

## ELECTRONIC NOSE AND ARTIFICIAL NEURAL NETWORK

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### ABSTRACT

Gas sensor array technology combined with multivariate data processing methods as artificial neural network has been demonstrated to have a promising potential for rapid non-destructive analysis of odour and flavour in foods. It may be applicable in quality control of raw material, food processing or products. This technique cannot completely replace reference methods like the use of sensory panels as the technique requires a frequent calibration against some valid reference method. As with all new techniques there remain some basic problems to be solved concerning sample handling and instrumental performance. The emerging research activity in the development of chemical sensors including hardware and software combined with applied research makes it realistic to expect applications with this technique implemented on-line in the food industry in near future. In particular, promising applications on meat seem to be within the field of spoilage, off-flavour, sensory analysis and fermentation processes.

### INTRODUCTION

Analysis of odour and flavour in food has traditionally been performed either by a trained sensory panel or by head-space gas chromatography mass spectrometry. These methods are time consuming and costly and there is a need in the food industry for objective automated non-destructive techniques that can characterise odour and flavour in food. New methods should allow a high number of samples to be analysed within a short period of time with a sufficient reproducibility and accuracy. During recent years there has been a rapid development of a concept named electronic nose (artificial nose) based on chemical gas-sensor technology which seems to fulfil these requirements.

### THE CONCEPT OF ELECTRONIC NOSE

With the term Electronic Nose is understood an array of chemical gas sensors with a broad and partly overlapping selectivity for measurement of volatile compounds within the headspace over a sample combined with computerised multivariate statistical data processing tools (Gardner and Bartlett, 1994). The electronic nose has derived its name because it in several aspects tries to resemble the human nose. Human olfactory perception is based on chemical interaction between volatile odour compounds and the olfactory receptors (primary neurones) in the nasal cavity. The signals generated are transferred to the brain through synapses and secondary neurones and further led to the limbic system in the cortex where identification of odour takes place based on neural network pattern recognition. In principle, the primary neurones correspond to the chemical sensors of the electronic nose with different sensitivity to different odours. By chemical interaction between odour compounds and the gas sensors the chemical state of the sensors is altered giving rise to electrical signals which are registered by the instrument analogue with the secondary neurones. In this way the signals from the individual sensors represent a pattern which is unique for the gas mixture measured and is interpreted by multivariate pattern recognition techniques like artificial neural network, the brain of the instrument. Samples with similar odours generally give rise to similar sensor response patterns and samples with different odours show differences in their patterns. When the sensor patterns for a series samples are compared, differences can be correlated with the perceived sample odour.

The sensor array of an electronic nose has a very large information potential and will give a unique overall pattern of the volatiles. In principle, both the electronic and the human nose operate by sensing simultaneously a high number of components giving rise to a specific response pattern. However, there are two basic differences between the human and the electronic nose that should be kept in mind. The electronic nose has both large differences in sensitivity and selectivity from the human nose. The sensors of an electronic nose respond to both odorous and odourless volatile compounds. Taking these constraints into consideration in the choice of sensors used for these instruments it is possible to design an electronic nose with a response similar to the human nose for specific compounds. Still, the mechanisms involved will be fundamentally different. In principle, the electronic nose can be applied to any product that gives off volatiles with or without smell provided that this occurs within the sensitivity range of the sensors.



## GAS SENSOR TECHNOLOGY

Several commercial gas sensor array instruments are now available on the market. In addition, a number of prototype gas-sensor array instruments are being used by research institutions and universities. Commercially available electronic noses cover a variety of chemical sensor principles, system design and data analysis techniques. The gas sensors are based on physical or chemical adsorption and desorption, optical adsorption or chemical reactions that take place on the surface and/or in the bulk of the sensor material. These interactions cause characteristic physical changes of the sensor to be detected. A series of different detection principles can be used in chemical gas sensors: heat generation, conductivity, electrical polarisation, electrochemical activity, optical properties, dielectric properties and magnetic properties.

In this context only the major principles used in gas sensors found in commercial electronic noses will be discussed. The most frequently used sensor technologies have shown to be successful and have become applicable in food analysis. These can be divided into two basic groups: hot and cold sensors.

