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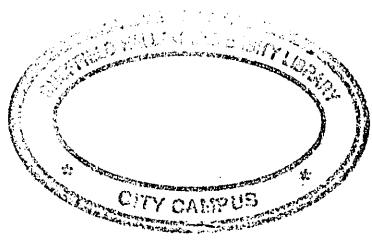
Odour Evaluation using Arrays of Conducting Polymer Sensors

David R Ellis

A thesis submitted in partial fulfilment of the requirements of
Sheffield Hallam University
for the degree of Master of Philosophy

February 1996

Collaborating organisation : Neotronics Scientific plc



Abstract.

Devices based upon the human olfactory system, comprising arrays of gas sensing elements with suitable data handling systems have shown much promise as being a viable alternative to human testing panels and established instrumental methods of assessing odours. The introductory chapter reviews the progress which has been made by various groups in developing these so called "electronic noses".

Chapters 3 and 4 deal with the characterisation of a series of water-based beverages and a range of tobacco samples. The results show promise, but also that sensor response is dominated by water which masks the responses of the analyte species. Results are presented in tabular and visual form, the latter being radar plots and ribbon diagrams. When the water signals are subtracted from the raw response data, different samples show individual and different visual patterns. The promise of these results is hampered by the impression of the data, as it is clear that the problem of water interference has to be reduced for the promise of sensor arrays to be fully realised.

In chapter 5, a series of structure/response mapping studies are considered. The effects of aliphatic chain length and of ring substitution are reported. Some discrimination is again evident, with water creating the same problems as in the previous studies.

Throughout the work a device comprising an array of polypyrrole-based conducting polymer gas sensors was employed. Some response data has been analysed using euclidean clustering techniques to determine the individuality of sensor responses. Groups of sensors, very often pairs or threes in an array have responded in a very similar fashion.

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Chapter 1 Introduction.

In many areas of industrial manufacture (cosmetics, foodstuffs, beverages, tobacco etc), the aroma of a final product can often be a key factor in consumer acceptability. Routine analysis of such materials is generally performed using either specially trained panels of odour evaluators or traditional instrumental methods such as gas chromatography or gas chromatography-mass spectrometry [1]. The use of odour evaluation panels yields subjective responses which are influenced by many factors such as the age, gender and general health of the panel members. Instrumental methods of analysis tend to be expensive and time consuming and in some applications may possess insufficient limits of detection to allow full characterisation of an aroma. A simple method by which odours could be rapidly, reproducibly and inexpensively characterised would be of great use [2].

Recent advances in gas sensing technology have led to the development of “electronic noses” based upon the highly sensitive human sense of smell. Gardner [24] has defined an electronic nose as being “an instrument which comprises an array of electronic chemical sensors with partial specificity and appropriate pattern recognition system, capable of recognising simple or complex odours”. These instruments respond to an odour as a whole rather than separating and detecting individual components as in chromatographic-based methods to produce a unique “fingerprint”, characteristic of an analyte. Using computer software, electronic noses are capable of discriminating between very similar odours such as different brands of coffee and classifying unknown species by comparison with previously learnt patterns. A wide range of applications have been envisaged for these devices [3, 4] and competition between manufacturers is steadily growing [5-7].

1.1 The human olfactory system. [8, 9]

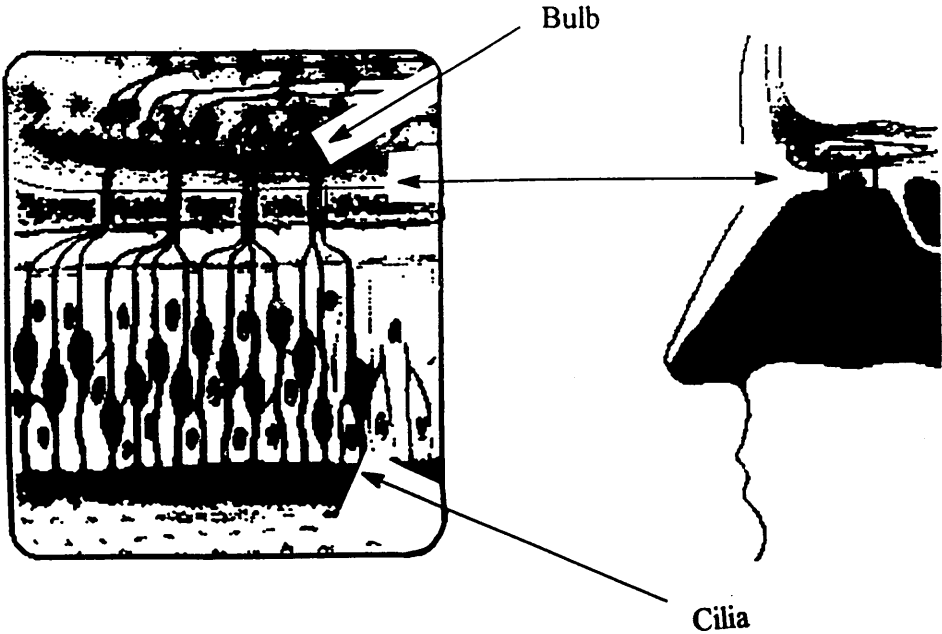
The molecular basis of olfaction is still poorly understood. A number of theories proposed to explain the mechanisms of this process [10-12] have been only partially successful. It is beyond the scope of this thesis to review the area of olfaction. However, more comprehensive reviews are presented elsewhere [13-15]. Instead, a brief overview is presented which concentrates upon features which would seem essential considerations when designing an electronic analogue of the human sense of smell.

The olfactory epithelium (figure 1) is an exposed odour-sensitive area containing approximately fifty million receptor neurone cells [16, 17]. These neurones have fine hair-like projections (cilia) which are immersed in a mucus layer which covers the epithelium. Volatile species reach the epithelium via the breathing process. The sniffing reflex increases the speed and volume of air reaching the epithelium, increasing sensitivity and allowing the detection of species which would be otherwise undetectable. Once dissolved in the mucus layer, odorants interact with the cilia which contain receptor proteins. Only approximately one hundred receptor proteins have been discovered, suggesting that the receptor neurones show overlapping response characteristics rather than being specific towards a certain class of compounds.

The olfactory bulb contains the secondary (mitral) cells of the olfactory system. Several thousand receptor neurones are connected to a single secondary cell and it is this convergence which is believed to be a key factor in explaining the high sensitivity of the system. Olfactory information from the array of primary neurones is pre-processed in the bulb before being fed to the higher olfactory centres of the brain.

The higher olfactory centres of the brain contain several targets for the bulb output. It is in these areas that odour classification, discrimination, perception, memory effects and initiation of behavioural responses occur.

Figure 1 The olfactory epithelium.



1.2 Realization of a practical electronic nose. [18 - 24]

An electronic analogue of the complex human olfactory system would necessarily be a simple system with the following requirements :

i) A method of introducing the sample into the sensing environment. A flow through system where the test sample is swept over the sensing array using an inert gas, mimicking the sniffing reflex, would be capable of performing this task. An alternative strategy would be to adopt a static headspace system where the sample is allowed to equilibrate (vaporise), and be separate from the sensing array until the point of analysis.

ii) An array of sensors [25] to act as artificial neurones, which is effectively a scaled down version of the many millions present in the olfactory system. These sensors would be required to respond rapidly, reversibly and reproducibly, preferably at ambient conditions. In modelling the olfactory system, there should be no need for individual sensors to respond with any great degree of specificity although clearly, an array of identical sensors would be of little value. Instead, an array in which each sensor responds to a broad range of species and has response characteristics offset from it's neighbours should prove to be adequate. Several types of gas sensor meet these criteria and will be considered in section 1.3.

iii) Some form of pre-processing algorithm, analogous to the pre-processing performed by the olfactory bulb to convert the sensor responses into a suitable form for statistical analysis. Various data transformations could be employed such as :

a) The difference in response (resistance, conductance etc.) between the analyte and a reference sample such as air. i.e. $\text{response}_{\text{sample}} - \text{response}_{\text{ref}}$

b) Relative response between the sample and a reference compound. i.e. $\text{response}_{\text{sample}} / \text{response}_{\text{ref}}$

c) Fractional response. e.g. $\text{response}_{\text{sample}} - \text{response}_{\text{ref}} / \text{response}_{\text{ref}}$

d) Logarithmic functions of the above strategies.

e) Normalisation (division of all responses by the largest or average response obtained).

f) Autoscaling where all data is adjusted such that it is mean centred with a standard deviation of one. This avoids inadvertent weighting of very small or very large data points.

iv) An evaluation system (a "brain") where the pattern of sensor responses to a given analyte may be compared with previously learnt patterns. This implies the use of pattern recognition techniques [26] which are considered in section 1.4.

Of course, the development of an electronic nose does not have to follow this design brief. Haskard and Mulcahy [27] have envisaged a design based on an alternative approach using an array of many thousands of sensors. Their proposed design is based upon the principle that in the biological system different receptor neurones are excited upon each inhalation yet for a given past history the same spatial pattern is generated in the olfactory bulb. They suggest that the bulb may be primed for a response by initially sampling the inhaled air and then focusing in on a specific feature. The authors envisage the use array of many thousands of simple sensors with threshold values beyond which they are activated to produce a pattern of sensor response which is related to odour concentration.

1.3 Sensors suitable for inclusion in an electronic nose.

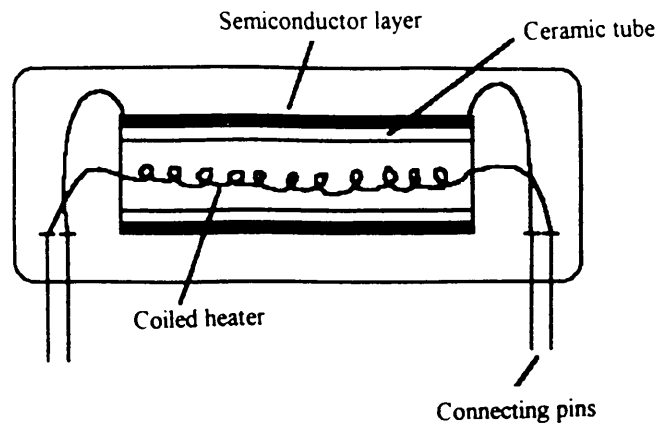
1.3.1 Metal oxide-based devices.

At temperatures of approximately 200-500 °C, the resistance of a semiconducting oxide such as tin oxide becomes dependent upon ambient gas composition [28]. Gas sensing devices based on this principle are very sensitive but unselective [29]. However, selectivity may be introduced using various strategies such as adopting an alternative operating temperature or by including catalytic additives and/or filters within the device [30].

The mechanism of conduction in these compounds is unclear. Several models have recently been proposed [31, 32]. It is generally agreed that conduction in these systems is a result of the reaction of adsorbed analyte gases with previously adsorbed atmospheric oxygen on the oxide surface layer [33, 34]. Tin (IV) oxide is a non-stoichiometric material, containing a deficiency of oxygen atoms. Charge neutrality is achieved by the presence of Sn^{2+} ions which act as electron donors. Atmospheric oxygen becomes adsorbed onto the surface of the tin oxide at elevated temperatures where it accepts electrons to yield charged oxygen species such as O^{2-} , O_2^- and O^- [35]. Adsorption of a reducing gas onto the oxide surface layer will decrease the resistance of the system by releasing electrons for conduction either by donating electrons or by reacting with the adsorbed oxygen species. An oxidising analyte will have the reverse effect whilst a multicomponent mixture such as an odour will exhibit competing effects.

Arguably the most well known and widely used commercially available semiconducting gas sensor is the Taguchi gas sensor [36] which is illustrated in figure 2. This device comprises of a small ceramic tube coated which has a sintered, porous semiconducting layer deposited onto its outer surface. This coating consists of tin oxide and catalytic additives such as palladium. The ceramic tube contains a heating element to allow operation at the optimum working temperature of 150-300 °C (poor sensitivity is obtained at lower temperatures). The power requirement of the heating element is typically about one Watt which constitutes a major disadvantage of these devices. The resistance or conductivity of Taguchi sensors may be conveniently measured as a function of gas concentration using simple circuitry.

Figure 2 Schematic representation of a Taguchi gas sensor.

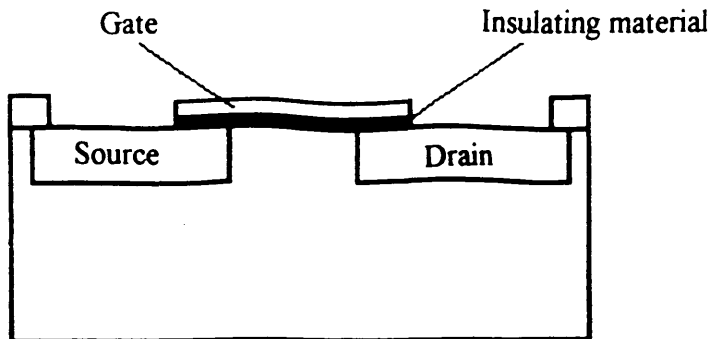


Taguchi sensors are sensitive to both temperature and humidity changes and the active surface is vulnerable to poisoning by various species. Responses to a few ppm of gases are in the order of a few seconds with recovery times typically in the order of sixty seconds. Olafsson et al [37] have applied tin oxide sensors to the monitoring of fish freshness.

1.3.2 MOSFET devices.

Metal oxide semiconductor field effect transistors (MOSFETS) [38, 39] consist of source and drain diffusions separated by a gate electrode. This design is illustrated in figure 3.

Figure 3 Schematic diagram of a basic MOSFET device

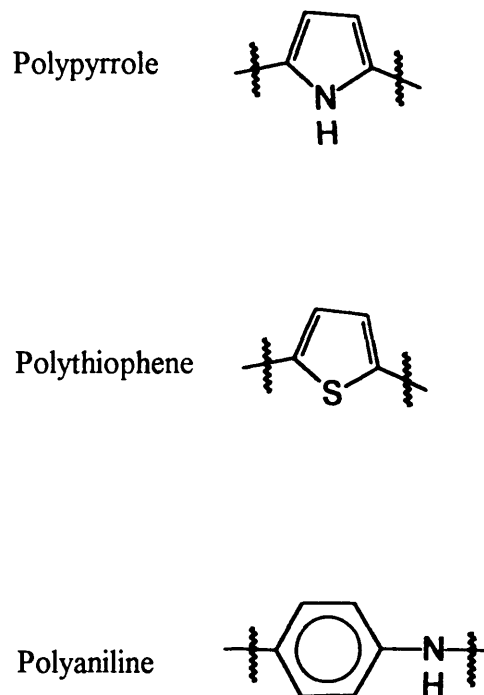


The n-type semiconducting source and drain are separated by an area of p-type semiconducting material which is covered by a thin film of insulating material. A metallic gate electrode is deposited on top of the insulating layer. The current that flows between the source and drain is governed by the voltage applied across the gate and substrate. At a certain gate voltage, termed the threshold voltage, the gate creates a field which is able to invert a thin layer of p-type material near the insulating layer to n-type material. This inversion process creates a channel between the source and drain which allows current to flow between them.

If the gate of a MOSFET device is made from a catalytic material, the threshold voltage can be made to be dependent upon the concentration of an analyte gas. For example a platinum or palladium gate device may be used as a hydrogen sensor. [40]

Over the past fifteen years, there has been a great expansion of research interest in the area of conducting polymers. A wide range of applications have been envisaged for these materials [43] including their use as gas sensors [44, 45]. Sensors based on heterocyclic derived conducting polymers such polypyrrole, polythiophene and polyaniline are well known. The repeat structures of these polymers are illustrated in figure 4. Gas sensing devices based on such polymeric materials exhibit rapid adsorption and desorption kinetics at ambient temperatures and are not prone to poisoning by analyte species.

Figure 4 Repeat structures of some common conducting polymers.



The most widely studied conducting polymer is polypyrrole. Chemical methods of preparing polypyrrole are well known but electropolymerisation methods [46-49] have proved to be most popular in the area of gas sensing as they allow thin polymer films to be deposited directly onto sensor substrates in their oxidised, conducting state. The first free standing, electrochemically prepared film of polypyrrole was reported by Diaz and co-workers in 1979 [50]. This pioneering work showed that conducting polymer films could be easily prepared using a simple two electrode cell by the application of a potential difference to a solution of monomer and supporting electrolyte dissolved in a suitable solvent. These polymerisation reactions proceed via radical cationic intermediates and hence are susceptible to nucleophilic species within the reaction environment. This obviously limits the choice of solvent and electrolyte and many reported methods employ weakly nucleophilic, aprotic solvents such as acetonitrile. It is also important to ensure that neither the solvent or supporting electrolyte undergo oxidative decomposition at the applied potential. The electrical, mechanical and other properties of the films may be changed by altering the identity of the supporting electrolyte and/or solvent, alteration of the duration of the electrodeposition reaction or by introducing substituents into the monomer structure. The redox properties and stability of conducting polymer films may be investigated using cyclic voltammetry [51] which essentially involves monitoring the current over a pre-set voltage scan range.

For a material to be electrically conducting it must possess a series of atomic orbitals which can overlap and interact to yield a series of band-like electronic states separated by forbidden regions (band gaps). Most polymers are electrically insulating as the sp^3 orbitals used in bond formation are spatially unsuited to allow sufficient overlap and interaction.

The previously described, heterocyclic based conducting polymers contain conjugated, unsaturated bonds. This arrangement of alternating double and single bonds yields a series of spatially compatible p_z orbitals which can overlap and create a continuous delocalised pi system.

In their neutral state, polymers such as polypyrrole are electrically insulating and it is only when they are oxidised (or reduced) that they become highly conducting. During the electropolymerisation of polypyrrole, an electron is removed from the polymer pi system. This creates a polaron state (figure 5a) which is essentially a free radical and a cation linked by local bond rearrangement. Electroneutrality is achieved by simultaneous incorporation of an anion from the supporting electrolyte (e.g. tetrafluoroborate, hexafluorophosphate, perchlorate, p-toluenesulphonate) into the polymer, this process is termed "doping". The formation of polarons creates new localised energy states within the bandgap. Upon further oxidation, a second electron is removed yielding a dication termed a bipolaron state (figure 5b). Formation of a bipolaron is thermodynamically more favourable than the production of two polarons by removal of another electron from the polymer chain. Bipolaron states are also accommodated within the bandgap.

Bipolarons are believed to be the primary charge carriers in polypyrrole [52] although charge transport mechanisms are still poorly understood. Doping of polymers is an inhomogeneous process which creates "islands" of highly conducting regions. Tunnelling or hopping of charge carriers between these domains is believed to occur.

Figure 5a Formation of a polaron state in polypyrrole.

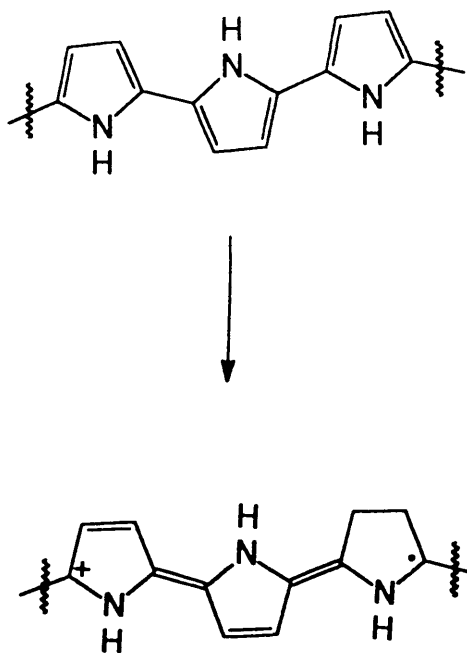
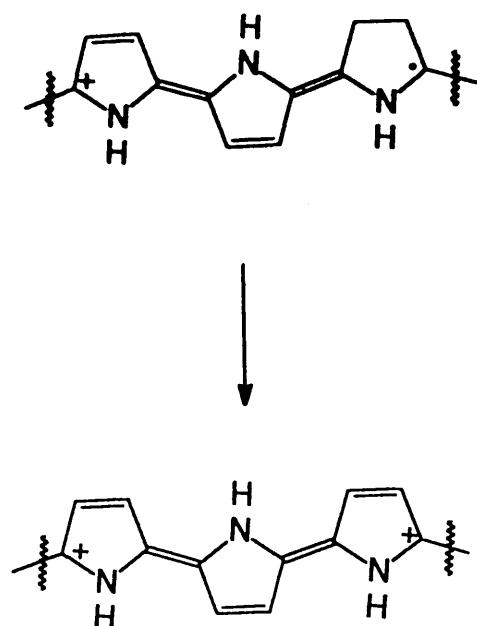


Figure 5b Formation of a bipolaron state in polypyrrole.



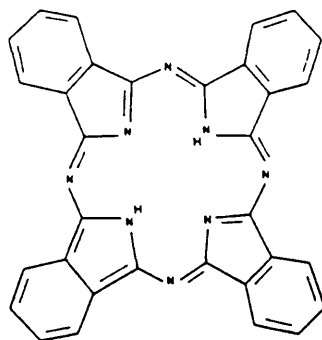
Sensors are generally fabricated by electrochemically growing polymer films across the gap between two metal electrodes on a suitable substrate. The change in resistance which is observed when these devices are exposed to gases such as NO_2 [53] and NH_3 [54] are thought to be caused by secondary doping of the polymer films by gaseous species which adsorb onto them. This adsorption process is only likely to involve weak, surface-based interactions since films of this kind may be returned to their equilibrium states by purging with gases such as air. Secondary doping effects probably involve interactions between the analyte species and the counter ions and/or solvent of the polymer or generation/removal of charge carriers.

Slater and co-workers [55] have described a novel gas sensing element comprising of a conducting polymer (polypyrrole or a derivative) coated array of eight electrodes deposited onto a single substrate. This design allowed the indirect investigation of the surface and bulk layers of conducting polymer films upon exposure to analyte species by determining the responses of pairs of electrodes. Exposure to methanol clearly showed differences in response between different zones of a single film indicating that analyte species do not fully penetrate into the polymer matrix.

1.3.4 Metal Phthalocyanine-based devices. [56]

The phthalocyanines (PC's) have polynuclear structures. The parent molecule, hydrogen phthalocyanine is shown in figure 6.

Figure 6 Structure of hydrogen phthalocyanine.

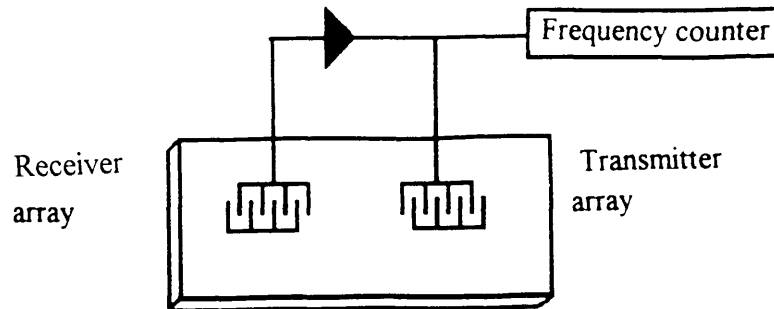


The central hydrogen atoms in the above structure may be replaced by metals such as copper and lead. Functional groups may be also introduced into the ring or central metal atom. Phthalocyanines behave as p-type (hole carrier) semiconductors at elevated temperatures [57, 58]. Simple devices comprising of thin PC films deposited on suitable substrates via vacuum sublimation or Langmuir-Blodgett techniques (see section 1.3.6) have shown good sensitivity towards strongly electrophilic gases such as NO_2 [59, 60]. The conductivity increase observed in electrophilic environments is thought to be due to the adsorbed analyte accepting a pi electron from the PC, leaving a hole which is delocalised throughout the PC structure. These devices suffer from memory effects and have slow recovery times. Recovery times may be improved via elevation of operating temperature but this can decrease the lifetime of the PC films.

1.3.5 Surface acoustic wave sensors.

Surface acoustic wave (SAW) devices [61, 62] are usually based upon the design shown below in figure 7

Figure 7 Typical SAW sensor design



Finger-like arrays of metal interdigital transducers (IDT) electrodes are evaporated/sputtered onto a piezoelectric substrate such as quartz or LiNbO_3 . Application of a radio frequency to the transmitter array creates deformations in the substrate which leads to the formation of surface Rayleigh waves which propagate along the device to the receiver array [63]. A shift is observed in this resonant frequency when a species is adsorbed onto the surface of the device. This frequency shift is proportional to the mass of the adsorbed material allowing devices of this type to be used as very sensitive microbalances [64]. The frequency shift is vulnerable to environmental effects such as temperature and humidity and so it is usual to have two sets of arrays on a single substrate with one acting as a reference.

Surface acoustic wave-based gas sensors [65-67] contain an adsorbent coating with some degree of selectivity towards the desired analyte in the surface region between the transmitter and receiver arrays. A diverse range of adsorbent materials have been reported in the literature including gas chromatography stationary phases [68, 69], polymeric materials [70], lipids [71-73], cyclodextrins [74], molecular sieves [75], Langmuir-Blodgett films [76], olfactory cell proteins [77], conducting polymers [78] and thermotropic nematic liquid crystals [79].

1.3.6 Langmuir-Blodgett techniques.[80, 81]

Langmuir-Blodgett (L-B) techniques have been extensively applied in the field of gas sensing. They essentially allow the deposition of ultrathin films of controlled thickness onto sensor substrates [82]. Such methods are limited to materials which possess long hydrocarbon chains terminated by a hydrophilic functionality at one end and a hydrophobic one at the other, such as fatty acids.

Compression of the monolayer formed by the deposition of a suitable material onto a liquid surface such as water yields a quasi-solid which is only one molecule thick. Monolayers of L-B film may then be transferred onto a substrate by continuous dipping and removal of the substrate through the monolayer. One layer is transferred with each movement through the surface with the molecules aligning in "head to tail" fashion. Simple gas sensors may be produced using these techniques by depositing a semiconducting material such as a metal phthalocyanine onto a substrate and monitoring conductivity changes upon exposure to a test atmosphere [83].

1.4 Pattern recognition techniques.

Pattern recognition techniques are essentially statistical methods of establishing relationships between data points in a set of data such as the responses of a sensor array to a series of analytes. Such methods are either based upon statistical analysis of mean and variance (parametric) or involve training of the system (non parametric). Training in non parametric methods may be either unsupervised where data is separated into groups or supervised where rules are developed in order to classify unknowns. Examples of some of these techniques are outlined below. For a more general review see Gardner and Bartlett [84].

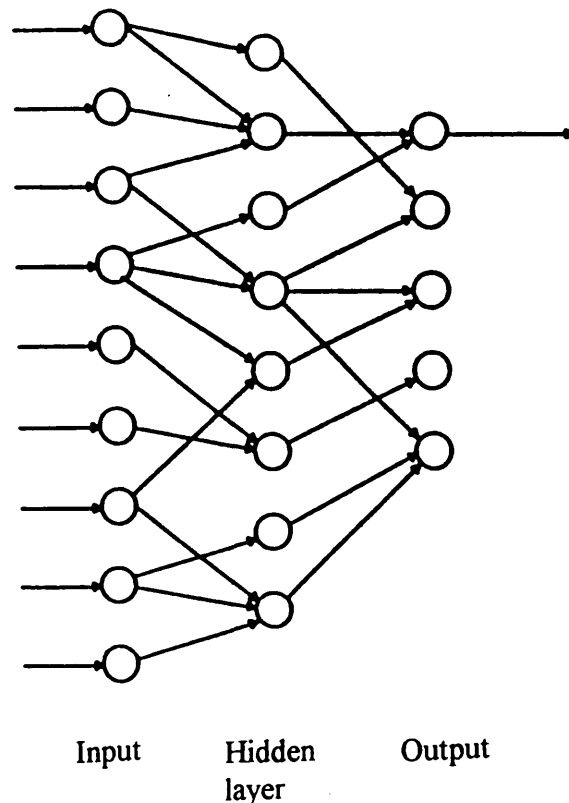
Principal component analysis (PCA) is a supervised parametric method which essentially involves the separation of unrelated pairs of data points on the basis of variance. It is usually possible to describe a data set using only a few principal components which exhibit a large % proportion of the total variance of the set. Principal component analysis is generally performed in conjunction with cluster analysis (CA) which is an unsupervised, non parametric method which groups a series of apparently unrelated data points into distinct sets (clusters) on the basis of their closeness in n-dimensional space. In heirarchical clustering methods, the initial clusters are grouped by comparison of pairs of points such as the two closest or most distant or by more complex methods involving all data points in a cluster. Gardner has described the application of clustering and principal component techniques to the discrimination of odours using an array of tin oxide sensors [85].

