Feasibility Study of an Electronic Nose Device for Meat Processing Odour Monitoring

For:
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Executive Summary

After considering the existing literature and information on the chemical composition of meat processing odours (RPDA.303), chemical mixtures that had odours of meat rendering plants were formulated and used to demonstrate that an electronic nose responded to such odours.

A sensor array device (e-nose) was constructed. Four sensors were chosen from a number of available sensors. In addition a fifth sensor, in a separate housing, was used to detect sulfur compounds. These two devices, used in combination, as a single effective e-nose, were sufficiently sensitive to detect odours sampled at a meat processing works. The sensitivity level for the e-nose was within the range of detection for these sample odours demonstrated by a panel of expert human odour judges.

Analysis of the raw output data from the e-nose by three methods showed that classification of the odours was feasible. The classes were determined by the source of the odour at the meat processing plant.

Chemical analysis of the processing plant odour samples showed that the e-nose was responding to the presence of aromatics (toluene, xylenes) aldehydes and dimethyl sulfide.

The study has shown:

- The e-nose can easily detect odours generated in a meat processing plant.
- It can discriminate between odorous sources.
- The e-nose tested had a detection limit around or below the 10 unit human threshold for meat processing odours (an odour intensity that is no longer detectable by a human if diluted ten-fold).

The study concludes that an e-nose could be used routinely to monitor odours at meat processing plants. It is suggested that a prototype “Sentinel” system, consisting of a number of e-noses installed at appropriate locations and linked to a central processor, be tested at a meat processing plant.

Glossary

2D	Two dimensional
BAW	Bulk Acoustic Wave device
CP	Conductive polymer
e-nose	Electronic Nose, see Appendix 1
EPA	Environmental Protection Agency
FOS	Fluorescence Optical Sensor
GC	Gas Chromatography - A method of analysing volatile chemicals
GC olfactometry	Gas Chromatography with human 'sniff' evaluation
IR	Infra Red
LDA	Linear Discriminant Analysis
MLA	Meat and Livestock Australia Limited
MOS	Metal Oxide Semiconductor
MOSFET	Metal Oxide Silicon -Field Effect Transistor
MS	Mass spectrometry
Odour Unit	Measure of the dilution of a gas sample needed before a human panel ceases to smell it.
Olfactometry	Method of determining the relative human impact of smells by dilution to the point of non-detection
PC	Personal Computer, Principal Component
PCA	Principal Components Analysis
pg	Picogram
ppb	parts per billion
ppt	parts per trillion
QCM	Quartz Crystal Microbalance
SAW	Surface Acoustic Wave device
Taguchi Sensor	Patent metal oxide semiconductor

Introduction

Odour release remains one of the greatest sources of community complaints and concerns regarding meat processing and rendering plants. Unfortunately, the objective measurement of the offensiveness or strength of odours in a manner that corresponds to that detected by the human nose remains extremely difficult and expensive.

One approach is to use an array of electronic sensors known as an ‘e-nose’. (See Appendix 1).

A preliminary study by MLA has shown that commercial electronic noses can distinguish between types of odour, although these are expensive ($100,000) and do not always provide the solutions that are claimed for such devices. There is scope for producing low-cost, portable systems that are programmed for a given situation, such as a meat processing works. These may be combined to provide total coverage for the plant (the “Sentinel” system).

This project is a proof of concept of such a system.

Objectives

Evaluation of the feasibility of producing low cost portable sensors for the meat processing industry, achieved by:

1. Undertaking a literature survey.
2. Identifying electronic sensors that respond to the compounds that represent typical meat processing odours.
3. Synthesis of a typical meat processing odour (as identified in the MLA report RPDA.303).
4. Assembling a number (up to six) of these sensors into an array (e-nose).
5. Calibrating the e-nose for mixtures of these compounds that correspond to odours
6. Calibrating the e-nose against human responses to the mixtures.
7. Demonstrating that the device can accurately track the human response to a given mixture
8. Demonstrating use of the device in a meat processing site[1]
9. Preparing a program of work to develop the instrument for on-line use in meat processing plants.

1 With agreement of the program manager, the e-nose was assessed using bagged odours from a meat rendering plant, and was not tested at the plant.

Literature Review[2]

Summary

The purpose of this review is to find documented examples of the use of electronic nose devices to monitor emissions from meat processing plants, or to monitor volatile mixtures analogous to those emissions.

There is no detailed literature dealing with the subject of the application of an electronic nose for the detection of odorous emissions from meat rendering plants, nor report of a study that is directly comparable to that conducted in 1999 by CH2MHill for Meat and Livestock Australia. Some studies have been conducted to investigate the feasibility of using an e-nose to monitor odours associated with livestock wastes. These wastes have a number of odorous components in common with meat processing emissions. There have also been a number of studies relating to the analysis of meat products by electronic nose, which have some relevance to the issue at hand. Aldehydes and reduced sulfur compounds have been detected successfully using various sensor technologies – for environmental purposes, and to monitor meat spoilage and classify types of meats.

It seems from the published literature that it is feasible to detect the volatile chemicals that comprise the odours emanated by meat processing plants using an e-nose device.

Objective 1 completed.

[2] The full literature review may be found in Appendix 2

Choice of Sensors

Sets of commercially available sensors of the low-current, doped tin-oxide, types have been obtained and suitable circuitry designed and built. The sensors we are using at present are of the printed sensor technology type, which require only about 30 – 50 mA for operation as compared with earlier types, which consumed 300 – 400 mA.

The particular sensors that we are testing are nominally sensitive to propane (TGS2610), methane (TGS2611), alcohols (TGS2620) and organic vapours (TGS2600). In practice there is considerable overlap of compounds sensed between different sensors a situation which is resolved by the pattern recognition software. Because the meat render odour has considerable sulfur compound content, including thiols, we included a thiol-specific sensor in the array (TGS 550).

There are other small sensors available in a related range including those that respond to carbon monoxide (TGS2442) and water vapour (TGS2180, TGS2281). These were evaluated and found not to be useful in this application.

The sensors have been mounted on a printed circuit board (PCB) in sets of the four types together with an air sampler fan incorporated into the housing. The PCB includes a regulated power supply and has arrangements for operation of the sensors and fan by an in-built rechargeable battery or from a step-down transformer from the mains.

Another PCB has been assembled for the particular operation of the thiol-sensitive sensor. This device has very distinctive power requirements and is subject to possible “poisoning” which has necessitated the incorporation of a periodic heating and cleaning cycle into the design. For these reasons the four-sensor array and the thiol sensor have been assembled in distinct packages but it is intended to eventually combine the whole assembly in a single housing.

The outputs from the above sensors consist of a set of DC voltages that vary as the sensors are exposed to various odorous mixtures. The signals are recorded by an interface and software package from Picotechnology Ltd. This system connects to IBM-compatible PCs via the parallel port and is powered from the PC itself. The associated software (PicoLog) displays up to eleven channels on the PC in real time and can save the data in a number of formats. The data is readily translated into a useful text file for manipulation by our statistical and pattern matching techniques. As our investigation proceeds we may produce our own custom interface but at present the above device is convenient and more than adequate.

The sensor assemblies are illustrated in the photographs below:

4 sensor array.
Dimensions (w x h x d)
100 x 40 x 180 mm
Weight (incl batteries) 650 g

4 sensor array with added thiol sensor.
Dimensions (thiol) (w x h x d)
80 x 30 x 150 mm
Weight (incl batteries) 400 g

The sensor arrays can be connected to a PC by several metres of cable or may be remotely monitored by telemetry (to be developed later).

