Organic vapour sensing using a coated piezoelectric quartz crystal sensor array

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ABSTRACT

The pattern of responses from a four sensor array have been used for the classification of methanol, propanol, butanol, hexane, heptane and toluene using artifical intelligence (AI) based pattern recognition methods. A feedforward forward network with backpropagation was trained using sensor array data with approximately 300 training vectors and 100 test cases and covering a period of four months. The network consisting of four input nodes, six output nodes, learning rate of 0.1 and momentum of 0 was built using a commercial package (NeuroShell). A classification success rate of 75% was achieved. The bulk of the mis-classifications arose from propanol being classified as butanol and hexane being classified as heptane. These mis-classifications are rational since the respective compounds are very similar in nature. A fuzzy logic algorithm where class membership functions are developed using the mean frequency change and standard deviation of individual sensors was developed for classification of the vapours. In this particular case, classification using the developed fuzzy logic gaussian algorithm was not as good as the feedforward network with backpropagation, but the guassian membership function offers a more rational approach than the previously published trapezoidal membership function.

Keywords: sensor array, fuzzy logic, neural network, organic vapours, chemical sensing

1. INTRODUCTION

The evaluation and control of odours and volatile compounds is important in a number of sectors including chemical, pharamceutical, food, environmental, forensic and medical . Conventional instrumental techniques for the analysis of volatile compounds are expensive, laboratory based and require technical skill to operate. Significant potential benefits are to be derived in terms of improved quality control, process control and product design by the introduction of an inexpensive and portable instrumental method for the analysis of volatiles.

Chemical and biosensors can be used for analysis of volatiles, they are, however, required to have both high selectivity and reversibility. Yet by their inherent nature these properties are mutually exclusive. A highly selective chemo/biosensor will have strong bonding between the chemo or bio-active component and the analyte will as a result will have poor reversibility. One approach to this problem is to use an array of chemical sensors with each component having only a limited selectivity to the measurand. The sensor array thus has good reversibility, selectivity can be achieved from analysis of the pattern of sensor array response which acts as a fingerprint for the analyte. When the volatiles sensed have an odour then these systems are referred to as an electronic nose[1].

A variety of gas sensors types are employed in sensor array systems; these can be divided into those that operate at high temperatures e.g. the metal oxide semiconductors (MOS) and metal oxide field effect transistor (MOSFET) and those that operate at around room temperature such as conducting polymers, piezoelectric quartz crystals (also known as bulk acoustic wave or BAW) and surface acoustic wave sensors (SAW)[2]. Optical sensor arrays are also being in investigated, these devices are often termed artifical noses[3]. Piezoelectric quartz crystal (BAW) and SAW sensors are two of the most common mass sensors. The two devices differ in that in the former an acoustic wave travels through the bulk of the material while in the latter case the acoustic wave travels on the surface. In both cases, the change in the device frequency is proportional to the mass deposited. A mathematical relationship between the mass of material on the piezoelectric quartz crystal and frequency shift was first derived by Sauerbrey[4] and is given in equation 1.

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Part of the SPIE Conference on Environmental Monitoring and Remediation Technologies II
Boston, Massachusetts • September 1999
SPIE Vol. 3853 • 0277-786X/99/$10.00

$$\Delta f = -2.3x10^6 . f_o^2 . \frac{\Delta M_s}{A} \quad (1)$$

Where Δf is the change in frequency of the quartz crystal (Hz), f_o is the resonant frequency of the quartz crystal (MHz), ΔM_s is the mass of the coating or substance sorbed (g) and A is the area coated (cm^2). They are converted into chemical or biosensors by incorportion of a chemical or biochemical layer on the device surface which will abstract the analyte from the sample stream. Since a wide range of coatings can be applied onto the device surface these sensors have very broad selectivity and have been applied to a wide variety of mass and chemical measurement applications[5]. These sensors do, however, suffer from poor batch-to-batch reproducibility.

The responses from the sensor array can be analysed by using pattern recognition methods[6]. These methods can be sub-divided into supervised or unsupervised techniques. Unsupervised methods such as principal component analysis (PCA), and cluster analysis are used in exploratory data analysis since they will attempt to identify a gas mixture without prior information. These techniques are most appropriate when no example of different sample groups is available or when hidden relationships between samples or variables is suspected. Supervised learning techniques such as canonical discriminant analysis (CDA), feature weighting (FW), artificial neural networks(ANN) and fuzzy logic classify a sample by developing a mathematical model relating training data to a set of descriptors. Test samples are then evaluated against a knowledge base and predicted class membership determined. ANN and fuzzy methods are attractive in sensor array applications since they are able to deal with non-linear problems.