Artificial neural networks (ANN's) [86. 87] consist of a network of interconnected, adaptable processing elements. A typical three layered system comprises of the following sections :

- i) An input layer with n inputs where n is equivalent to the number of sensing elements.
- ii) A hidden layer containing fewer elements than the input layer, mimicing the convergence in the biological system.
- iii) An output layer where the number of elements is dependent upon the number of target analytes.

Each element in the network is connected to all elements in the preceeding layer. The output from each element is a weighted function of it's input and is connected to all elements in the layer above as illustrated in figure 8.

Figure 8 A diagrammatic representation of a three layer artificial neural network.



A network is trained using a series of standard compounds. The results obtained from a training session are compared with the expected output. Any differences which exist between the two are back propagated through the network, adjusting the weighting on each element. This training continues until the network output matches the target output. The network gains experience during the learning process which it can subsequently apply to make judgements about unknown samples which are presented to the sensing array.

1.5 The development of electronic noses.

The first odour evaluation instrument based upon the olfactory system was developed at the University of Warwick in 1982 [88]. This simple device consisted of an array of three commercially available Taguchi tin oxide gas sensors, with a light emitting diode acting as a discrimination indicator. This pioneering work showed that a small array of non-selective gas sensors had the potential to discriminate between a large number of odours and this led to a great deal of research interest in the area of artificial olfaction by a number of research groups.

The subsequent development of a practical odour sensing device at the University of Warwick [89-93] has involved the investigation of tin oxide and conducting polymer sensors using simple static test rigs and the development of improved measurement circuitry and pattern recognition systems [94-96]. These investigations ultimately led to a DTI funded link scheme for the development of an instrument which underwent trials at a brewery (discussed later). Some of this work has been patented [97, 98].

Initial testing of Taguchi tin oxide sensors was performed using a simple test rig comprising of three sensors mounted and sealed into a five litre flask fitted with a stirrer paddle and sample injection port. The flask was immersed in a water bath to maintain a constant temperature within the test environment. Resistance changes caused by exposure of the sensors to various test species were monitored using a simple potential divider circuit. Experimental work was controlled using purpose written software running on a BBC microcomputer. Promising results were obtained from these initial studies [99].

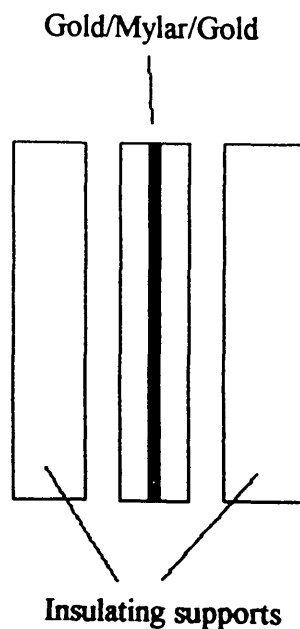
A three element array with improved circuitry was subsequently applied to the characterisation of tobacco smoke and alcoholic beverages [100]. Application of simple statistical techniques to the response data obtained in these studies allowed adequate discrimination between samples.

The initial test rig was subsequently upgraded to incorporate twelve sensors [101, 102]. Sensitivity was improved by two orders of magnitude by replacing the simple potential divider circuitry with an a.c bridge design [103]. The improved twelve element array was applied to the discrimination of brands of coffee [104]. Application of statistical techniques to the response data allowed samples to be classified with a success rate of 88.1 %

By consideration of the heat loss mechanisms in similar devices, the Warwick group have constructed low powered integrated tin oxide gas sensors of a novel design [105-107]. Thermal efficiency was improved by either mounting the sensing elements on a ceramic package or by suspending them by their bond wires. These sensors consume only approximately 20 % of the power required by Taguchi gas sensors under similar operating conditions.

Conducting polymers have also been investigated as potential gas sensing elements for inclusion in the Warwick instrument. Rapid and reversible responses to methanol were observed using a sensor fabricated by the electropolymerisation of pyrrole across two gold electrodes using a sandwich design [108] which is illustrated in figure 9.

Figure 9 Schematic diagram of a sandwich electrode

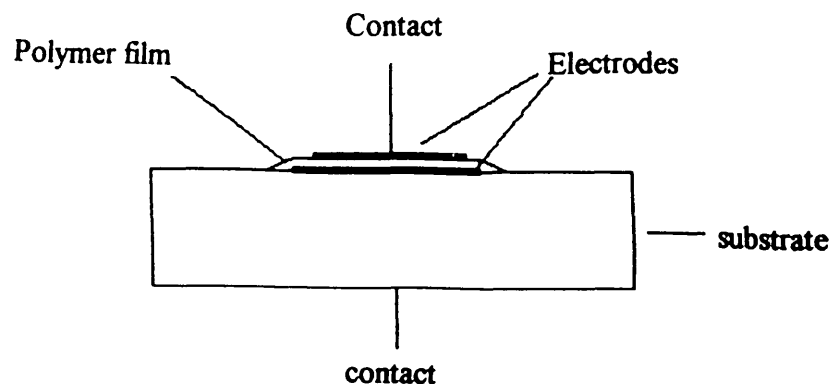


In this design, gold was sputtered onto both sides of a strip of insulating Mylar film which was then sandwiched between two insulating supports. This strategy allows sensors with a range of inter-electrode gaps to be prepared.

A series of polypyrrole sensors of this design were prepared and characterised using cyclic voltametry. A subsequent paper [109] reported the effects of temperature, analyte concentration and film thickness upon sensor response. The sensors were found to yield reproducible responses to methanol vapour but their baseline resistances were found to increase during storage. A further series of polymers based on alternative monomers (poly-n-methyl pyrrole, polyaniline and poly-5-carboxyindole) were subsequently investigated by exposing each sensor to a series of organic vapours [110]. Of the three polymers investigated, poly-5-carboxyindole was found to yield the most stable and reproducible responses.

An alternative conducting polymer sensor design has also been reported [111] in which poly-n-methyl pyrrole was electropolymerised onto a gold electrode on an alumina substrate. A second electrode (gold or indium) was then vacuum deposited onto the polymer film. This is illustrated in figure 10.

Figure 10 University of Warwick electrode design.



Shurmer et al [112] have suggested that the introduction of different response characteristics into an array of initially identical polypyrrole sensors could be achieved by using Langmuir-Blodgett films of arachidic acid to inhibit the sensitivity of the polymer films. They proposed that the L-B films would act as passive molecular sieves and would not interfere with the conduction mechanism of the polymer. A simple study using polypyrrole sensors with varying numbers of L-B monolayers deposited onto their active surfaces showed that sensor response may be significantly modified by this method but the L-B films seemed to play a more complex role than just as passive molecular sieves.

A LINK scheme involving the University of Warwick, Neotronics, Bass brewery and the government led to the patenting of sensor technology [97] and the development of an electronic nose for industrial use [113]. In an initial study [114], polypyrrole, polyaniline and poly-3-methyl thiophene based sensors incorporating a wide range of dopant (electrolyte) materials were investigated. Each of the sensors investigated contained three individual elements on a single substrate. The instrumental hardware comprised a glass sample vessel fitted with a motorised fan, immersed in a water bath to ensure constant temperature within the test environment. Beer samples were allowed to equilibrate in the sealed sample vessel until the point of analysis when the sensor head was inserted at a defined analysis point. Cluster analysis of the responses from a range of tests showed the potential of the system for application in the brewing industry.

A second paper summarising the results of the three year research programme was subsequently published [115]. The improved hardware consisted of an array comprising of up to twenty four conducting polymer sensors, an automated flow injection system and sophisticated classification software involving neural network pattern recognition. The improved system was capable of detecting taints in beer samples with a high rate of success.

An electronic nose has been commercialised and launched by Essex-based Neotronics Scientific LTD [116] a spin off company formed by Neotronics technology plc to exploit the technology developed during the previously discussed DTI LINK project [117-119].

The Neotronics olfactory sensing equipment (NOSETM) is a static system which measures the headspace above a sample using an array of up to twelve sensors [120].

Each NOSETM sensor consists of a conducting polymer electropolymerised onto a ceramic substrate. Polypyrrole-based sensors have mainly been employed but other materials are currently undergoing investigation. Different response characteristics are introduced into the array by variation of the dopant (electrolyte) material used in the electropolymerisation reaction. The sensors are reported to be manufactured extremely reproducibly, allowing them to be replaced without compromising subsequent tests. A d.c. power supply maintains a constant current through the sensors and voltage changes caused by alteration of the resistance of the polymer films by adsorption of analyte species are measured and fed to a computer system. WindowsTM-based software allows a comprehensive description of the sample and analysis conditions to be stored with the sample results.

The NOSETM has been successfully applied to several areas of industrial manufacture [121]. Neural computing technology has also been developed to be used in conjunction with the system and will be incorporated into subsequent models [122].

AROMASCAN plc [123, 124], based in Crewe was formed to commercialise the results of research into artificial olfaction performed in the Department of Instrumentation and Analytical Science at the University of Manchester Institute of Science and Technology (UMIST) [125, 126]. AROMASCAN'S electronic nose, "AROMASCANNER" is a benchtop unit incorporating an array of thirty two conducting polymer-based sensors all located on a single substrate. Sample introduction into the instrument is achieved using a flow through system which incorporates single use sample bags to minimise memory effects. Sample discrimination is performed using sophisticated neural network software.

Early research efforts at UMIST concentrated on assessing the suitability of conducting polymers as potential sensing elements in an artificial nose. In an initial investigation, a series of monomers were electropolymerised onto steel anodes [127, 128]. Polypyrrole was found to yield robust, easy to handle films and was the basis of subsequent research efforts. New sensors were fabricated by electropolymerising a series of monomers namely, 2-chloroaniline, thiophene-2-acetonitrile, indole and 2-isobutylthiazole onto polypyrrole sensors. The polypyrrole film was used to allow improved adhesion of the polymer films onto the sensor substrate and did not affect the conduction of the other materials. The responses of these sensors to a series of simple test compounds showed their potential to be used to discriminate between a variety of analytes. Many of the sensors exhibited different magnitudes of resistance change towards each of the test compounds and in some cases decreases in resistance were observed. The sensors exhibited no drift in response over a period of several months and were not poisoned by any of the test compounds studied. The methods of fabricating these devices were subsequently patented [129].

The development of an artificial nose [130] quickly followed, with arrays of conducting polymer sensors being employed in subsequent investigations [131, 132]. An application specific integrated circuit (ASIC) was developed [133, 134] as an improved means of measuring absolute values of resistance and changes in resistance associated with a sensor array. This strategy overcame previously encountered problems of high noise and long measurement times associated with traditional bridge-based measurement systems.

The measurement of d.c. conductivity changes in conducting polymer films is a well established method of determining their resistances. The use of high frequency a.c. methods are poorly understood and have been investigated at UMIST as an alternative method of interrogating sensor arrays [135, 136]. Several electrical parameters namely resistance, capacitance, conduction and capacitance were determined using this strategy and showed much promise to be used in conjunction with or as an alternative to d.c.-based measurement strategies.

The AROMASCAN technology has been applied to many areas of application such as the food industry [137, 138] where foodstuffs and beverages such as wheat, coffee, soya and cheese have all been assessed. An interesting paper [139], which concerns the detection of taints in milk samples, outlines a method of “washing” the sensor array between tests using an aqueous solution of butanol which is described as a suitable cleanser since it is rapidly adsorbed and desorbed from the polymer films. The system has also been compared to various other techniques in the assessment of offensive odours from livestock waste [140] and was found to be capable of discriminating between different animal wastes.

The “FOX 2000” electronic nose has recently been developed via the collaboration of Alpha MOS (France) and the Universities of Warwick and Southampton. The instrument is comprised of up to eighteen sensors in arrays of six elements located in three chambers, linked in series. The first array consists of various oxide sensors with the second and third comprising of conducting polymer and other oxide sensors such as tin, zinc and tungsten oxide. More than forty sensors have been developed which can be easily fitted into and removed from the instrument which allows the potential construction of analysis-specific arrays. Each sensor chamber is also fitted with a temperature and humidity sensor to allow the monitoring of conditions within the test environment. Sample introduction is via a flow through system. The instrument has been successfully applied to the analysis of beverages and foodstuffs [141] and also in studies involving perfumes and body odours [142].

An electronic nose for monitoring solid state fermentations has been reported by Wang [77]. The device comprises an array of five quartz surface acoustic wave sensors coated with fractions of receptor proteins obtained from the olfactory system of bullfrogs in conjunction with a lipid coated reference electrode. The nose has been applied to the monitoring of alcoholic beverages and the decay processes of solid hog waste. The results of these tests were analysed using simple statistical techniques such as cluster analysis. The instrument was capable of discriminating between a variety of alcoholic beverages and also between raw and stabilised composts.

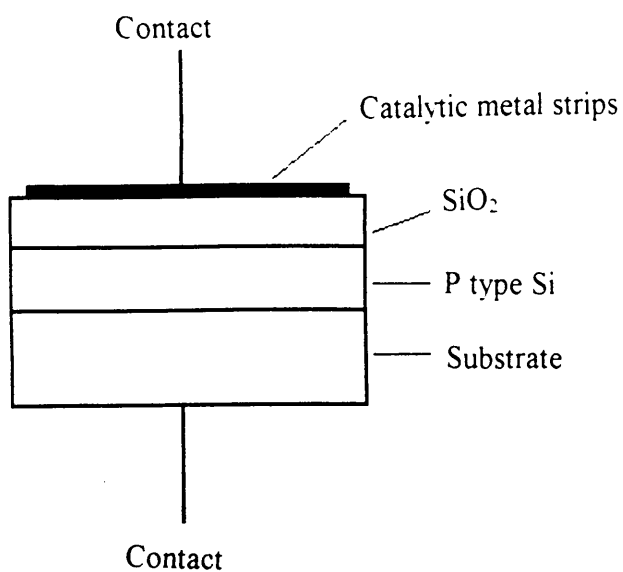
Winqvist et al [143] have described the application of an an electronic nose to the estimation of the quality of ground meats stored under polyethylene sheets. The device is comprises a flow system which sweeps sample odours through two cells, the first containing ten catalytic metal gate MOSFET devices and the second containing four commercially available Taguchi tin oxide gas sensors. A carbon dioxide sensor based upon infrared absorbance was adopted in some studies since micro organisms associated with meat decay evolve carbon dioxide. Ground samples of beef and pork were analysed over a period of seven days to assess spoilage. The results from these studies were used to train an artificial neural network to predict meat identity and time of storage. The carbon dioxide responses were omitted from some network training sessions due to the high cost of the sensor which would raise the cost of a practical measurement system of this type. Initial predictions of storage time, based upon training sets with and without the inclusion of the carbon dioxide sensor data, were rather poor. More satisfactory results were obtained using a network with fewer inputs based upon the responses of ten sensors which were considered to be the most important in terms of their contribution towards sample classification. This instrument has recently been applied to the estimation of paper quality [144]. The response data obtained from this study was screened using both principal component and clustering techniques and was predictively classified using a back propagation neural network. The authors have reported the successful discrimination of five classes of paper using these techniques based upon the responses of only four sensors.

The application of electronic odour sensing technology to robot guidance has been suggested by Deveza and co-workers [145]. They propose a strategy based upon a mobile robot detecting a trail of suitable, short-lived odorant marker material. Promising results have been obtained using a guidance system whereby a robot follows camphor floor trails using a surface acoustic wave-based odour detection system.

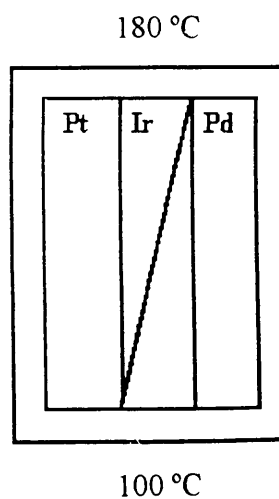
Lundstrom and co-workers have been active in the area of field effect devices for use in an artificial nose [146]. They have envisaged the construction of an "olfactory camera" comprising of a large array of field effect devices. Selectivity is to be introduced into such an array by employing a temperature gradient in one direction whilst altering sensor identity (gate composition) in the other. Hence, different areas of the array will exhibit different response characteristics towards a given analyte and a unique "picture" may be recorded. These workers have also described a gas sensor capable of yielding "olfactory images" [147]. This device is based on a field effect sensor and comprises three thin, overlapping catalytic metal strips (Pt, Ir, Pd) deposited onto a silicon dioxide surface layer. This layer has been deposited onto a p-type silicon layer which in turn has been deposited onto a substrate (figure 11). One end of the device is heated to approximately 100 °C, the other to approximately 180 °C, creating a temperature gradient which alters the properties of the metal strips along their length.

Figure 11 Schematic diagrams of a catalytic odour sensing device (Lundstrom et al)

Side view



Overhead view



A scanning light pulse technique is used to detect changes in the electronic properties of the catalytic strips caused by surface adsorption and reaction of analyte species. This yields an "olfactory image", characteristic of the analyte. Images of this type have been produced which clearly discriminate between two brands of cheese [148].

Bourronet et al [149] have applied an array of commercially available Taguchi tin oxide gas sensors to the determination of strong, unpleasant "boar taint" cooking odours in samples of pork products. An initial evaluation of fourteen Taguchi sensors allowed five sensors which exhibited the greatest degree of specificity towards a series of test mixtures to be identified and adopted in subsequent studies. A simple test rig was developed and applied to the classification of the volatile species associated with samples of pork fat. Initial results were promising but the authors envisage that the realization of a practical taint detector will require a great deal more work.

A portable odour sensing device is undergoing development at Argonne National laboratory, Illinois [150]. This instrument is designed to allow coast guard personnel to detect and identify potentially hazardous materials in situations involving shipwrecks or spillages. A prototype device comprising of a compact array of amperometric sensors was exposed to series of test vapours. Application of a variety of pattern recognition methods to the test responses including clustering and pattern recognition techniques showed that the device is capable of discriminating between all of the test series.

Yokoyama and Ebishawa have developed an "artificial olfactory sensor" which they have used to evaluate a series of fragrances [151]. An eight element surface acoustic wave array coated with a range of polymeric materials was exposed to a series of thirty seven fragrances. The responses obtained were quantified using pattern recognition techniques and then correlated to responses obtained by an odour evaluation panel by performing multiple regression analysis. The authors have reported that their array is capable of predicting human reactions to fragrances, indicating the possibility of developing a practical odour sensing device for application within the perfume industry.

The University of Leeds and Mastif Electronic Security Systems have developed an odour evaluation system named "Sentinel" which comprises of an array of conducting polymer sensors [152]. The device is to be used as an advanced door security system, identifying whether the odour response generated by a potential visitor's palm matches patterns of known individuals which are stored in memory. The sensors are reputed to contain some form of biological olfactory cells.

Ohnishi and co-workers [76] have described an odour recognition system incorporating surface acoustic wave sensors coated with Langmuir-Blodgett films. Pattern recognition techniques were applied to the responses of the sensing array to a series of commercial fragrances resulting in successful discrimination.

Xinxia and co-workers have described [73] the preparation and testing of a novel interdigital electrode lipid film odour sensor (ILOS). This device consists of a dioctadecyldimethylammonium polystyrene sulphonate film deposited onto Au/Cr finger electrodes on an Si/SiO₂ substrate. The authors have reported that their film electrode may be applied to the detection of a variety of organic species.

Nakamoto and co-workers have been active in the development of instruments based upon the mechanisms of biological olfaction. A surface acoustic wave-based device incorporating neural network pattern recognition software has been applied to the discrimination of brands of whisky where a recognition success rate of 94% was achieved [153]. This system has also been used to characterise a series of perfumes and flavourings [154]. The design was subsequently improved by the incorporation of an automatic sampling system [155]. The authors have also investigated the possibility of developing a portable gas monitor incorporating Taguchi gas sensors and neural network pattern recognition [156].

An odour evaluation system incorporating a headspace concentration system has been described by Aishima [157]. The measurement system comprises of two arrays of Taguchi tin oxide sensors, with one acting as a reference. The headspace concentrator is based upon adsorption of species on tenax and has proved most useful in studies involving alcoholic beverages by separating the aroma compounds present in each sample from the large ethanol background signal. The system was able to discriminate between a range of alcoholic beverages using pattern recognition techniques and was subsequently applied to the characterisation of coffee samples, essential oils and a range of organic compounds [158].

Abe and co-workers [159] have applied pattern recognition techniques to the responses of an eight element Taguchi tin oxide array gained from a study involving a series of odourants. The test series of odourants were classified by odour evaluation using terms such as “minty”, “ethereal” and so on. The responses of the array were investigated to determine whether any correlations existed between response and human odour description. The responses of thirty compounds produced four obvious clusters describing different odour classes.

It can be seen from the review of the literature within this area that the most significant progress towards a practical odour sensing system appears to have been achieved by workers using arrays of conducting polymer gas sensors. Indeed, the two most successful instruments of this kind to date, namely Aromascan's “AROMASCANNER” and the Neotronics “NOSETM” are based on such technology. Many prototype devices based upon Taguchi sensors, MOSFETS etc have been reported but no practical instrument has yet been developed to challenge the two previously mentioned instruments. This may be a consequence of the power requirements associated with heating such sensors to their optimum working temperatures. There is no such requirement with conducting polymer-based sensors which show relatively rapid and reproducible responses at ambient temperatures. The popularity of arrays of such sensors is probably due to their ease of preparation. An almost limitless range of materials may be polymerised in a simple controlled reaction. The properties of such polymers may also be easily modified to introduce selectivity within an array. It will be extremely interesting to see if the initial promise of arrays of conducting polymer gas sensors is fulfilled.

1.6 Aims of this work

The use of arrays of conducting polymer-based gas sensors as a potential method of routinely characterising and discriminating aromas has been investigated. Arrays of sensors connected to a computer system with appropriate software (Neotronics scientific plc) have been used to characterise a series of beverages. The system has also been applied to the discrimination of a series of tobacco samples to allow its performance to be compared to an established tobacco analysis technique, namely headspace gas chromatography.

A programme of structure response mapping using a series of individual compounds has been undertaken in an attempt to identify the specific feature(s) of an analyte to which each of the sensors respond. For example polarity, molecular size/shape, functional groups/atoms etc. The effects of aliphatic chain length in a series of esters and positional substitution in aromatic systems have also been investigated.

Some sample test results have been analysed using statistical techniques in an attempt to identify trends in the response data. This has led us to investigate alternative methods of manipulating and displaying test data since only limited options are available with the current version of the Neotronics software.

Chapter 2 Experimental.

2.1 Overview of the analysis system.

A model C NOSETM (Neotronics Scientific ltd) with associated software was used throughout the investigations. Schematic diagrams of the system hardware are shown in figure 12. This instrument does not possess any neural network capabilities.

Two different arrays of sensors, which will be referred to as head 1 and head 2, have been utilised. Each array comprised a range of polypyrrole-based sensors whose response characteristics are determined by the identity of the counter ions and solvents used during their manufacture. The identities of these materials are of a confidential nature. Head 1 was supplied with the system whilst head 2 comprised of novel sensors which were produced at this institution. Each individual sensor consists of a polymer film which is electrochemically grown over a gap between two gold electrodes on a ceramic substrate as illustrated in figure 13. Arrays are constructed by arranging the sensors in circular fashion, facing inwardly in special sealed units. This arrangement is illustrated in figure 14

Figure 12 a Schematic diagram of Nose™ hardware

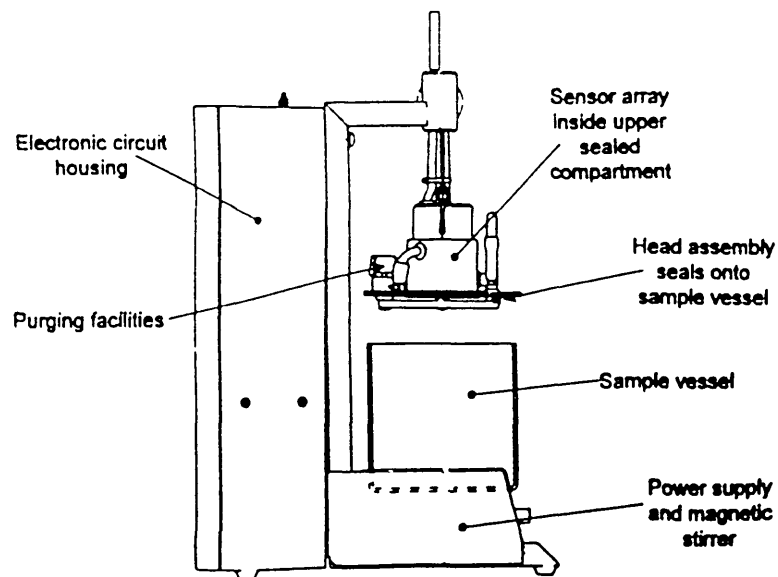


Figure 12 b Simplified diagram of system electronics

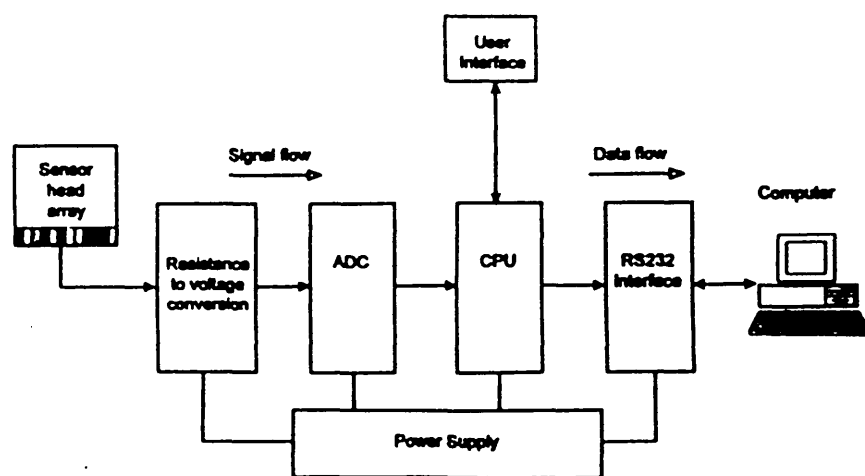


Figure 13 A typical NOSE™ sensor.

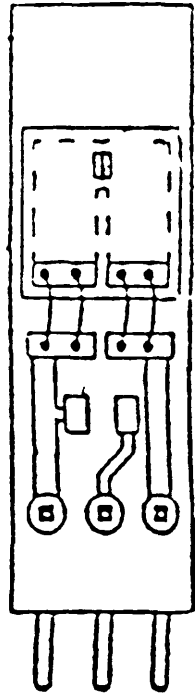
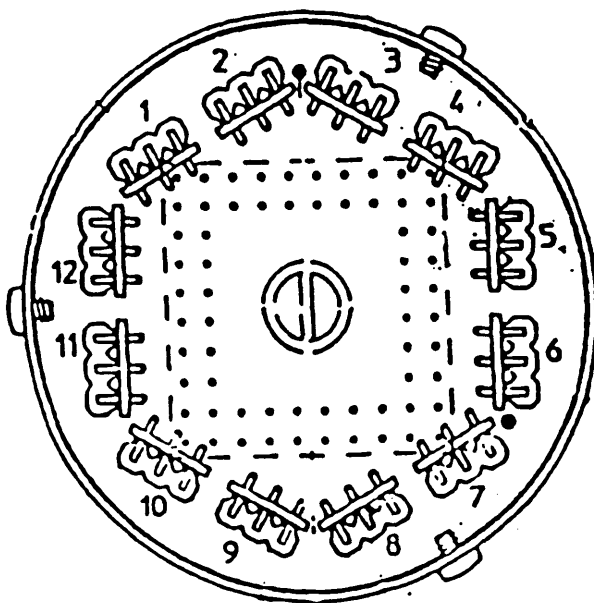


Figure 14 Underside view of a typical sensor array.