Objective 2 completed
Objective 4 completed

Tests

Preparation of synthetic meat odour

The synthetic meat odour described in MLA RPDA.303 was prepared.

The mixture contained hydrogen sulfide, methyl mercaptan, dimethylsulfide, dimethyldisulfide, 2-methylpropanal, 3-methylbutanal, hexanal, heptanal, methanol and ethanol (For details see Appendix 3).

Objective 3 completed.

Analysis of odour mixtures

As an extra piece of work conducted within the original time scale and budget, gas chromatography mass spectrometry (GC-MS) was used to analyse bagged odours. Sufficient gas sample was available for only three of the bags from the Biofilter inlet, Biofilter outlet and Wastewater plant.

Distinct profiles of compounds were discovered in the Biofilter inlet, outlet and Wastewater plant. The gaseous composition appeared different to the synthetic odour but all the samples were characterised by the presence of considerable amounts of aromatics (toluene, xylenes), aldehydes and dimethyl sulfide which appear to be detected by the sensor system.

Details are collected in Appendix 4.

Additional objective completed.

Response to synthetic odour mixture

The sensor array was exposed to the synthetic meat odour

Figure 1 shows the output of the array to a series of exposures of the synthetic meat odour followed by fresh air. The response was fast and clearly followed the rise and fall of the odour.

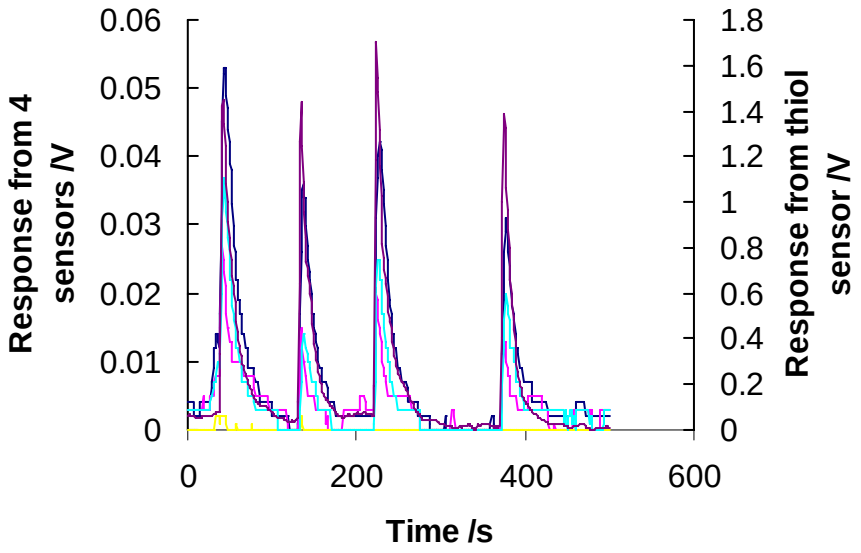

Figure 1: Output of sensor array analysing consecutive exposures to the synthetic odour mixture.

Response to meat odours

The bagged odours were collected by staff from The Odour Unit Pty Ltd (T. Schulz), Australian Technology Park, Eveleigh, who determined the odour unit value of each sample by dilution analysis and human panel.

The bags were from the following locations in Southern Meats, Goulburn, NSW: Biofilter Outlet, Biofilter Inlet, Wastewater Plant, Kill Floor Vent, Sheep Holding Pens. (Details of samples are given in Appendix 5).

The bags were passed to the Centre For Chemosensory Research for examination with the sensor arrays. (Details of the experimental procedure are given in Appendix 6).

Results

The electronic nose responded to each bagged odour and the magnitude of the response followed the strength of the odours. The small sample size (number of bags and different odours) limited the extent of the statistical analysis. However it was possible to use the electronic nose to discriminate between the types of odour and to give an indication of whether the odour was ‘high’ or ‘low’.

Calibration

Figure 2 shows the results of a procedure called ‘cluster analysis’ that analyses all the data and groups the samples. There are three main groups. The first contains all the low odour samples and the second and third cover the high odour samples. One of these groups only contains odours from the Biofilter Inlet which had a separate and distinct odour.

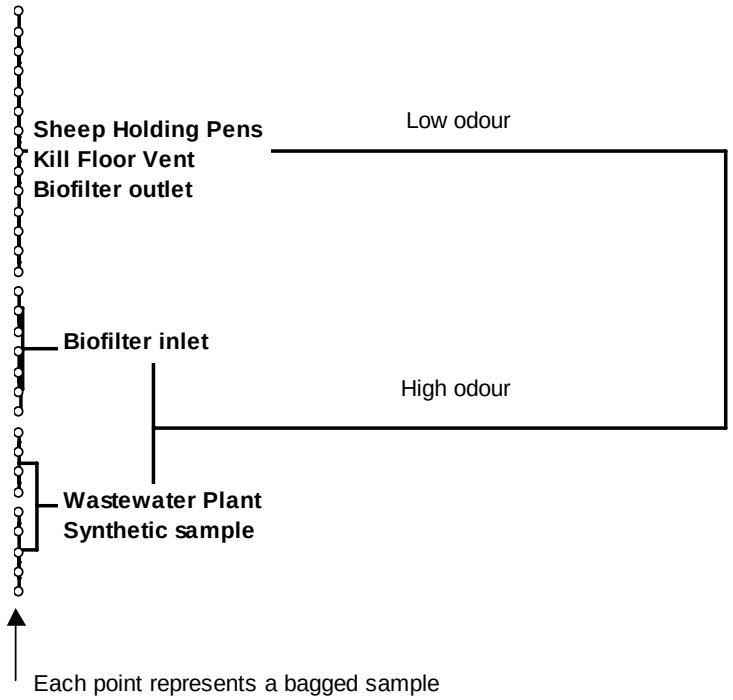

Figure 2: Discrimination between high and low odour sources

In Figure 3, a different technique (principal components analysis) shows groupings, first between low and high odours, and then within the high odours between the synthetic samples, the Biofilter Inlet and the Wastewater Plant.

A more detailed account of the statistical methods used is giving in Appendix 7

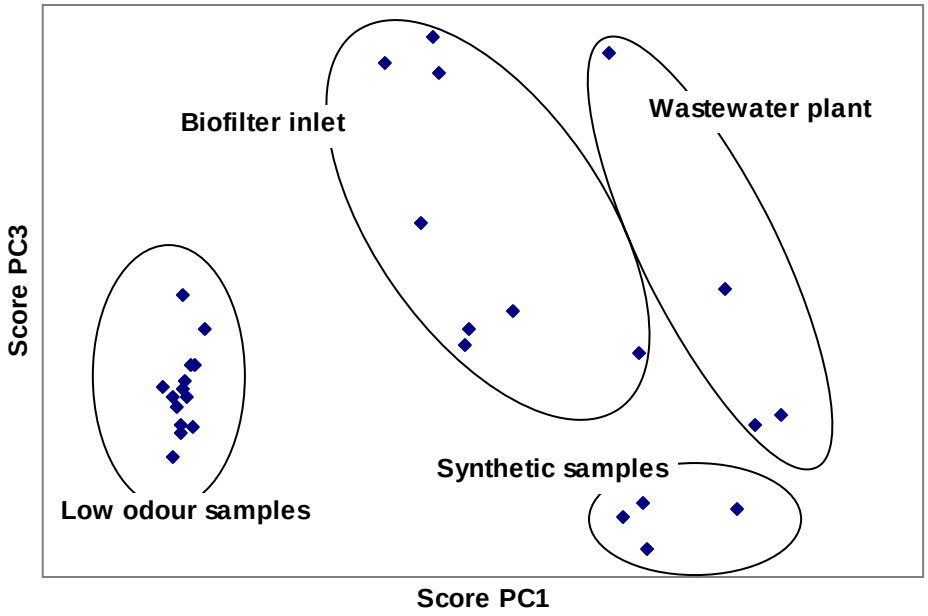

Figure 3: Statistical analysis of electronic nose output showing discrimination between locations of sampling.

