



Assessment of Conducting Polymer Odour Sensors for Agricultural Malodour Measurements

Krishna C. Persaud, Soad Mohialdin Khaffaf, Philip J. Hobbs¹ and Robert W. Sneath²

Department of Instrumentation and Analytical Science, UMIST, Manchester M60 1QD, ¹AFRC Institute of Grassland and Environmental Research, North Wyke Research Station, Okehampton, Devon EX20 2SB and ²Silsoe Research Institute, Wrest Park, Silsoe, Bedfordshire MK45 4HS, UK

Correspondence to be sent to: K.C. Persaud, DIAS, UMIST, PO Box 88, Sackville Street, Manchester M60 1QD, UK

Abstract

The major odoriferous components of fresh pig slurry were identified using gas chromatography coupled to mass spectrometry. From the analytical data, a standard artificial slurry was reconstituted. The performance of conducting polymer odour sensor arrays was evaluated using the individual chemical volatile components and the artificial slurry itself. Most of the components are discriminated from each other, when presented singly to the sensor array. The sensors are not poisoned by the chemicals and give reproducible responses over a 3 month period. The odour components being detected from an artificial alkaline pig slurry appear to be associated with patterns obtained from indole, skatole and ammonia. The intensity of the signal is proportional to the concentration of the volatiles presented to the sensor. The results indicate that conducting polymer sensor arrays show promise for measurement of agricultural malodours, and may complement olfactometric techniques. *Chem. Senses* 21: 495–505, 1996.

Introduction

The practice of intensive livestock farming, and the problems associated with the treatment and disposal of waste has raised public awareness of agricultural malodours as environmental pollutants (Jones, 1977; Shusterman, 1992). Such odours may be released from ventilation systems in farm buildings, waste storage and slurry treatment systems, and the spreading of slurries on agricultural land. Malodours emanating from cow and pig slurries are an increasing source of environmental pollution (O'Neill and Phillips, 1991). Many substances produced during the anaerobic digestion of faeces have very low human olfactory thresholds and so are perceived as odour nuisances even when their concentrations in air are very low. These include volatile fatty acids, p-cresol, amines,

sulphides, disulphides, mercaptans and many heterocyclic compounds (Schaeffer, 1977; Williams, 1984). It has been reported that environmental odours greatly affect the physiological and psychological status of a human population. A recent study on the effect on a population exposed to malodours from pig farms reports more tension, depression and anger, reduced vigour, increased fatigue and more confusion than a control population (Schiffman *et al.*, 1995).

The nature of very odourous compounds is such that they are detected by the human nose even when less odourous compounds are present at higher concentrations. For an odorant, the perceived intensity of odour is proportional to a fractional power of the concentration. Methods of odour

measurement traditionally rely on dilutions of odour samples with clean odour-free air to the 50% human detection thresholds assessed by odour panels and calculation of 'odour units' (Hoshika *et al.*, 1981; Hobbs *et al.*, 1995). Strict adherence to set procedures and statistical methods is essential to minimize subjectivity and take into account variations in the response of the panelists. This is a laborious and expensive measurement, and with the increasing need to assess malodour in agriculture, very often on site, rapid odour measurement systems are required to give intensity and quality information, rather than olfactometric data based on human panels. Until recently, instrumentation for automated odour measurements did not exist, but several types of sensing systems for odours are now becoming commercially available. The trend has been towards arrays of sensors that may be based on several different types of sensor technologies. These include metal oxide sensor arrays (Gardner and Bartlett, 1994), quartz crystal arrays and surface acoustic wave devices (Ballantine *et al.*, 1986; Nakamoto *et al.*, 1993), arrays of electrochemical cells (Stetter *et al.*, 1986), and conducting polymer arrays (Hatfield *et al.*, 1994). We have been involved for some time in the chemistry and applications of organic conducting polymers for sensing of volatile chemicals. The strategy has been to develop sensing systems where individual elements in an array show broad, overlapping selectivity to chemical species, each sensor element responding more selectively to certain chemicals. This approach has the advantage that the array can respond to many thousands of chemical species due to the broad selectivity of the adsorbent surfaces. On the other hand, extremely selective information for discrimination between adsorbed chemical species or mixtures can be obtained by analysis of the cross-sensitivities between sensor elements. The relative responses between sensor elements produce patterns that may be unique 'fingerprints' that may be used as odour descriptors.

Polymers of some heterocyclic materials show reversible changes in electrical conductance with adsorption and subsequent desorption of odour molecules. There is high sensitivity to polar molecules, and although chemical selectivity of individual polymers is broad, arrays of sensors that contain different functional groups on the surface show different but overlapping responses to different chemical families. Functionalization of conducting polymers and their applications have recently been reviewed (Imisides *et al.*, 1991). There is a quantitative relationship to odour

concentration since the change in conductance measured is almost directly proportional to the concentration of adsorbed odour molecules and their binding affinity to the conducting polymers (Pelosi and Persaud, 1988; Persaud *et al.*, 1992). Of advantage in these kinds of sensing materials is the ability to react rapidly and reversibly at ambient temperatures, and that they are more sensitive to polar volatiles than to nonpolar volatiles. This correlates well with the range of volatile chemicals to which the human nose is most sensitive, and therefore in many cases the sensor responses can be related to human perception, albeit indirectly.