2.2 Sample preparation and introduction to sensing array.

Minimal sample preparation is required using this system but contamination of the equilibration vessel can lead to carry over of sample to subsequent tests. To minimise this effect test samples were either placed into glass sample tubes or on watch glasses rather than being placed directly into the equilibration vessel.

Sample introduction is based upon a static headspace design. With reference to figure 12a, the test sample is sealed into the glass vessel by lowering the sensor array to form an airtight seal. Initially, the sensor array and sample vapour remain in separate sealed compartments. Purging of the sample and/or array may be performed simultaneously (section 2.4). Once the sample has reached equilibrium (typically after a period of ten to fifteen minutes) the trap door between the two compartments is opened which initiates the acquisition of sample data .

2.3 Sensor response and recovery.

Many of the sensors that have been investigated do not achieve a steady state response even after being exposed to an analyte for several minutes. Experience has shown that the sensors appear to exhibit one the following response behaviours :

- i) An initial, rapid change in response followed by a more gradual change.
- ii) A slow, gradual response change over the acquisition period.

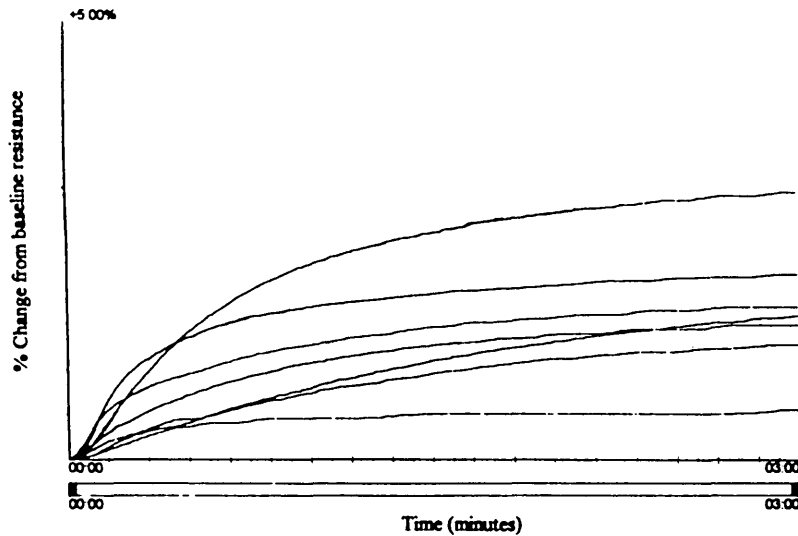
A typical set of responses is shown in figure 15 where both types of behaviour can be clearly seen.

In most cases, a large proportion of the full change in sensor response is observed after approximately sixty to ninety seconds of exposure to an analyte. The responses of the sensors may be determined at any point during the acquisition period. It is usual to quote the responses obtained after sixty seconds of exposure to an analyte as being the test results.

Changes in temperature can affect both the sensitivity of the sensors and the volatility of test samples. Lagging of the sample vessel and head assembly with insulating material was found to be impractical and we must assume that test results have been affected to some degree by temperature effects resulting from the day to day variation in the temperature of the laboratory.

It is important to allow sufficient time between tests for the sensors to recover. If the array is exposed to another sample before the sensors have fully recovered, sensitivity will be affected. The system software contains a preset minimum recovery time and will not allow further acquisition of data until at least fifteen minutes has elapsed from the end of the previous test. In all investigations therefore, a standard recovery time of fifteen minutes was allowed between tests. Recovery was aided by purging the array with air which is considered in section 2.4.

Figure 15 A typical set of responses (red wine).

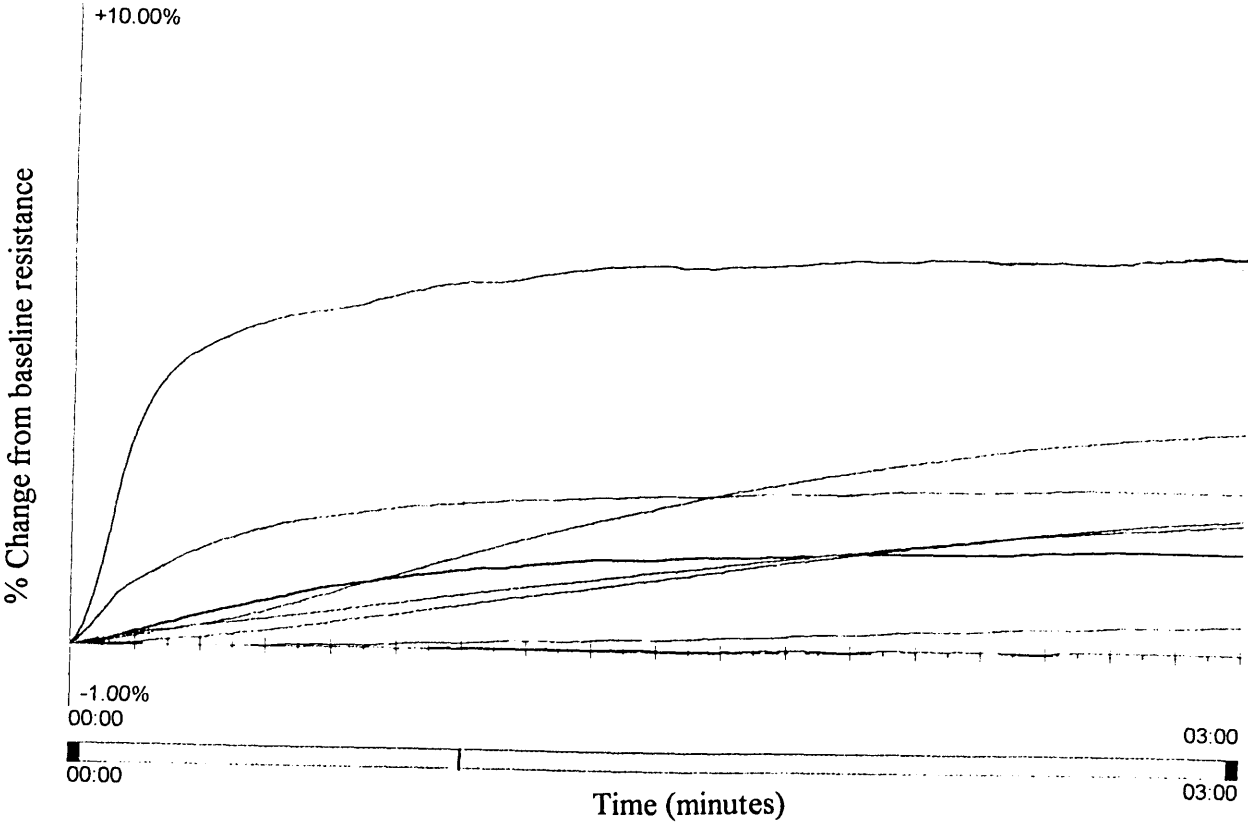


2.4 Purging.

We have used air as reference compound in our studies. The response of the array to cylinder air (BOC) was determined at the beginning of each working day to ensure that the system was responding satisfactorily. A satisfactory response was defined as all sensors in the array exhibiting a change in baseline resistance no greater than 0.05 %. If necessary, the test procedure was repeated until all sensor responses were of this magnitude.

In our early investigations, the array was purged with dry air directly from a cylinder. This practice caused permanent damage to the sensors in head 1 which began to yield very high responses to the cylinder air (as illustrated in figure 16) and erratic responses to test samples. This damage was probably caused by cracking of the polymer films as they dried out. A bubbler containing a saturated solution of potassium chloride was introduced into the purging line to allowing purging to be performed at approximately 30 % relative humidity. Purging at this level of humidity appeared to have no adverse effect on either the response or performance of the sensors. Due to financial constraints, head 1 could not be replaced and subsequent investigations were performed using head 2 which had been prepared to perform contracted work.

Figure 16 Response of head 1 to cylinder air after prolonged purging with dry air.

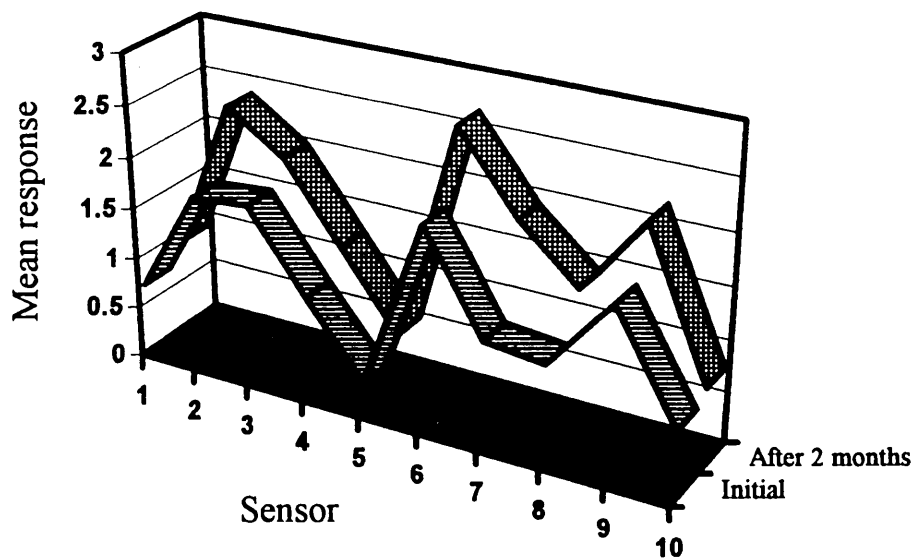


2.5 Calibration.

Figure 17 presents the results of a simple test in which an array was exposed to samples of methanol on two separate occasions, two months apart. It is clear from this investigation that the responses of the sensors drift with time. It is therefore essential that the array is calibrated on a routine basis. This essentially involves setting up a fixed voltage across each sensor using calibration potentiometers. Calibration was performed at the beginning of each new program of work. Sensor calibration can be significantly affected if the instrument is moved or disturbed and therefore all investigations were performed in a vibration free environment.

Figure 17 Drift of sensor response to methanol over a two month period.

(All sensor responses are the averaged results of ten tests).



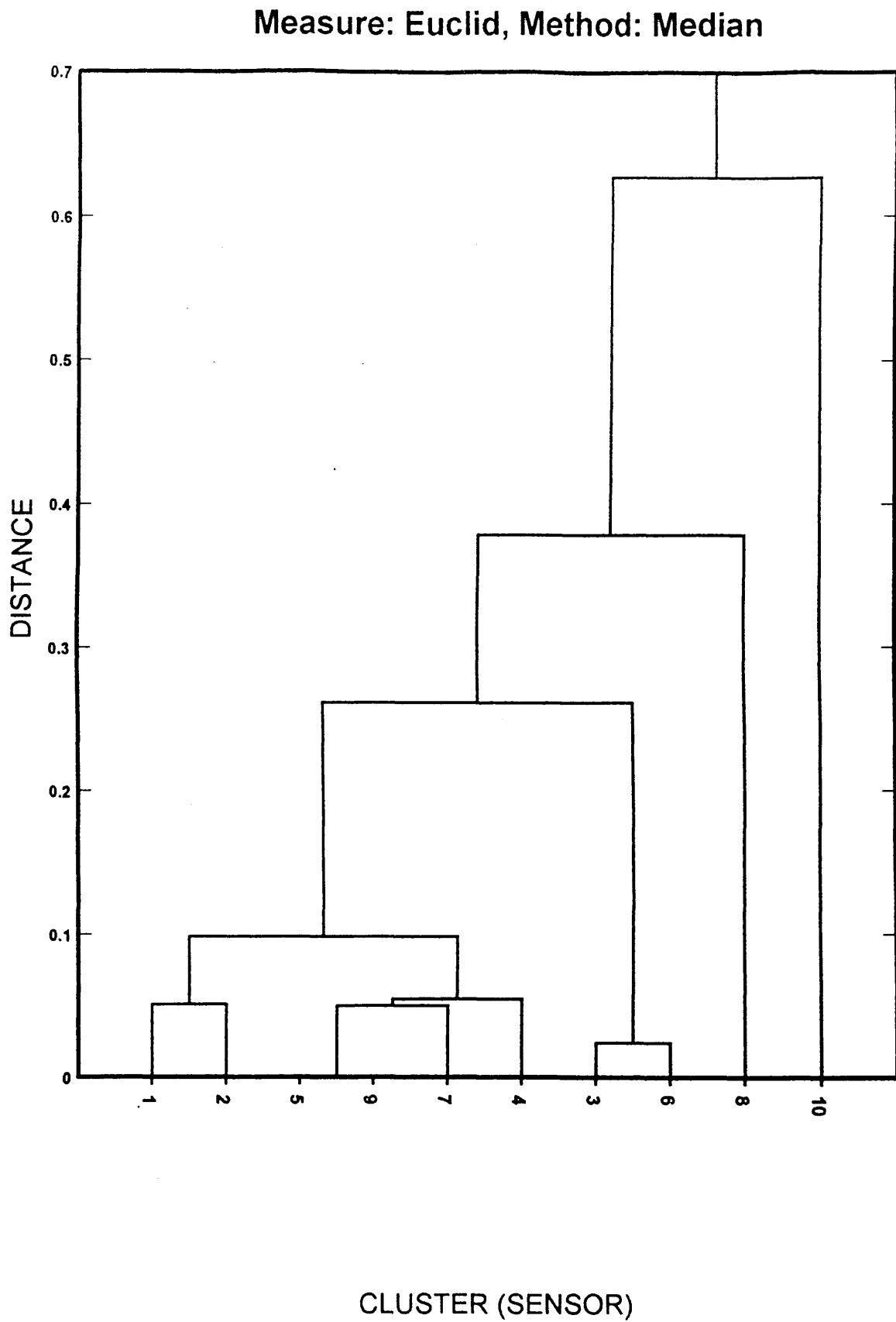
2.6 Cluster analysis.

Response data obtained from some of the investigations were analysed using five different Euclidean distance cluster methods using a suitable software package (UNISTAT 3.0). The methods adopted were median, centroid, single linkage, complete linkage and group average. Results from these analyses are displayed as dendograms which link variables according to their similarity. An example dendogram created from the responses of a ten sensor array to three samples of snuff tobacco (presented in table 1) is shown in figure 18. The y-axis of the plot indicates the relative distance or similarity between data points. Variables which exhibit a high degree of similarity link at low distances. For example, sensors 3 and 6 exhibit very similar responses for the three samples. Sensors 9 and 5 have identical responses for each sample (indicated by the vertical line between these values on the x axis) which are also similar to the responses of sensor 7 which are in turn similar to those of sensor 4 which exists in a lone cluster. The cluster containing these four sensors links with the cluster containing sensors 1 and 2 at a relative distance of 0.1 indicating some degree of similarity. Sensors 8 and 10 exist in lone clusters and exhibit very dissimilar response behaviour. The dendogram therefore indicates that several sensors in the array are responding in a very similar fashion, leading to a reduction in the potential discrimination possible with the array. This is a straightforward example to illustrate cluster analysis whose usefulness increases when dealing with larger data sets.

Table 1 Sensor responses to three samples of snuff tobacco

Sensor	Sample 1	Sample 2	Sample 3
1	0.19	0.20	0.15
2	0.23	0.23	0.16
3	0.40	0.45	0.34
4	0.25	0.35	0.23
5	0.20	0.30	0.20
6	0.41	0.46	0.36
7	0.25	0.30	0.20
8	0.10	0.01	0.05
9	0.20	0.30	0.20
10	0.31	0.56	0.8

Figure 18 An example dendrogram.



2.7 Manipulation of sample test results.

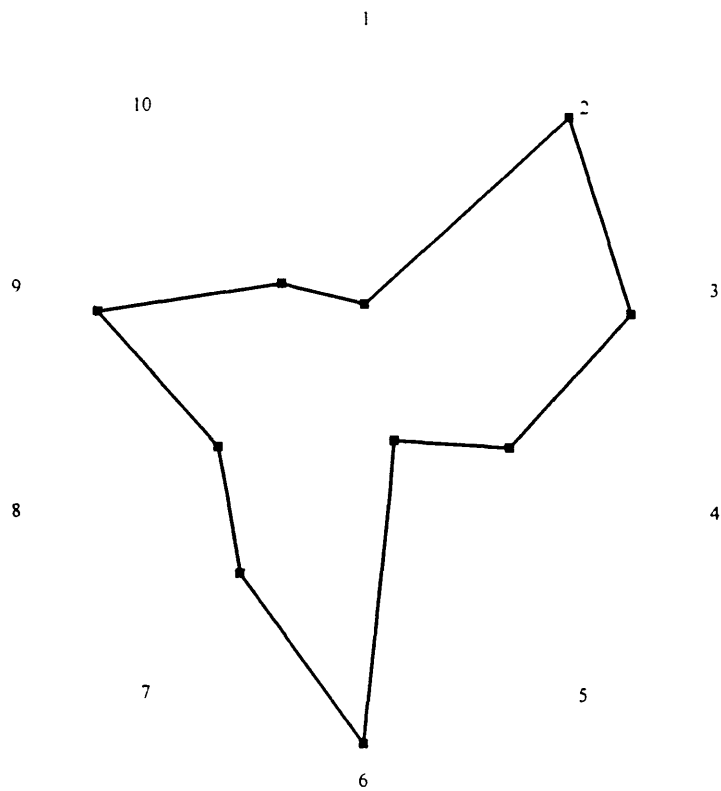
2.7.1 Reference templates.

Test results may be combined using the system software to create a reference template. Sensor responses are averaged over the tests selected and standard deviation data is automatically calculated for templates comprising of three or more sample tests. In practise, a reference template may be used to establish a standard for a particular analyte against which subsequent sample tests may be compared. This is a procedure recommended by Neotronics. Experience has shown that a template produced from several tests on water alone to be an adequate blank to subtract from sample response data to yield adjusted data and response patterns.

2.7.2 Presentation of test results.

Results may have been displayed in a variety of styles which were created using suitable software packages (Microsoft Excel 4.0 and UNISTAT 3.0). Radar plots have been adopted to study the unique nature of the response pattern generated by the array for a given test compound. Note the use of these “fingerprints” to compare the magnitude of responses between different compounds is impractical since they are displayed at a variety of scales. An example radar plot which displays the pattern of response generated by a sample of n-hexane is illustrated in figure 19

Figure 19 Pattern of response generated by a sample of n-hexane presented as a radar plot. The numbering indicates the identity of each sensor



Ribbon diagrams have also be adopted which are sometimes a clearer alternative means of comparing the profiles of different samples.

Chapter 3 Analysis of beverages.

3.1 Mineral waters.

In a number of areas of industry, overdosing or underdosing of an ingredient during production could have a marked effect upon the quality of the final product. Routine quality control analysis of the final product may not detect the problem until significant wastage has occurred. A method by which samples removed from various stages of production could be rapidly profiled and compared to standards of known quality would prove to be of great use.

The industrial scenario was simulated in the laboratory using a ten bottle batch of sparkling citrus flavoured mineral water. Underdosing of the flavouring was simulated by diluting aliquots of the mineral water with distilled water. The response patterns of these samples were compared to the pattern of a reference template (created by averaging the response patterns generated by ten samples from the batch) to determine whether the array was capable of distinguishing between subtle changes in the level of flavouring present in the presence of a high water background.

A small aliquot of mineral water was removed from each bottle in the batch to yield a series of ten test samples. All samples were degassed in an ultrasonic bath for a period of fifteen minutes prior to analysis to remove carbon dioxide which is known to affect sensor response. Each of the samples was then exposed to the array in turn. The responses generated by these ten tests were combined to produce a reference template. The experimental conditions adopted in these tests are outlined below :

Array : Head 1.

Sample size : 10 drops.

Equilibration time: 10 minutes.

Purging : 2 minutes (sensors) with dry air.

Acquisition time : 3 minutes.

Analysis point : @ 1 minute.

A randomly chosen bottle from the batch was used to produce a series of test samples exhibiting a flavouring deficiency. Aliquots of degassed mineral water (2, 4, 6 and 8 ml) were diluted to 10 ml using distilled water and then profiled under the same test conditions used to create the reference template. Each sample was profiled once only.

The sensor response data presented in table 2 illustrate that significant differences exist between some of the individual sensor responses to each sample. However, there appears to be no simple correlation between the level of flavouring present in a sample and the magnitude of the sensor responses it generates.

The normalised (division of responses by the highest response obtained for each sample) response data presented in table 3 illustrate that the ratio in which the individual sensors respond with respect to each other is virtually identical for all of the test samples and the reference template. Thus, although individual sensor responses are different for each sample, the patterns of response they generate are virtually identical. These response patterns are presented in figure 20.

Table 2 Responses of an array of sensors to a series of mineral water test samples.

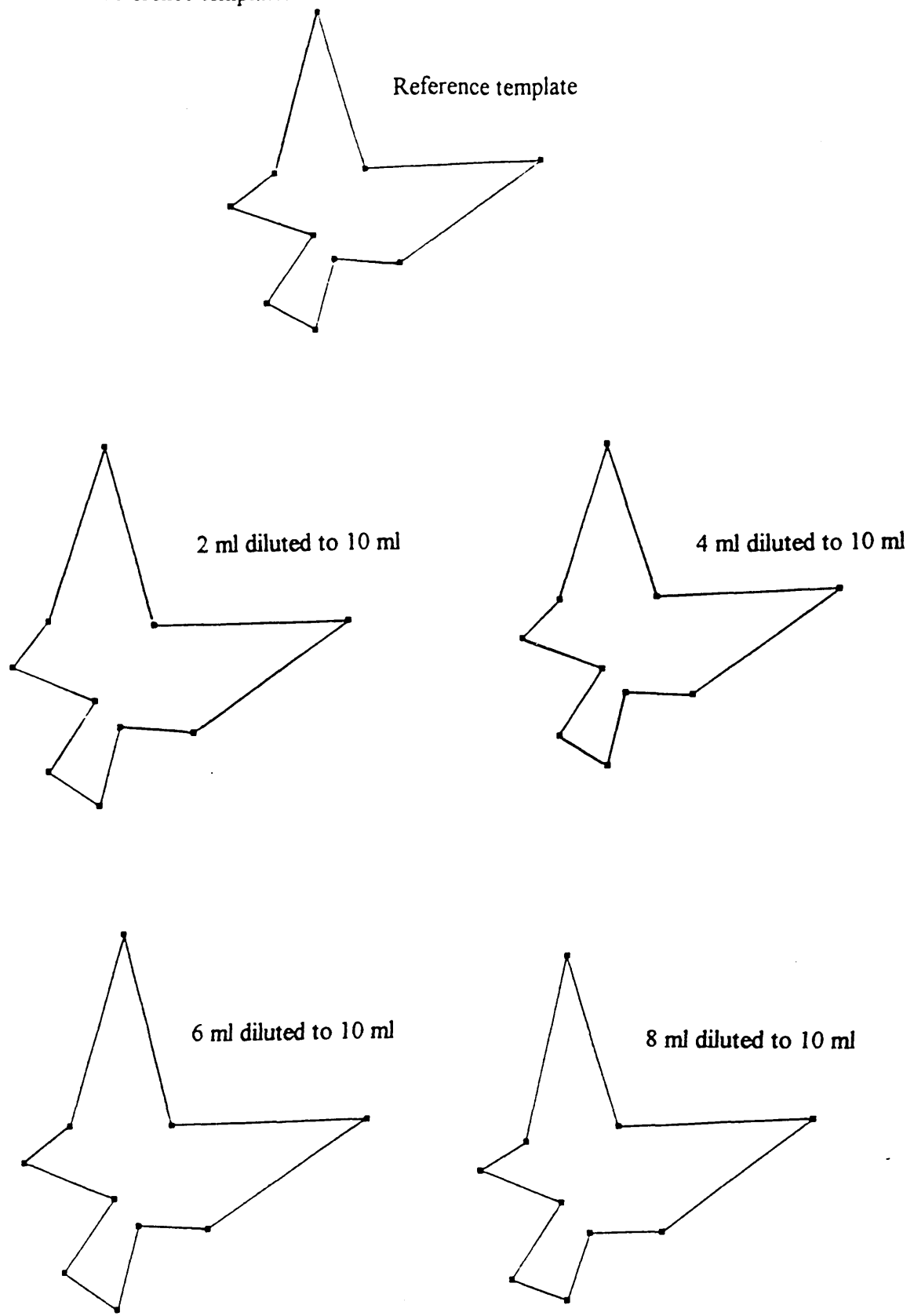
Sensor	Reference template	8 ml diluted to 10 ml	6 ml diluted to 10 ml	4 ml diluted to 10 ml	2 ml diluted to 10 ml
1	2.86	2.70	2.92	2.87	2.79
2	1.07	1.01	1.01	1.12	1.03
3	3.12	2.88	2.97	3.17	2.96
4	1.16	1.12	1.07	1.17	1.13
5	0.40	0.44	0.38	0.41	0.38
6	1.24	1.10	1.24	1.27	1.18
7	1.10	1.08	1.04	1.10	1.01
8	0.05	0.07	0.06	0.07	0.07
9	1.22	1.06	1.16	1.20	1.08
10	0.98	0.80	0.97	1.07	1.05

Table 3 Normalised response data for the tests involving mineral water.

Sensor	Reference template	8 ml diluted to 10 ml	6 ml diluted to 10 ml	4 ml diluted to 10 ml	2 ml diluted to 10 ml
1	0.94	0.94	0.98	0.91	0.94
2	0.35	0.35	0.34	0.35	0.35
3	1.00	1.00	1.00	1.00	1.00
4	0.37	0.39	0.36	0.37	0.38
5	0.13	0.15	0.13	0.13	0.13
6	0.39	0.38	0.42	0.40	0.40
7	0.35	0.38	0.35	0.35	0.34
8	0.02	0.02	0.02	0.02	0.02
9	0.39	0.37	0.39	0.38	0.36
10	0.31	0.28	0.33	0.34	0.35

Figure 20 Response patterns generated by each mineral water test sample and the

reference template.



The level of discrimination achieved between the different samples is very poor.

However, when the reference template is subtracted from each of the test samples, a series of unique patterns is produced. The four response patterns given in figure 21 show that we can clearly discriminate between the different levels of flavouring in the test samples.

The standard deviation data for the tests used to create the reference template are presented in table 4. This data can be considered to be of limited value as it does not take the magnitude of the sensor responses into account. For example, a standard deviation of 0.5 can be considered to be insignificant for very large response values but highly significant for very small ones. More meaningful data are obtained by calculating the % relative standard deviation (% RSD) for each sensor :

$$\% \text{ RSD} = \frac{\text{Standard deviation}}{\text{Mean response}} \times 100$$

The % relative standard deviation data presented in table 4 clearly indicate that the responses of sensor 8 (% RSD of 80) should be viewed with little confidence. It would seem advisable to either ignore this sensor or replace it with an alternative one.

The results from this investigation show great promise. However, it is difficult to place a confidence level on this investigation due to the lack of standard deviation data for the tests for each of the flavouring deficiency samples. Unfortunately, it was unfeasible to repeat this investigation since head 1 could not be replaced.

Figure 21 Unique patterns are created for each flavouring deficiency sample by subtraction of the reference template from the raw response patterns.