Objective 5 completed

Sensitivity

If the sensor voltage is plotted against the odour units of the sample on a log-log plot an approximately straight line is obtained (Figure 4). The odour unit threshold for the EPA is 10 units (horizontal dotted line), and the threshold for measurement is about 2 mV above baseline (vertical dotted line). The thiol sensor (S5) can detect meat plant odours at the 10 unit level. Sensor 2 (representative of the other sensors) just reaches the level and with optimisation it is clear that the device as a whole would certainly achieve the EPA limits.

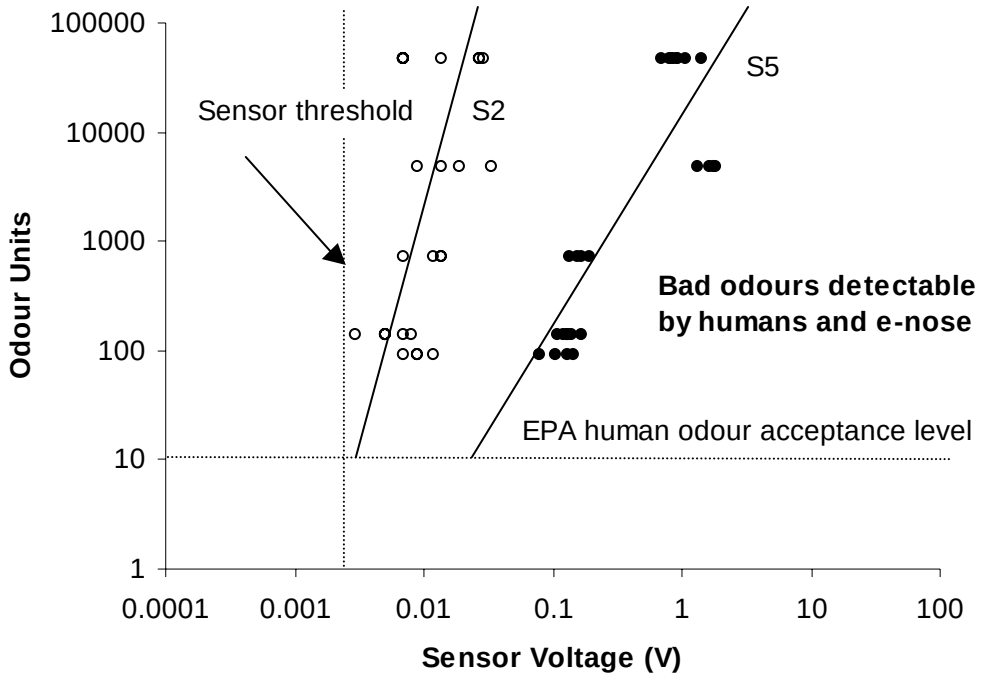

Figure 4 : Correlation between sensor responses and odour levels

The linear response of the sensors to the human odour unit values shows that the e-nose can track the human perception of the odour.

Objective 6 completed

Objective 7 completed

Future Directions

This project has demonstrated the capacity of the e-nose to detect and distinguish among odours. We believe the next phase of development should be a pilot study at a meat rendering plant, in which a number of sensor arrays are deployed for a period of time. This would be a realisation of the "Sentinel" concept described in earlier reports.

The objectives of this phase would be:

1. Demonstrate the capacities of the e-nose arrays to detect odours in a plant.

2. Optimise the physical arrangement of the arrays (particularly in relation to the potential source of odours), and the numbers and types of sensors.

3. Set up a central control point to which all data is transmitted, and where software will process the sensor output to give real time advice to plant operatives.

4. Collect human sensory data in the plant for comparison/ calibration of the nose.

The outcomes of the program will be:

- A prototype system that detects unwanted odours and gives an indication of the location and likely impact on the public.

- Intellectual property and a demonstration system that will be patentable for "Sentinel" systems.

Objective 9 completed

Conclusions

- The e-nose can easily detect odours in the plant.
- It can discriminate among the more odorous sources.
- The e-nose used here has detection limits around or below the 10 unit threshold.
- Future optimised systems will provide warning and information about all odours that pose problems to meat processing plants.

The success of this trial gives us great confidence that a “Sentinel” system could be set up as envisaged, with arrays of sensors in the plant near sources of odour and on the boundary of the factory.

Calibration and monitoring should allow a clear picture of the odour profile of the plant, with indication of both the sources of odour and the likely nuisance levels to the public.

Acknowledgments

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For the authors:

Signed:

APPENDICES

Appendix 1: What is an Electronic Nose?

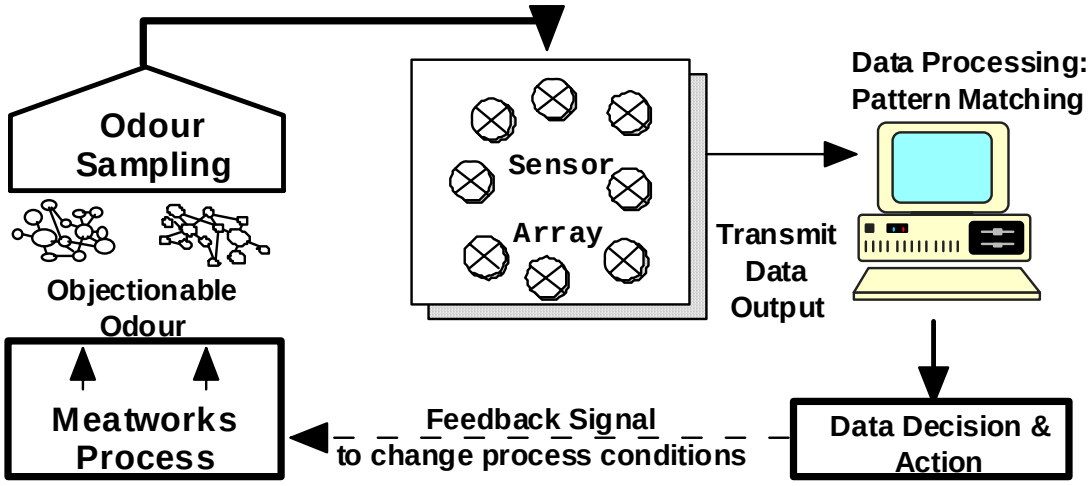
The term ‘Electronic Nose’ is a generic name for an analytical instrument that profiles the headspace volatiles over or around a sample. The technology is based on an array of partially-specific chemical sensors whose outputs are integrated by advanced signal processing to rapidly identify complex odour mixtures. These devices offer the food, packaging and other industries a method of rapid chemical analysis for the improvement of production efficiency and quality control, by classifying complex volatile mixtures. Current analytical methods, such as gas chromatography and mass spectrometry are unsuitable or unable to satisfy the requirement for rapid, simple operation which is demanded in the factory situation.
Presently, commercially electronic noses are not adapted to on-line monitoring or process control. Their sensitivity and speed of operation leaves much to be desired. Additionally, demonstrated software and data analysis techniques of the commercial systems are not generally suitable for feedback or alarm situations.
The electronic nose to some extent mimics the human sense of smell, but humans have a sensitivity and response repertoire greatly exceeding electronic noses. However, the noses can respond to certain chemicals that humans cannot smell or dare not smell for reasons of safety. Additionally the electronic nose does not, like the human nose, become fatigued or no longer respond to an odour due to adaption.