Hot sensors are metal oxide semiconductors (MOS) and the metal oxide semiconducting field effect transistors (MOSFET) which operate at elevated temperatures. The MOSFET sensor consists of a doped semiconductor and an insulator (oxide) covered by a catalytic metal (Lundström et al., 1990). The output signal is based on a change of potential in the sensor due to electrical polarisation when molecules react on the catalytic surface. The sensors operate at temperatures between 100-200 °C. The MOS sensors (Gardner et al., 1991) are based on reaction between adsorbed oxygen on the oxide surface with incoming molecules. The output signal is derived by a change in conductivity of the oxide caused by the reaction with volatile compounds. They operate at a temperature from 200-500 °C. In both type of sensors red-ox processes take place i.e. when respectively reducing or oxidising compounds are interacting with the sensor surfaces. Their selectivity and sensitivity characteristics are dependent on temperature and choice of metal.

Cold sensors operate at ambient temperature. They consist of the conducting organic polymers (CP), oscillating sensors, optical sensors or electrochemical cells. Conducting organic polymers (Bartlett et al., 1989) are based on two main classes of polymers, the pyrroles and the anilines. The most used property to measure is the alteration of the conductivity of the polymers when volatiles interact with the polymer. By altering the functional groups or the structure of the polymer and using different doping ions, the selectivity and sensitivity can be altered.

Oscillating sensors are based on the principle that adsorption of molecules onto the sensing layer result in a decrease in frequency due to increased mass and sometimes a changed viscosity of the sensing layer. The QMB (quartz micro balance) also called BAW (bulk acoustic wave) and SAW (surface acoustic wave) sensors are based on such interactions. QMB sensors (Nakamoto et al., 1995) consist of a piezoelectric quartz oscillator coated with a sensing membrane, whereas the SAW (Liron et al., 1997) sensors consist of two pairs of finger structure electrodes fabricated onto a piezoelectric substrate with a sensing layer between them. The selectivity and sensitivity is determined by the composition of the coated sensing layer and the operating frequency. SAW sensors operate at much higher frequencies (50-1000 MHz) than the QMB sensors (5-30 MHz).

Optical gas sensors are another type of sensors used in electronic noses. In these sensors a light source excites the gas resulting in a signal from optical properties as absorbance, reflectance, fluorescence or chemiluminescence.

Electrochemical cells consist of several electrodes and an electrolyte. The gas molecules are either oxidised or reduced at the working electrode, while the opposite reaction takes place at the counter electrode. The reaction between the analyte generates a voltage between the electrodes which is measured as the output signal.

The most frequently used sensors in commercial instruments are the metal oxide semiconductors and the organic polymers. More recently the SAW and QMB sensors have been implemented in commercial instruments (Alpha MOS, NST). Commercial hybrid electronic noses are also being produced. By combining different kind of sensor technologies in the same instrument (MOS, MOSFET, QMB and CP) the instruments become adapted for many different applications. It remains to see how well these hybrid instruments perform when different sensors techniques are being applied simultaneously since they operate at very different conditions (temperature, flow rate, carrier gas). A summary of the performance of the different sensor techniques is presented in Table 1. It should be emphasised that the table only should be used as a general guideline. In principle, the hot sensors are expected to be more robust and less sensitive to moisture. Their sensitivity is in the range of 100 ppm to 0,1 ppm (Gardner and Bartlett, 1994). The conducting organic polymer sensors and SAW sensors seem to be more sensitive with the ability to detect volatiles down to ppb levels (Gardner, 1996; Shaffer et al., in press). In comparison, the odour threshold of the

human nose may vary from 1000 ppm down to ppt dependent on the chemical compound and matrix (Belitz and Grosch, 1987). The response and recovery times for any of the sensor types will be dependent on the particular compound and its concentration.

**Table 1. Comparative properties and performance of the most frequently used gas sensors**

| Performance                | MOS                             | MOSFET                          | CP                                        | QMB                                       | SAW                                       |
|----------------------------|---------------------------------|---------------------------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|
| Selectivity                | Poor                            | Moderate                        | Moderate                                  | High                                      | High                                      |
| Sensitivity                | >0,1 ppm                        | >0,1 ppm                        | 0,01 ppm                                  | >0,1 ppm                                  | ppb                                       |
| Reproducibility            | Poor                            | Good                            | Good                                      | Moderate                                  | Moderate                                  |
| Temperature dependence     | Low                             | Low                             | High                                      | Moderate                                  | High                                      |
| Carrier gas                | Synthetic air (O <sub>2</sub> ) | Synthetic air (O <sub>2</sub> ) | Inert/<br>Synthetic air (O <sub>2</sub> ) | Inert/<br>Synthetic air (O <sub>2</sub> ) | Inert/<br>Synthetic air (O <sub>2</sub> ) |
| Humidity dependence        | Low                             | Moderate                        | High                                      | Low                                       | Low                                       |
| Operating temperature (°C) | 300-400                         | 100-200                         | Ambient                                   | Ambient                                   | Ambient                                   |
| Response time (sec.)       | (0,5-5)                         | (0,5-5)                         | (20-50)                                   | (20-50)                                   | (20-50)                                   |
| Recovery time              | Fast                            | Fast                            | Slow                                      | Slow                                      | Slow                                      |
| Lifetime (years)           | 3-5                             | 1-4                             | 1-2                                       | <2                                        | <2                                        |