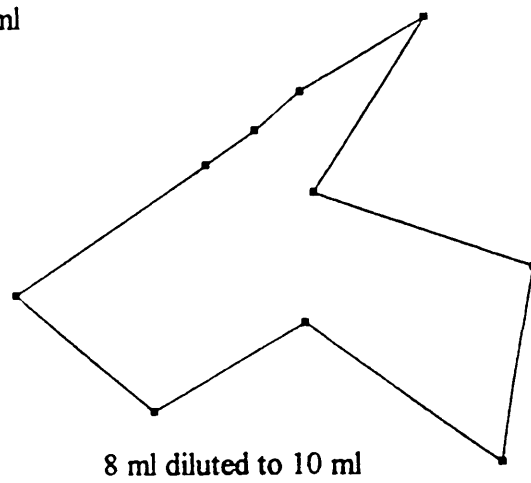
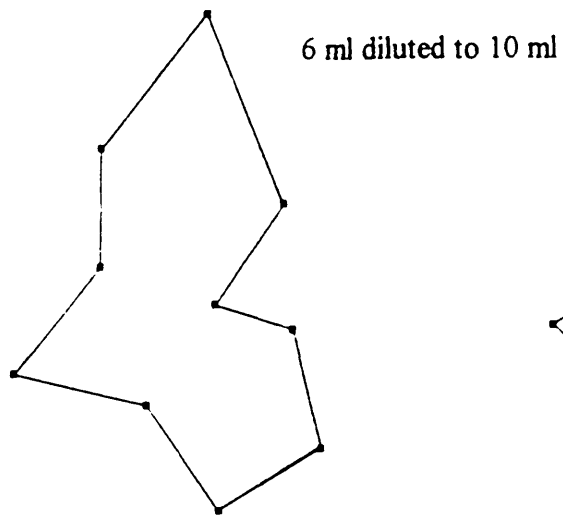
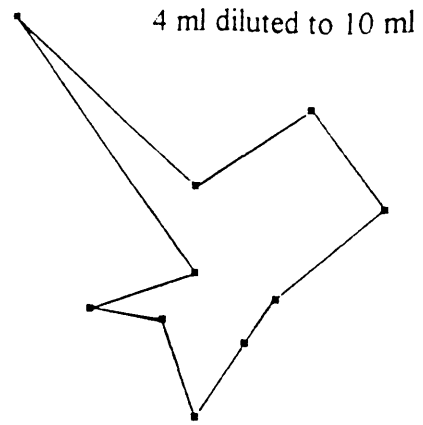
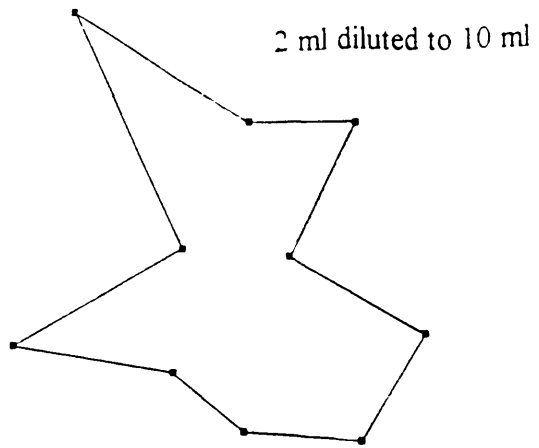


Table 4 Standard deviation and % relative standard deviation of the ten tests which were combined to produce the reference template.

Sensor	Standard deviation	% RSD
1	0.74	26
2	0.17	16
3	0.47	15
4	0.12	10
5	0.06	15
6	0.20	16
7	0.13	12
8	0.04	80
9	0.30	25
10	0.29	30

3.2 Cola drinks.

The reference template subtraction procedure used in the mineral water analysis investigation was adopted to profile a series of cola soft drinks. Again, the flavourings in the drinks are present in samples in which water is the major component. Subtraction of a water reference template (blank) from the response pattern of each cola drink should theoretically yield a series of unique response patterns based solely upon the flavourings present in each drink.

Four cola samples were profiled :

- i) A well known American brand name.
- ii) The diet version of the above.
- iii) The Caffeine free diet version of the above.
- iv) A British supermarket brand.

A small aliquot of each cola was placed in an ultrasonic bath for a period of fifteen minutes to ensure total degassing prior to analysis. Five replicate tests were performed on each cola to allow the calculation of standard deviation data from the mean responses. A water reference template (blank) was prepared in a similar manner using distilled water. The following test conditions were adopted :

Array : Head 2.

Sample size : 5 drops.

Equilibration time : 15 minutes.

Purging : 15 minute (sensors) with 30 % r.h air.

Aquisition time : 3 minutes.

Analysis point : @ 1 minute.

At first sight the sensor responses generated by each sample exhibit sufficient differences to allow discrimination between the different brands of cola, these data are presented in table 5. The standard deviation of the tests are presented in table 6. It is interesting to note that the response patterns generated by the four brands which are presented in figure 22 are all very similar to the pattern of the water reference template. This may indicate that the responses are dominated by the water in the drinks which is masking the response due to the flavourings. Discrimination on the basis of the raw patterns is therefore not practical. The magnitude of the response to each cola is quite different and suggests that a modified approach may be fruitful.

Figure 23 shows that a unique “fingerprint” is indeed produced for each cola brand by subtracting the water reference template from each of the response patterns. However, the data presented in table 7 show that the majority of sensors display totally unacceptable % relative standard deviation values. This is a consequence of the small differences which exist between some of the cola responses and those obtained for the water blank. For example, the difference between the responses obtained for the blank and the brand name cola is only 0.02% change from baseline resistance in the case of sensor 1. The level of precision achieved in this investigation is therefore very poor and many of the results can be viewed with little confidence. It is important to realise that this discussion is based upon % RSD calculated from the raw response data and it would seem better practice to base such an analysis on the adjusted response data which was the basis of the “unique” radar plots and these data are presented in table 8. The standard deviation and % RSD calculated from the adjusted data are presented in tables 9 and 10 respectively. It is possible that the poor test reproducibility may have been caused by inefficient recovery of sensors between tests. Many of the responses were rather high and the sensors may have had insufficient time to return to their equilibrium conditions before subsequent tests. It may therefore be necessary to adopt a longer purging time or a different purging strategy in an attempt to optimise sensor recovery and test reproducibility.

It would seem highly advisable to repeat this study on a regular (weekly/monthly) basis to investigate the poor level of precision which has been encountered. The high % RSD values which were observed for some sensors may mean that significantly different response patterns would be obtained in a repeat study.

If the problems associated with poor precision could be overcome, this characterisation procedure could prove to be extremely useful in many areas of application. For example, in the area of detecting fake perfumes the integrity of a sample could be checked in a matter of minutes which is far faster than by using established chromatographic-based techniques. It may also be possible to apply this strategy to other sample types such as subtraction of an ethanol template when profiling spirits to yield response patterns which would theoretically be based solely upon the flavourings present in each brand.

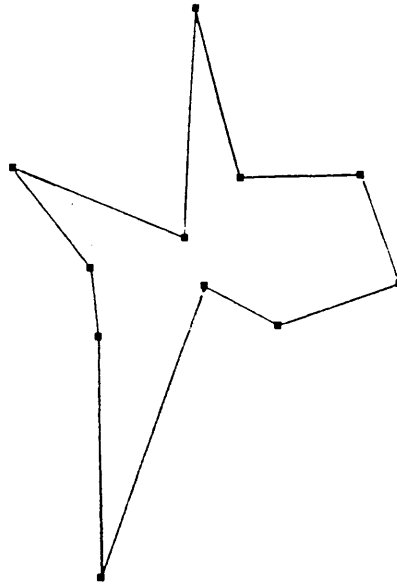
Table 5 Responses of an array of sensors to a series of cola soft drinks and a sample of water.

Sensor	Brand name	Diet	Diet caffeine free	Supermarket	Reference template
1	4.23	5.30	5.06	3.94	4.21
2	1.74	1.38	1.30	1.75	1.56
3	3.34	3.58	3.59	3.31	3.24
4	3.96	3.53	3.36	3.98	3.67
5	2.20	1.97	2.02	2.10	1.95
6	0.64	0.70	0.68	0.62	0.61
7	9.67	6.03	6.75	6.89	5.90
8	2.57	2.50	2.62	2.30	2.25
9	2.05	1.99	2.04	1.96	1.88
10	3.88	3.53	3.54	3.76	3.54
11	0.22	0.05	-0.24	-0.02	0.31

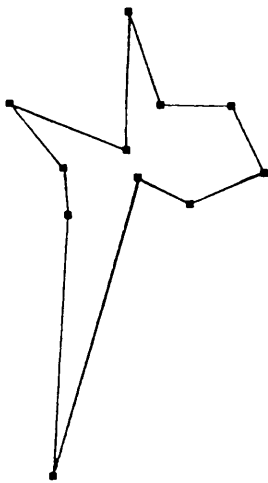
Table 6 Standard deviation of the tests involving a series of cola drinks.

Sensor	Brand name	Diet	Diet caffeine free	Supermarket	Reference template
1	0.58	0.19	0.28	0.36	0.66
2	0.14	0.07	0.06	0.21	0.04
3	0.38	0.28	0.24	0.47	0.15
4	0.31	0.24	0.11	0.53	0.15
5	0.18	0.11	0.09	0.20	0.10
6	0.03	0.06	0.04	0.07	0.02
7	4.03	1.00	0.71	1.52	0.49
8	0.32	0.18	0.14	0.27	0.13
9	0.14	0.07	0.12	0.12	0.09
10	0.31	0.20	0.15	0.34	0.15
11	0.48	0.60	0.55	0.51	0.29

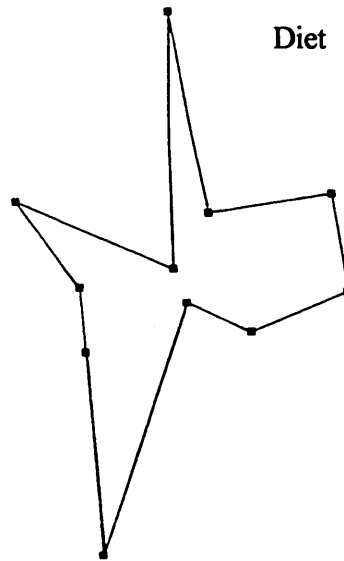
Figure 22 Response patterns generated by the water blank and the four brands of cola.



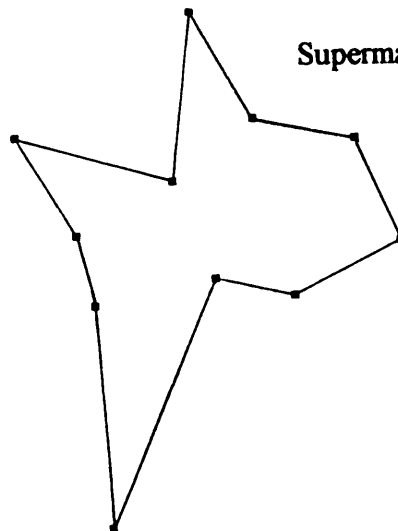
Brand name



Diet



Supermarket



Diet Caffeine free

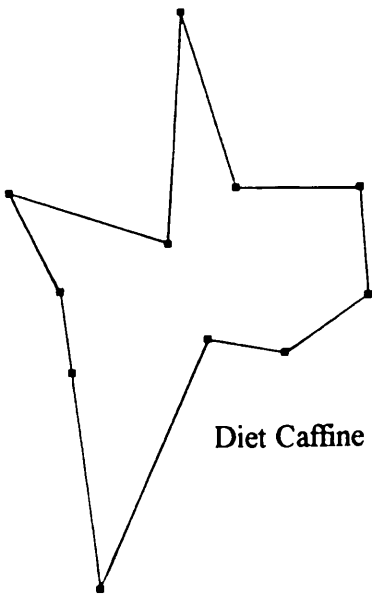


Figure 23 A unique “fingerprint” pattern is produced for each cola by subtracting the water reference template from the raw patterns

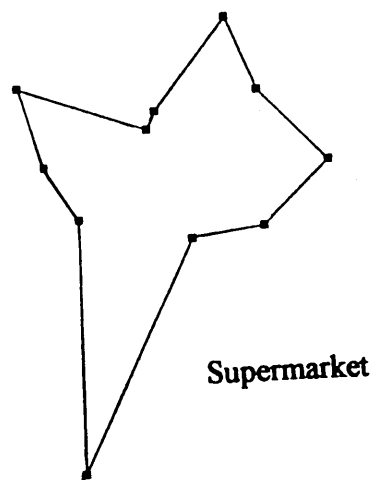
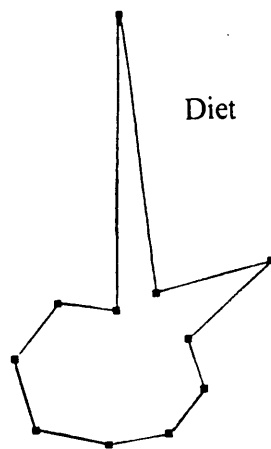
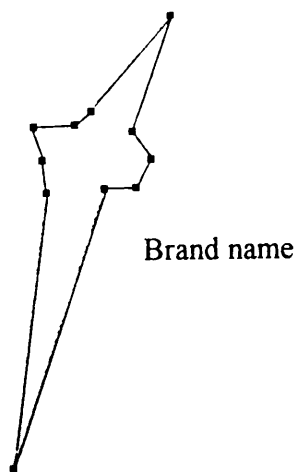


Table 7 % relative standard deviation of the cola drink tests.

Sensor	Brand name	Diet	Diet caffeine free	Supermarket	Reference template
1	2900	17	33	133	16
2	380	39	23	111	3
3	107	82	69	671	5
4	62	171	37	171	4
5	72	550	129	133	5
6	100	67	57	700	3
7	107	769	84	154	8
8	100	72	38	540	5
9	82	39	75	150	5
10	91	2000	0	425	4
11	533	231	100	155	94

Table 8 Adjusted response data for the cola drinks.

Sensor	Brand name	Diet	Diet Caffeine free	Supermarket
1	0.02	1.09	0.85	-0.27
2	1.56	-0.18	-0.26	0.19
3	0.10	0.34	0.35	0.07
4	0.29	-0.14	-0.31	0.31
5	0.25	0.02	0.07	0.15
6	0.03	0.09	0.07	0.01
7	3.77	0.13	0.85	0.99
8	0.32	0.25	0.37	0.05
9	0.17	0.18	0.16	0.08
10	0.34	-0.01	0.00	0.22
11	-0.09	-0.26	-0.55	-0.33

Table 9 Standard deviation of the adjusted response data for the cola drinks.

Sensor	Brand name	Diet	Diet caffeine free	Supermarket
1	0.46	0.56	0.32	0.33
2	0.07	0.04	0.03	0.10
3	0.18	0.14	0.13	0.22
4	0.15	0.13	0.08	0.25
5	0.09	0.07	0.06	0.10
6	0.02	0.01	0.02	0.03
7	1.81	0.50	0.39	0.71
8	0.15	0.10	0.09	0.13
9	0.07	0.05	0.07	0.07
10	0.15	0.11	0.09	0.17
11	0.25	0.30	0.28	0.26

Table 10 % relative standard deviation for the adjusted response data.

Sensor	Brand name	Diet	Diet caffeine free	Supermarket
1	2300	51	38	122
2	4	22	12	53
3	180	41	37	32
4	52	93	26	124
5	36	350	86	67
6	67	11	29	33
7	48	384	46	72
8	47	40	24	260
9	41	28	44	88
10	44	1110	0	129
11	36	115	51	79

Chapter 4 Discrimination of tobacco samples.

4.1 Introduction

Tobacco leaves contain many thousands of compounds [160, 161] and hence their aromas are rather complex. Tobacco is categorised into varieties such as Burley, Oriental (Turkish) and Virginia (Flue-cured) which differ in their growth conditions, aromas etc. Cigarette tobacco is usually a blend of these three varieties. The characterisation of tobacco blends is generally performed by gas chromatography-based methods which can be rather time consuming and reflect the composition of a sample rather than its aroma. The application of the sensing array to produce sample profiles based on aroma could therefore yield potentially very useful information. The ability of the array to discriminate between a series of tobacco samples was critically compared with an alternative technique, namely headspace gas chromatography.

4.2 Experimental.

Headspace gas chromatography [162-164] is essentially the analysis of the volatile species in equilibrium with a sample rather than the sample itself. All analysis was performed using a Perkin-Elmer HS6 headspace injection system [165] installed on a model 8600 instrument. In this system, samples are sealed into glass vials using ptfelined aluminium caps. The vials are then equilibrated in a temperature programmable sample magazine to allow sample vaporisation. A schematic diagram of this arrangement is presented in figure 24 a.

The sampling needle is connected to the carrier gas line and is isolated by a septum to prevent loss of carrier gas during equilibration. Sample injection is initiated manually by raising the sample magazine which causes the needle to pierce the septum and enter the sample vial. Carrier gas enters the vial until the pressure within the vial is equal to that at the column head. This process is illustrated in figure 24 b.

Transfer of the sample onto the column is initiated by a solenoid valve which stops the flow of carrier gas into the vial. This results in the sample volatiles expanding through the needle and onto the column. Finally, the solenoid valve reopens, stopping the injection and starting the chromatogram as shown in figure 24 c.

Figure 24 a Sample equilibration in Perkin Elmer HS6 headspace injection system.

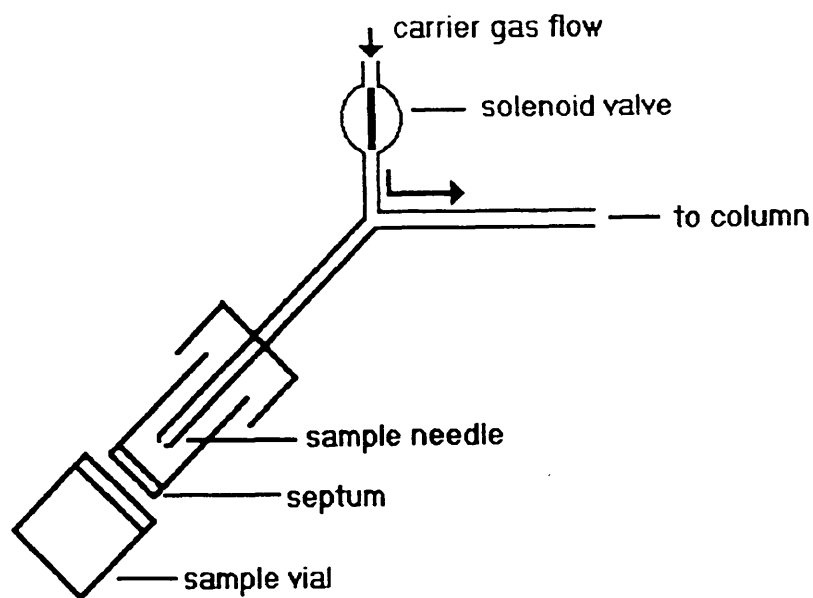


Figure 24 b Pressurisation of sample vial.

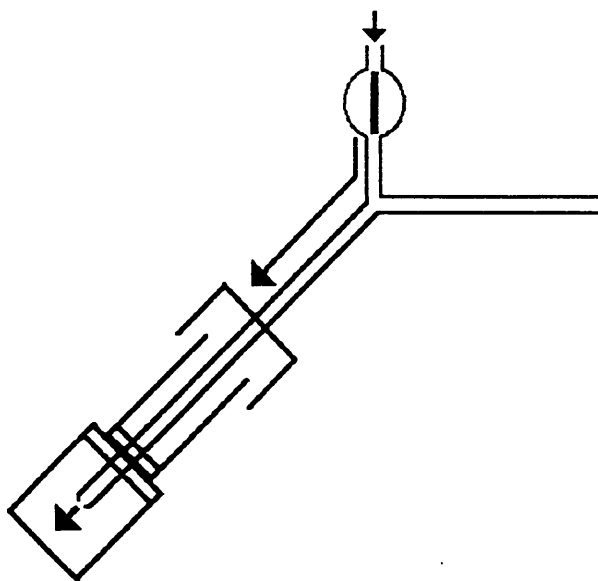
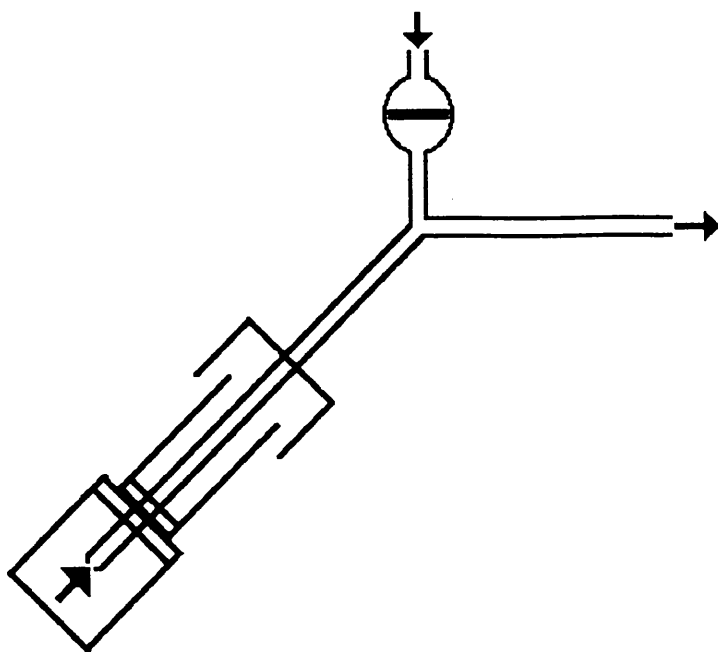


Figure 24 c Injection of sample headspace onto column.



Samples of Burley, Oriental and Virginia tobaccos were stored at approximately 60% relative humidity prior to analysis to re-introduce some moisture into the leaves since they had become very dry during transit. In total, nine samples were profiled, namely two samples of American origin and one sample of German origin for each of the three varieties.

Five replicate test were performed on each tobacco sample to allow the calculation of standard deviation from the averaged response data. The following test conditions were adopted :

Array : Head 1

Sample size : 0.1g

Equilibration time : 15 Minutes.

Purging : 5 minutes (vessel and sensors) with dry air.

Acquisition time : 3 minutes.

Analysis point : @ 1 minute.

Many problems were encountered during the chromatographic analysis and much method development was required to produce adequate chromatograms. The two most serious instrumental problems were the presence of water within the carrier gas line leading to poor run reproducibility and poor detector performance due to bad alignment of the jet assembly. Attempts to realign the jet proved to be unsuccessful and several parts of the detector had to be replaced.

Very little information has been reported on this area in the literature and hence each experimental parameter (sample equilibration time/temperature, temperature program, column identity etc) had to be individually optimised to create an analysis method. Three different columns, namely Carbowax, 2% BPX and 5% BPX were available and each was investigated in turn. The 5% BPX column appeared to yield the most satisfactory separations and was the basis of all subsequent studies. Variation of the sample equilibration temperature indicated that the samples were prone to burning at temperatures in excess of 150 °C whilst chromatograms of poor quality (too few peaks) were produced by adopting a temperature below 120 °C. A variety of temperature programs were investigated, with the best separations achieved using a relatively slow (10 °C/min) ramp. A holding period at the initial temperature was found to be essential to achieve adequate separation of the most volatile tobacco constituents at the beginning of the chromatogram. The experimental conditions which were finally adopted are summarised below :

Column : BPX5 (12.5 M, 0.32 mm id)

Detection : Flame ionization (@ 330 °C)

HS6 headspace injection system conditions : Samples equilibrated at 150 °C for 45 minutes prior to injection.

Temperature program : 35 °C (held for 2 minutes) to 280 °C at 10 °C/ min.

4.3 Discrimination on the basis of response patterns.

The sensor responses obtained for each of the tobacco samples are presented in tables 11-13. The standard deviation associated with these tests are presented in tables 14-16. The response patterns resulting from these data are given in figure 25 and show that the tobacco samples yield a series of very similar response patterns. It is possible to discriminate between samples of different varieties to a limited extent but extremely difficult to distinguish between samples within a given single variety. It is interesting to note that all of the tobacco patterns closely resemble the pattern of the water template that was employed in the beverage investigations. This would appear to indicate that the array is responding to moisture within the test environment which is masking the signal due to the volatile species associated with the tobacco samples.

The raw response data were adjusted by subtracting the responses of a water reference template from the averaged responses of each tobacco sample. These adjusted data are presented in tables 17-19. the standard deviation associated with these adjusted data are presented in tables 20-22 . A second series of radar plots (difference plots) was created using the adjusted data which should theoretically be based solely upon the aroma of each tobacco. These patterns which are presented in figure 26 show that a much greater level of discrimination may be achieved between the samples using this strategy. Many of the samples now exhibit a unique “fingerprint” response pattern allowing discrimination not only between samples of different varieties but also between samples within a single variety. However, the patterns obtained for the second American Oriental sample, the German Oriental sample and the German Virginia sample are all very similar and it is more difficult to distinguish between these samples. This situation may be improved by presenting the data in an alternative form. The responses of the three samples within each variety are compared as ribbon diagrams in figure 27. These plots show clearer discrimination between the Virginia tobacco and the two Oriental samples but suggest that the second American Oriental sample and the German Oriental sample have almost identical aromas which cannot be easily distinguished.

Table 11 Responses of an array to three samples of Burley Tobacco.

Sensor	American 1	American 2	German
1	0.71	0.55	0.70
2	0.17	0.13	0.15
3	0.60	0.45	0.62
4	0.10	0.09	0.12
5	0.04	0.01	0.02
6	0.17	0.13	0.18
7	0.12	0.10	0.14
8	0.00	0.00	0.00
9	0.36	0.25	0.37
10	0.31	0.23	0.24

Table 12 Responses of an array to three samples of Oriental Tobacco.

Sensor	American 1	American 2	German
1	0.64	0.35	0.35
2	0.11	0.05	0.08
3	0.47	0.27	0.27
4	0.03	0.01	0.06
5	0.00	-0.02	0.00
6	0.11	0.07	0.07
7	0.07	0.05	0.07
8	0.01	0.00	0.00
9	0.28	0.14	0.16
10	0.28	0.14	0.14

Table 13 Responses of an array to three samples of Virginia tobacco.

Sensor	American 1	American 2	German
1	0.83	0.73	0.41
2	0.21	0.14	0.10
3	0.73	0.58	0.37
4	0.10	0.08	0.07
5	0.00	0.00	0.00
6	0.22	0.17	0.10
7	0.14	0.10	0.08
8	0.00	0.01	0.01
9	0.44	0.34	0.24
10	0.43	0.31	0.22

Table 14 Standard deviation of the responses obtained for the Burley samples.

Sensor	American 1	American 2	German
1	0.17	0.10	0.27
2	0.04	0.03	0.03
3	0.15	0.04	0.18
4	0.04	0.02	0.03
5	0.02	0.01	0.03
6	0.03	0.03	0.05
7	0.05	0.00	0.03
8	0.00	0.00	0.03
9	0.11	0.04	0.11
10	0.10	0.06	0.11

Table 15 Standard deviation of the responses obtained for the Oriental samples.

Sensor	American 1	American 2	German
1	0.20	0.11	0.11
2	0.05	0.03	0.03
3	0.14	0.08	0.10
4	0.03	0.02	0.02
5	0.03	0.03	0.00
6	0.04	0.03	0.03
7	0.03	0.00	0.03
8	0.03	0.00	0.00
9	0.06	0.05	0.07
10	0.08	0.05	0.07

Table 16 Standard deviation of the responses obtained for the Virginia samples.

Sensor	American 1	American 2	German
1	0.28	0.29	0.12
2	0.07	0.07	0.04
3	0.17	0.16	0.07
4	0.01	0.06	0.03
5	0.00	0.04	0.00
6	0.08	0.05	0.05
7	0.04	0.05	0.03
8	0.00	0.02	0.02
9	0.11	0.13	0.06
10	0.10	0.13	0.07

Figure 25 Radar plot response patterns for each tobacco sample based upon raw response data.

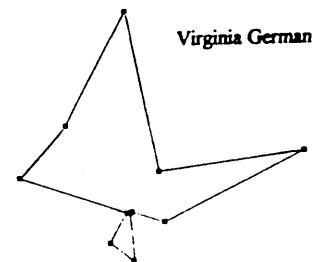
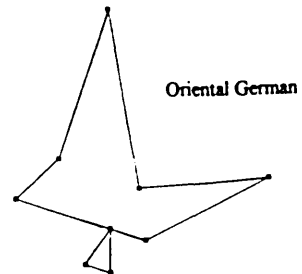
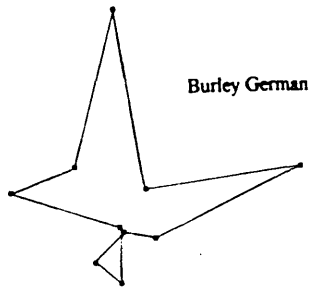
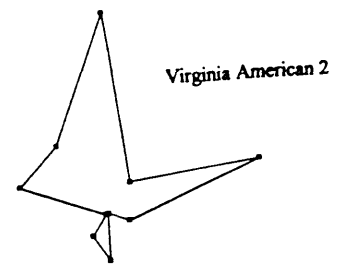
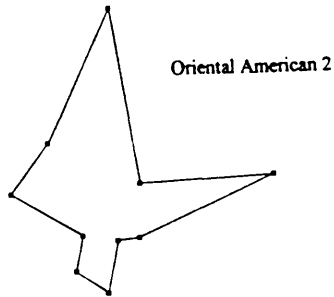
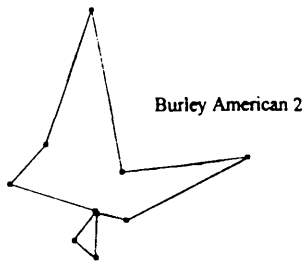
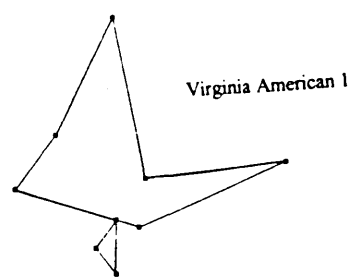
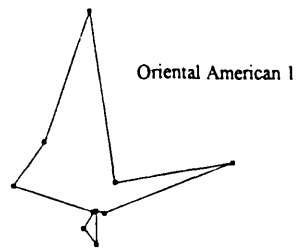
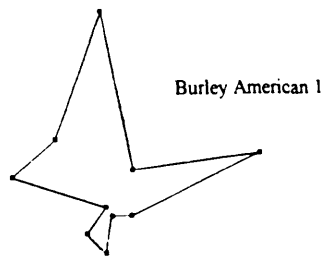


Table 17 Adjusted responses of the Burley samples.