Current electronic noses are a comparative technique only and will produce a classification or “fingerprint” of the volatiles in a headspace. There is no identification of the components in the mixture. To achieve recognition of samples the noses require training. Electronic nose outputs are not generally considered quantitative.

The main features of the technique are:

- The response can be rapid and highly reproducible.
- The chemical fingerprint is unique and can be matched to a library for rapid identification.
- Once a protocol has been established the instrument does not require a highly skilled operative and frequently an icon driven screen is simply used to control operations.

To illustrate the concept, a possible way of applying electronic noses to the control of nuisance odours is indicated in the diagram below. The sampling could be made at various points inside or on the perimeter of a plant and information relayed to the operation centre for action by plant engineers. Alarm levels could be set which when reached would trigger appropriate responses to avoid environmental consequences.



Use of an 'Electronic Nose' as a meat process control device.

Appendix 2: Literature survey

BACKGROUND: Preliminary study by CH2MHill (1)

The first object of this study was to identify the “most nuisance compounds” producing the bulk of odours associated with meat rendering. The results are shown below in Table A2.1.

Table A2.1

Compound	Chemical Group
Hydrogen sulfide	Reduced sulfur compounds
Dimethyl sulfide	
Dimethyldisulfide	
Methyl mercaptan	
3-methyl butanal	Aldehydes
2-methyl butanal	
2-methyl propanal	
heptanal	

The study also found that amines might also play a large part in odorous emissions in some cases.

Olfactometry, GC-MS and 2 types of e-nose were used in this analysis, in order to compare the efficiency of the 3 techniques. The 2 e-noses used were the Aromascan e-nose (conducting polymer sensor), and the Fox 4000 metal oxide sensor from Alpha M.O.S.

The conducting polymer sensor e-nose was found to be very sensitive to water, and was therefore judged to be unsuitable for monitoring purposes, whereas the metal oxide sensor was not water sensitive, and was thus used for most of the analyses.

The conclusion of this study was that e-nose technology has a real potential for use as an environmental monitor of odour emissions. The e-nose technology was found to be most effective at differentiating between overall odours, rather than individual components, although it was able to differentiate between different concentrations of the same odour. E-nose technology seemed to correspond well to the human nose.

Advantages & Disadvantages of Different E-nose Sensors

As was found in the study described above some sensors are more suitable than others for monitoring purposes. A brief description of different sensor types is given below:

Metal oxide sensors (MOS):

These sensors usually have a lesser selectivity than other sensor technologies (CP, BAW, SAW, or MOSFET) (2). However, they do have an extreme sensitivity to ethanol, which may blind them. They also may be poisoned by irreversible binding of sulfur compounds (2, 3), which could prove

to be a problem when applied to meat processing and rendering odours. They are, though, the most used of all the sensor technologies so far.

Conducting polymer sensors (CP):

These sensors show good sensitivity, but require a low operating temperature (<50ºC) which makes them sensitive to humidity (2, 3), as was discovered in the CH2MHill study (1). They are resistant to poisoning, but only have a lifetime of around 9-18 months (2).

Piezoelectric crystal sensors (including surface acoustic wave, SAW, and bulk acoustic wave, BAW, devices):

These crystals may be coated with an unlimited number of materials (2), and so offer the greatest selectivity of all the sensors. However, at the moment it is difficult to produce a reproducible coating from one batch to another (2,3). They are also sensitive to temperature and humidity fluctuations.

Fibre Optic Sensors (FOS):

These are optical sensors in which the light is delivered and monitored by an optical fibre. They show rapid response and are of small size, but lack sensitivity (3).

Metal oxide semiconductor field-effect transistor (MOSFET):

A great deal of expertise is needed to manufacture a good quality sensor. However, these sensors are very robust and have a low sensitivity to moisture. (2)

Environmental Monitoring and the E-Nose

An area relevant to the subject of meat-related emissions is the analysis of odours from agricultural practices such as the application of animal slurries to land.

Hobbs *et al* (4) used an e-nose comprised of an array of 20 polypyrrole sensors to assess odours from livestock waste (pig and poultry slurry). GC-MS was used to identify odourants such as dimethyl disulfide and dimethyl trisulfide in the chicken slurry. The sensitivity of the e-nose was found to be low, compared to olfactometry. The e-nose was good at discriminating between different odours, but was only able to detect odour concentrations down to 60 000 OU m^{-3}. Moisture was found to be a factor in reducing the sensitivity of the polypyrrole sensors.

In a more recent study by the same group (5), two different CP type e-noses were used (an Aromascan, and the Odormapper) in the detection of odours from cattle slurry. This time the e-noses were found to have a greater sensitivity to odourants (down to 10 000 Ou m^{-3}).

An instrument that has been developed recently is the “zNose” manufactured by “Electronic Sensor Technology” (ESTCAL). Although this instrument is not strictly an e-nose, it is a combination of fast chromatography, an integrating SAW sensor, and a programmable gate array (PGA) microprocessor (6). It is able to identify individual volatile components and also gives a visual fragrance pattern that identifies overall odours for the user. This group is investigating odours from meat rendering plants. EJ Staples of ESTCAL (private communication) claims that the zNose is able to quantify and identify the concentration of chemicals in the odours (but does not specify what these chemicals are in any of these communications). The detection of odours associated with swine production is mentioned in one paper, but is not elaborated upon (although methane is mentioned). The zNose is claimed to have a minimum detection level for volatile organic compounds of 1 ppb, and for semivolatiles, 1 pg or ppt.

The E-Nose and Food

In 1998 Schaller *et al* (2) published a review of the e-nose and its application to food. They reported that within the area of analysis of food by e-nose, the greatest interest has been in the analysis of meat and meat products.

E-nose to detect meat spoilage

Most research applying an e-nose to meat odours has been related to the detection of off-odours by analysis of sample headspace, rather than to the measurement of processing or rendering emissions in the environment. Studies have shown that the chemicals produced by bacterial action on meat include aldehydes (such as heptanal, hexanal and octanal) and some ketones (7), and sometimes alcohols and indoles (8). There is a general belief that the e-nose, particularly coupled with an artificial neural network (9) shows promise when it comes to detecting meat spoilage and off-flavour.

Some research has been done using the e-nose for classification of microorganisms on meat products by their chemical products (10-11). The instrument used in these studies was a Fox 2000 e-nose consisting of 6 MOSs. Bacterial strains used for curing meat, or pathogenic strains, were identified by analysis of the meat’s headspace. In another study conducted in 1998 (8) an e-nose using CP sensors, coupled with artificial neural network software, was used to measure volatile compounds produced by bacteria on chicken.

Most recently (1999) a study conducted by Siegmund *et al* (12) compared the efficacy of an electronic nose to that of GC-MS and GC olfactometry, for the measurement of the volatile fraction of chicken during storage. This study analyzed for saturated and unsaturated aldehydes. The e-nose results showed a good correlation with those obtained from GC techniques.

Also in 1999, Blixt *et al* (13) used an e-nose composed of 10 MOSFET transistors, 4 Taguchi sensors and one CO2 sensitive sensor to check on the spoilage of vacuum packed beef. In the end the degree of spoilage was calculated using only 2 Taguchi (semiconductor oxide) sensors, and was found to correlate well with the ratings of a sensory panel.