2. EXPERIMENTAL

2.1 APPARATUS

The piezoelectric(pz) quartz crystal based sensor array was developed at the University of Teesside. A sensor array consisting of six pz quartz crystals with fundamental frequencies of 10MHz were used (Piezo Products Ltd., Portsmouth, Hants. UK). In this study only four quartz crystals were employed. Each crystal was coated with a commonly utilised gas chromatography stationary phase, each containing a different functional group to allow limited selectivity. The coated pz quartz crystals are housed in a 10ml PTFE sensor chamber. The pz quartz crystals are offset to their neighbour to provide mixing of the sample in the chamber. A reference pz quartz crystal is used for differencing, allowing for compensation of drift and also allows the frequency of each crystal to be determined. The frequency of each pz quartz crystal is fed to a PC and the data is acquired using a PC-30AT interface card.

2.2 PZ QUARTZ CRYSTAL COATING

The crystal coatings used were Diethylene glycol succinate, Silar 10C, OV1 and Squalene (Phase Separations Ltd). These were chosen to give a wide range of functional groups and polarities. Dilute solutions (0.1w/w) of each coating were prepared in a volatile solvent, either dichloromethane (CH_2Cl_2) or an 80:20 v/v mixture toluene:methanol. The solutions were applied to both sides of each crystal by means of a fine brush. The frequencies of the pz quartz crystals were monitored during the coating procedure to enable similar frequency shifts to be observed for each coating. The sensors were conditioned by passing nitrogen over the sensor array for a period of two days.

2.3 SAMPLING

Dreschel bottles, volume $125cm^3$, were filled with a $5cm^3$ aliquot of the analyte and left for 30 mintues. A PTFE four-way valve was used to switch between reference air and sample air, in both cases a sample flow rate of 20 cm^3 was maintained through the sensor chamber. After exposure of the sensor array to sample air for six minutes, reference dry air was passed through the sensor chamber for the same period to obtain a stable baseline. Sensor array frequency measurements are made every 10 seconds.

2.4 DATA ANALYSIS

The feedforward backpropagation network of 4 input nodes and 6 output nodes and gradient descent was developed using Neuroshell (Ward Systems Group, Inc.). For every three samples used for training, one was used for testing. Training was preformed using a learning rate of 0.1 and momentum 0. Classification using a gaussian membership fuzzy logic algorithm was developed, as described in section 3.2, and performed on the sensor array data.

3. RESULTS AND DISCUSSION

Data from the sensor array was analysed using both a feedforward network with backpropagation and a fuzzy logic classification algorithm. Data from the sensor array was split in both cases into training and testing in a 3:1 ratio. The results of the classifications for the test samples for both the neural network and fuzzy logic algorithm are shown in table 1. It can be seen that the feedforward network has a higher classification success rate.

Compound	Neural network		Fuzzy logic	
	Correctly Classified	Incorrectly Classified	Correctly Classified	Incorrectly Classified
Methanol	13	1	11	3
Propanol	3	17	0	20
Butanol	21	0	12	9
Hexane	5	7	4	8
Heptane	15	0	13	2
Toluene	19	0	5	14

Table 1 Summary of classification results for test samples using neural network and fuzzy logic

3.1 FEEDFORWARD NETWORK WITH BACKPROPAGATION

Table 1 shows that the neural network has a 75% classification success rate. Output values were in the range 1.0 – 0.0; when the correct compound had the highest output value but if this value did not exceed 0.5, the classification was deemed to be incorrect. The bulk of mis-classifications arose from propanol being classified as butanol or hexane being classified as heptane. The mis-classifications are rational since butanol is similar in nature to propanol and likewise hexane is very similar to heptane.

Given the imprecision of the sensor array, the neural network has performed reasonably well; being able to generalise well. Classification could have been improved by increasing the numbers of sensors in the sensor array or alternatively choosing different coating materials for the sensors. This would have given greater discrimination amongst the mis-classified data set. Results could also have been improved by including input nodes for time and temperature. It is possible that by further adjustment of network parameters, improved classification could have been obtained. A network with a single hidden layer was chosen since this reduces the number of nodes and thus the number of training vectors required. Too few nodes leads to large errors. We have used approximately 300 training vectors and 100 test cases. It has been previously shown that the use of two or more hidden layers only has a marginal effect on the network performance[7]. Bishop has shown that the number of hidden nodes has a significant effect on the ability of a multi-layer preceptron to generalise. A limitation of this work is that the optimisation of the network parameters was carried out on an ad-hoc basis. It has been recently shown that genetic algorithms can be usefully employed to determine the optimal training parameters[8].