It is clear that odour sensing systems may have wide applications in the agricultural area. However, few odour sensor systems have previously been tested for agricultural odour applications. Important aspects of any sensing system are the characteristics of the response, reproducibility and stability over time. In applying odour sensors to agricultural applications, it is important to have a good understanding of the chemicals that cause odour nuisances. Some attempts have been made previously to relate chemical characteristics to the odour of excreta from various farm animal sources, and volatile fatty acids, ammonia, sulphides and p-cresol are well correlated with perception of offensive odour characteristics (Spoelstra, 1980). We have analysed the chemicals present in pig slurry odours and investigated the quantitative and qualitative responses of conducting polymer odour sensor arrays to individual components that have low human olfactory thresholds, as well as to the complex mixture of chemicals that are present in slurries.

Materials and methods

Analysis of pig slurry

Fresh liquid slurry produced by three pigs fed on fixed diets was analysed by gas chromatograph-mass spectrometry (GC/MS). All slurries were thoroughly mixed to ensure that the solids were evenly distributed. Prior to analysis the supernatant fractions of slurries were obtained by centrifugation, and the soluble components were analysed by GC/MS. Major components with high olfactory impact are shown in Table 1 and represent the averaged aqueous concentrations of these components for slurries obtained from the three pigs.

A requirement for the evaluation of the responses to sensors was a mixture of chemicals representative of pig

Table 1 Major odoriferous constituents of fresh pig slurry as measured by GCMS

| Chemicals | Averaged concentration ($\mu\text{g/ml}$) |
|------------------------|---|
| Acetic acid | 1365 |
| Propanoic acid | 358 |
| 2-Methylpropanoic acid | 604 |
| Butanoic acid | 237 |
| 3-Methylbutanoic acid | 301 |
| Pentanoic acid | 90 |
| Phenol | 21 |
| 4-Methylphenol | 62 |
| Indole | 6.6 |
| 3-Methylindole | 3.7 |

slurry that could easily be reproduced from day to day. An artificial pig slurry was made by reconstitution of these components in aqueous solution. This solution had a pH of 3.1. This was then increased to pH 8.2 by addition of ammonia (aq.), this being representative of the pH of normal pig slurry. Both acidic and basic forms of the artificial slurry were used for experiments.

Phenol, p-cresol and volatile fatty acids have previously been used as odour indicators of swine waste (Schaeffer, 1977; Bourque *et al.*, 1987). Although sulphides also contribute to pig slurry odour, these were not included in the measurements because of problems in making stable solutions of these compounds. However, the conducting polymer sensors do respond to hydrogen sulphide, mercaptans and other compounds.

Measurement of the response characteristics of conducting polymer sensors

A system for presenting known concentrations of volatiles to a sensor array consisted of a 4.0 l sealed glass vessel with a motorized PTFE stirrer and a septum through which volatile chemicals could be introduced either as liquids that evaporate or as vapours of known concentration, producing a static headspace. A sensor array consisting of 20 polymers based on substituted pyrroles was sealed into the vessel. The vessel was maintained at constant temperature (room temperature—22°C) by immersion into a large water bath with large thermal inertia, so that minor fluctuations in room temperature during the course of the experiments did not change the equilibrium headspace concentrations being

generated. The measurement system consisted of a computer controlled multiplexed system capable of measuring changes in sensor resistance to a precision of 0.001 Ω in 10 K Ω . The amplified output of the sensor array was recorded digitally to 12 bit accuracy. A multiplexed input allowed each sensor in the array to be interrogated in turn, and the sampling frequency was 5 points per second. Signals from the entire array were averaged over 1 s and output through an RS232 port to an external computer that was used for data manipulation and display. The experimental procedure generally consisted of injecting known volumes of a volatile chemical into the container, waiting for an equilibrium vapour to be established (30 min) and measuring the changes in resistance of each sensor. Methanol vapour was used as a standard for testing the repeatability of the measurements and reproducibility of the manufacture of the sensor array.

Because the measurement technique was incremental in terms of the introduction of increasing analyte concentrations into the headspace and then waiting for an equilibrium to be established, the sensors would normally have been exposed to the analyte over several hours. Between measurements, the system was flushed with clean air for at least 30 min. For replicate measurements chemicals were presented in random order, and at least five replicates were done for each experiment.