Sensor	Burley USA 1	Burley USA 2	Burley German
1	0.18	0.02	0.17
2	0.02	-0.02	0.00
3	0.05	-0.10	0.07
4	-0.08	-0.09	-0.06
5	0.02	-0.01	0.00
6	-0.01	-0.05	0.00
7	-0.02	-0.04	0.00
8	-0.02	-0.02	-0.02
9	0.09	-0.02	0.10
10	0.10	0.02	0.03

Table 18 Adjusted responses of the Oriental Samples.

Sensor	Oriental USA 1	Oriental USA 2	Oriental German
1	0.11	-0.18	-0.18
2	-0.04	-0.10	-0.07
3	-0.08	-0.28	-0.28
4	-0.15	-0.17	-0.12
5	-0.02	-0.04	-0.02
6	-0.07	-0.11	-0.11
7	-0.07	-0.09	-0.07
8	-0.01	-0.02	-0.02
9	0.01	-0.13	-0.11
10	0.07	-0.07	-0.07

Table 19 Adjusted responses of the Virginia samples.

Sensor	Virginia USA 1	Virginia USA 2	Virginia German
1	0.3	0.20	-0.12
2	0.06	0.01	-0.05
3	0.18	0.03	-0.18
4	-0.08	-0.10	-0.11
5	-0.02	-0.02	-0.02
6	0.04	-0.03	-0.08
7	0.00	-0.04	-0.06
8	-0.02	-0.01	-0.01
9	0.17	0.07	-0.03
10	0.22	0.10	0.01

Table 20 Standard deviation of the adjusted Burley responses

Sensor	Burley USA 1	Burley USA 2	Burley German
1	0.12	0.11	0.16
2	0.04	0.04	0.04
3	0.12	0.10	0.12
4	0.03	0.03	0.03
5	0.02	0.01	0.02
6	0.04	0.04	0.04
7	0.03	0.00	0.03
8	0.00	0.00	0.02
9	0.07	0.04	0.06
10	0.06	0.04	0.06

Table 21 Standard deviation of the adjusted Oriental responses.

Sensor	Oriental USA 1	Oriental USA 2	Oriental German
1	0.14	0.10	0.10
2	0.04	0.04	0.04
3	0.11	0.10	0.10
4	0.03	0.03	0.03
5	0.02	0.02	0.00
6	0.04	0.04	0.04
7	0.03	0.00	0.03
8	0.02	0.00	0.00
9	0.04	0.04	0.04
10	0.05	0.04	0.05

Table 22 Standard deviation of the adjusted Virginia responses.

Sensor	Virginia USA 1	Virginia USA 2	Virginia German
1	0.16	0.16	0.11
2	0.05	0.05	0.04
3	0.12	0.12	0.10
4	0.03	0.04	0.03
5	0.00	0.02	0.00
6	0.05	0.04	0.04
7	0.03	0.03	0.01
8	0.00	0.02	0.02
9	0.06	0.07	0.04
10	0.06	0.07	0.05

Figure 26 Secondary radar plot response patterns formed by subtracting a water reference template from each of the raw patterns.

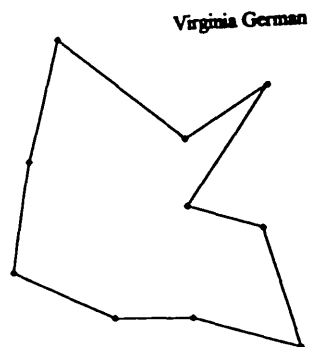
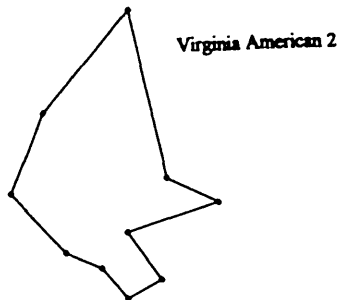
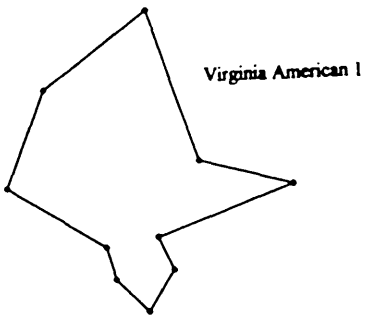
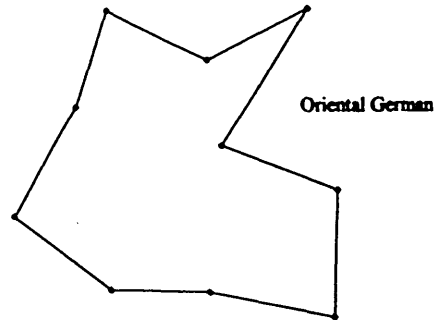
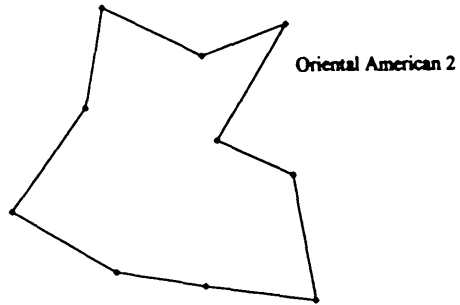
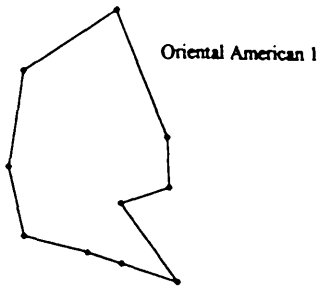
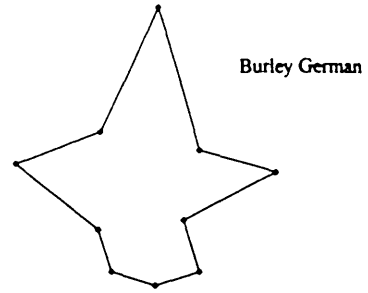
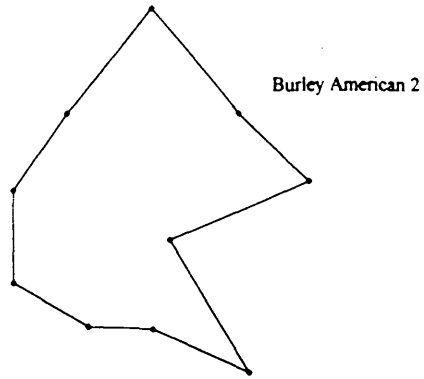
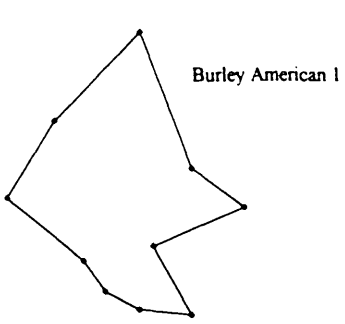
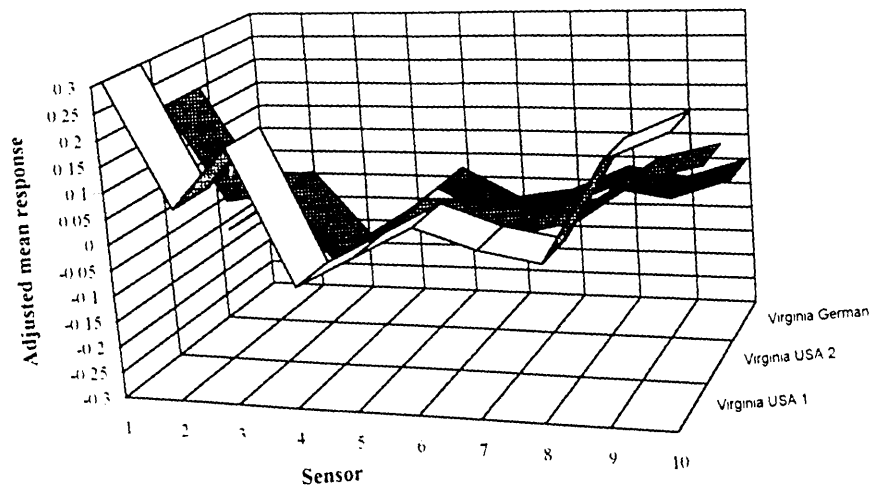
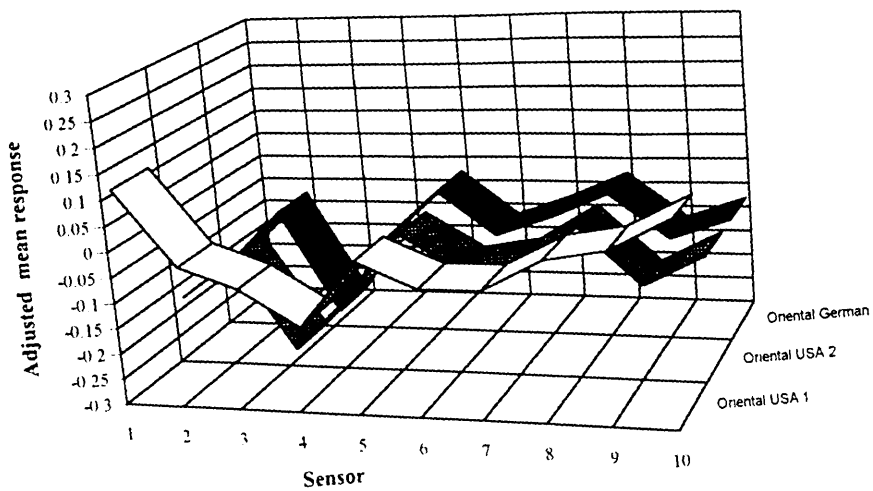
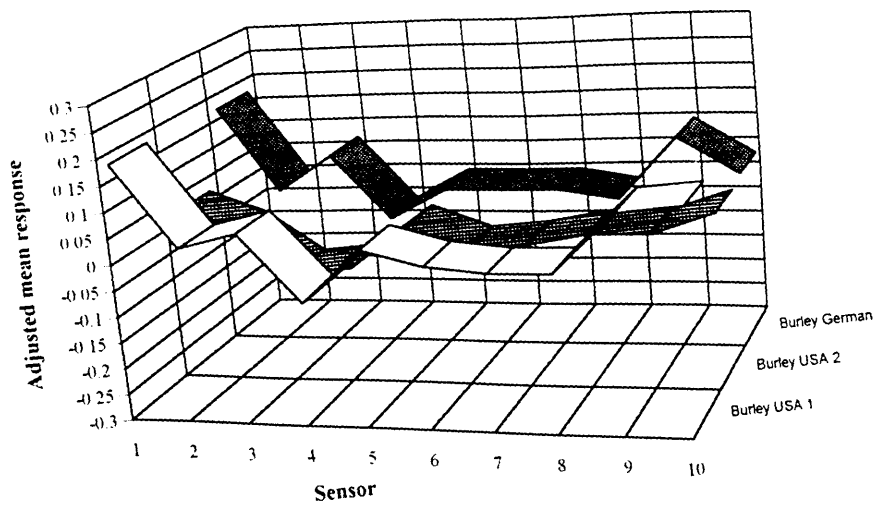


Figure 27 Comparison of the responses obtained for each of the three samples within a single variety using ribbon diagrams.

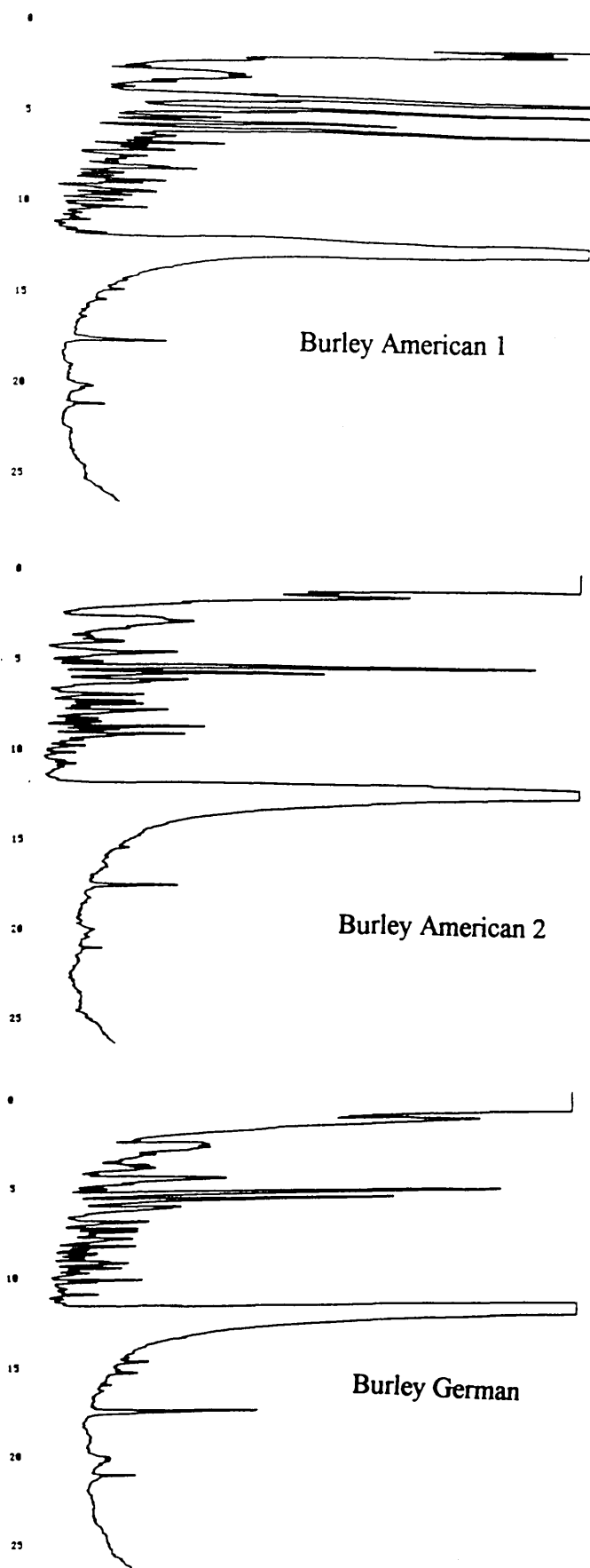


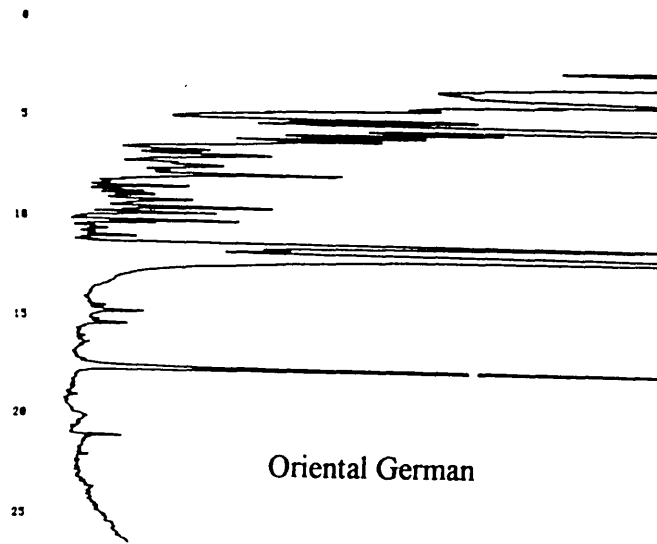
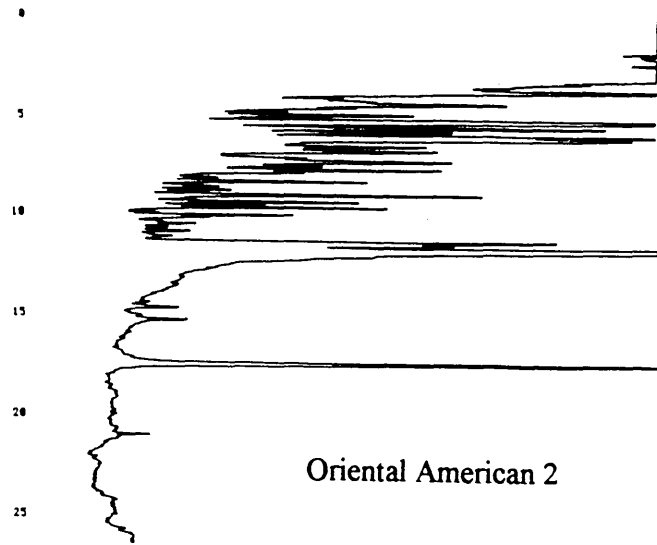
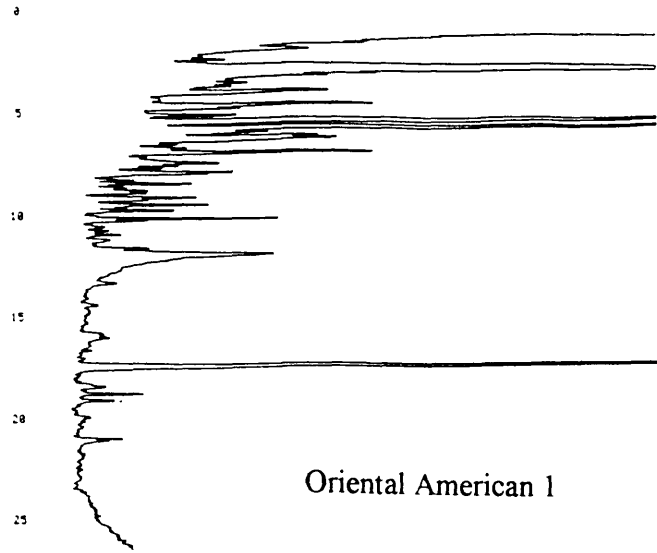
4.4 Discrimination on the basis of gas chromatography.

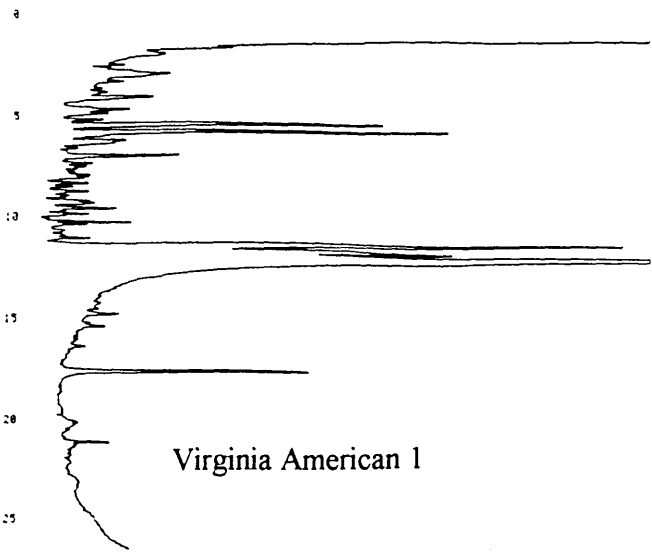
The chromatograms presented in figure 28 clearly differentiate between the different varieties of tobacco and allow adequate classification of samples within a single variety. However, it is possible that they may not give a true representation of the composition of each sample as some tobacco leaf components are known to undergo thermal reactions at elevated temperatures [167]. Visual comparison of chromatograms in some cases can be rather problematic and it may be better practise to list and compare the retention times of the most significant peaks. It should then be possible to apply pattern recognition techniques to such retention data in an attempt to improve the discrimination between samples. This chromatographic analysis clearly sets a target performance level that must be achieved by the arrays before they can be considered as a viable alternative to established chromatographic-based methods of analysis in this area of application.

Figure 28 Chromatograms obtained for each tobacco sample

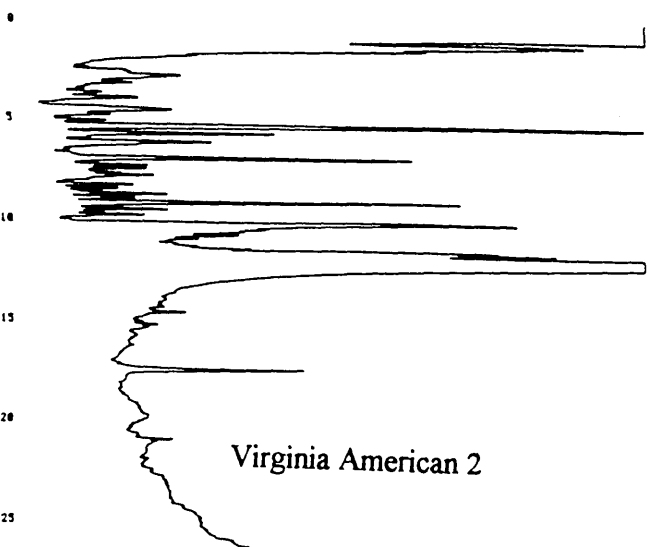
(all shown at attenuation 4).



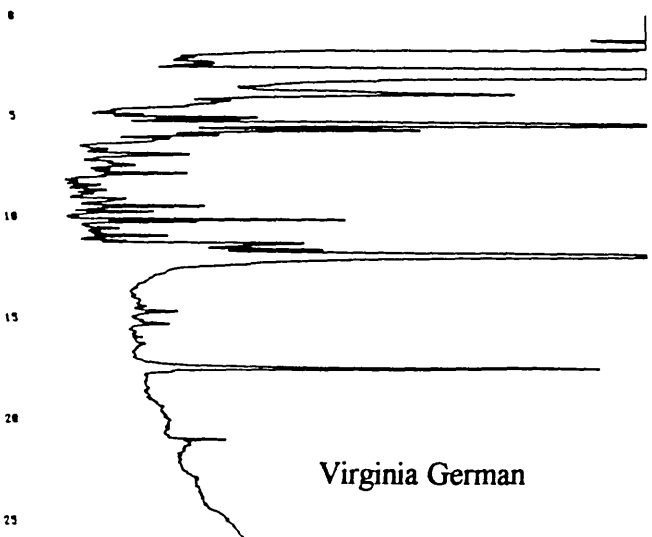




Virginia American 1



Virginia American 2



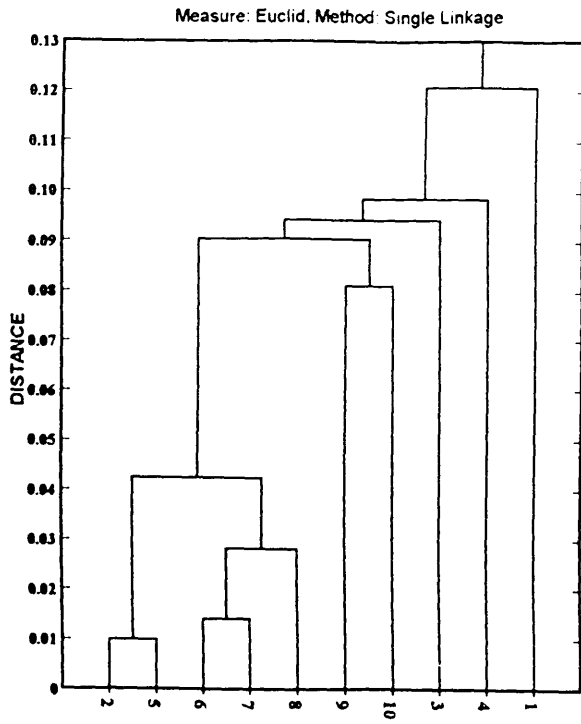
Virginia German

4.5 Cluster analysis.

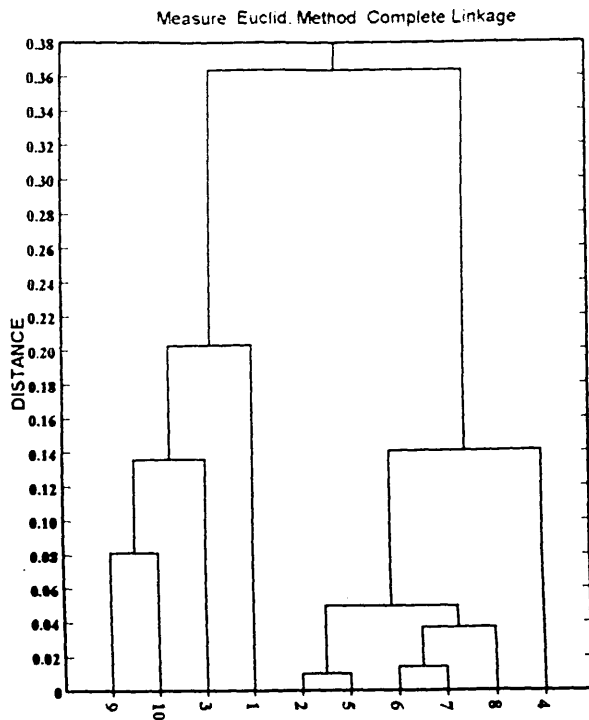
Five euclidean clustering techniques were applied to the adjusted tobacco response data to identify which sensors respond in a similar fashion to the three samples within a given variety. This analysis gives an insight into the efficiency of the discrimination achieved by the array. Dendograms prepared by the application of a series of clustering methods to a single set of data may exhibit slight differences. These differences are due to the different methods used by each technique to decide when two clusters are merged. There is no accepted “best” method for analysing the results from this type of analysis. Experience has shown that a strategy whereby all of the dendograms are studied as a whole to yield a representative picture of clustering behaviour is an adequate method of data analysis.

Analysis of the dendograms created from the Burley tests shown in figure 29 indicate that sensors 2 and 5 have almost identical responses to each sample as do the pair comprising of sensors 6 and 7. The responses of sensor 8 show a high degree of similarity with sensors 6 and 7 and this sub group of three sensors links with the cluster comprising of sensors 2 and 5 at low relative distance indicating that all five sensors display similar response behaviour. The next most similar pairing are sensors 9 and 10 but these two sensors exhibit sufficiently different responses to the three samples to be considered to have dissimilar response characteristics. These results suggest that adequate discrimination could have been achieved between the three samples using only seven sensors, namely numbers 1, 3, 4, 9 and 10 with one sensor from each of the two clusters comprising of sensor 2 with 5 and sensors 6 with 7 and 8 respectively. Greater discrimination could theoretically be achieved by replacement of one sensor from each of these two groupings with an alternative one.

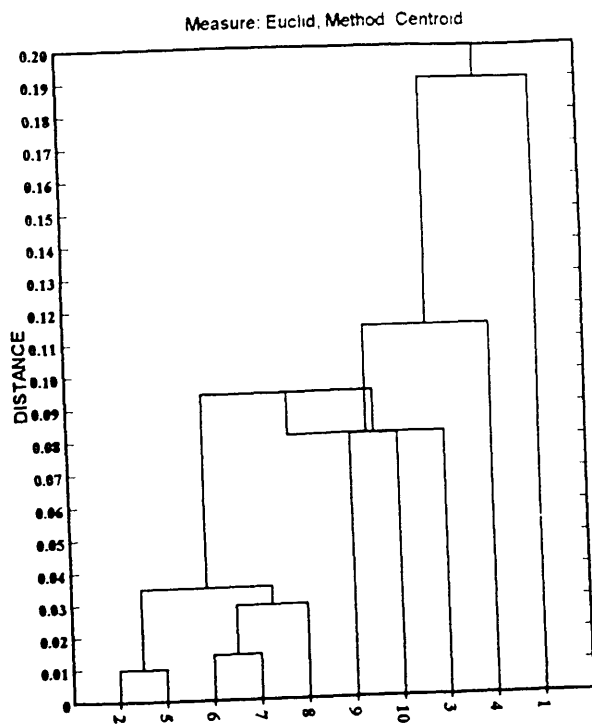
Figure 29 Dendograms created by applying five euclidean clustering techniques to the sensor responses obtained from studies involving three samples of Burley tobacco.