Table A2.2: E-nose applications in the meat industry

Application	Type of E-Nose	Reference
Pig and poultry slurries (reduced sulfides)	20 CP sensors	4
Cattle slurry	CP sensors	5
Meat rendering odours	"zNose" SAW sensor	6
Measurement of volatile compounds off chicken	CP sensors	8
Analysis of headspace generated by microbial species on meat to classify bacteria	Fox 2000 – array of 6 MOSs	10
Analysis of headspace of sausage and hams to classify meat	Fox 2000 – array of 6 MOSs	11
Aldehydes off chicken	Not specified	12
Beef spoilage	2 Taguchi sensors	13
Identifying hams and sausages	MOS CP	14
Type of ground meat, storage time	10 MOSFET 1 MOS 1 IR sensor	15

Identifying Meat

Other studies have concentrated on identifying an odour pattern in order to recognise and discriminate between different types of meat (14, 15), rather than looking at their volatile compounds individually. Moy *et al* (14) used a combination of MOS and CP elements to distinguish between samples such as hams and sausages.

The type of meat and storage time of ground meat was investigated by Winquist *et al* (15) using an e-nose with 10 MOSFET, 4 MOS and 1 infrared sensor. Sensor signals were treated with pattern recognition software based on an artificial neural network system. The type of meat was easily determined, but the time of storage was not so successful.

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Appendix 3 Recipe for the Synthetic Gas Mixture

		(Table values are microlitres required)		
	Form	***1 Litre - 1st dilution (ppm Concentrate)***		***ppb***
Hydrogen Sulfide	Gas	0.25 mL		**1000**
Methyl Mercaptan *(Methanethiol)*	1% in MeOH	4.92	These volumes will exceed the MeOH concentration required by 1.5 times	**1000**
Dimethylsulfide *(Methyl Sulfide)*	Liquid	0.06		**10**
Dimethyldisulfide *(Methyl Disulfide)*	Liquid	1.93		**200**
2-Methylpropanal *(iso-Butyraldehyde)*	Liquid	7.37		**1000**
3-Methylbutanal *(iso Valeraldehyde)*	Liquid	35.21		**4000**
Hexanal	Liquid	2.05		**200**
Heptanal	Liquid	0.23		**20**
Methanol	Liquid	3.27	Not required - See above	**1000**
Ethanol	Liquid	96.22		**20000**

Take 4mL of the 1L Concentrate above and dilute into a 1 Litre vessel to obtain the required ppb.

Appendix 4: Analysis of bagged odours by GC/MS

The analysis was performed by Gas Chromatography Mass Spectrometry following sorption and thermal desorption from Tenax.

Experimental

The collected volatiles were transferred from the collection bags by application of gentle pressure, over about 2 hours, to stainless steel sample tubes, which contained 200 mg of Tenax (TA 60/80).

The samples were analysed using an Automated Thermal Desorption (ATD) system connected to a Hewlett Packard GC/MS.

Apparatus

Perkin Elmer ATD 400 (with Cryogenic concentrator and automated sample injector).

Hewlett Packard GC 6890 series MS 5973 Mass Selective Detector

Column: HP-5MS

GC Conditions: Column: Programmed from 30° – 220°C at 4 °C/min

Interface Temperature: 280 °C

ATD Conditions

The ATD is connected to the GC by a heated transfer line which was set at 200°C. The samples were purged for 1 min with He gas to remove any oxygen. The samples were desorbed for 5 min and transferred to the cold trap (–30°C), which was then heated rapidly (40 °C s^{-1}) to 250°C. Finally the samples are transferred through the heated line into the GC/MS for analysis.

Identification of compounds

The compounds were identified by matching with a Reference Library (HP). Compounds with a match of 60% or better are listed in Table A4.1 below. The GC traces and the Library identification are available on CD-ROM, which can be read only with appropriate software.

It is seen from the GC traces (below) that the profile of the Biofilter samples is quite different from that of the Wastewater plant, and that the Biofilter does indeed reduce the number of compounds.

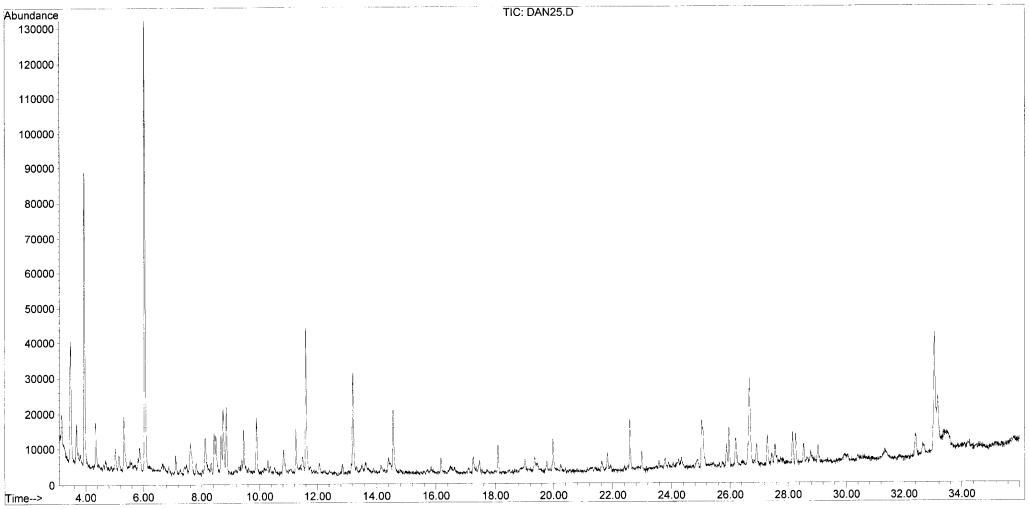

Figure A4.1: GC trace of Bag C703 (Biofilter Outlet)

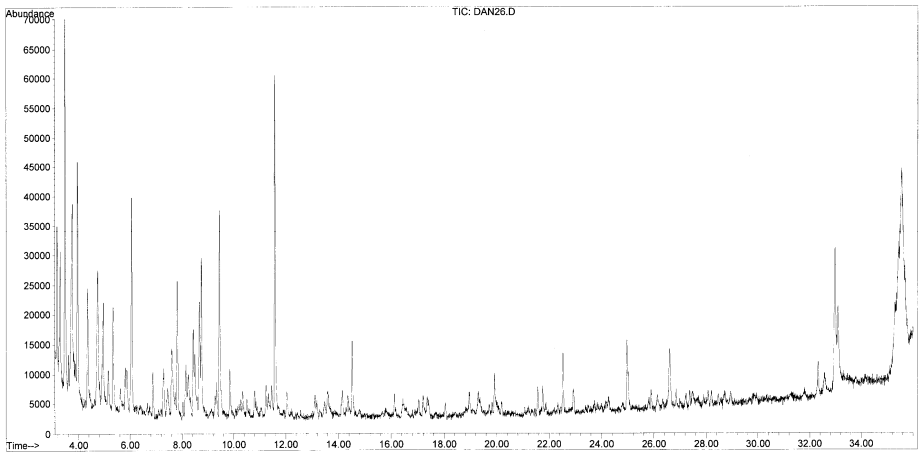

Figure A4.2: GC trace of Bag C705 (Biofilter Inlet)