Results and discussion

Concentration–response relationships

Figure 1 shows concentration–response curves obtained to methanol vapour for each sensor in the array. The change in resistance when presented with a volatile chemical relative to the base-resistance in air ($\Delta R/R$) is a convenient measure of response. The standard deviations are the result of six experiments carried out over a period of 1 week. For methanol, the response was almost linearly proportional to concentration. Each sensor element showed different sensitivity to methanol, reflecting the differences in affinities of each conducting polymer for this ligand. With acetic acid vapour, shown in Figure 2, the response was of opposite polarity to methanol, and nonlinear relationships were observed. The nonlinearity may be due to the competition between polar and nonpolar forms of acetic acid competing for interaction with the adsorbent, this being dependent on the relative concentration of the two species and the

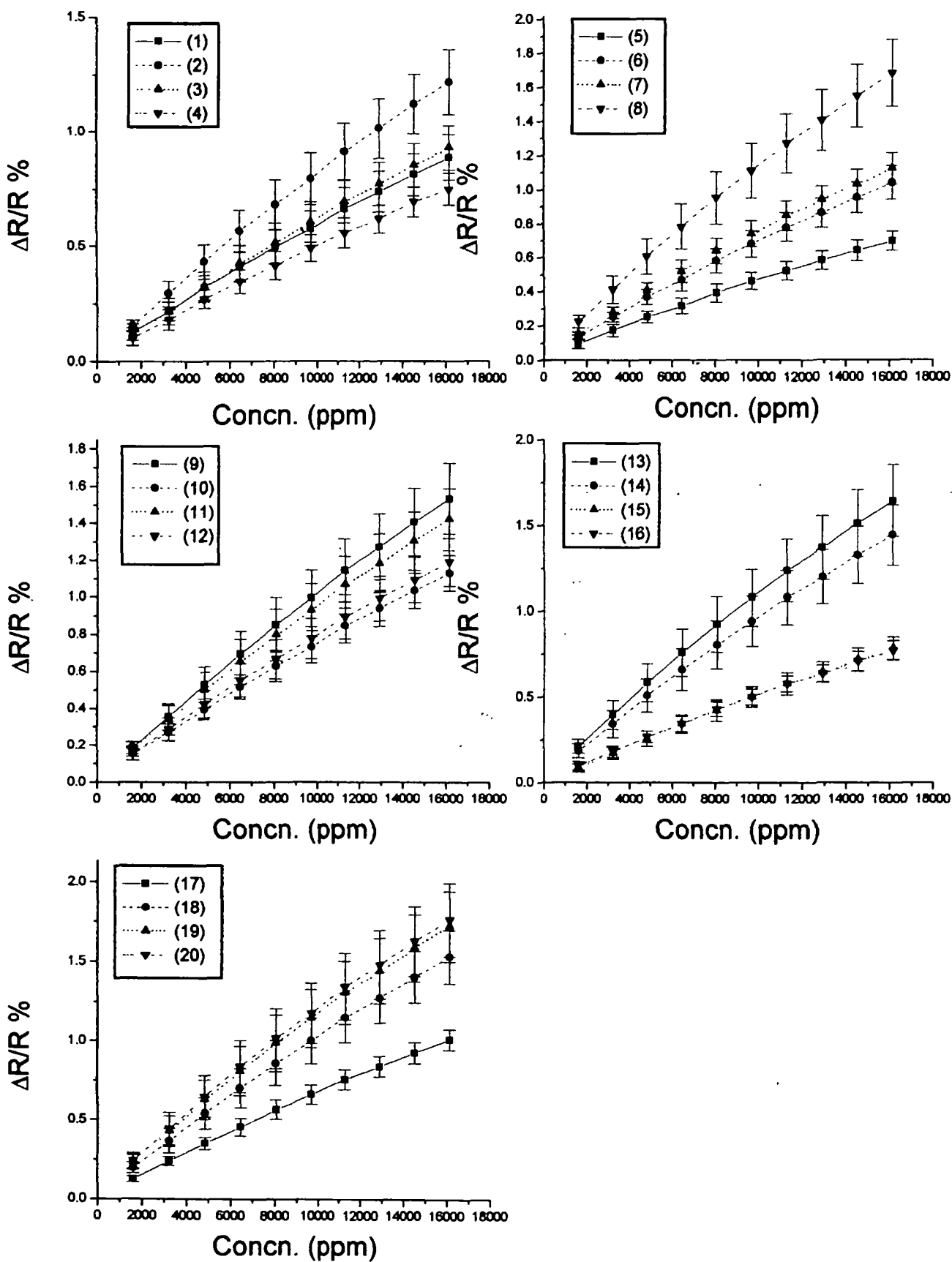


Figure 1 Concentration–response curves for 20 conducting polymer sensors in an array. The data shown are for methanol vapour. Each graph shows data from four sensors from the array numbered from 1 to 20.