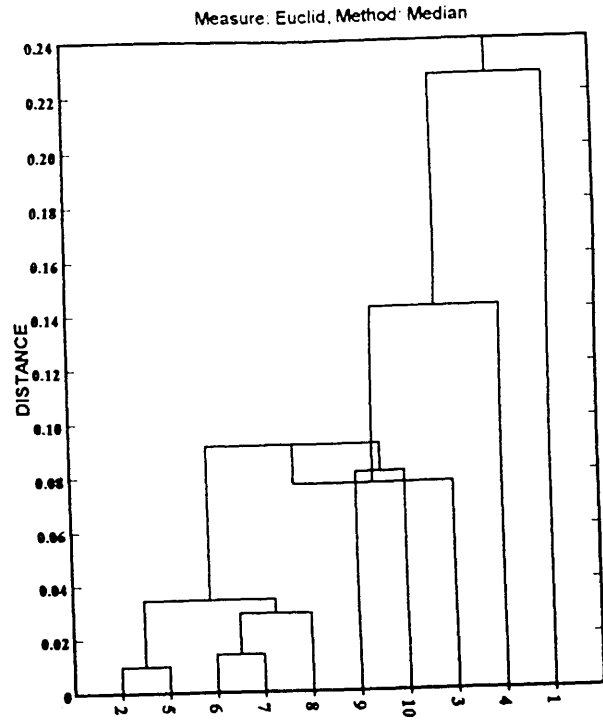
CLUSTERS (SENSOR)



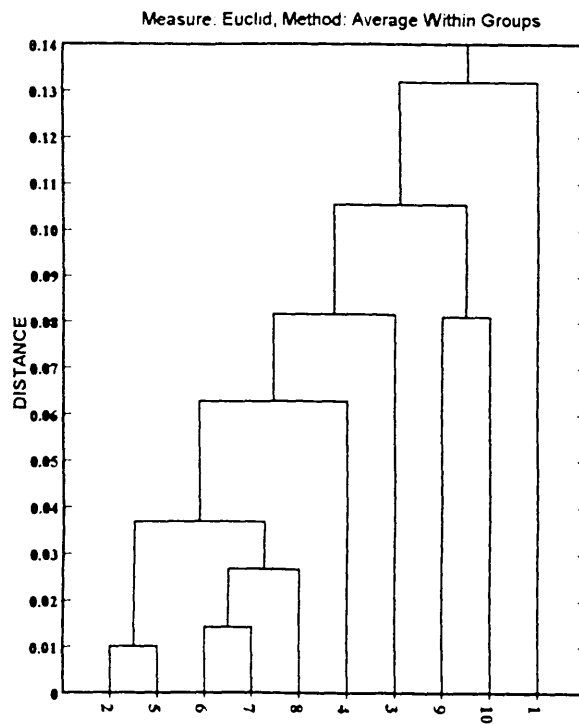
CLUSTERS (SENSOR)



CLUSTERS (SENSOR)



CLUSTERS (SENSOR)



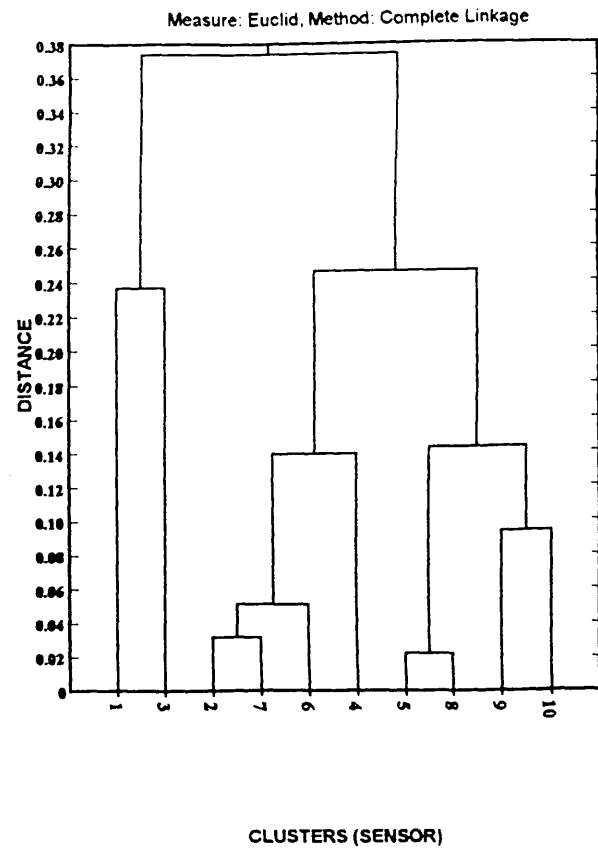
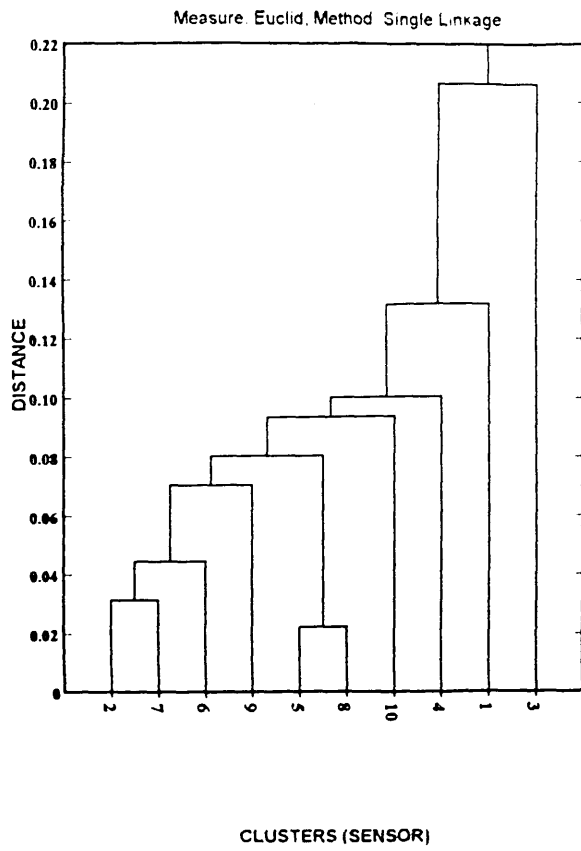
CLUSTERS (SENSOR)

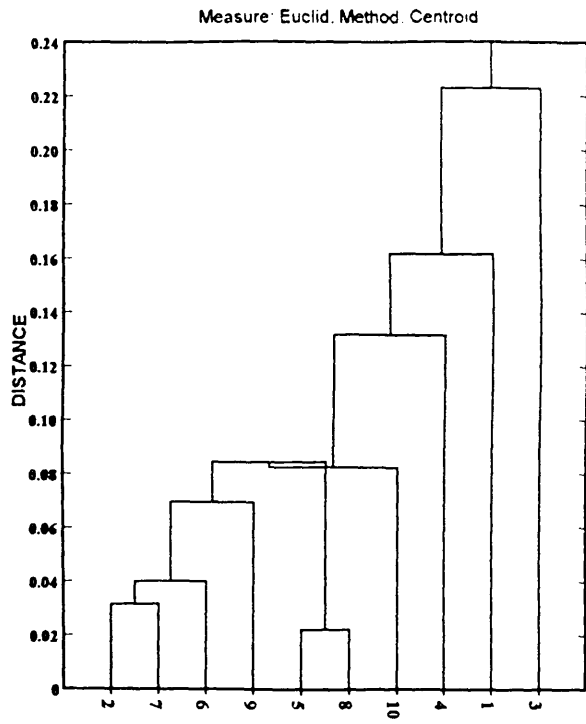
Pairing of sensors on the basis of similar responses is also observed in the Oriental tests. Figure 30 shows that sensors 5 and 8 have the most similar response behaviour. Sensors 2 and 7 also cluster into a pairing which links with sensor 6 at low relative distance indicating similarity between these three sensors. The most unique behaviour is displayed by sensor 3. Again, discrimination could have been achieved using only seven sensors, namely numbers 1, 3, 4, 9 and 10 with one from each of the two groupings comprising of sensors 2 with 6 and 7 and number 5 with 8 respectively.

The sensors also formed pairs in the Virginia tests. Figure 31 shows that each pair, namely sensors 5 with 8, 2 with 6 and 9 with 10 link at higher relative distances than was observed with the other two varieties. This indicates that the similarity of responses within a given pairing is reduced. Sensor 3 displays the most unique response behaviour. Again, the three samples could have been discriminated using less than ten sensors.

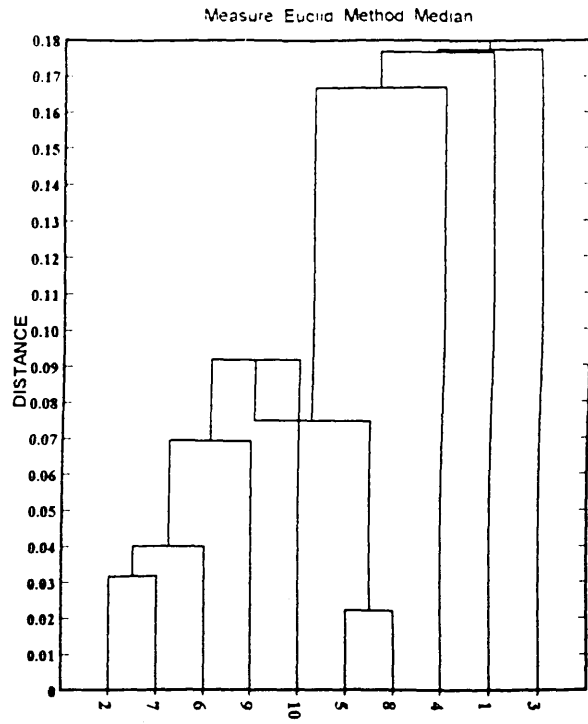
It may be extremely useful to create a large data base by applying clustering techniques to the responses of a large range of sensors to a range of tobaccos (or any other sample type). Sensors exhibiting different response characteristics to a given analyte could be chosen from this data base allowing the potential construction of analyte-specific arrays capable of discriminating between very similar test compounds.

Figure 30 Dendograms created by applying five euclidean clustering techniques to the response data obtained from studies involving three samples of Oriental tobacco.

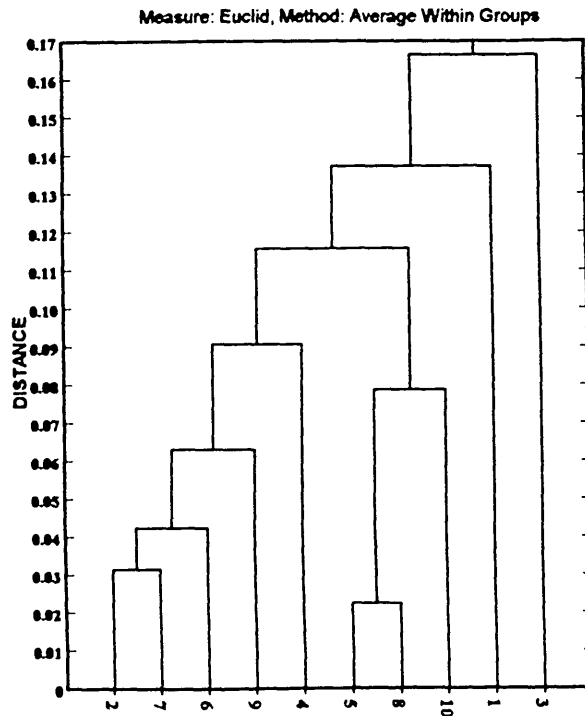




CLUSTERS (SENSOR)

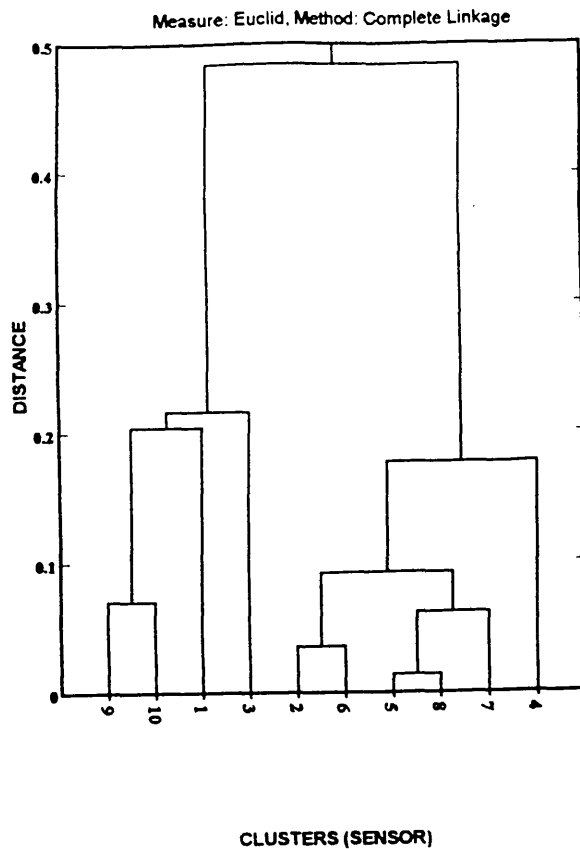
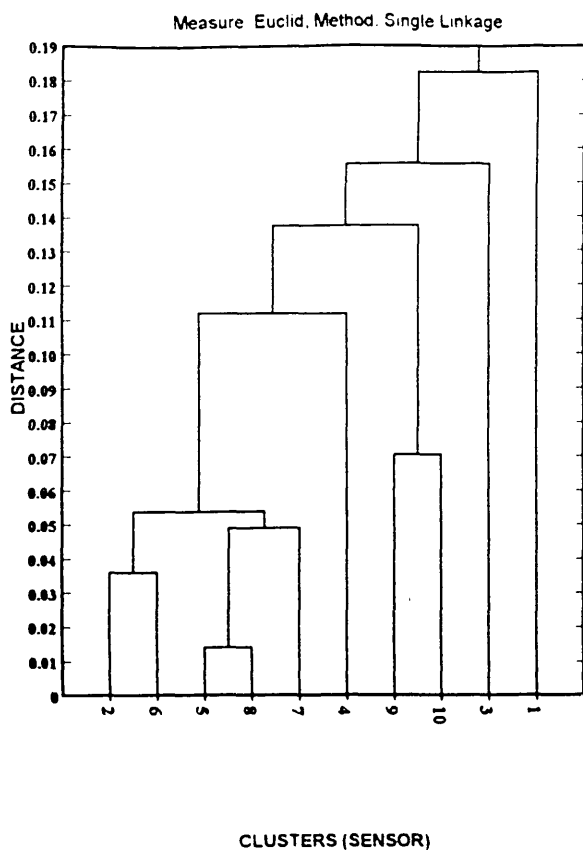


CLUSTERS (SENSOR)

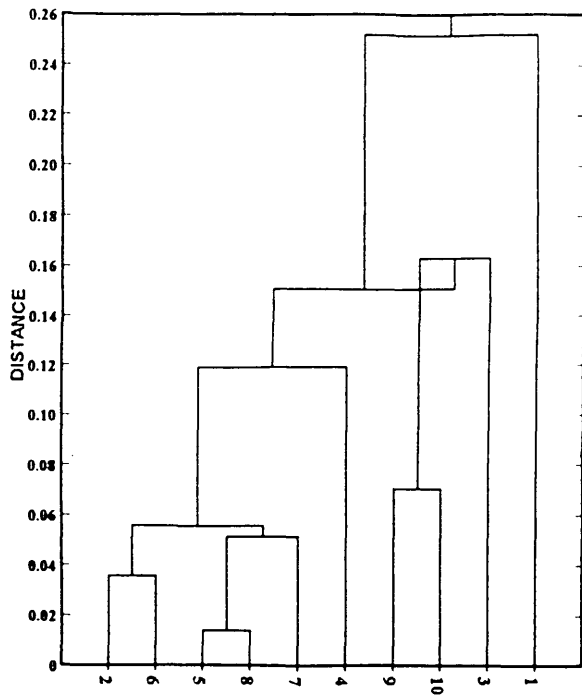


CLUSTERS (SENSOR)

Figure 31 Dendograms created by applying five euclidean clustering techniques to the response data obtained from studies involving three samples of Virginia tobacco.

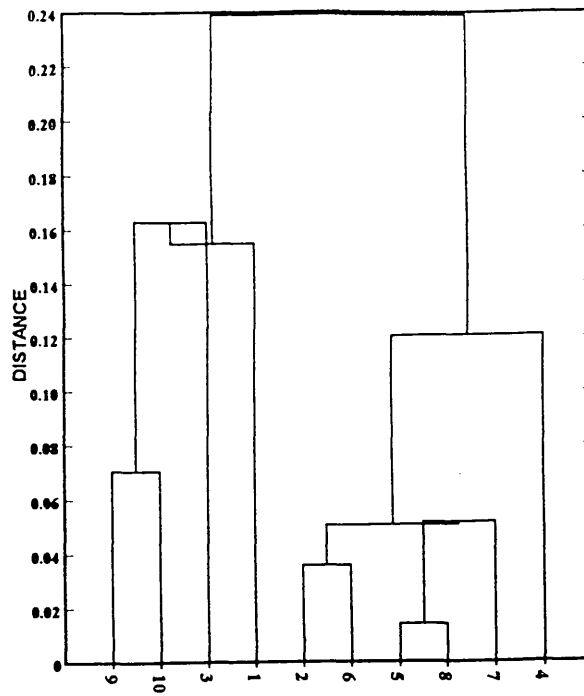


Measure: Euclid, Method: Centroid



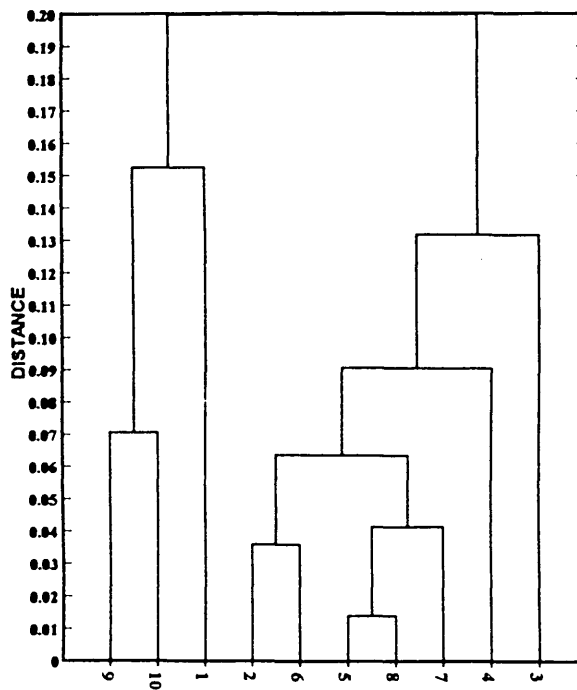
CLUSTERS (SENSOR)

Measure: Euclid, Method: Median



CLUSTERS (SENSOR)

Measure: Euclid, Method: Average Within Groups



CLUSTERS (SENSOR)

4.6 Conclusions.

At first sight, the array shows much promise in this area of application, comparing favourably with the chromatographic analysis in terms of the discrimination achieved between samples and the time taken for analysis. However, the % relative standard deviation presented in tables 23-25, which are based upon the standard deviation of the adjusted average sensor responses show that the precision achieved in most cases is extremely unsatisfactory. We again appear to be experiencing difficulties with test reproducibility as a consequence of water dominating the responses of the array. It is difficult to envisage how this effect could be minimised since there is a requirement that the arrays are purged with moist air. However, it may be possible to improve the situation by increasing the concentration of analyte volatiles in the sample headspace so that they are masked to a lesser extent. This could theoretically be achieved by increasing the sample size and/or the sample equilibration time. An alternative strategy which has recently been suggested by a co-worker [166] is to place samples onto a raised, porous platform below which a magnetic stirrer bar is used to agitate the atmosphere within the equilibration vessel.

The two major problems which have been encountered are the similarity of response between sensors and the generally dominant effect of water within the test environment which largely masks the effects of the volatile species associated with the tobaccos. It is recommended therefore as a first step in future work in this area that the water response problem be addressed. One approach may be to coat the sensors with a thin layer of hydrophobic material. However, there is a requirement that the sensors are purged with moist air to stop them cracking. It may be possible to incorporate plasticisers within the polymer matrix which would give the films a degree of flexibility although this would be unlikely to stop the evaporation of the solvent within each polymer matrix when purged with a dried gas.

Table 23 % RSD based on the adjusted Burley responses

Sensor	Burley USA 1	Burley USA 2	Burley German
1	66	18	94
2	50	200	0
3	42	100	171
4	267	33	50
5	100	100	0
6	250	263	0
7	66	0	0
8	0	0	100
9	129	200	60
10	167	200	200

Table 24 % RSD based on the adjusted Oriental responses

Sensor	Oriental USA 1	Oriental USA 2	Oriental German
1	127	56	56
2	100	40	57
3	138	36	36
4	20	18	25
5	100	50	0
6	57	36	36
7	43	0	43
8	200	0	0
9	400	31	36
10	29	57	71

Table 25 % RSD based on the adjusted Virginia responses

Sensor	Virginia USA 1	Virginia USA 2	Virginia German
1	53	43	92
2	83	500	80
3	67	400	56
4	38	40	27
5	0	100	0
6	125	100	50
7	0	0	17
8	0	100	200
9	35	41	125
10	27	32	500

5.1 Investigation of a range of small molecules.

The mechanisms by which a polypyrrole-based sensor comprising of a given solvent and counter ion responds in a certain fashion to a molecule which displays particular physical and structural parameters are poorly understood. An understanding of the manner by which an analyte is “recognised” by a sensor would be invaluable by guiding the choice of specific structure responsive sensors to synthesise.

A series of compounds comprising a variety of functionalities was profiled using a ten sensor array in an attempt to identify any relationships which exist between the structural and/or physical properties displayed by a given analyte and the sensor responses it generates. The structures of the test compounds are presented in figure 32. Three replicate tests were performed on each test compound to allow the calculation of standard deviation data from the averaged response data. The test conditions that were adopted in these investigation are outlined below :

Array : Head 2.

Sample size : 0.01 Moles.

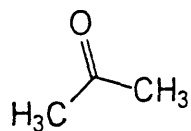
Equilibration time : 10 minutes.

Purging : 10 minutes (sensors) with 30 % r.h cylinder air.

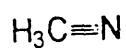
Acquisition time : 3 minutes

Analysis point : @ 1 minute

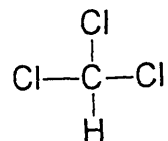
Figure 32 Structures of the series of simple compounds used in the structure response mapping investigation. The numbering scheme identifies each compound in subsequent graphical displays.



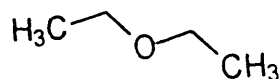
1) Acetone



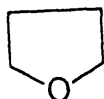
2) Acetonitrile



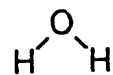
3) Chloroform



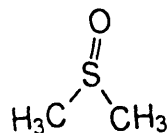
4) Diethyl ether



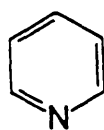
5) Tetrahydrofuran (thf)



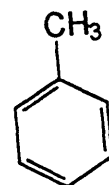
6) Water



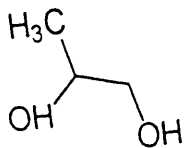
7) Dimethyl sulphoxide (dmsO)



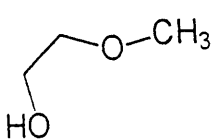
8) Pyridine



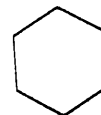
9) Toluene



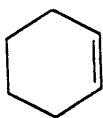
10) 1, 2 propanediol



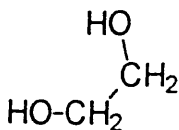
11) 2 methoxy ethanol



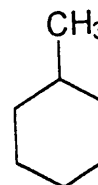
12) Cyclohexane



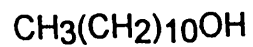
13) Cyclohexene



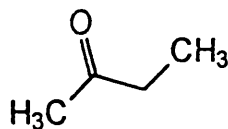
14) Ethylene glycol



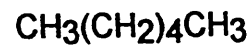
15) Methyl cyclohexane



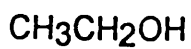
16) n-Undecanol



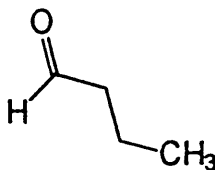
17) Butan-2-one



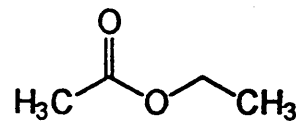
18) n-hexane



19) Ethanol



20) Butyraldehyde



21) Ethyl acetate

The sensor responses obtained for each test sample are presented in table 26. The standard deviation associated with these data are presented in table 27. It was initially anticipated that the array would yield a unique “fingerprint” response pattern for each of the compounds since the test series display a variety of structural features. The patterns obtained for each test compound are illustrated in figure 33 and seem to indicate that this is not the case since many of the patterns are very similar. However, it is evident that many of these patterns closely resemble the pattern generated by water. This supports our previous proposal that the array is responding to moisture within the test environment which is masking the responses due to the test compounds. The response data were therefore adjusted by subtracting the average response values of water. The adjusted data are presented in table 28, the standard deviations in table 29. A second series of response patterns was created from this adjusted data which are displayed in figure 34. These show improved discrimination between the members of the test series, and it is possible to distinguish between many of the compounds on the basis of these new patterns. However, the patterns of acetone, acetonitrile, tetrahydrofuran, propanediol and methoxy ethanol are very similar to each other as are those of cyclohexene and cyclohexane. It is possible to improve the visual discrimination between these six compounds by displaying them using an alternative method of presentation. The ribbon plots shown in figure 35 allow adequate discrimination between the two cyclohexane-based structures and also between propanediol and methoxy ethanol. The latter two compounds may now also be distinguished from acetone and acetonitrile but these two compounds are still virtually indistinguishable from each other.

Table 26 Sensor responses obtained for each member of the test series.

Sensor	Acetone	Acetonitrile	Chloroform	Ether	Thf	Water	Dmso	Pyridine	Toluene	Propanediol	Methoxyethanol
1	0.31	0.30	0.28	0.21	0.18	0.46	0.46	0.94	0.80	0.24	0.22
2	1.03	1.03	1.11	0.83	0.66	1.57	1.73	2.84	2.32	0.89	0.73
3	0.72	0.73	0.74	0.56	0.47	1.06	1.16	2.16	1.84	0.60	0.50
4	0.52	0.49	0.53	0.42	0.28	0.85	0.87	1.36	1.11	0.42	0.36
5	0.32	0.29	0.28	0.23	0.16	0.41	0.50	0.59	0.42	0.25	0.20
6	1.22	1.20	1.20	0.95	0.67	2.11	2.45	3.00	2.19	1.00	0.81
7	0.95	0.96	0.89	0.74	0.55	1.54	1.70	2.11	1.65	0.86	0.69
8	0.67	0.67	0.64	0.57	0.38	1.10	1.13	1.49	1.22	0.60	0.49
9	0.81	0.77	0.86	0.63	0.51	1.38	1.36	2.40	2.10	0.73	0.59
10	0.33	0.29	0.28	0.23	0.18	0.61	1.44	2.12	0.45	0.28	0.24

Sensor	Cyclohexane	Cyclohexene	Ethylene glycol	Me cyclohexane	n-Undecanol	Butan-2-one	n-Hexane	Ethanol	Butyraldehyde	Ethyl acetate
1	0.75	0.74	0.80	0.81	0.41	0.41	0.68	0.61	0.57	0.43
2	2.34	2.32	2.73	2.36	1.49	1.76	2.48	2.13	2.32	1.59
3	1.80	1.83	1.99	1.87	0.99	1.29	2.01	1.71	1.75	1.25
4	1.07	1.13	1.29	1.10	0.69	0.70	1.09	0.90	0.95	0.64
5	0.44	0.45	0.53	0.46	0.35	0.26	0.36	0.31	0.34	0.20
6	2.27	2.37	2.84	2.28	1.60	1.36	2.43	1.84	2.00	1.26
7	1.71	1.69	2.11	1.68	1.24	1.01	1.52	1.19	1.38	0.90
8	1.21	1.25	1.45	1.23	0.86	0.74	1.10	0.87	0.98	0.66
9	2.00	2.03	2.28	2.06	1.16	1.31	2.01	1.67	1.79	1.24
10	0.49	0.55	2.00	0.55	0.31	0.17	1.01	0.79	0.65	0.50

Table 27 Standard deviation of the raw response data.