For the moment the major problems related to gas sensors are poor sensitivity, instability, susceptibility to humidity and a rather limited life time. The limited sensitivity can partly be overcome by increasing the sample amount relative to headspace volume, headspace conditioning time or the sensor measuring time.

In order to compare results over time (weeks, months or years) it is required that these instruments give the same signal when identical samples are being measured over time. However, due to dynamic processes taking place in the sensors over time, the signals from a sensor array may vary significantly. The long term reproducibility (1-3 months) of the gas-sensors used in these instruments vary from 1 to 10% (Persaud et al., 1996; Gardner, 1996; Eklöv et al., 1997). Calibration of the system based on control/reference samples in order to check the performance of the sensors is, therefore, a crucial part of the quality assurance of these instruments. If a good precision is required in order to discriminate between similar samples, and the drift extends the sample distances in the multidimensional space (euclidian distance) drift correction will be necessary. This can be done by applying drift counteraction algorithms on the measurement raw data before further data analysis (Di Natale et al., 1995; Holmberg et al., 1996,1997). The sample to sample reproducibility of replicates of real samples will be strongly dependent on the sample matrix. In particular, when replicates of raw meat samples with a very heterogeneous composition are being analysed, the precision may become poor.

Since sensors have a limited life time, they must be replaced after some time and new sensors from another batch will differ in performance. A recalibration on reference samples is then necessary in order to continue using the previously reference database of the original sensor array. This can be achieved by using a neural network that will make it possible to predict what the response of a particular sensor should be. If the entire array should be replaced, the whole system needs to be recalibrated and retrained (Mielle, 1997).

Sensors responding to polar molecules (CP, MOS, MOSFET, and QMB and SAW with a polar active layer) will also respond to water vapour. In most situations when meat is being measured water vapour will be generated in the headspace during sampling due to the water activity in the meat. This problem may be addressed in several ways. The carrier gas can be humidified and adjusted to the same humidity as the sample headspace gas or to maximum humidity. Another alternative is to run samples of purified water with the same relative humidity as the real samples and make a water background correction by simply subtracting the calibrated water responses from the signal obtained from the real samples. In this way the water responses will be eliminated and the signal from the real analytes obtained. This procedure provides that the responses fall within the linear range of the sensors. A variety of gas-sensors may exhibit a non-linear response, so this alternative should be handled in a critical way. Addition of a desiccant could be another choice. In particular, when there is a significant variation in water activity in the samples being measured i.e. during fermentation processes it is crucial that the water problem is being handled properly.

Accordingly, as with all analytical techniques a number of instrumental variables have to be optimised. In particular, this is valid for the sample treatment prior to the instrumental gas analysis which is based on headspace sampling. The sampling is a critical part of the analysis when it comes to achieve good results. Other considerations are sample headspace temperature, equilibration time, sample quantity, sample surface area, etc. There is no room for going into this topic in this context and it has been discussed in detail elsewhere (Kolb, 1980; Gardner, 1996).

### DATA ANALYSIS. ARTIFICIAL NEURAL NETWORK

The data processing of the multivariate output data generated by the gas sensor array represent an essential part of the electronic nose concept. The statistical techniques used are based on commercial or specially designed software using pattern recognition routines like principal component analysis (PCA), partial least squares (PLS), functional discriminant analysis (FDA), cluster analysis, fuzzy logic or artificial neural network (ANN). (Martens and Næs, 1989). More recently a combination of different of these techniques have been used and show promising results (Ping and Jun 1996; Singh et al. 1996). Another new technique which seems to have an interesting potential is multiway decomposition (Bro, 1996; Shaffer et al., in press).

All these methods apart from ANN are based on a linear approach. Gas sensor array data may often be non-linear in nature. Simple transformations of the data such as logarithms may help, but it may be that the non-linearities are more complex. Another problem is that while good models may be obtained where the variation between samples is large, this is seldom the case where variation between samples is very small. In such cases linear models may not provide robust models. It is therefore very important to use data that span the space we want to investigate and that there is as little collinearity as possible between the variables. By introducing non linear methods like artificial neural network, it will be possible to model electronic nose data in a better way. By combining statistical methods like PCR and neural nets we will have a new powerful approach of modelling electronic nose data. Artificial neural nets in many cases seems to give higher recognition and prediction probability than conventional multivariate analysis if the data relations are non-linear.