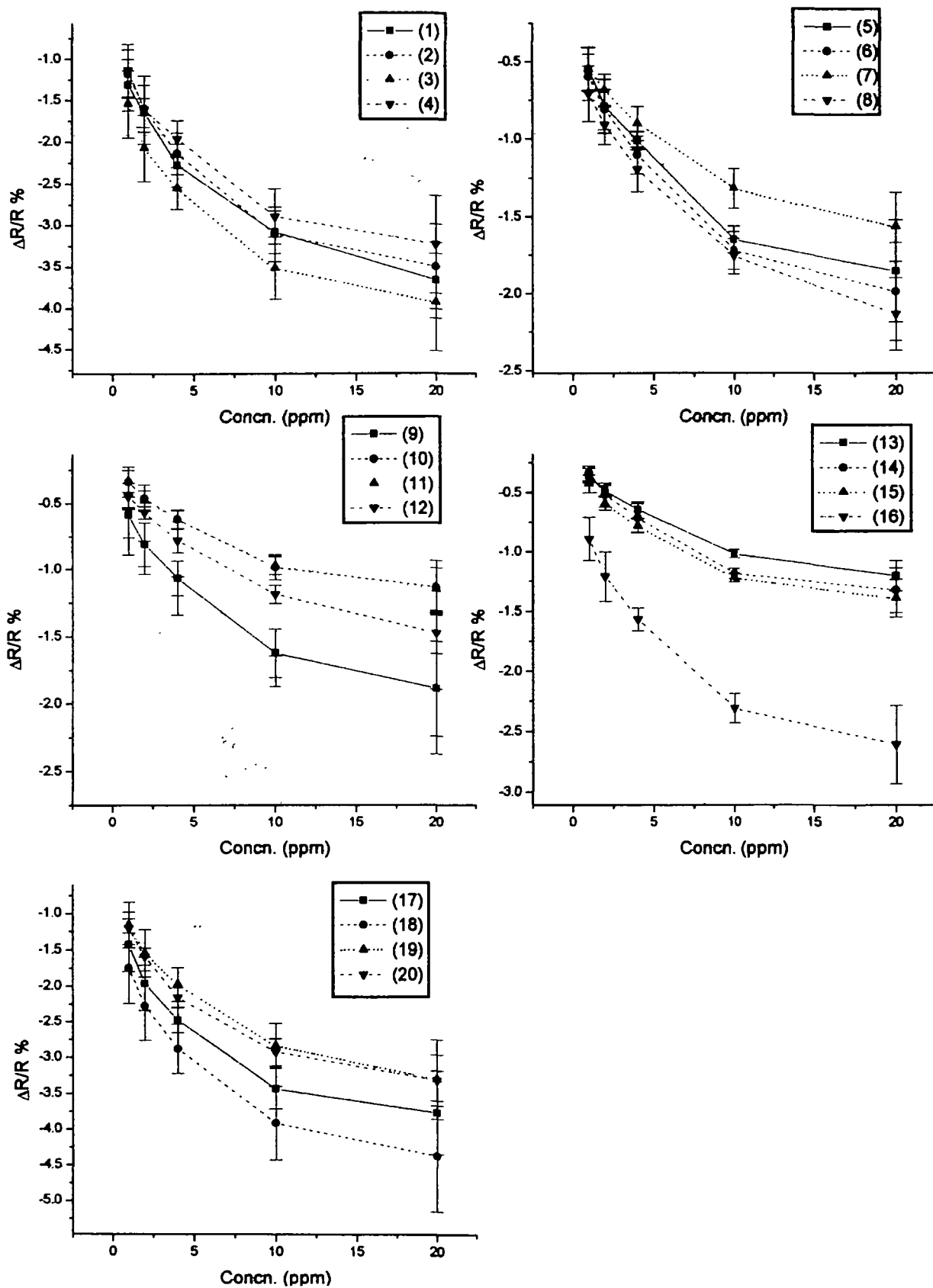


Figure 2 Concentration–response curves for 20 conducting polymer sensors in an array. The data shown are for acetic acid vapour. Each graph shows data from four sensors from the array numbered from 1 to 20.

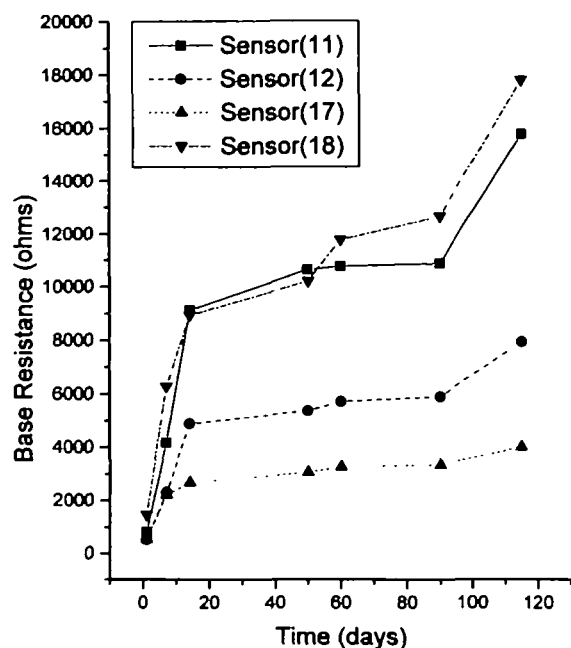


Figure 3 The stability of the base resistance of the sensors with time. The data shown are for four representative sensors in the array (sensors 11, 12, 17 and 18).

affinities of the interaction with the conducting polymer. Again each sensor in the array showed different sensitivity to the acetic acid vapour. The polarity of the response is dependent on the nature of the electronic perturbation induced on binding of the molecules to the polymer. However, the physicochemical mechanisms involved in inducing a reversible change of resistance are not yet known in detail. The dynamic range of the concentrations used was limited by laboratory difficulties in generating lower concentrations in a repeatable manner. Hence the data presented do not necessarily represent limitations in the sensitivity of the instrument to particular vapours. They illustrate that the initial slopes of the concentration response curves, as well as the linearity of the responses, are dependent on the analytes being measured as well as the chemical characteristics of the individual sensor elements.