Sensor	Acetone	Acetonitrile	Chloroform	Ether	Thf	Water	Dmso	Pyridine	Toluene	Propanediol	Methoxyethanol
1	0.06	0.07	0.01	0.02	0.09	0.44	0.05	0.04	0.04	0.08	0.11
2	0.22	0.20	0.11	0.09	0.26	0.20	0.29	0.16	0.08	0.20	0.25
3	0.18	0.19	0.06	0.05	0.20	0.14	0.18	0.13	0.07	0.16	0.21
4	0.10	0.14	0.07	0.02	0.15	0.41	0.13	0.16	0.04	0.12	0.17
5	0.08	0.08	0.03	0.03	0.09	0.12	0.06	0.06	0.00	0.06	0.07
6	0.26	0.31	0.09	0.05	0.36	0.06	0.33	0.17	0.07	0.23	0.31
7	0.21	0.19	0.09	0.06	0.28	0.18	0.26	0.21	0.07	0.16	0.21
8	0.13	0.13	0.09	0.03	0.21	0.11	0.15	0.20	0.05	0.11	0.17
9	0.22	0.19	0.08	0.06	0.21	0.05	0.21	0.19	0.07	0.19	0.25
10	0.09	0.08	0.03	0.03	0.12	0.28	0.5	0.25	0.02	0.05	0.12

Sensor	Cyclohexane	Cyclohexene	Ethylene glycol	Me cyclohexane	n-Undecanol	Butan-2-one	n-Hexane	Ethanol	Butyraldehyde	Ethyl acetate
1	0.15	0.06	0.05	0.24	0.19	0.03	0.03	0.06	0.07	0.03
2	0.36	0.17	0.07	0.17	0.04	0.08	0.12	0.29	0.15	0.19
3	0.32	0.12	0.03	0.1	0.21	0.06	0.05	0.18	0.16	0.11
4	0.24	0.09	0.05	0.05	0.12	0.05	0.02	0.09	0.09	0.08
5	0.07	0.07	0.02	0.2	0.09	0.03	0.02	0.04	0.04	0.04
6	0.51	0.28	0.07	0.17	0.03	0.08	0.07	0.19	0.26	0.14
7	0.52	0.11	0.06	0.11	0.2	0.04	0.07	0.17	0.12	0.14
8	0.26	0.1	0.06	0.11	0.14	0.04	0.05	0.09	0.09	0.08
9	0.37	0.13	0.1	0.19	0.07	0.08	0.04	0.17	0.15	0.14
10	0.12	0.55	0.08	0.19	0.12	0.17	0.08	0.18	0.26	0.10

Figure 33 Response patterns obtained for the series of test compounds

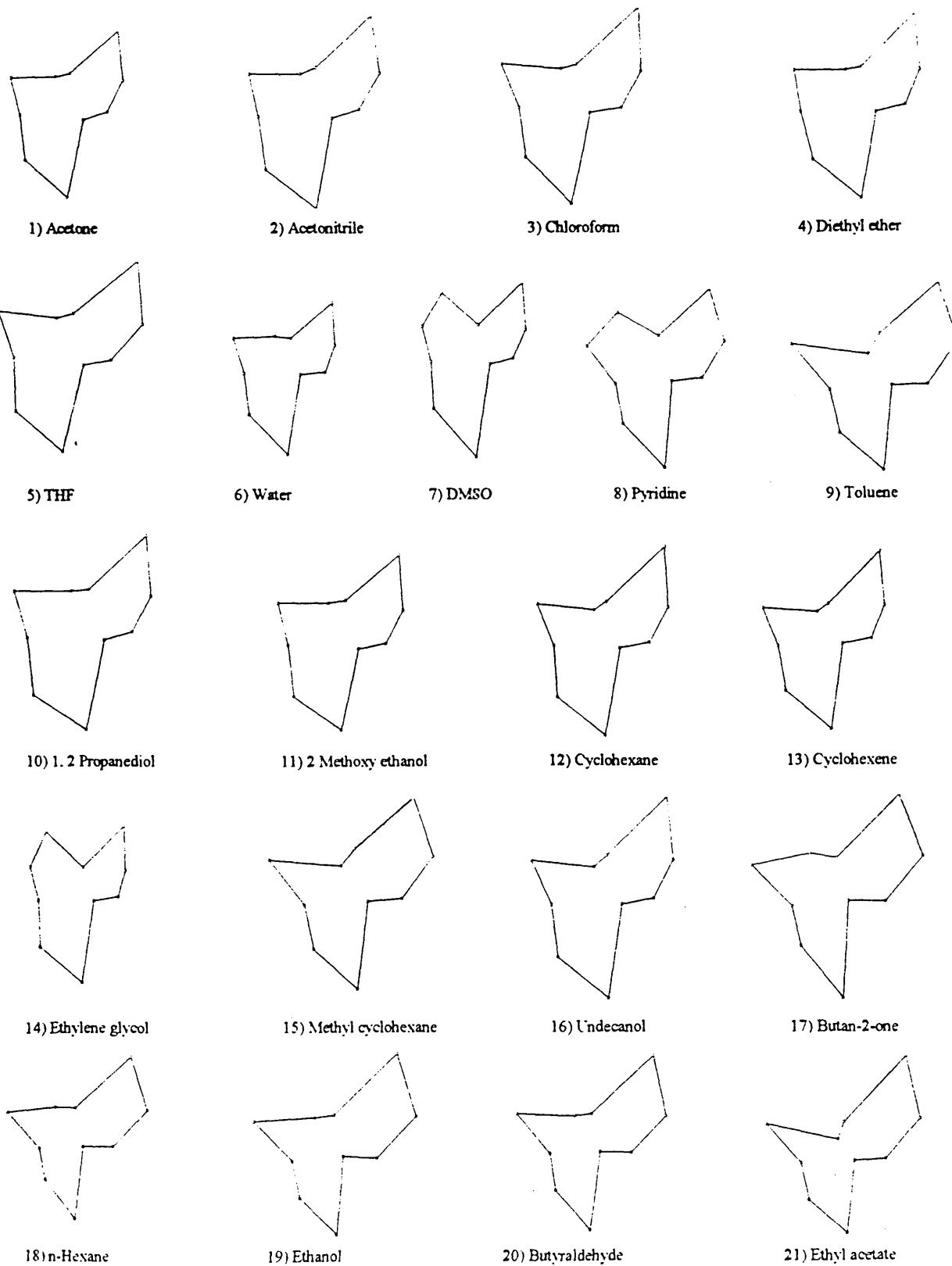
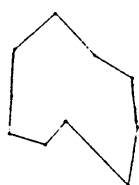
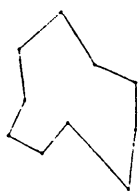


Figure 34 Secondary response patterns based on adjusted data



1) Acetone



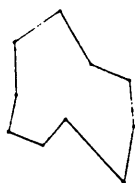
2) Acetonitrile



3) Chloroform



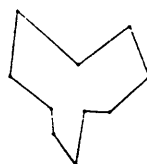
4) Diethyl ether



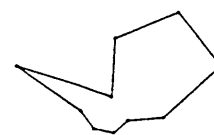
5) THF



7) DMSO



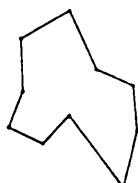
8) Pyridine



9) Toluene



10) 1, 2 Propanediol



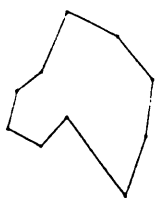
11) 2 Methoxy ethanol



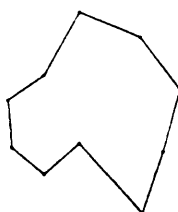
12) Cyclohexane



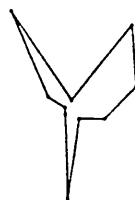
13) Cyclohexene



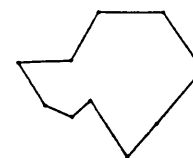
14) Ethylene glycol



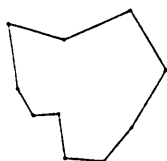
15) Methyl cyclohexane



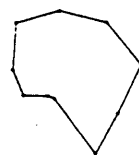
16) Undecanol



17) Butan-2-one



18) n-Hexane



19) Ethanol

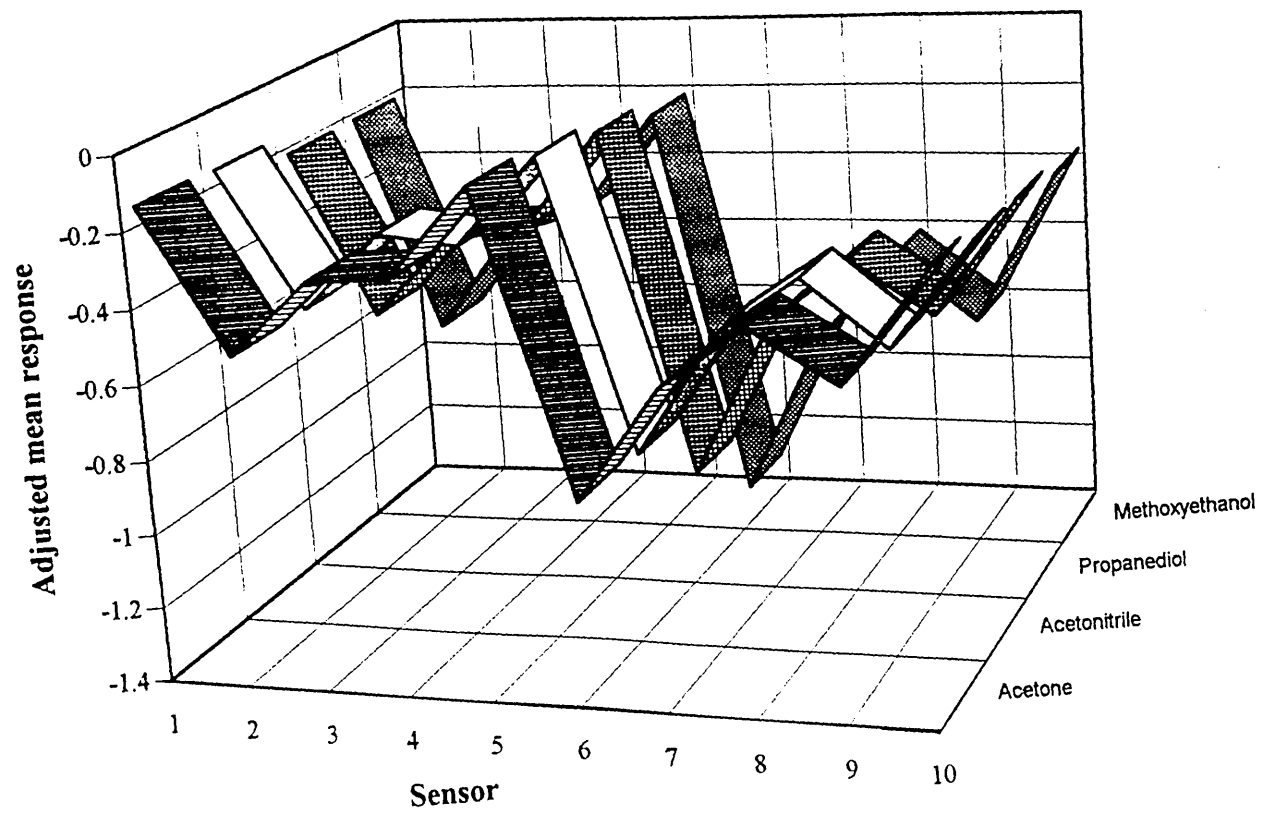
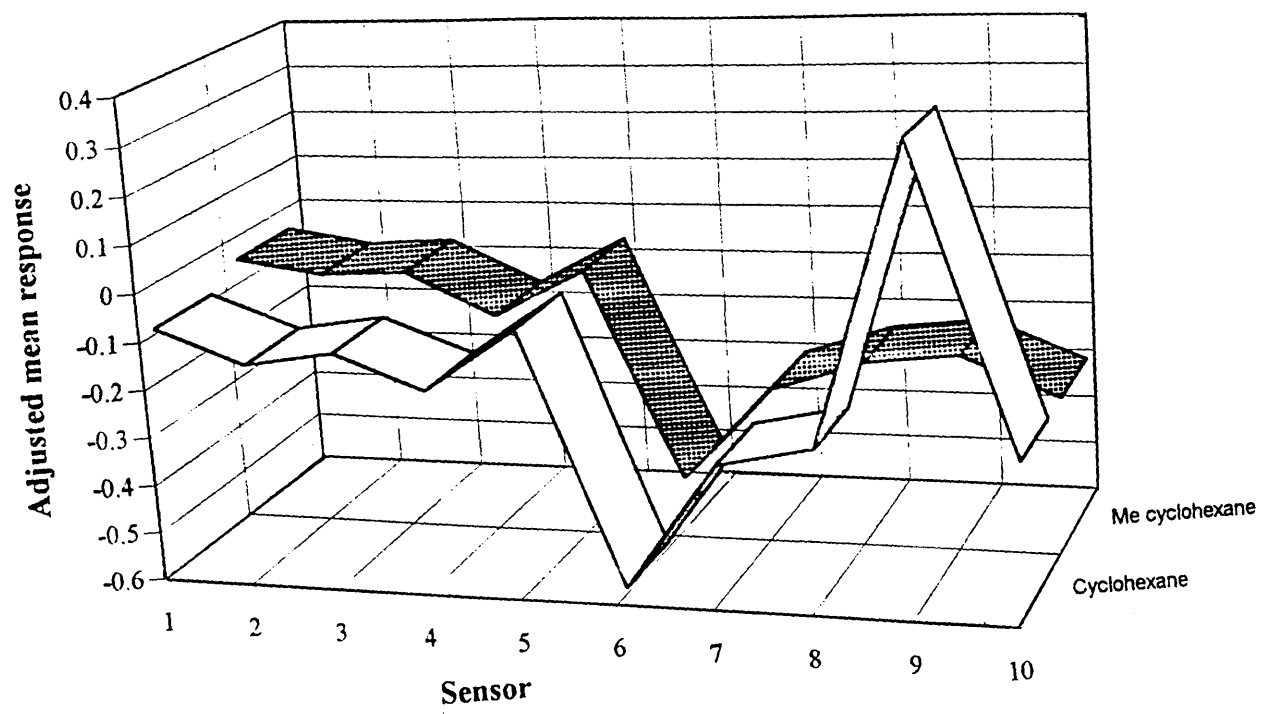


20) Butyraldehyde



21) Ethyl acetate

Figure 35 Comparison of some members of the test series using ribbon diagrams allows improved discrimination between some compounds.

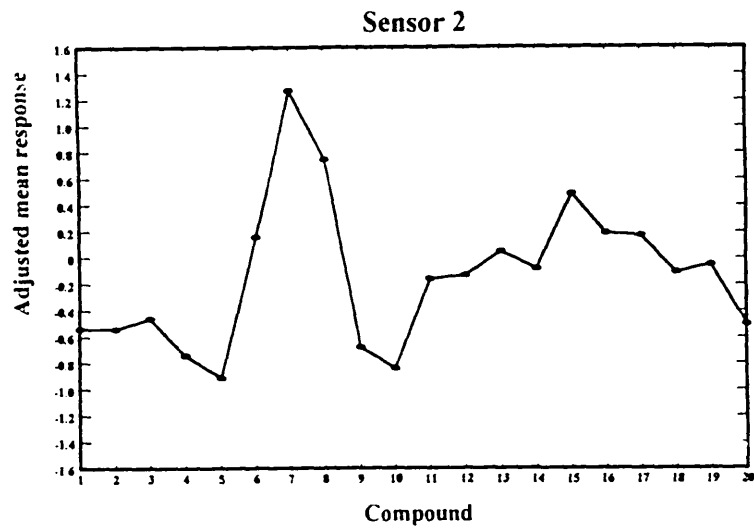
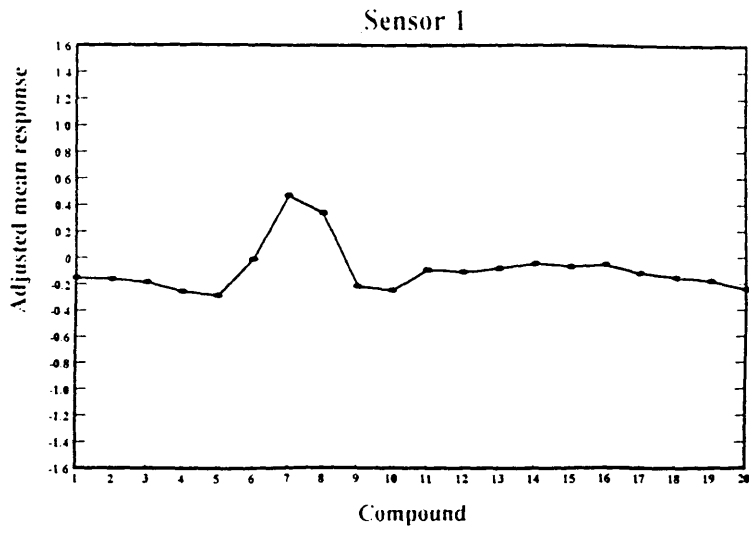


5.2 Individual sensor responses.

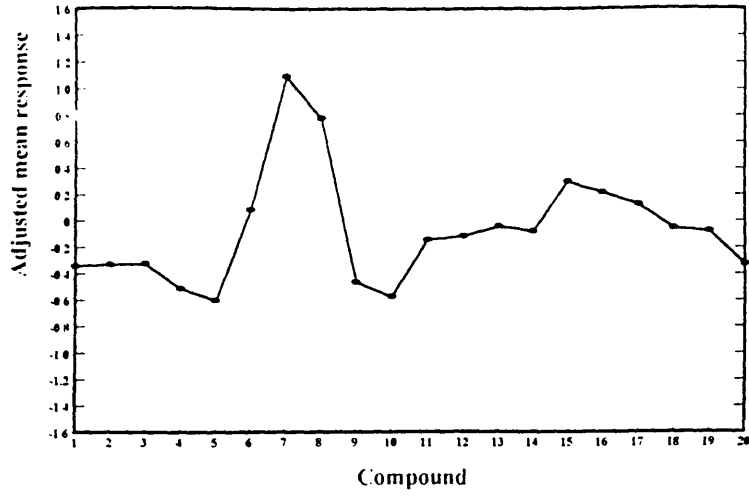
The adjusted responses of individual sensors to each test compound are presented graphically in figure 36. These plots indicate that although the actual magnitudes of response for each sensor are different for each compound, the pattern of response across the test series is fairly similar for all of the sensors within the array. This was quite a surprising discovery as the sensors were believed to display significantly dissimilar response behaviour and be of a more selective nature.

There appears to be no simple correlation between solvent/counter ion identity and magnitude of response. Sensors 5 and 7 were manufactured using the same counter ion but different solvents. The responses of these two sensors are markedly different and show how the response characteristics of sensors of this type may be tailored by careful selection of the solvent used in their electrochemical preparation. It is difficult to propose a theory to explain this difference in response characteristics. The two different solvents may either determine the electrical properties of the polymer films to a different extent or may exhibit different effects when an analyte interacts with the active sites of the sensor.

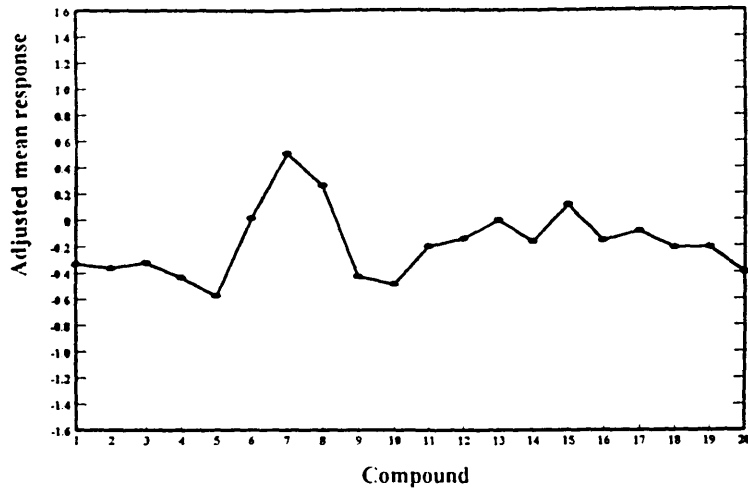
Figure 36 Responses of the individual sensors to the test series.



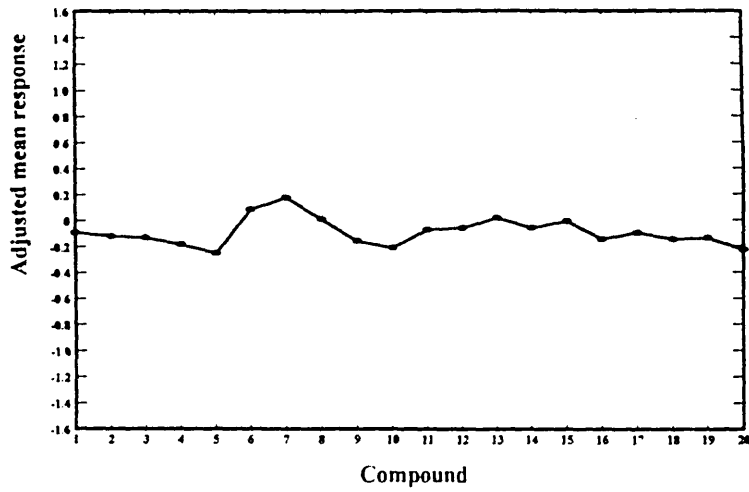
Sensor 3

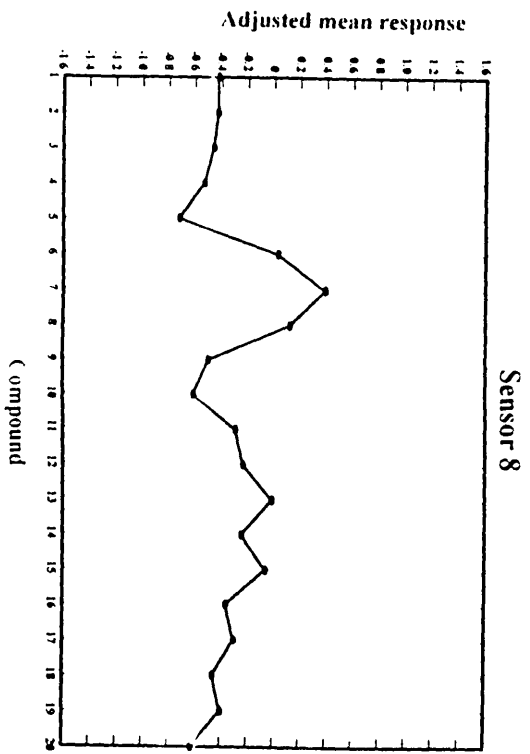
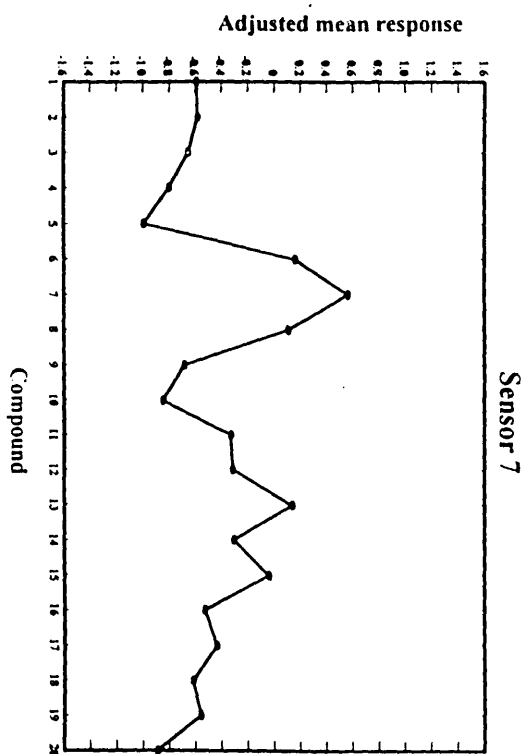
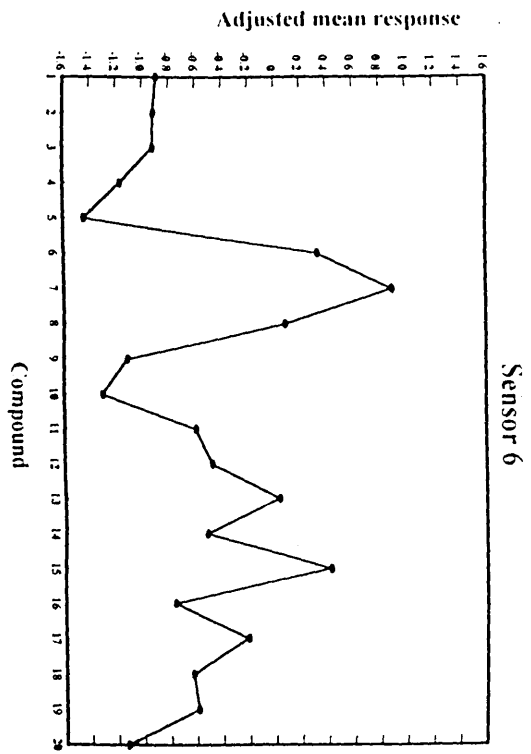


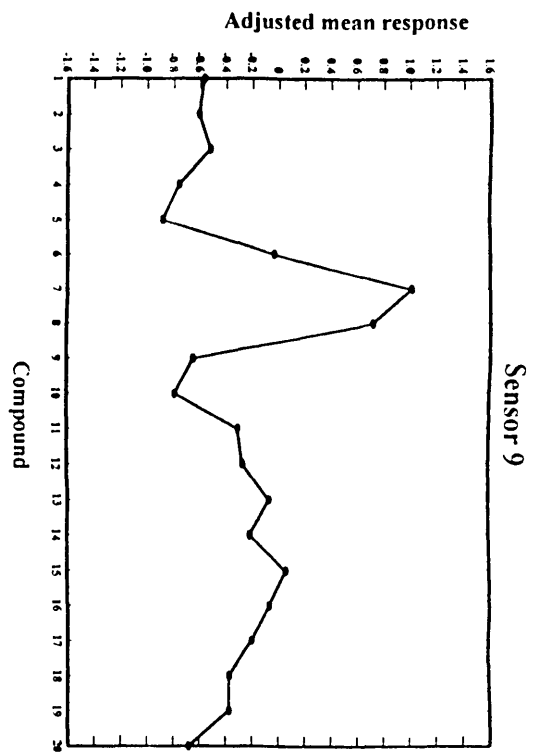
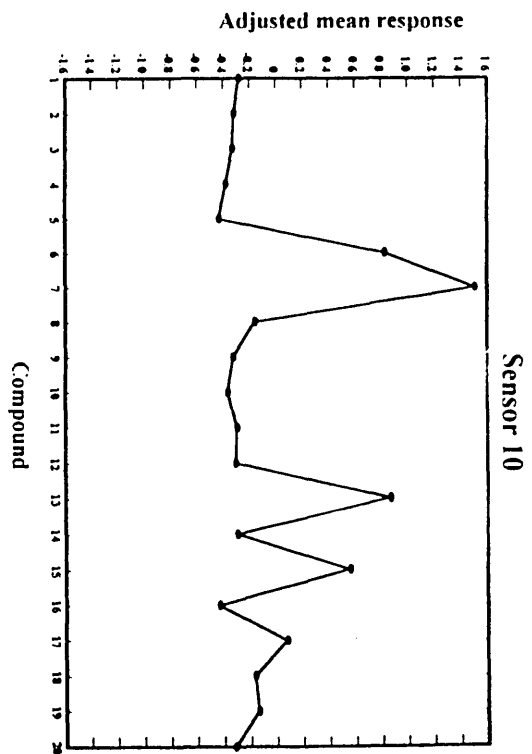
Sensor 4



Sensor 5







The adjusted response data was analysed using five euclidean clustering techniques in an attempt to identify which compounds appear most similar to the array. The dendograms presented in figure 37 indicate that the test series cluster into the following groups of compounds which display a similar degree of response behaviour :

- i) Acetone, acetonitrile and chloroform.
- ii) Ether, propanediol, 2 methoxy ethanol and ethyl acetate.
- iii) Dimethyl sulphoxide and ethylene glycol.
- iv) Cyclohexene, methylcyclohexene and cyclohexane.
- v) Ethanol and butyraldehyde.