To achieve this we will use statistical pre-processing of the data. By using the principal components as inputs to a neural network, it is possible to reduce the collinearity. The principal components are constructed in such way that their bases are orthogonal and that the main variation of the data is to be described in the first components. The noise is being effectively taken away in the higher components.

Working with neural networks is a challenge of trial and error, and it is also very important to have a good knowledge of the history of the data being analysed. There is, however, a growing market for more "intelligent" programs to guide the user in the modelling process. Good programs for building neural networks seem to grow in strength and neural networking will be a good add-on to model building in gas sensor array science.

#### What neural network should be used?

With neural network modelling still in its early stages of development and understanding, addressing the questions on when and why neural networks should be used poses some problems. However, through reading and discussion, a number of general guidelines should be considered. Different topologies have been used to investigate the potential of the method when it comes to modelling ability of gas sensor array relations (Ping and Jun, 1996; Winqvist et al., 1993). Normally a standard feed forward topology is sufficient to use. Other interesting classification networks like Kohonen self organising networks should be considered (Kohonen, 1988). This kind of network is in some cases able to do good classifications of samples.

It is difficult to choose appropriate neural network models for work with gas sensor arrays. Feed forward nets are normally preferred for prediction of responses on continuous scales or in classifications. In this case the neural net may be considered as a function mapping device generalising on the basis of unknown samples. The design of the transfer function is essential in the design of what kind of problems the user wants to solve. Most often the sigmoid transfer function gives useful results. Most software packages have the option to change to other transfer functions according to the data taken into account. In cases where the predictions are to be performed on discrete data there are network topologies to use. These may be constructed as a combination of self organising networks and feed forward nets (Hierarchical nets). This process on choosing the right network design is a trial and error process. However some guidelines might be considered.

As a neural network may model non-linearities it is a natural choice to use this method. If the data are purely linear, methods like PCR and PLS are most likely to be used. The user is recommended to start with PCR/PLS to get a good knowledge of the data set with the tools that this methods have. This will indicate that there might exist non-linear relations that a neural network might be able to solve. The flexible nature of neural nets forces the user to be aware of the overfitting problem. A neural net is supposed to model a X/Y relation. The problem is the generalisation on unknown Y's. It is very important to understand this fact, because we often see neural network models that are perfect in respect to the actual X/Y being used in the learning.

The question whether neural networks should be used depends on the precision of generalisations the user wants. Neural computing should be used as it provides a powerful alternative to traditional statistical methods for the prediction of responses. If only generalisations are wanted the neural network computes this more easy in a well defined function. If diagnostic tools are essential together with generalisations, a mixture of linear and non-linear methods should be taken into account.

### Relationship to other methods

The artificial neural network models have strong relations to other statistical methods that have been frequently used in the past. An extensive discussion of the relations will be found in Næs et al., (1993). When a network is trained, the weights are estimated in such way that prediction error is as small as possible. The design of the feed forward network is closely related to multiple linear regression (MLR) when the linear transfer function is used and the hidden layer is removed. In this case the neural network may be solved directly and no training is necessary. If the data has a purely linear relationship, the MLR method may give good results. If, however, the data has non-linear relationship, the MLR method will not give satisfactory predictions. Non-linear methods like neural networks should be taken into account to detect the non-linear relations in the data. The transfer function used in the neural net is designed to detect both linear and non-linear relations in the data. Reports in combining MLR and neural nets into one network topology claims success to guarantee optimal solutions on data sets with unknown relationships (Borgaard et al., 1992).

In order to translate the functionality of the brain into a computer environment, it is first necessary to break the processing of information into a number of levels and components. The first level will be the input of which there may be several components. For example, an individual is given some chocolate from which he perceives a number of sensory attributes. The chocolate and the individual form the stimulus, and for the sake of argument it will be assumed that the sensory attributes are the input variables, as these can be recorded in the physical world.