Stability of the responses

The usefulness of any sensor system is dependent on the stability of the sensors and longevity of the sensors with constant use. The data in Figure 3 show examples of the change in base resistance with time for four sensors in the array and are representative of the other sensors in the array. After manufacture, the sensors showed a steep increase in base resistance over 2–3 weeks, and then the slope of the change decreased but the resistance continued

to rise with time. The causes of these changes in base resistance are probably very complex and may include oxidation of the materials, physical changes induced by repeated adsorption and desorption, movement of counterions within the matrix and other unknown factors. In this case the usable resistance of the sensors is up to ~500 K Ω , after which the resistance measurement becomes too noisy. This means that the expected lifetime of the sensor array may be >2 years. The measured parameter $\Delta R/R$ appeared to be relatively independent of the slow change in base resistance with time.

Figure 4 shows the concentration–response curves for methanol for the four sensors of Figure 3 at 0 days and after 100 days. The response curves were almost superimposable for sensor 17, while the other sensors showed a change of ~10% over the period. The sensors had been in active use for 10–20 h per week over the period monitored. These data provide evidence that the inherent pattern stability from a conducting polymer array is likely to be good over the long term, though methods of recalibration of the sensors will need to be introduced if the system is to be used over long periods. The stability data for all the sensors in the array were quite similar.

Response patterns

When each individual sensor element is responding to an identical concentration of a volatile chemical at any particular instant, the relative response of each individual sensor produces a pattern. These patterns of responses may be used as ‘fingerprints’ that are characteristic of the chemical species adsorbed. A convenient way of normalizing the responses so that the intensity components are nearly eliminated is to express each sensor response as

$$\frac{\frac{\Delta R}{R}}{\sum_{i=1}^n \left| \frac{\Delta R}{R} \right|} \quad (1)$$

where the change in resistance (ΔR) relative to the base resistance in clean air (R) in response to an odour is measured for the entire array. For compounds where the sensor response is relatively linear to change in concentration, such as methanol, the patterns produced using this method are independent of concentration, while with compounds that give a nonlinear response with concentration the patterns will change with concentration.

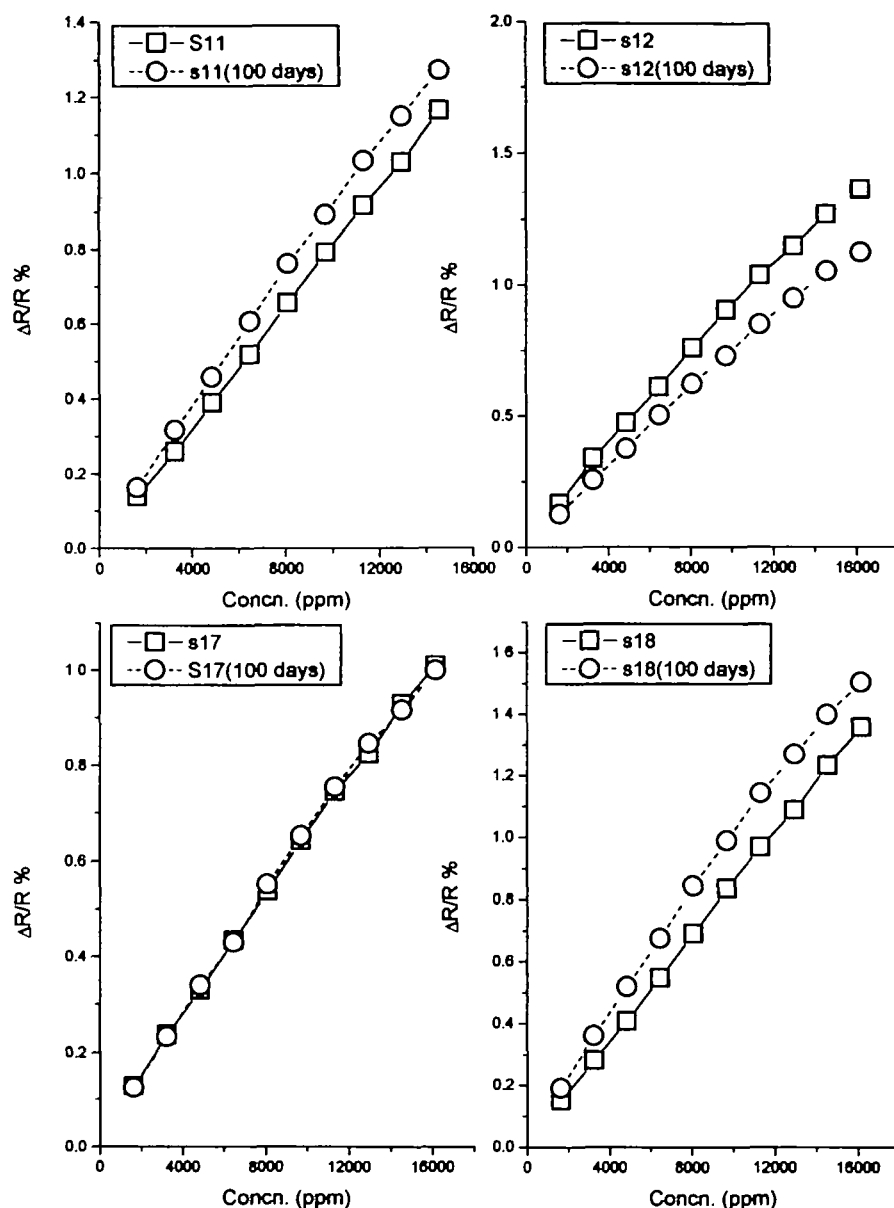


Figure 4 The stability of the response with time. Concentration–response curves are shown for methanol at day 0 and after 100 days of continuous sensor use for sensors 11, 12, 17 and 18.