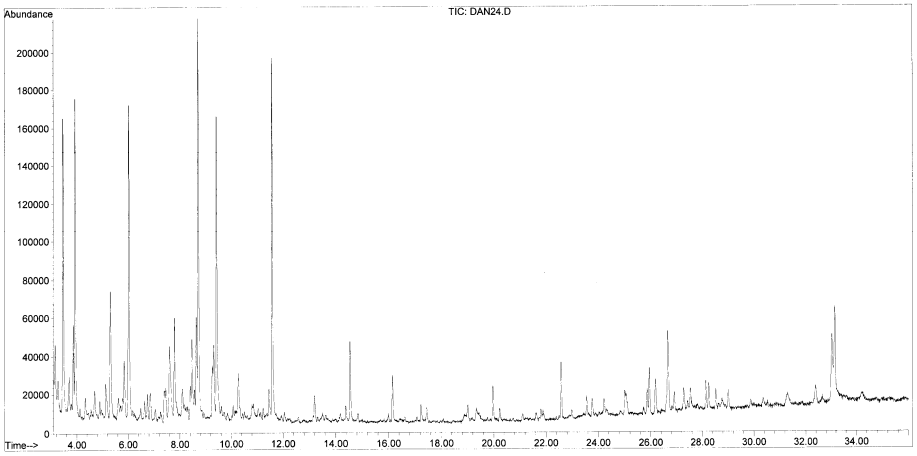

Figure A4.1: GC trace of Bag C707 (Wastewater plant)

Table A4.1: Compounds found by GC-MS in three bagged samples

Compounds in red are common to each sample.
Compounds in **bold** are in the Synthetic mixture (See Appendix 3)

Sample Name: C0703 Biofilter outlet	**% match**	**Sample Name: C0705 Biofilter inlet**	**% match**	**Sample Name: C0707 Wastewater plant**	**% match**
		Benzaldehyde	81		
		Benzaldehyde, 2-hydroxy-	81		
Benzene, 1,2,3-trimethyl-	87				
				Benzene, 1,2,4-trimethyl-	95
Benzene, 1,3,5-trimethyl-	87	Benzene, 1,3,5-trimethyl-	93		
				Benzene, 1-ethyl-2-methyl-	86
				Benzene, 1-ethyl-3-methyl-	94
				Benzene, 1-methyl-4-(l-methylethyl	97
		Butanoic acid	90	Butanoic acid	72
				1,4-Cyclohexadiene, 1-methyl-4-(l-	90
Decanal	68	Decanal	60	Decanal	80
				Decane	95
				Dibutyl phthalate	96
Diethyl Phthalate	96	Diethyl Phthalate	95		
Disulfide, dimethyl	**38**	**Disulfide, dimethyl**	**91**	**Disulfide, dimethyl**	**91**
D-Limonene	96	D-Limonene	94	D-Limonene	96
				Dodecane	64
				Ethylbenzene	81
Heptanal	**94**	**Heptanal**	**87**	**Heptanal**	**58**
Hexadecanoic acid	96	Hexadecanoic acid	97	Hexadecanoic acid	96
Hexanal	**90**	**Hexanal**	**72**	**Hexanal**	**74**
				Methane, dibromochloro-	97
Nonanal	91	Nonanal	86	Nonanal	91
Octanal	87	Octanal	87	Octanal	95
2-Octanone	72	2-Octanone	74	2-Octanone	72
Pentadecane	96	Pentadecane	83	Pentadecane	98
p/m-Xylene	93	p/m-Xylene	94	p/m-Xylene	97
Tetradecane	89	Tetradecane	60	Tetradecane	96
1-Tetradecanamine	72				
Toluene	93	Toluene	95	Toluene	91
				Tridecane	76
		Trisulfide, dimethyl	95	Trisulfide, dimethyl	94
				Undecane	76

Appendix 5: Details of bagged odours received from CH2MHill

Five samples from Southern Meats, Goulburn, NSW were received for examination by the electronic nose. The locations and bag numbers are given in Table A5.1. The level of odour in odour units per cubic metre was determined by CH2MHill and is given in the Table.

Table A5.1 : Bagged samples received for examination by the e-nose.

LOCATION IN PLANT	**TOU SAMPLE NUMBER**	**ODOUR CONCENTRATION (OU / m^3)**
Biofilter Outlet	C0703	724
Biofilter Inlet	C0704 / 705	46,300
Wastewater Plant	C0707	4,870
Kill Floor Vent	C0708 / 721	139
Sheep Holding Pens	C0722 / 723	91

These samples were the remains or duplicates of the bagged samples used for odour dilution examination.

Appendix 6: Experimental procedure for analysing bagged odours

The samples were prepared in 30 Litre sample bags.

Figure A6.1: Bagged Odours in 30 L sample bags

The method of examination of the bagged odours was as follows: The sensors were mounted at the rear of a sample chamber (approx. volume 2.5L). The array has two small fans which draw air through the chamber at about 500mL/min.

The bags were opened at the Swagelok seal and the outlet tube was introduced into the inlet of the sample chamber (which was partially covered with a polythene cover to reduce drafts) and the bag depressed manually so as to expel about 500 mL of gas sample into the chamber. The bag was then removed and sealed. The odour injection was repeated four times and, in each case, the responses of the sensors monitored and recorded by computer. The data was saved in a text file to be later replotted and analysed.

The raw data has been plotted in a standard form via Excel and the sensor outputs can be compared.

Appendix 7: Statistical analysis of e-nose data

A five sensor e-nose was used to analyse the bagged odours. As each sensor responds to a number of gas phase molecules, the data is analysed by methods of 'pattern recognition', which looks for trends in the totality of the responses.
Principal components analysis (PCA) is a commonly used method that projects out of the data set independent patterns called principal components, and the contribution each sample (here bagged odour) makes to the PCs. Plots of these contributions can show groupings in the data and allow calibration of the e-nose in terms of, for example, odour units.

Sensor output

The output from the sensors was imported as a text file into Excel. The baseline was subtracted giving the traces shown in Figure A7.1, which is for the Biofilter inlet (C0704). It was found that one sensor (Sensor 5 – the thiol sensor) responded very strongly to the odours, while the other sensors' contribution was less but still observable.
In the analysis, although the thiol sensor clearly dominates the output, this is largely due to the nature of the electronics and set up of this particular sensor. Two other sensors contribute strongly to the discriminating ability between odours.

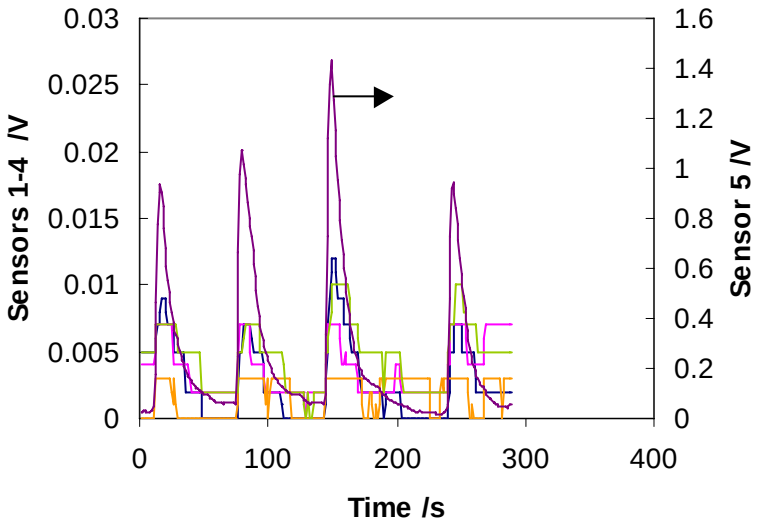

Figure A7.1: Traces for C0705 (Biofilter Inlet) with baseline subtracted

Data set

The data set consisted of a matrix with five columns (each sensor) and 31 rows (each sampling action). Eight bags were monitored about four times each. These were the seven bags described in Table A7.1 plus the synthetic sample. The data was the maximum height of the peaks.

