Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 371-381

GAS-SENSING SYSTEM USING AN ARRAY OF COATED QUARTZ CRYSTAL MICROBALANCES WITH A FUZZY INFERENCE SYSTEM

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Abstract

Quartz crystal microbalances have high mass sensitivities. Their application in gas sensing has been limited because they are required to have both high selectivity and reversibility. Yet by the inherent nature of their operation these properties are mutually exclusive. One approach to this problem is to use an array of quartz crystal microbalances. We have used an array of six coated quartz crystal microbalances for the classification of methanol, propan-1-ol, butan-1-ol, hexane, heptane and toluene. A novel classification scheme using fuzzy membership functions was found to be highly efficient.

Keywords: fuzzy logic, gas, QCM, sensing, sensor array

Introduction

Application of a mass onto a quartz crystal microbalance (QCM) causes the resonant frequency of the quartz crystal to change in a quantitative manner; the QCM may thus be used as mass balance of high sensitivity. A mathematical relationship between the mass of material on the QCM and frequency shift was first derived by Sauerbrey [1].

$$\Delta f = -2.3\times10^{6} f_o^2 \frac{\Delta M_s}{A} \tag{1}$$

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). QCMs have been applied to a wide variety of mass and chemical measurement applications [2].

QCMs may be used as chemical sensors if they are coated with a material which selectively and reversibly binds to the analyte. Commercialisation of these devices for gaseous sensing has been limited. This is in part due to the se-

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest

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lectivity and reversibility to the analyte being entirely dependent on the chemical coating on the quartz crystal. If the binding mechanism between the chemical coating and the analyte is either adsorption or absorption then the selectivity for the gas detection system will be poor but the reversibility will be good. If the binding mechanism is chemisorption then selectivity will be high but reversibility will be poor. Selectivity and reversibility thus appear to be mutually exclusive properties.

One approach that we have taken previously to overcome this problem is to introduce a sampling device, such as a denuder tube, prior to the QCM [3]. The denuder tube introduces an additional stage of selectivity so that the selectivity of the QCM does not have to be high. The denuder tube has the additional advantage that any particulates present in the sample stream can be removed and also preconcentration is allowed. A possible drawback is the increase in analysis time. Another approach that has been taken is to use an array of chemical sensors with each component having only a limited selectivity to the measurand. Selectivity to the analyte is achieved through the use of pattern recognition techniques [4–6]. This strategy is attractive since the system then has potential for high selectivity and reversibility and a short analysis time.

A further drawback to the use of QCMs for chemical sensing is that reproducibility is often regarded tc be poor. In recent years fuzzy logic has been usefully employed in systems where the data may be imprecise or even incomplete. We have previously employed fuzzy logic for the analysis of automobile components [7, 8]. We now report on the use of a fuzzy inference system in a QCM sensor array for the classification of gaseous components. The fuzzy inference system allows incorporation of uncertainty into the rule-based expert-like system.

Experimental

QCM sensor array

The QCMs used were 10 MHz, fundamental mode, AT-cut with 5 mm diameter circular silver electrodes on both sides of the 8 mm quartz slab, supplied by Piezo Products, Southampton, UK. An array of six coated QCMs were placed in a sealed measuring chamber with a volume of 30 cm^3. The sensor array chamber is constructed from teflon to avoid adsorption of contaminant materials. The QCMs were made part of parallel crystal oscillator circuit [9], trimmed to 10 MHz operation. Circuits were powered from a 12 V d.c. power supply. The output frequency of each quartz crystal was measured sequentially by a Fluke PM6685 frequency counter.

Sensor coatings

Prior to coating, all QCMs were cleaned by sequential wash of HPLC grade ethanol and deionised water. The QCMs were brush coated with adsorbent material until a stable frequency shift (Δf) of approximately 2–4 kHz was obtained after evaporation of the volatile solvent:

$$\Delta f = f_0 - f_1 \tag{2}$$

where f_1 is the frequency of the quartz crystal after it has been coated with an adsorptive material. Table 1 shows the coating materials used in this study as well as the frequency shifts due to coating.