3.2 FUZZY LOGIC CLASSIFICATION

Fuzzy logic tries to handle imprecise information rather than exact or crisp data. Fuzzy reasoning in pattern classification involves the development of membership functions. The approach we have taken in our algorithm is similar to that taken by Yea *et.al.*[9]. Yea *et.al.* developed trapezoidal membership functions based on experience. In our algorithm, gaussian membership functions were developed for each class and sensor using training data thus each sensor has a gaussian membership function associated with each class. The membership functions are developed using the mean frequency change and standard deviation for each class and sensor (figure 1)

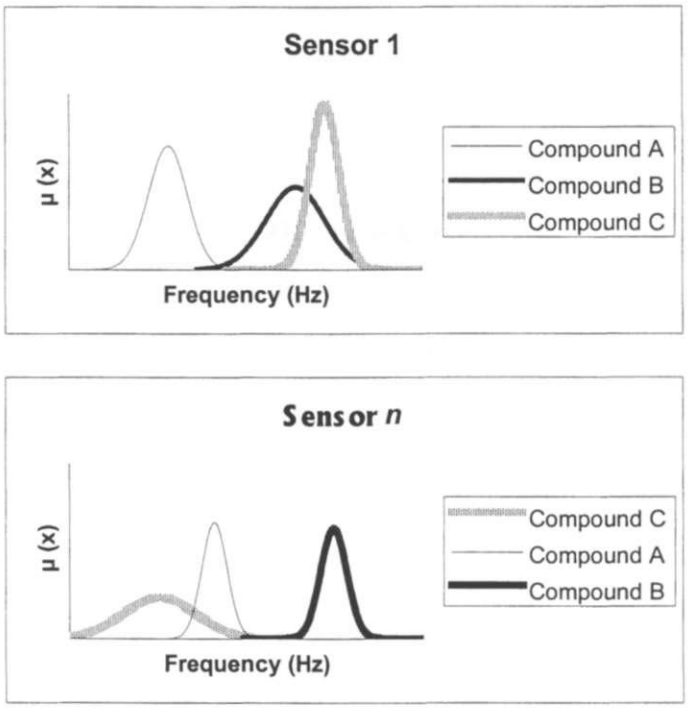

Figure 1 Membership functions for three compounds and *n* sensors

The information can be represented as a fuzzy system.

$$Group = \begin{array}{c} \\ f_1 \\ f_2 \\ f_3 \\ f_4 \end{array} \begin{vmatrix} \mu_{GMet} & \mu_{GEth} & \mu_{GPro} & \mu_{GBut} & \mu_{GHex} & \mu_{GHep} \\ \mu_{GMet1} & \mu_{GEth1} & \mu_{GPro1} & \mu_{GBut1} & \mu_{GHex1} & \mu_{GHep1} \\ \mu_{GMet2} & \mu_{GEth2} & \mu_{GPro2} & \mu_{GBut2} & \mu_{GHex2} & \mu_{GHep2} \\ \mu_{GMet3} & \mu_{GEth3} & \mu_{GPro3} & \mu_{GBut3} & \mu_{GHex3} & \mu_{GHep3} \\ \mu_{GMet4} & \mu_{GEth4} & \mu_{GPro4} & \mu_{GBut4} & \mu_{GHex4} & \mu_{GHep4} \end{vmatrix}$$

The grade of membership for an unknown compound is calculated using equation 2

$$\mu_G = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\left(\frac{(X-\mu)^2}{2\sigma^2}\right)} \qquad (2)$$

The output membership functions can be determined by the fuzzy union of each column.

$$\mu_{Gmet} = \mu_{GMet1} \cup \mu_{GMet2} \cup \mu_{GMet3} \cup \mu_{GMet4}$$

$$\mu_{Geth} = \mu_{GEth1} \cup \mu_{GEth2} \cup \mu_{GEth3} \cup \mu_{GeEth4}$$

.....

$$Group = \left\{ \mu_{GMet}, \mu_{GEth}, \mu_{G\,Pro}, \mu_{GBut}, \mu_{GHex}, \mu_{GHep} \right\}$$

The unknown compound can be classified by the defuzzification of the fuzzy set GROUP, i.e. taking the α cut with the supremum of the fuzzy set GROUP. It can be seen from table 1 that in this case, classification of vapours using fuzzy logic is not as successful as the common feedforward with backpropagation network.

4. CONCLUSION

A 75% success rate was achieved for classification of closely related organic volatiles with a four sensor array and classification using a feedforward network with backpropagation. The network could be further optimised by changing it's architecture. The developed fuzzy logic algorithm did not perform as well. Improvement in classification could be obtained by using a larger number of sensors, giving different information about the system.

5. ACKNOWLEDGEMENTS

This work has been partially supported by HEFCE and the European Regional Development fund under contract 70/41/001. The authors are grateful for the help in construction of the system by J. Legg and K. Middleton.

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