Table A7.1: Source of odours bagged and analysed

Source of odour	Abbreviation on graph	Bag number
Biofilter Outlet	BO	C0703
Biofilter Inlet	BI	C0704
Biofilter Inlet	BI	C0705
Wastewater Plant	W	C0707
Kill Floor Vent	K	C0708
Kill Floor Vent	K	C0721
Sheep Holding Pens	Sh	C0723
Synthetic sample	S	—

Odour identification

Statistical analysis of the raw output data from the e-nose by three methods showed that classification of the odours into different classes was feasible. The classes were determined by the source of the odour at the meat processing plant.

Cluster analysis

Cluster analysis attempts to group objects (here each peak corresponding to one analysis of a bag) together with similar profiles of variables (here the sensor outputs). The output is in the form of a ‘dendrogram’ which plots the similarity between objects. Figure A7.2 is a dendrogram of the 31 samples. There are 3 significant groups determined by this method (A, B and C on the figures). The most odorous samples (S, BI and W) are clustered together in groups B and C with most of the BI samples grouped separately from the rest in group C. The less odorous samples also group together in group A. This method does not discriminate among the less odorous samples.

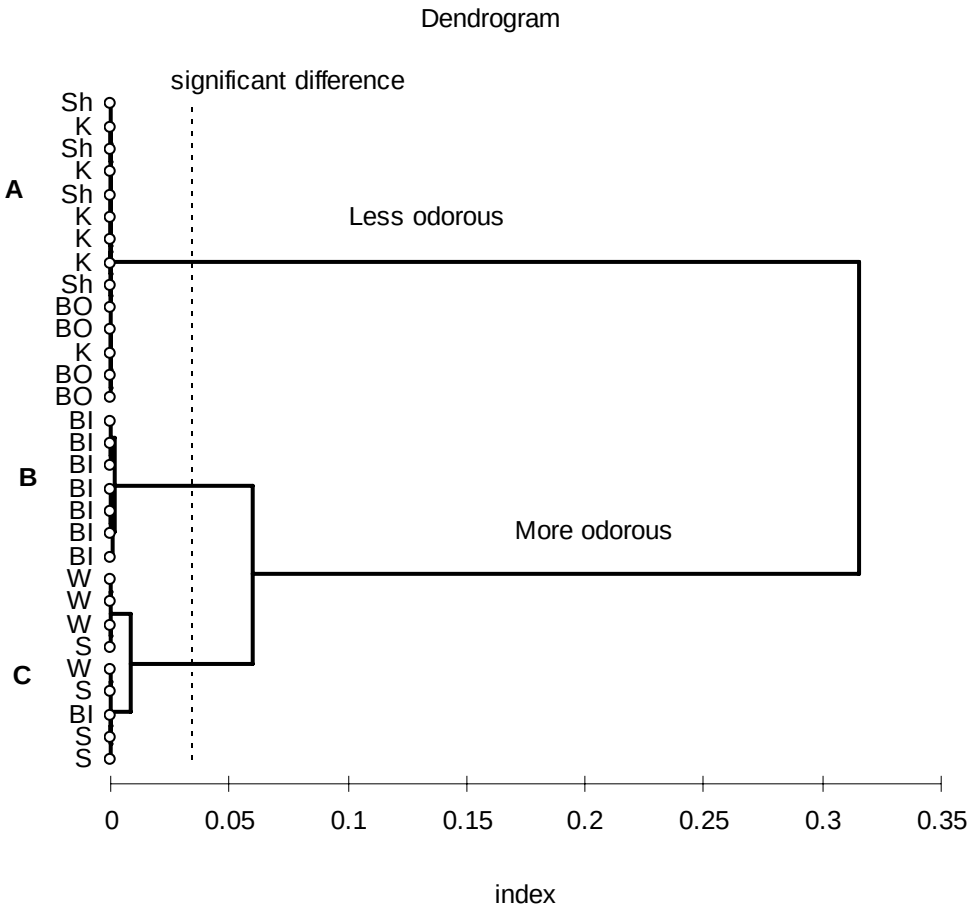

Figure A7.2: Hierarchical cluster analysis of odours.

Principal components analysis (PCA)

A PCA resulted in three PCs explaining 96% of the variance of the data. A PCA decomposes the data matrix into a matrix of “scores” which give information about the objects and “loadings” which give information about the variables. Figure A7.3 is a plot of the scores of the first PC, showing easy discrimination between the more and less odorous samples.

Further discrimination is obtained between the more odorous samples by plotting in two dimensions the scores of the first and third PCs (Fig A7.4). A proper calibration with more samples should result in much improved discrimination.

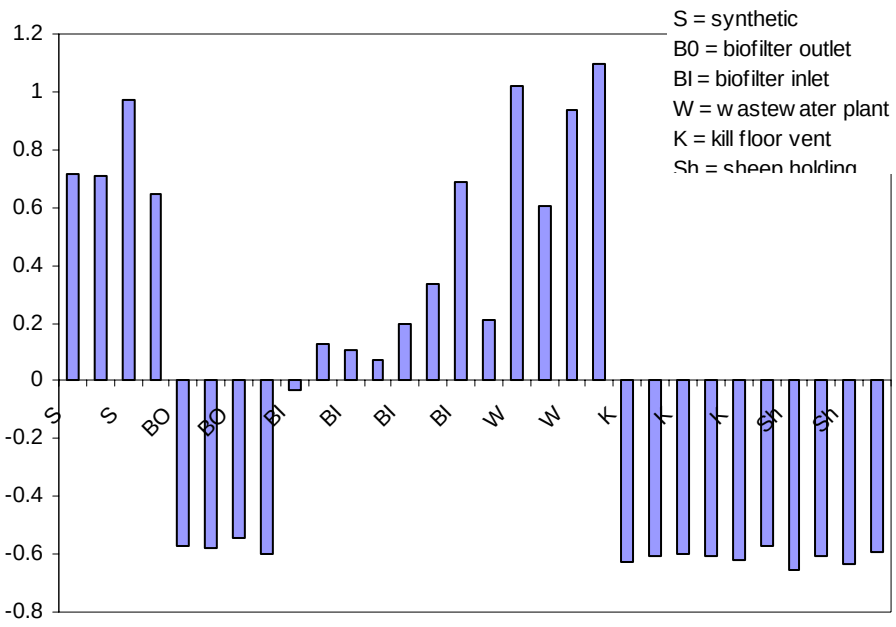

Figure A7.3: PCA scores of the first principal component showing discrimination between high odour samples (positive on graph) and low odour samples (negative on graph).