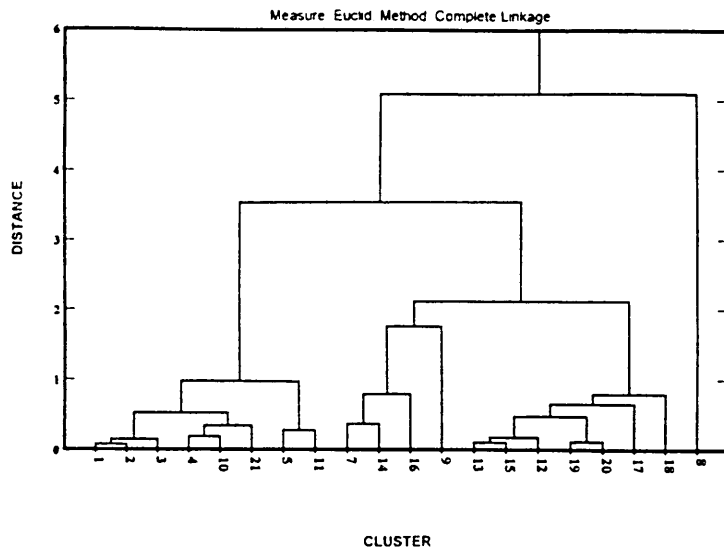
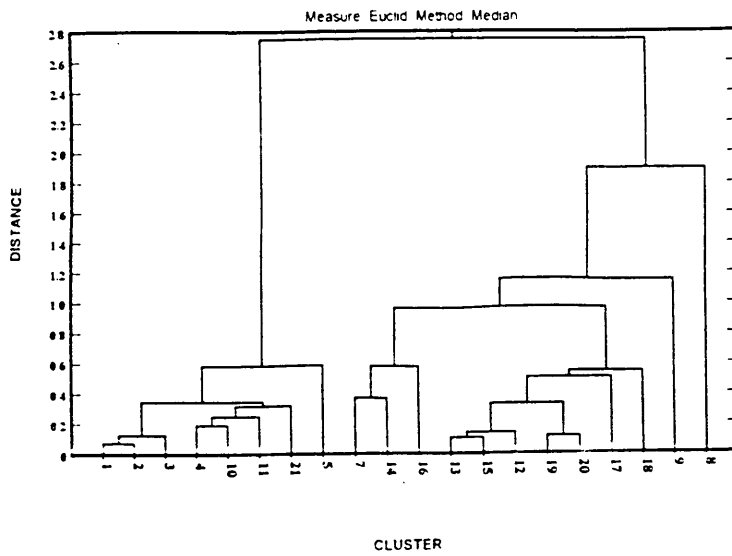
The dendograms also indicate that acetone (1) and acetonitrile (2) appear most similar to the array whilst pyridine (8) displays the most unique behaviour. The compounds within each of the above clusters do not appear to display any immediately obvious trends of structural and/or physical parameters such as polarity, functionality or volatility and it is extremely difficult to make correlations on these few data.

It is safe to assume that the volatility of a test compound will play a significant role in sensor response since measurements are based on the concentration of species in the sample headspace. The fact that the more volatile members of the test series such as chloroform and ether do not exhibit the highest responses indicates the expected conclusion that the basis of sensor response is more complex than a simple linear vapour phase concentration/response relationship.

Once in the vapour phase, sample molecules must somehow interact with the conducting polymer matrix to generate a response. The mechanisms of this process are poorly understood. Initial interactions between the analyte and the polymer are likely to involve hydrogen bonding and other inter molecular attractions. It would therefore seem logical to assume that the polarity of a test compound will have an effect upon sensor response. Unfortunately, there does not seem to be any simple method for determining what contribution the volatility or any other property of a molecule will have towards response since it is difficult to envisage how a single property may be studied whilst keeping other parameters constant. For example, the test series may be arranged into order of polarity but the fact each compound possesses a different volatility/functionality and so on makes analysis of the effect of polarity on response rather problematic. There is obviously a need to somehow develop a profiling strategy so that a study of the effects of single parameters can be made. Such a programme of response mapping would obviously need to incorporate a far more comprehensive series of test compounds and sensors. Cluster analysis and other statistical techniques would prove to be invaluable tools when analysing such a large set of response data.

The % relative standard deviation data based upon the standard deviation of the adjusted sensor responses are presented in table 30. With a few exceptions, the majority of the sensors display highly unsatisfactory values which obviously means that the response data cannot be studied with any degree of confidence. To successfully map the range of structural features of interest will require the problems of sensor response to water to be addressed and require a test strategy to be designed which allows the investigation of single parameters.

Figure 37 Dendograms created by the application of five euclidean clustering techniques to the responses obtained from the test series.



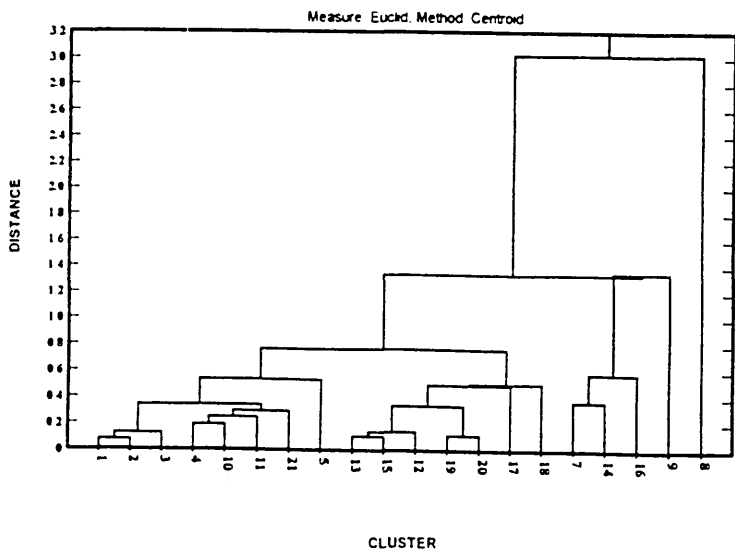
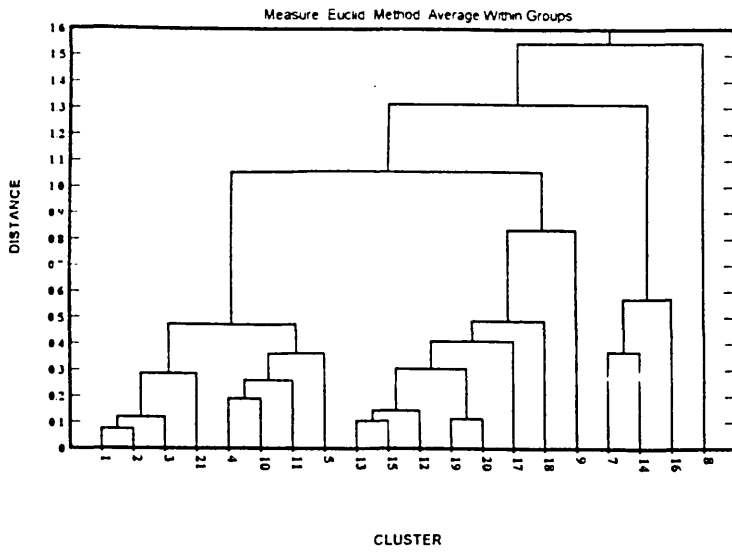
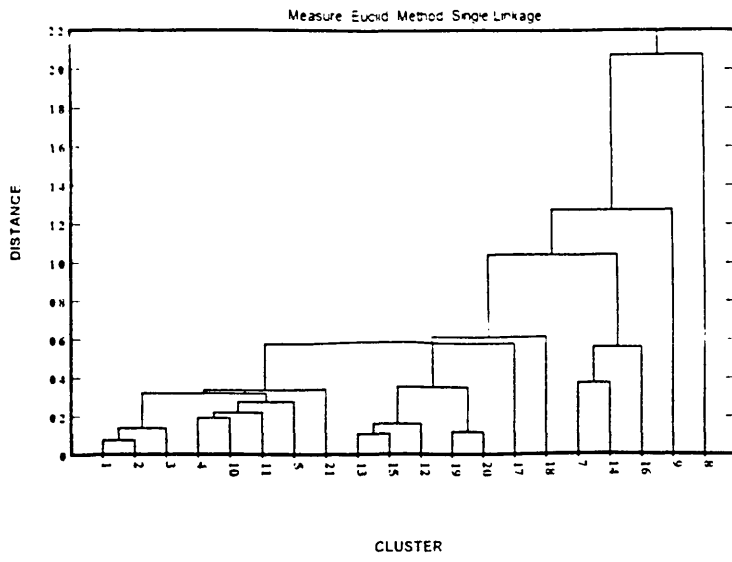


Table 30 % RSD based on the adjusted sensor responses.

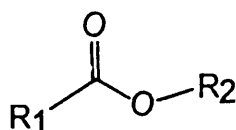
Sensor	Acetone	Acetonitrile	Chloroform	Ether	Thf	DmsO	Pyridine	Toluene	Propanediol	Methoxyethanol
1	173	163	161	100	92	0	52	83	118	108
2	31	30	28	16	20	194	12	16	24	21
3	38	42	28	16	24	1300	10	12	26	27
4	73	69	75	55	44	13	49	88	58	53
5	100	75	54	40	36	89	44	0	50	38
6	20	20	7	4	15	56	11	63	13	14
7	24	16	12	14	19	113	28	100	21	27
8	19	19	13	6	22	433	33	58	18	20
9	37	33	33	4	16	700	11	7	17	19
10	122	34	30	43	41	40	15	100	48	49

Sensor	Cyclohexane	Cyclohexene	Ethylene glycol	Me cyclohexane	n-Undecanol	Butan-2-one	n-Hexane	Ethanol	Butyraldehyde	Ethyl acetate
1	300	260	371	580	400	500	208	163	144	104
2	150	115	240	188	24	63	76	182	280	32
3	154	100	200	143	35	39	69	217	150	30
4	135	171	0	150	208	160	575	219	219	115
5	114	133	350	217	900	47	70	47	50	9
6	51	36	325	500	9	8	26	19	25	7
7	33	23	357	40	400	8	25	23	21	15
8	55	39	700	38	166	19	23	17	20	13
9	71	30	86	50	100	71	20	27	24	13
10	60	55	20	57	32	43	213	11	157	53

response.

The odour properties of some molecules are related to carbon chain length. This complex inter-relationship may be illustrated by considering a series of aliphatic esters. With reference to figure 38, variation of the length of one of the aliphatic chains (R_1 or R_2) whilst keeping the identity of the other constant yields an homologous series which exhibit different odour properties [89].

Figure 38 Diagrammatic representation of an aliphatic ester.



The effect of aliphatic chain length on the response behaviour of a sensor array has been investigated using an homologous series of acetate esters where R_1 remained as CH_3 whilst R_2 was increased from C_1 to C_6 (methyl to hexyl). Three replicate tests were performed on each ester to allow the calculation of standard deviation based on the averaged response data. The test conditions which were adopted are outlined below:

Array : Head 2

Sample size : 0.01 moles

Equilibration time : 15 minutes

Purging : 10 minutes (sensors) with 30 % r.h cylinder air.

Acquisition time : 3 minutes

Analysis point : @ 1 minute

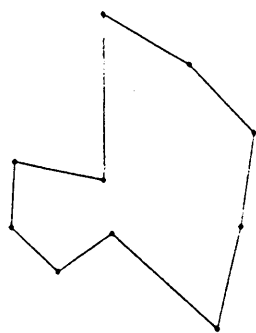
A series of response patterns (difference plots) have been prepared from adjusted response data obtained by subtracting a water reference template from the raw response data. These patterns, which are presented in figure 39 show that methyl acetate and ethyl acetate are very similar to each other but are different to propyl, butyl, amyl and hexyl acetate which display no obvious differences from each other. On the basis of these results, the array has difficulty in discriminating between molecules which differ only in their hydrocarbon chain length. The % relative standard deviation data based upon the standard deviation of the adjusted sensor responses which are presented in table 31 are again unacceptable in most cases and hence it is extremely difficult to propose any conclusions concerning the effects of aliphatic chain length on the basis of these studies.

Table 31 % RSD of the tests involving a series of acetate esters.

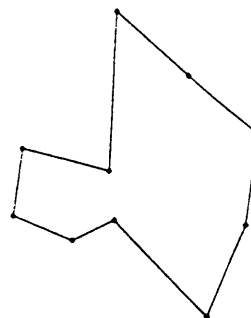
Sensor	Methyl	Ethyl	Propyl	Butyl	Amyl	Hexyl
1	21	17	60	31	40	0
2	58	50	15	23	44	122
3	19	39	6	19	0	350
4	13	23	140	73	120	250
5	27	26	20	3	0	150
6	15	12	55	107	40	29
7	18	19	77	94	22	46
8	0	16	45	92	71	100
9	10	24	80	48	63	550
10	3	6	16	8	7	14

Figure 39 Response patterns for a series of acetate esters based on adjusted response

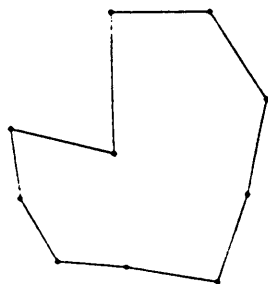
data.



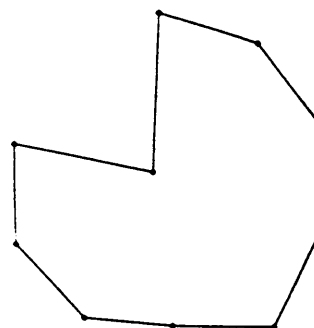
Methyl (C₁)



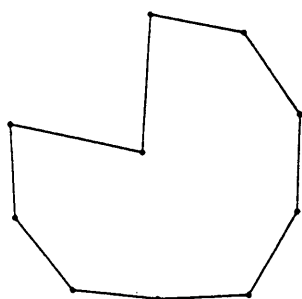
Ethyl (C₂)



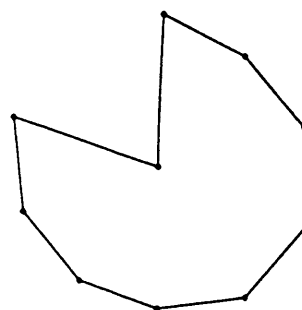
Propyl (C₃)



Butyl (C₄)



Amyl (C₅)



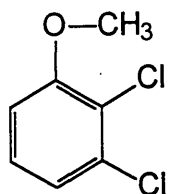
Hexyl (C₆)

5.4 Investigation of positional substitution in aromatic systems.

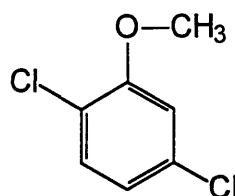
The effects of structural variation in analyte species on the response of an array have been investigated using a series of chloroanisole isomers which display subtle variations in positional substitution. The structures of the test isomers are presented in figure 40.

Figure 40 Structures of the chloroanisole isomers profiled during the investigation.

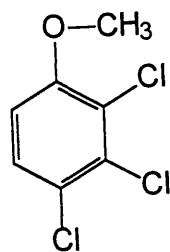
2, 3 Dichloroanisole



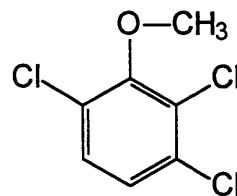
3, 6 Dichloroanisole



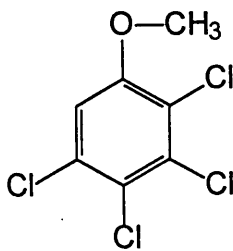
2, 3, 4 Trichloroanisole



2, 3, 6 Trichloroanisole



2, 3, 4, 5 Tetrachloroanisole



Three replicate tests were performed on each isomer to allow the standard deviation of the averaged sensor responses to be calculated. The test conditions which were adopted are outlined below :

Array : Head 2

Sample size : 0.01 Moles.

Equilibration time : 15 minutes.

Purging : 10 minutes (sensors), 5 minutes (vessel) with 30% r.h air.

Acquisition time : 3 minutes.

Analysis point : @ 1 minute.

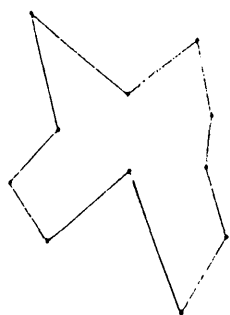
The responses obtained for each isomer were again adjusted by subtracting a water reference template from the raw data. The adjusted sensor responses for each chloroanisole isomer are shown in table 32. These values are extremely similar and it is very difficult to distinguish between some of the isomers on the basis of these data. The trichloro isomers exhibit higher responses than the dichloro isomers whilst the responses of the trichloro isomers are virtually identical to those of the tetrachloro isomer. On the basis of this study, it would seem that the introduction of increasing numbers of chlorine atoms into the aromatic system does not cause any significant change in the responses of any of the sensors. A series of patterns based upon the adjusted response data are presented in figure 41. It is virtually impossible to distinguish between the isomers on the basis of these patterns. Comparison of the response data using ribbon plots does not improve visual discrimination as shown in figure 42.

Table 32 Adjusted responses for the tests involving a series of chloroanisoole isomers.

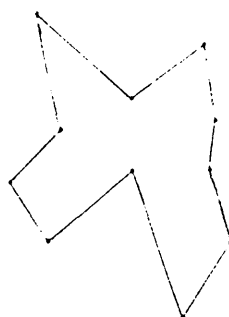
Sensor	2, 3 Dichloro	3, 5 Dichloro	2, 3, 4 Trichloro	2, 3, 6 Trichloro	2, 3, 4, 5 Tetrachloro
1	-3.87	-3.88	-3.93	-3.94	-3.93
2	-1.49	-1.49	-1.51	-1.51	-1.50
3	-2.90	-2.90	-2.98	-2.98	-2.97
4	-3.44	-3.45	-3.49	-3.49	-3.48
5	-1.82	-1.83	-1.85	-1.88	-1.86
6	-0.56	-0.55	-0.58	-0.57	-0.58
7	-5.66	-5.67	-5.72	-5.74	-5.72
8	-2.06	-2.03	-2.11	-2.1	-2.09
9	-1.71	-1.74	-1.76	-1.75	-1.76
10	-3.28	-3.29	-3.35	-3.34	-3.34
11	-0.16	-0.24	-0.26	-0.25	-0.25

Figure 41 Response patterns for a series of chloroanisole isomers based on adjusted response data.

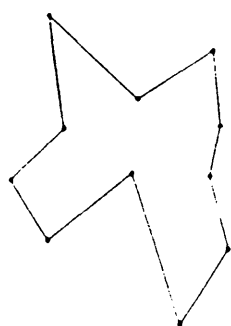
2, 3 Dichloro



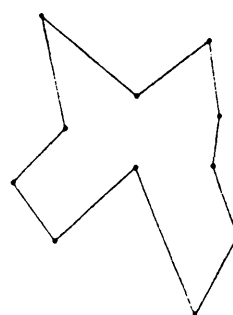
3, 5 Dichloro



2, 3, 4 Trichloro



2, 3, 6 Trichloro



2, 3, 4, 5 Tetrachloro

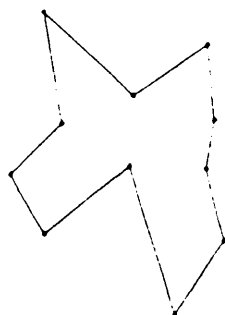
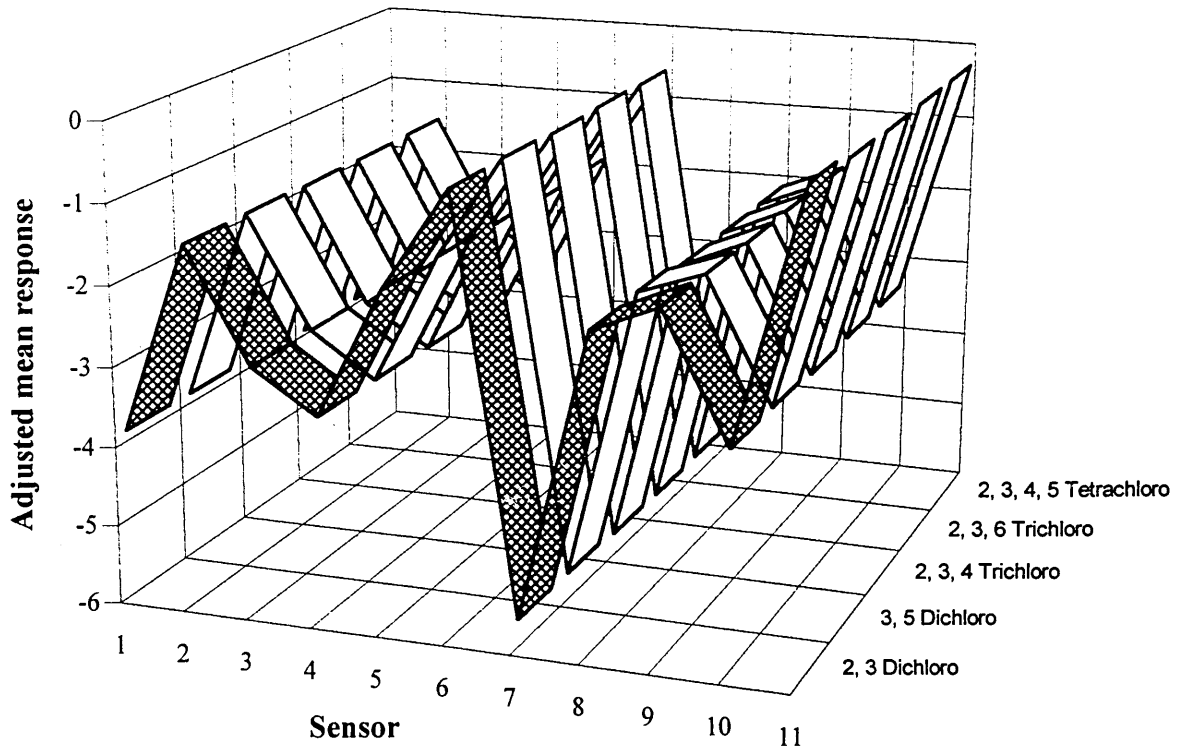


Figure 42 Comparison of the responses obtained for a series of chloroanisoole isomers.



The polymer matrix of each sensor presumably interacts to some degree with the ether functionality in each of the chloro anisole isomers since it is the most polar area of each structure. It may therefore seem logical to assume that sensor response would be influenced by steric hindrance around the oxygen atom. This effect, if it exists would appear to be minimal based upon the response data obtained for the 2, 3, 4 trichloro isomer and the more hindered 2, 3, 6 trichloro isomer which exhibit virtually identical responses.

With the exception of sensor 11, the majority of the % RSD values based on the adjusted response data are within an acceptable range of 2-10%. However, the mean responses obtained for the water reference template are far higher than those obtained for the chloroanisole isomers which suggests that the water response effect has been drastically over compensated for in this case. Obviously, there is a need to determine the extent of the response to water before future investigations can be performed. Again, the results of this investigation are rather inconclusive, it may be possible that the response mechanism of the sensors is based on "identification" of the steric features exhibited by each isomer but there appears to be no simple relationship between response and positional substitution on the basis of these results.

Table 33 %RSD of the chloroanisole tests based on adjusted sensor responses.

Sensor	2, 3 Dichloro	3, 5 Dichloro	2, 3, 4 Trichloro	2, 3, 6 Trichloro	2, 3, 4, 5 Tetrachloro
1	10	10	10	10	10
2	2	2	0	2	2
3	3	3	3	3	4
4	3	3	3	3	3
5	3	3	3	3	3
6	5	4	4	3	5
7	5	5	5	5	5
8	4	3	4	4	4
9	3	3	3	3	3
10	3	3	3	3	3
11	116	70	65	68	67

Chapter 6 Conclusions

The use of arrays of polypyrrole-based gas sensors to characterise volatile species is hindered by the fact that the sensor responses are dominated by water within the test environment. It is difficult to envisage how this effect could be minimised since there is a requirement that the sensors are purged with moist air between sample tests to aid their recovery to equilibrium conditions and avoid drying out the polymer films. Subtraction of a water reference template (blank) from a set of sample responses allows the creation of response patterns which are theoretically based solely upon the analyte in question and in most cases these patterns, on the face of it, allow adequate discrimination between a series of samples. However, this strategy is only an approximation and in some cases the subtraction of a blank based upon water may have over compensated for the moisture effect. This strategy could be significantly improved by subtracting a blank whose magnitude was based upon the measured humidity within the test environment (ie subtraction of large blank for high humidity and low blank for low humidity). This would require the investigation of the effects of humidity upon sensor response. A series of repeat tests would be required whereby a series of humidity levels are generated and measured within the test environment. There would also be a requirement to study the inter-dependency between temperature and humidity. The problems associated with temperature variation could easily be overcome by redesigning the instrument such that the sensing array and equilibration vessel were contained within a temperature controlled environment as in the "AROMASCANNER" instrument.

The adjusted sensor responses associated with the blank subtraction procedure exhibit very poor precision and many of the results from our investigations can be viewed with limited confidence. There is an obvious need for a series of repeat investigations to be performed on a regular basis to investigate the extremely poor reproducibility that has been observed. Unfortunately, it was impossible to repeat many of the investigations to determine the causes of this problem. The major contribution appears to be from the effects of water response but it is feasible that temperature effects and inefficient purging of the arrays between sample tests leading to only partial recovery of sensors to their equilibrium states may also have been significant factors in the poor response reproducibility achieved in some tests. Studies involving individual sensor elements in a simple test rig [168] have shown that sensors of this design do not return to their equilibrium resistance states after exposure to an analyte even after being purged with cylinder air for periods in excess of fifteen minutes. The design of the head unit in which the sensor arrays are housed does not appear to allow uniform purging of the polymer films and experience has shown that it is extremely difficult to ensure that a standard air flow rate is used at each purging session, even with the incorporation of a flow meter in the gas line. This suggests the adoption of an increased purging time but this strategy would compromise the rapid testing times associated with the system. It would therefore seem prudent to investigate alternative purging strategies which ensure efficient sensor recovery. It may also be advisable to investigate alternative methods of housing the sensors which would allow uniform purging of the array. Many of the reported flow through sample introduction-based devices reported in the literature exhibit extremely rapid recovery times (for example [109]) and it may be prudent to investigate this type of instrumental design.

It would be extremely interesting to investigate the claim that the sensors are manufactured extremely reproducibly allowing replacement of individual elements or complete heads without compromising test results. It would also seem prudent to investigate whether the performance of an array is reproducible between different instruments.

The use of euclidean clustering techniques have shown much promise in our studies, allowing the investigation of the similarity of the response behaviour exhibited by a series of sensors or test compounds. These techniques would undoubtedly become invaluable if a more extensive programme of research which generated much larger sets of data was undertaken in this area. It has also been demonstrated that visual discrimination may be improved between some test samples by simply displaying the response data an alternative style of presentation. These plots and all of the clustering techniques have been developed off line using suitable software packages. It is therefore suggested that the NOSETM software should be improved upon to allow more sophisticated data presentation, manipulation and analysis.

The NOSETM has shown great promise and has great potential in many areas of application. However, although the arrays compare favourably with established techniques such as gas chromatography in terms of sample analysis time they are unlikely to be considered a practical alternative analysis technique until the problems associated with their significant response to water are solved

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