This will also be true when mixtures of volatile chemicals are presented to the sensor array, as each chemical species will compete for binding on the basis of its relative affinity and concentration. Figure 5 shows examples of patterns obtained for some of the individual components of pig slurry at fixed concentration. For most of the compounds measured, the nonlinearity of the concentration–response curves meant that the patterns changed over the concentration range. It is, however, necessary to be able to differentiate compounds over a range of concentrations. The 20 sensors in the array can be considered to produce vectors in multidimensional space. A convenient way to

examine the separation of classes in multidimensional space is to use methods of reduction of the data to two or three dimensions where the human eye can easily be used to determine whether pattern classes are separable from each other. One such method, known as Sammon mapping, reduces multidimensional vectors into two or three dimensions on the basis of the distance between the patterns (Sammon, 1969). The distance measure most commonly used is the Euclidean distance, but other measures may also be used. This mapping procedure is useful because no prior assumptions are made that the patterns belong to any particular class. In many cases where the distribution of

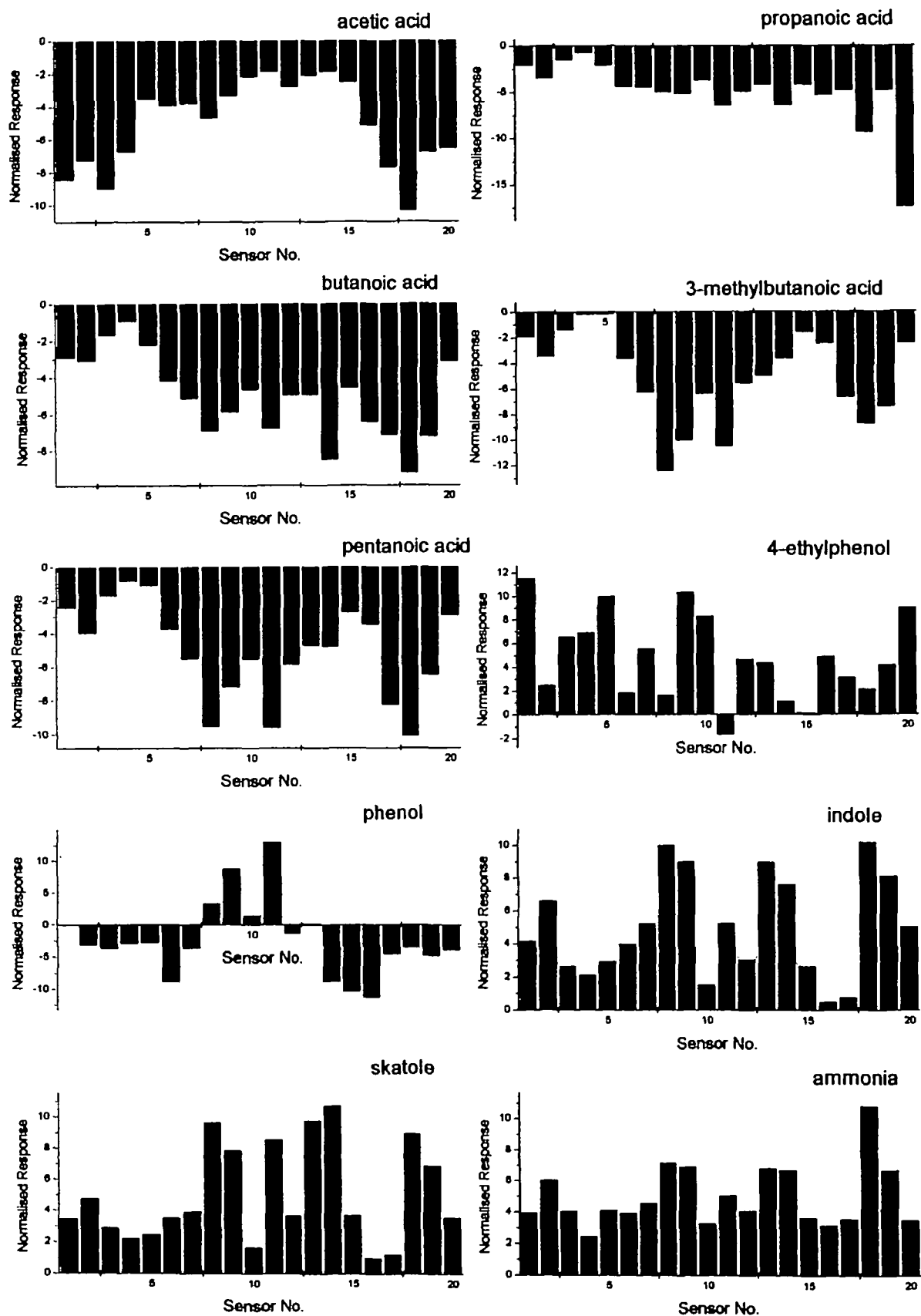


Figure 5 Response patterns to components of fresh pig slurry. The patterns consist of the normalized response of each sensor relative to the response of the entire array. They show unique features for each chemical species measured, and allow discrimination between them.

