽⁶⁾ Consistent with this is the observation that many common amines will induce resistance changes in PAN films,^(24, 26) as also seen qualitatively in the course of the present work.

Use of a PAN sensor in solution presents practical difficulties, the most obvious being the inability to achieve steady state resistance measurements. The solution behaviour exactly parallels that observed in the gas phase when the sensor is held below dewpoint.

5. Conclusions

This work has demonstrated that it is possible to make durable sensors for ammonia with a threshold sensitivity below the 10 ppm level. The response to ammonia is dependent on the temperature of the sensor itself which in turn affects the concentration of water present at the sensor surface. At temperatures below the dewpoint for any given gas mixture, equilibrium responses to ammonia cannot be obtained, suggesting continuous partitioning of ammonia into the water layer that forms on or in the PAN surface.

The following practical implications are suggested for a PAN-based ammonia sensor: the measurement system must include a means of defining the dewpoint of the analyte gas stream (utilising RH and temperature data); and the temperature of the PAN film must be under independent control to enable it to be set accurately to a value above the dewpoint. In this way the usefulness and reliability of such sensors for ammonia and other volatile amines under ambient atmospheric conditions is greatly enhanced.

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