Experimental procedures

Each quartz crystal was tested to its response to the diluted headspace of methanol, propan-1-ol, butan-1-ol, hexane, heptane and toluene. A schematic diagram of the test rig used is shown in Fig. 1. The tubing and four port valve was supplied by Omnifit (Cambridge, UK) and is of teflon material to avoid adsorption of material and thus preventing memory effects.

Table 1 Coating materials used and associated frequency shifts

QCM	Coating	Δf, frequency shift/ kHz
1	PEG 400	2.525
2	Nujol	4.045
3	Ucon 50	2.910
4	Squalene	2.280
5	Silicone DC-710	3.640
6	Triton X-305	2.475

The test rig shown has referencing and detection modes. Switching from one mode to the other is carried out by changing the four port valve. In the referencing mode nitrogen is passed through the sensor array chamber while the headspace of the organic compound is passed to waste. In the detection mode the diluted headspace of the organic compound is passed to the sensor array chamber while the nitrogen is sent to waste. Gas flows were controlled by Platon flowmeters.

In a typical cycle the sensor array chamber was first flushed for five minutes with reference nitrogen. The frequency of all QCMs were recorded. The diluted headspace of the organic compound was then passed into the sensor array chamber for five mintues prior to recording of frequency of the QCM array. This cycle was repeated 12 times for each organic compound. The mean frequency change of the quartz crystal array and the standard deviation were computed. The data obtained was used to build a knowledge base for classification of the organic compounds. After a period of two weeks these experiments were repeated in or-

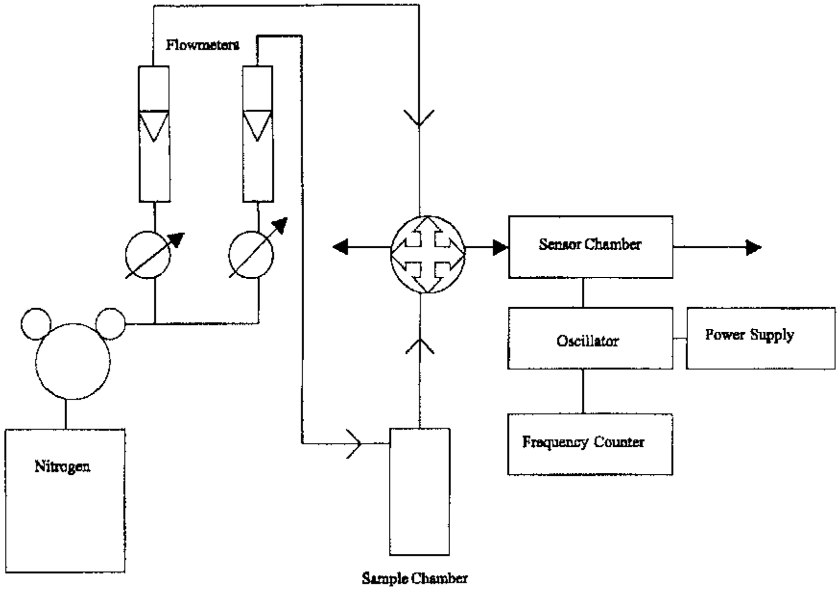

Fig. 1 Apparatus for the analysis of organic components using an array of coated quartz crystals

der to test how well the fuzzy inference system was able to classify the test compounds.

The frequency of each QCM was monitored over a period of three weeks to determine the stability of each coating. An increase in the frequency of the coated quartz crystal would indicate that some of the coating material had been removed from the surface of the quartz crystal.

Results and discussion

Pattern recognition system

Fuzzy logic based on fuzzy set theory is employed and constructed according to the structure of IF-THEN fuzzy inference rules. Hence, an efficient 1-D determination (classification) of organic gaseous components is made possible.

In the data analysis, the attributes of the object (frequency change due to a particular class of organic component) are extracted as described in the experimental section. The specific values of the attributes are those data needed for the analysis. The main objective here is to find some structural information about these data. This may be achieved by way of classifying the large amount of data into relatively few classes of similar objects – clustering. Data analysis can thus be viewed as the search for structure in data.