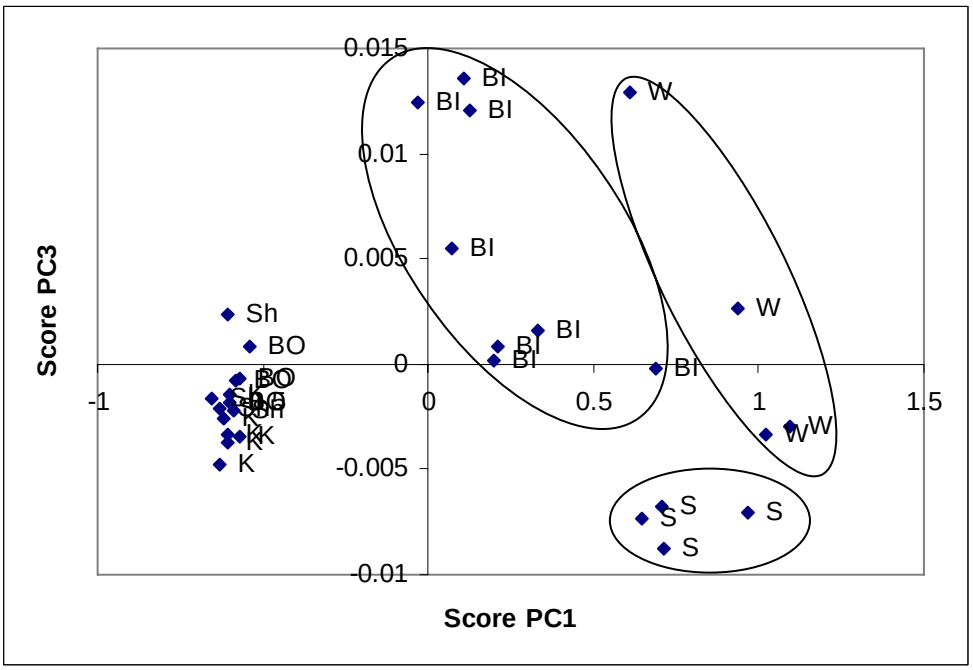

Figure A7.4: Principal Component Analysis (PCA) - Scores plot of PC1 and PC3

Linear Discriminant Analysis (LDA)

LDA is a supervised pattern recognition method in which a model is trained to recognise classes in the data. Here we have specified two classes H – high odour (Synthetic, Biofilter inlet and Wastewater plant) and L – low odour (Biofilter outlet, Kill floor vent and Sheep holding pens).

Figure A7.5 gives the discriminant scores for the members of the two classes and again it is seen that clear discrimination is achieved.

The result of the LDA is a formula that converts sensor output to a score that determines which class the sample belongs to. Thus if an unknown odour were presented to the calibrated e-nose, it would give an answer as “high” or “low” odour.

With more samples from different locations it will be possible to define classes such as “High odour from the Wastewater plant”.

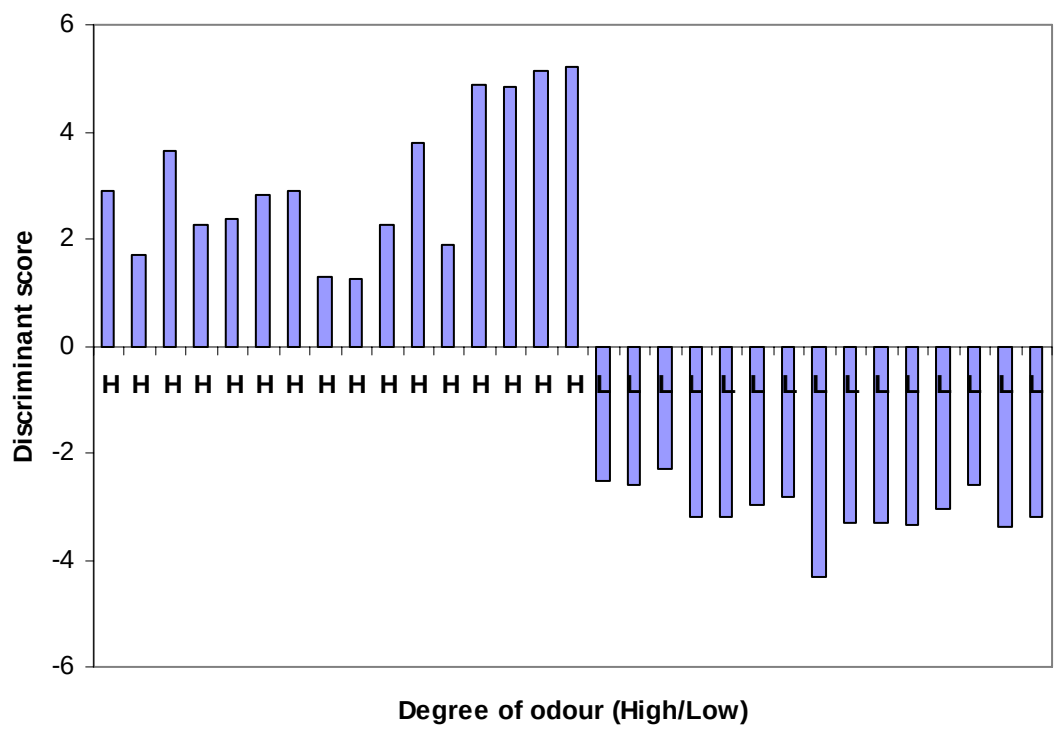

Figure A7.5: Linear discriminant analysis discriminant score for high and low odours showing perfect discrimination.

Detection limit

We have made no attempt to optimise the sensors for very low odours. However it is possible to estimate the detection limit of the sensors in terms of odour units.

If the sensor voltage is plotted against the odour units of the sample on a log-log plot an approximately straight line is obtained (Figure 4). The odour unit threshold for the EPA is 10 units (horizontal dotted line), and the threshold for measurement is about 2 mV above baseline (vertical dotted line). The thiol sensor (S5) can detect meat plant odours at the 10 unit level. Sensor 2 (representative of the other sensors) just reaches the level and with optimisation it is clear that the device as a whole would certainly achieve the EPA limits.

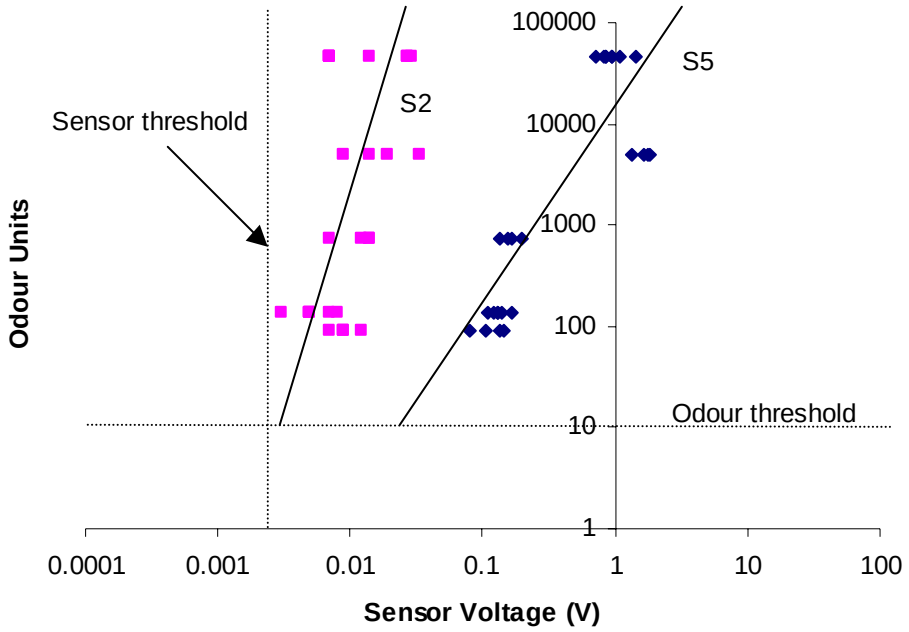

Figure A7.6 : Sensor response plotted against measured odour units