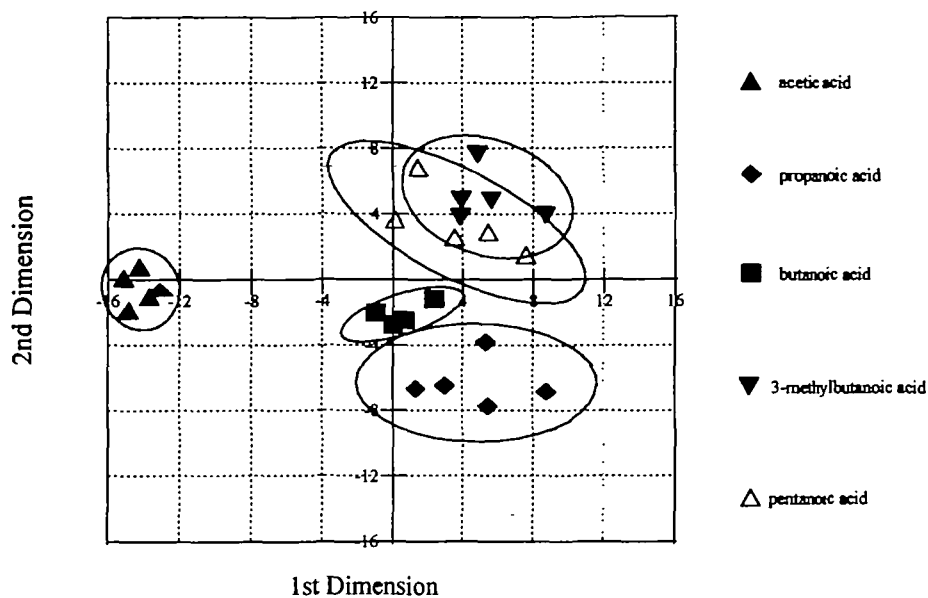


Figure 6 Sammon map of fatty acids showing discrimination between classes. Each point correspond to a pattern such as those in Figure 5, that has been reduced from 20 dimensions to two dimensions, while retaining the relative Euclidean distances between patterns.

data is non-Gaussian, it gives a better representation of the data than principal component analysis, because the latter is essentially a linear procedure. However, some data are inevitably lost in going from a multidimensional space to a lower dimensional space.

If n input patterns with l -dimensional space are designated X_i , $i = 1, 2, \dots, n$, and, corresponding to these n patterns with d ($d = 2, 3$), dimensional space is also designated Y_j , $j = 1, 2, \dots, n$, the distance between the patterns X_i and X_j in l -dimensional space is defined by $d_{ij}^* = \text{distance}[X_i, X_j]$, and the distance between corresponding patterns Y_i and Y_j in the d -dimensional space is defined by $d_{ij} = \text{distance}[Y_i, Y_j]$. All the new d -dimensional space distances d_{ij} are then used to define an error, which represents how well the present new configuration of n patterns in d -dimensional space fits the n patterns with l -dimensional space, such that

$$E = \frac{1}{\sum_{i < j} [d_{ij}^*]} \sum_{i < j} \frac{[d_{ij}^* - d_{ij}]^2}{d_{ij}^*} \quad (2)$$

From equation (2), the minimization attempts to preserve interpoint distances by finding d_{ij} s that are as close as possible to d_{ij}^* s. Since the d_{ij}^* s are constants for any original patterns given application, the unknowns in this error function are the new d -dimensional configuration distance d_{ij} . The distance functions between the original patterns, and the new configuration patterns, use the common Euclidean

distance measurement in this application. Sammon's non-linear mapping technique attempts to emphasize the fit of small l -dimensional space distances since the d_{ij}^* term in the denominator of equation (2) acts as a weighting function which is large when d_{ij}^* is small. This weighting produces the effect of mapping l -dimensional space clusters into two- or three-dimensional space clusters.

Figure 6 shows the map produced for the fatty acids. Each point corresponds to a single pattern and each cluster contains points obtained over different concentrations of fatty acids. Each point corresponds to the mean of 3–5 replicate experiments. Clear discrimination between clusters corresponding to acetic acid, propanoic acid, butanoic acid and pentanoic acid could be observed. Interestingly, the 3-methylbutanoic acid and pentanoic acid clusters overlapped, but 3-methylbutanoic acid could be discriminated if the concentration was high enough.