The primary objective of clustering is to partition given data into so-called homogenous clusters. In fact, homogenous indicates that all points in the same group are close to each other and are not close to points in other groups. The clustering algorithm is then used to build pattern classes or to reduce the size of a set of data while retaining relevant information. The separation of cluster is a fuzzy notion, and the representation of clusters by fuzzy sets may seem more appropriate in certain situations. A brief description of a general pattern recognition system is presented as follows:

Data acquisition

This is normally the first part of a pattern recognition system. The method for obtaining the frequency change of the quartz crystals on exposure to a particular gaseous component are obtained using the system shown in Fig. 1.

Feature extraction

The aim of feature extraction is to reduce the dimensionality of the data by keeping only the information believed to be important for discrimination (Fig. 2).

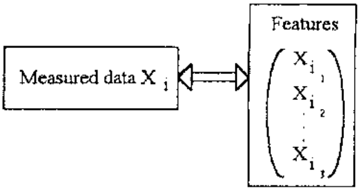

Fig. 2 Feature extraction

Classifier design

The essential concept of pattern recognition may be expressed by mapping from feature space to decision space. The mapping operator which performs the function of classification is often called a classifier. The design of a classifier consists of two parts. The first part is to collect data samples from various classes

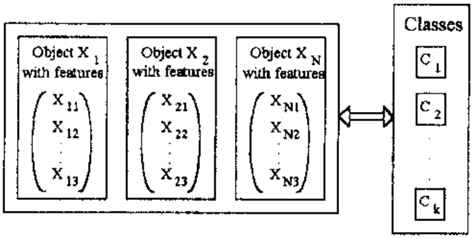

Fig. 3 Classifier design

(organic compounds) and to find the boundaries which separate the classes, this process is called the classifier training, or the learning (Fig. 3). The other is to test the designed classifier by feeding the samples for which the class identities are known.

Classification

The classification stage involves assigning the examining objects to the appropriate classes based on the object's properties (Fig. 4).

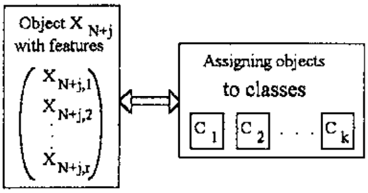

Fig. 4 Classification

Classification using Neuro-fuzzy algorithm

Principle of fuzzy set theory

One way of dealing with the real world phenomena is qualitative and non-numerical in nature. In decision-making processes, numerical data are converted into some qualitative form and thus are dealt with only in aggregation. This form of aggregation gives rise to a set of linguistic labels and is sometimes referred to as information granules. This aggregation of information makes the partition of space more manageable for further processing. All cognition and inference processing are then carried out at the level of the granules. This process of aggregation or granulation implies that we deal with the relationships of functions between linguistic label rather than with numerical quantities. To cope with this style of cognition, a suitable modelling technique is developed using the theory of fuzzy sets since this theory deals with such granularity of our perception.

Principle of Neuro-fuzzy

In general, Neuro-fuzzy is a neural network (connectionist) model designed to incorporate fuzzy sets theory into neural networks. This connectionist model, in the form of a feedforward multi-layer net, incorporates the knowledge structure of fuzzy logic into the neural network structure, resulting in structure neural networks to enable fuzzy systems to learn and make neural networks interpretable. The distinctive feature of the Neuro-fuzzy is that its internal state can be analysed according to the rule structure, and the problematic position can be easily located and improved.

Modelling of the Neuro-Fuzzy System

Radial Basis Function (RBF)-networks typically have linear nodes in the input and output layer and a hidden layer of n-RBF nodes. The response transfer function of the RBF-nodes are described through the Gaussian-distribution form. For 1-D input x, the node n is given by [10, 11],

$$f_k = e^{-(x-\mu_k)^2/\sigma_k^2}, \quad k = 1,\dots, n \tag{3}$$

In fact, the Neuro-fuzzy algorithm proves to be a variant of the RBF-network and exhibits very good characteristics. For the RBF, a weighted sum of (multi-dimensional) Gaussian functions are applied,

$$y_j(x) = \sum_{i=1}^{n} y_{j,i} e^{-c_i|x-x_i|^2} = \sum_{i=1}^{n} y_{j,i} e^{-c_i\sum_{k=1}^{n}(x_k-x_{k,i})^2} \tag{4}$$

where $i=1,\dots, q$ and $y_{i,j}$, c_i and $x_{k,i}$ represent the parameters of the network.