The neural network model applied in a gas sensor array context is shown in Figure 1. The different inputs are the electronic nose responses. At the output level, that is the observable response or behaviour, is one component called acceptability, which can also be measured. The output response,  $y$ , shown in Figure 1a may be one or several measured data items. Both chemical, sensory and physical data may be modelled at the same time. The hidden layers will process the information initiated at the input. The fundamental building block in a neural network is the neurone. The neurone receives input from the neurones in a earlier layer and adds the inputs after having weighted the inputs. The response of the neurone is a result of a non-linear treatment in different regions in the input space. The neurones in the hidden layer may be identified as feature detectors. Several hidden layers may exist, but in practice only one is sufficient. This is represented in Figure 1b. The next problem is how to join the levels of the network. In the human brain there is a complex network of connections between the different levels, and the complexity of their use will depend on the amount and type of information processing required.

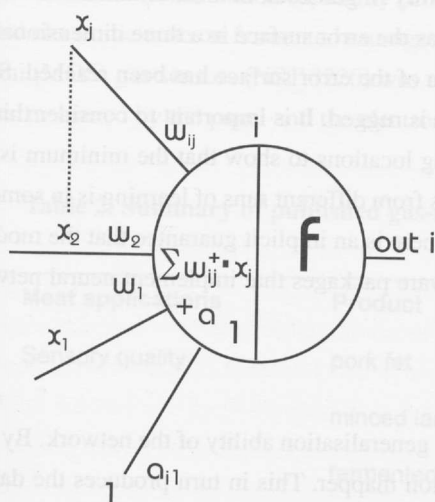


fig a

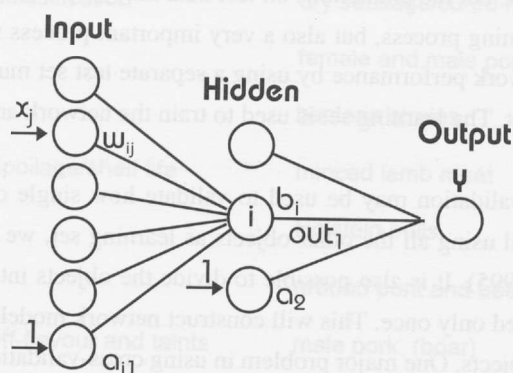


fig b

fig c

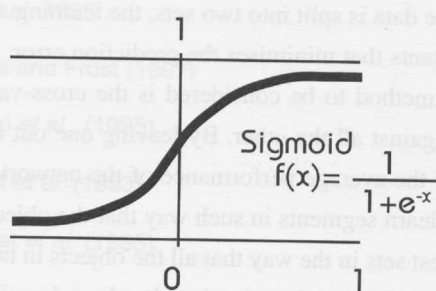


Figure 1.

(a) A diagram illustrating the structure of a simple neural network applied to an gas sensor array equipment. The fundamental building block in a neural network is the neurone. (b) The connections between different connections in the neural network. The input paths to processing elements in the hidden layers are combined in the form of a weighted summation. (c) A sigmoid transfer function is then used to get to the output level. The inputs corresponds to the gas sensor array responses. The output  $y$  may correspond to a sensory attribute (vector or scalar).

The feed-forward neural network in Figure 1 is defined by an equation of the form  $y = f[\sum_i b_i f(\sum_j w_{ij} x_j + a_{i1}) + a_2] + e$  where  $y$  is the output variable, the  $x$ 's are the input variables,  $e$  is a random error term,  $f$  is the transfer function and  $b_i$ ,  $w_{ij}$ ,  $a_1$  and  $a_2$  are constants to be determined. The constants  $w_{ij}$  are the weights that each input element must be multiplied by before their contributions are added in node  $i$  in the hidden layer. In this node, the sum over  $j$  of all elements  $w_{ij}x_j$  is used as input to the transfer function  $f$ . This is in turn multiplied by a weight constants  $b_i$  before the summation over  $i$ . The constants  $b_i$  are the weights that each output from the hidden layer must be multiplied by before their contributions are added in the output neurone. At last the sum over  $i$  is used as input for the transfer function  $f$ . More than one hidden layer can be used resulting in a similar, but more complicated, function. The constants  $a_1$  and  $a_2$  acts as bias signals to the network. They play the same role as the intercept constants in linear regression.

The learning of the neural network is performed by optimising a cost function (error function) of the squared differences in predicted output and wanted output. In short, information flows from the input towards output, and error propagates back from output to input (Backpropagation learning rule). The weights are calculated in an iteration process. The weights are given initially random values. By presenting a pattern to net network, the weights are updated by computing the layer errors and the weight changes. The learning process will stop when the network has reached a proper minimum error.