A map with all of the components of the artificial slurry can now be examined and compared with the acidic and basic artificial slurry itself in Figure 7. This is a complex figure that may be divided into three zones. On the left, the fatty acids and the acidic artificial pig slurry map in the same region. On the top, the phenol, p-cresol and 4-ethylphenol tend to group together, but the map indicates that the patterns change substantially with different concentrations, possibly reflecting changes in the equilibria between different species at different concentrations. The basic

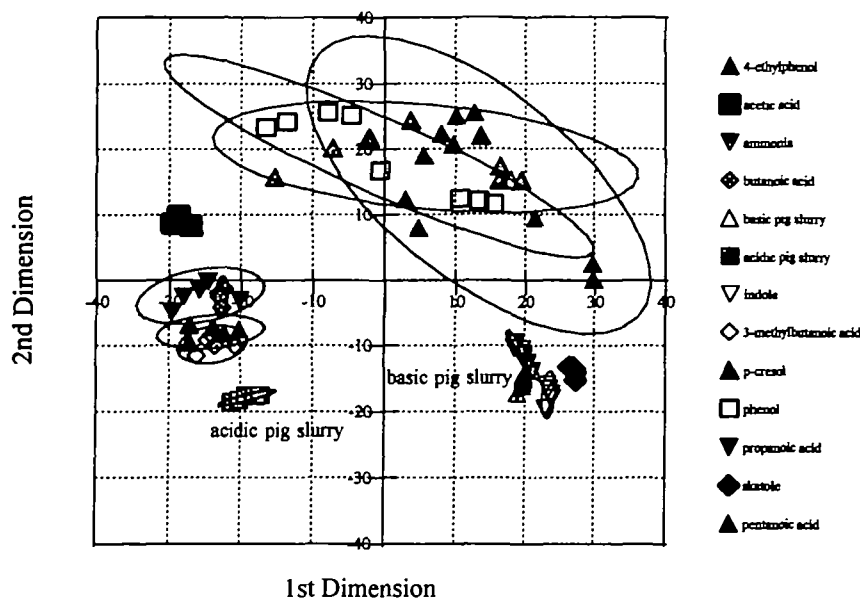


Figure 7 Sammon map of the components of artificial pig slurry and the acidic and basic pig slurry mixtures. The plot shows the distribution of patterns obtained for 4-ethylphenol, acetic acid, ammonia, butanoic acid, basic pig slurry, acidic pig slurry, indole, 3-methylbutanoic acid, p-cresol, phenol, propanoic acid, skatole and pentanoic acid obtained over a range of concentrations. Alkaline artificial pig slurry clusters closely to ammonia, indole and skatole, while acidic artificial slurry clusters closely to the fatty acids.

artificial pig slurry clusters closely with ammonia, indole and skatole on the lower right of the figure. Since natural pig slurry is predominantly alkaline with a pH of ~ 8.2 , these results indicate that the skatole, indole and ammonia content of the slurry may dominate the chemical species to which the conducting polymers are more sensitive to and thus may serve as odour markers. The pH of the slurry will change the equilibrium between the ionized and uncharged forms of the volatile fatty acids in the slurry and Henry's law will apply. Conducting polymer sensors are very insensitive to nonpolar compounds. Therefore at an alkaline pH the contribution of the fatty acids to the pattern produced by the sensor array is likely to be very small, since they are trapped within the slurry as the involatile salts. Ammonia, indole and skatole as well as water have a high affinity for the conducting polymers and these will predominantly contribute to the patterns that are produced from the alkaline artificial pig slurry. While ammonia has been correlated with odour concentration for specific experiments, no universal relationship has been found (Pain and Misselbrook, 1991). A sensor that responds to ammonia will not be consistently able to predict odour in different situations. Thus the system would need to be calibrated to measure odour from individual odour sources. Since conducting polymers are sensitive to water, this means that sampling of agricultural malodours would also need to be correlated with independent humidity measurements, which

can be used as correction factors. The correlation between the sensor sensitivity and human sensitivity to agricultural malodours still has to be done and the concentration ranges of chemicals that were investigated were well above human olfactory thresholds. A systematic investigation on real pig slurry samples is underway.

Conclusion

The data presented give evidence that conducting polymer sensor arrays are capable of detecting to high sensitivity the major odoriferous components of fresh pig slurry. However, we did not measure H_2S , which is also an important odorous component in pig slurry. Most of the components may be discriminated from each other when presented singly to the sensor array, even though the patterns for individual chemicals may change with concentration. The sensors are not poisoned by the chemicals and give reproducible responses over a 3 month period. The odour components detected from an artificial alkaline pig slurry consisting of a mixture of the odoriferous components appear to be similar to patterns obtained from indole, skatole and ammonia. Similar patterns have since been produced from fresh pig slurry. The intensity of the signal is proportional to the concentration of the volatiles presented to the sensor.

Objective malodour measurement is a difficult task since the sensor signals need to be correlated to human sensory

perception of the odour. The perception of an objectionable malodour is very often dominated by components that may be present in low concentration but which have very low human olfactory thresholds. With agricultural malodours, sensors to be used for objective odour measurement need to

be tuned to be most responsive to the odour components with low human olfactory thresholds. The results of the present study indicate that conducting polymer sensor arrays may soon be suitable tools for objective malodour measurements.

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