The RBF-network has an advantage over the Multi-layer Preceptron (MLP) as the backpropagation principle is not required.

The general form of the RBF network is given as,

$$y_j(x) = \frac{\sum_{i=1}^{n} \varphi_{j,i} y_{j,i} e^{-\sum_{k=1}^{p} c_{k,i}(x_k-x_{k,i})^2}}{\sum_{i=1}^{n} \varphi_{j,i} e^{-\sum_{k=1}^{p} c_{k,i}(x_k-x_{k,i})^2}} \tag{5}$$

where $j=1,\dots, q$.

The Neuro-fuzzy algorithm can be represented as:

$$Y_i = \frac{\sum_{k=1}^{n} c_{i,k} d_{i,k} f_k}{\sum_{k=1}^{n} c_{i,k} f_k} \quad i=1,\dots, q$$
$$= e^{-\sum_{j=1}^{p}(x_j-\mu_{j,k})^2/2\delta_{j,k}^2} \tag{6}$$

where $f_k = \prod_{j=1}^{p} e^{(x_j-\mu_{j,k})^2/2\delta_{j,k}^2}$.

In addition, $X_1...X_p$ are the inputs from the frequency counter and $Y_1...Y_p$ are outputs for the classification.

Application of Neuro-fuzzy to classification

Development of membership functions

In this section, a classifier is developed based on the development of a membership function using a special form of the radial basis function – the Gaussian function:

$$\mu(x_i) = h\exp\left[-\frac{(x_i - \bar{x})^2}{2\sigma^2}\right] \quad i=1, 2, 3,... \tag{7}$$

where $\bar{x}$ is the mean of x (the central position), σ is the standard deviation (the width) and,

$$h = \frac{1}{\sigma\sqrt{2\Pi}} \tag{8}$$

is a real constant which represents the height of this function. A graphical representation of the membership function is shown in Fig. 6. By comparing these three attributive parameters of the membership function, an efficient and confident organic compound identification can be obtained.

Fuzzy cross-correlation

In order to obtain a recognition system which is able to cope with uncertain, imprecise, or incomplete data, a classification algorithm based on the concept of fuzzy cross-correlation is proposed. A detailed explanation of this algorithm is given as follows.

Fuzzy similarity measure

Equations (9) and (10) illustrates the mathematical expression to compute the fuzzy cross-correlation algorithm,

$$\mu_{ref*test} = \omega_{ref}^{n} * \omega_{test}^{n} \tag{9}$$

or,

$$\mu_{ref\cdot test} = \frac{\sum_{i=1}^{n}\min[R_i, T_i]}{\sum_{i=1}^{n}\max[R_i, T_i]} = \frac{[R_1 \cap T_1] + [R_2 \cap T_2] + ...}{[R_1 \cup T_1] + [R_2 \cup T_2] + ...} \quad i=1, 2, 3,... \tag{10}$$

where $\omega_{ref}^{n}=[R_i]$ and $\omega_{ref}^{n}=[T_i]$ represent the reference and the testing feature matrices respectively, n is the number of element in the matrix, and the $[R_i]$ and $[T_i]$ are the elements in the matrix. The symbol '*' represents the fuzzy cross-correlation operator, the 'min' represents the fuzzy logic intersection, the 'max' represents the fuzzy logic union and the $\mu_{ref*test}$ is the grades of similarity of the testing component to the reference component ranging from 0 to 1. A value of 1 represents that the reference and test compounds are identical.

Gas classification system

The grade of similarity between a reference and test gas is determined by carrying out a Fuzzy cross-correlation of the attributive parameters (mean, standard deviation and height of the frequency response of the quartz crystal array) of the reference and test gases. A summary of the grade of similarity of all six gaseous compounds are illustrated in Table 2.