## Local and global minima of the error

One of the major disadvantages of the backpropagation learning rule is its ability to get stuck in local minima. The error is a function of all the weights in a multidimensional space. This may be visualised as the error surface in a three dimensional space as a landscape with hills and valleys. There is no proof that the global minimum of the error surface has been reached. Starting with different randomised weights leads to different minima if the error surface is rugged. It is important to consider this when analysing the final minimum. The learning is run repeatedly at different starting locations to show that the minimum is reasonable. This problem of not being able to reproduce the same result of predictions from different runs of learning is in some cases problematic to a novice user. When statistical methods like PCR/PLS are used there is an implicit guarantee that the models are reproduced after separate modelling runs. This rises a custom problem in software packages that implement neural network as the main modelling system.

## Validation of the performance

Validation of the performance is very important when we want to monitor the generalisation ability of the network. By adding more neurones in the hidden layer, the network becomes a very flexible function mapper. This in turn produces the danger of overfitting. The network may be able to map the learning data perfect, but the predictions on test data may be poor. The validation is by this concept not only to find the iteration count in the learning process, but also a very important process when evaluating the number of nodes in the hidden layers. Validating the network performance by using a separate test set must be considered. The data is split into two sets, the learning set and the test set. The learning set is used to train the network and find the set of constants that minimises the prediction error.

Another method to be considered is the cross-validation. Cross-validation may be used to validate how single objects are modelled against all the other. By leaving one out to the test set and using all the other objects as learning set, we may get a measure of the average performance of the network (Kvaal et al., 1995). It is also possible to divide the objects into test segments and learn segments in such way that the objects are being tested only once. This will construct network models based on learn and test sets in the way that all the objects in turn will be test objects. One major problem in using cross-validation on neural nets is the danger of getting into local minima. There will be one new model at each segment validation. This in turn gives different local minima.

## MEAT APPLICATIONS

In principle, the results obtained from a gas-sensor array represent qualitative and quantitative information of the composition of the headspace gas mixture of a sample. The technique should therefore have a great potential in a number of applications related to meat. Quality control is of great importance within the food industry and with this technique it would be possible to monitor the food from the raw material throughout the process and to the final product by analysing volatile compounds released from the food matrix. There are several aspects of quality control that may be the issue in the context of meat; Sensory quality, shelf life, spoilage, off-flavour and taints and authenticity. In addition, the electronic nose may have a potential in product development when it comes to the design of a product with certain flavour characteristics. Table 2 summarises different meat applications with gas-sensors that have been published in the scientific literature and which are described in this section.

Recently, comparative studies on meat with gas sensor arrays and sensory analysis have been carried out in order to find out whether gas-sensors can be used to predict sensory attributes of meat. Narum Nilsen et al., (1996) showed that by using a commercial electronic nose based on 10 MOSFET and 5 MOS sensors and an IR-based CO<sub>2</sub> sensor (NST 3210) it was obtained a correlation (PLS) between sensory odour and flavour scores and electronic nose measurements for pork loins of  $r=0,6-0,8$ . This was a study where they compared meat from pigs given five different feeds. By using artificial neural network they could make a unique classification of 90% of the meat samples according to their feeding pattern. Braggins and Frost (1997) looked at the odour and flavour of raw and cooked minced meat of lamb of extended chilled storage in CO<sub>2</sub> atmosphere and frozen vacuum packed storage by using a sensory panel and a commercial electronic nose (Alpha MOS Fox 4000). The sensor array consisted of 18 different MOS sensors. By using canonical discriminant analysis they could reliably distinguish between lamb mince samples of different storage conditions over a period from 4 to 14 weeks. Eklöv et al., (1997) made a comparison between sensory analysis and electronic nose of fermented sausages. The gas-sensor array used consisted of 10 MOSFET and 4 Taguchi

(MOS) gas-sensors. Both techniques were sensitive to small quality differences between batches of sausages and there was a good agreement in discrimination capability between the two techniques. We have carried out a comparative study with sensory panel and electronic nose on fermented sausages. An gas sensor array consisting of one IR-based CO<sub>2</sub> sensor, 10 MOSFET and 5 Taguchi (MOS) gas-sensors (NST 3220) was used. High correlations ( $r=0,8-0,9$ ) were found between sensory odour and taste attributes measured by the panel and the electronic nose measurements (unpublished data).

**Table 2. Summary of published gas-sensor array meat applications described in the text**

| Meat applications      | Product                  | Reference                           |
|------------------------|--------------------------|-------------------------------------|
| Sensory quality        | pork fat                 | Narum Nilsen <i>et al.</i> , (1996) |
|                        | minced lamb meat         | Braggins and Frost (1997)           |
|                        | fermented sausages       | Eklöv <i>et al.</i> , (1997)        |
| Classification         | dry sausage/cured ham    | Vernat-Rossi <i>et al.</i> , (1996) |
|                        | female and male pork fat | Berdagué and Talou (1993)           |
|                        | bacteria strains         | Rossi <i>et al.</i> 1995            |
| Spoilage/shelf life    | minced lamb meat         | Braggins and Frost (1997)           |
|                        | Holstein bulls           | Funazaki <i>et al.</i> , (1995)     |
|                        | ground pork and beef     | Winquist <i>et al.</i> (1993)       |
| Off-flavour and taints | male pork (boar)         | Bourronet <i>et al.</i> (1995)      |
|                        | male pork (boar)         | Annor-Frempong <i>et al.</i> (1997) |
| Processing             | fermented sausages       | Eklöv <i>et al.</i> , (1997)        |
|                        | fermented sausages       | Berdagué and Talou (1993)           |

These examples demonstrate that the electronic nose may have the ability to describe and predict sensory properties of meat characteristics. However, it should be emphasised that the result from the sensory analysis always will be the ultimate answer when it comes to characterise flavour of a food product. Provided that the instrument has been calibrated against sensory analysis and performs according to the required sensory properties, accuracy and reproducibility, it could be applied to partly replace a sensory panel in the industry.

Electronic nose techniques have also been used on several applications concerned with classification of meat samples. Vernat-Rossi *et al.*, (1996) used a commercial nose (Alpha MOS Fox 2000) with an array of six semiconducting metal oxides to classify varieties of dry sausages and cured ham samples of different quality. With factorial discriminant analysis 94 % of the dry sausage samples were classified correctly. For the cured ham samples which consisted of two groups of samples, respectively normal samples and abnormal samples with an aroma defect after slicing, 87 % of the samples were correctly classified. Only two sensors were necessary for the classification of the ham samples. With the same instrument Rossi *et al.* 1995 also were able to discriminate between seven species of the bacteria *Micrococcaceae* that can be found in fermented meat products (also reported in Vernat-Rossi *et al.*, 1996). The species investigated in culture were respectively four aromatic (*Micrococcus* and *Staphylococcus*) and three pathogenic (*Staphylococcus*) bacteria strains. 100 % of the bacteria samples were classified correctly into their respective groups based on factorial discriminant analysis. It remains, however, to be demonstrated that these sensors can specifically detect bacterial strains in real meat samples with a high number of other volatiles present in the headspace that also may interact with the sensors. This would represent a major progress in the area of food security were the sensors could be applied to detect pathogenic bacteria at an early stage.

Another application where the electronic nose seems to have a great potential is the pointing out of spoilage and off-flavour of meat. The cause at issue may be the classification of meat according to certain well-defined odour or flavour quality criteria. Boar taint is an example of off-flavour that the meat industry has to handle. Frequently, sensory assessment fails in identifying boar taint represented by the chemical compounds androstenone and skatole. This is partly due to anosmia, low odour thresholds to these compounds or misclassification due to other interfering off-odours than boar taint (i.e. rancidity). It would therefore be useful to have an objective method in order to sort out these meat samples. Bourronet et al. (1995) used five different Taguchi type gas sensors (MOS) to measure pork fat with different levels of androstenone. They achieved a 84 % successful classification of the samples belonging to low ( $<1,7 \mu\text{g/g}$ ) and high ( $>1,7 \mu\text{g/g}$ ) androstenone content, respectively. Annor-Frempong et al., (1997) used 12 conducting polymer sensors combined with discriminant analysis to classify boar tainted meat samples of two sets of pigs containing up to  $4 \mu\text{g/g}$  androstenone and  $1,6 \mu\text{g/g}$  skatole. Respectively 84 and 90 % correct classification for the two training sample sets were obtained according to low, intermediate and high concentration classes of androstenone and skatole.

The spoilage of raw meat caused by microbiological processes taking place during storage represents a great problem in the meat industry and there is considerable waste in storage and handling of meat. Funazaki et al., (1995) used one single semi-conducting metal oxide gas sensor to determine freshness of sirloins from Holstein bulls. The sensor was specially designed to have a high specificity and sensitivity to ethyl acetate, one of the major components produced during the early stage of bacterial putrefaction in meat. The sensor had a linear range from 1-200 ppm. They found a correlation factor of  $r^2=0,8$  between gas-sensor responses and bacterial counts. This example suggests that in some cases the sensor arrays of electronic noses have a too broad selectivity and that more specific and sensitive single gas sensors will be required for specific applications.

Winqvist et al. (1993) used an array of respectively 10 MOSFET, 5 Taguchi (MOS) and one IR-based  $\text{CO}_2$ -sensor (prototype of the commercial electronic nose of Nordic Sensor Technologies, Linköping, Sweden) for measuring ground pork and ground beef during storage up to 8 days at  $4^\circ\text{C}$ . The storage time could be well predicted even with a reduced number of sensors by using artificial neural network. By supervised training of an artificial neural network they also obtained a clear separation of the two classes of samples.

The gas sensor array technology may as well be interesting to use in the monitoring of food processing. By adding starter cultures the desired aroma and flavour characteristics of fermented sausages are obtained. Eklöv et al., (1997) evaluated the use of a gas sensor array for monitoring the fermentation of sausages over a 52 hours period. They used a sensor array consisting of 10 MOSFET and 4 Taguchi (MOS) gas-sensors. With an artificial neural network model they could predict the fermentation process of 52 hours duration with an error of 2,7 hours. Berdagué and Talou (1993) used a chamber with a one semiconductor gas sensor to monitor the maturation of unspiced sausages over a 90 days period. The sensor responses correlated with increased odour intensity with time and odour maximum at the late stage of maturation. They also analysed back fat from female and male pigs and could demonstrate significant differences in sensor responses related to sex. Accordingly, this technique should represent a rapid way to identify meat from male and female pigs.

Lipid oxidation taking place during storage of meat represents another issue in the food industry. We have measured freeze-stored chicken with different treatment before freezing (salt, antioxidants, modified atmospheres) with a commercial electronic nose consisting of 10 MOSFET, 5 MOS and one IR-based  $\text{CO}_2$  sensor nose (NST 3220). With a PLS model a correlation of  $r=0,9$  with TBA-values was obtained (unpublished results). This suggests that the electronic nose may have a potential for measuring rancidity in freeze stored chicken.

## FUTURE PERSPECTIVES

The gas sensor array technology applied on food must be regarded as being in its early stage. So far, the applications in the scientific literature seem promising for future use in the food industry. There is a rapidly advancing research and development going on both on sensors and instrument hardware and software in order to enhance selectivity, sensitivity and reproducibility of the gas sensors. Much effort is also put into solving the drift problem of the sensors by increasing the stability and life-time of the sensors. There is also carried out research in order to develop improved mathematical algorithms for drift counteraction and automatic calibration. At the same time development of different applications by the industry and research centres in different fields is proceeding.

Interfacing of a pre-concentration sampler (tenax, silica) combined with an automated thermal desorption (ATD) device to the inlet of the gas-sensor array seems to be a promising approach to handle the selectivity and sensitivity issue. Due to a different desorption from the adsorbent of the trapped volatile compounds it would be possible to detect small quantities of target vapor in the presence of high concentrations of background vapors that would normally mask the minor components (Shaffer et al., in press).

There may also be significant information available in the transient response curve of these sensors that not has been fully utilised in order to improve the selectivity and precision of the sensors (Eklöv et al., 1997). The use of new multivariate statistical methods as multiway decomposition, can be applied to get a better exploitation of these data in order to extract relevant information (Shaffer et al., in press; Eklöv, 1997; Bro, 1996).

One ongoing research activity that seems very promising is the development of fiber-optic based sensors. By combining the responses from a multitude of sensors a dramatical increased selectivity and sensitivity is achieved. Such sensor bundles have been used to discriminate large number of compounds (Dickinson et al., 1996; Walt et al., 1997). They are not yet commercially available, but will also be fit for use in electronic noses.

Commercial gas sensor arrays with a broad selectivity as represented by the electronic nose concept may for some applications not prove to be useful. The manufacturers of electronic noses have to face the fact that for several applications there will be a need for a few very specific and sensitive gas-sensors instead of the broad selectivity sensors which normally are implemented in commercial instruments.

On-line sensors play a key role in the automation of food control and processing. In near future when the basic issues of the gas-sensors have been solved, we will see more on-line gas-sensors implemented in the industry. For each application, however, technical problems have to be solved for implementation on-line. One interesting vision for the future would be to have a fully automated platform of different kind of sensors to monitor the essential information required for the characterising of quality of the raw material, process or product. Gas-sensors would make up a vital part of such a multi-sensor system. This may be realised in the food industry in the future.

#### ACKNOWLEDGEMENTS

Critical comments to the manuscript made by Einar Risvik, Tomas Eklöv and Oddvin Sørheim are highly appreciated.

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