Table 2 Summary of the final $\mu_{ref*test}$ for each gas

Test gas	$\mu_{methanol*test}$	$\mu_{propanol*test}$	$\mu_{butanol*test}$	$\mu_{hexane*test}$	$\mu_{heptane*test}$	$\mu_{toluene*test}$
Methanol	0.891	0.601	0.537	0.464	0.375	0.826
Propan-1-ol	0.638	0.941	0.898	0.789	0.669	0.686
Butan-1-ol	0593	0.875	0.980	0.827	0.720	0.637
Hexane	0.419	0.623	0.699	0.799	0.944	0.453
Heptane	0.404	0.594	0.665	0.759	0.899	0.432
Toluene	0.841	0.801	0.715	0.620	0.501	0.909

Measured results

The results above show that the system is capable of classifying different classes of gaseous compounds. One of the classifications in Table 2 can be seen to be incorrect. One reason for this is a possible change of the QCM array response with time i.e. a change in QCM array response between building the

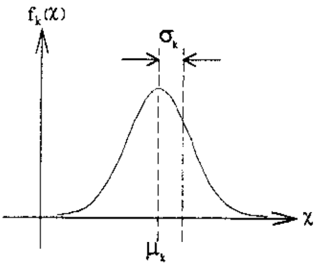

Fig. 5 Transfer function of a one-dimensional radial basis function

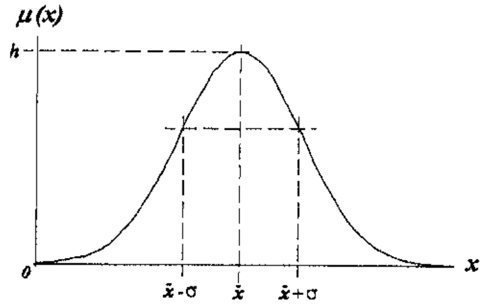

Fig. 6 Graphical explanation of the membership function

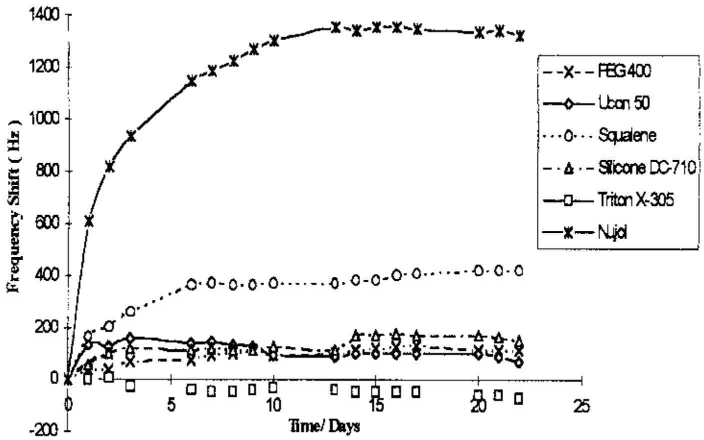

Fig. 7 Frequency drifts the coated QCMs with respect to time

knowledge base and actual testing. The frequency change of the coated quartz crystals over a period of three weeks is shown in Fig. 7. It can be seen that in most cases the frequency of the QCM has increased suggesting that a certain amount of coating has been displaced from the crystal surface. A very large frequency increase was observed for the nujol coated QCM. The change in the QCM array would clearly lead to a changed response with time. Despite this the fuzzy cross-correlation algorithm performs well and shows its effectiveness to uncertain data. Improvements can, however, be made by building into the algorithm the change in response of the QCM array with time.

Conclusions

We have developed a QCM sensor array with a Fuzzy inference system for the classification of various organic compounds. The classification algorithm was found to be highly efficient and able to cope with uncertain data. It is important to note that the classification process is an aggregation or a granulation in which the relationships of the components are dealt with as linguistic labels rather than numerical quantities. It is possible to extend the capabilities of the design of the inference rules in order to be able to handle a large number of rules pertaining to changes in the sensor array response. The speed of the inference is almost independent of the number of rules.

References

1 G. Sauerbrey, Z. Phys., 155 (1959) 206.
2 J. J. McCallum, Analyst, 114 (1989) 1173.
3 Z. Ali, C. L. P. Thomas, J. F. Alder and G. B. Marshall, Analyst, 117 (1992) 899.
4 K. Persaud and G. H. Dodd, Nature (London), 299 (1982) 352.
5 T. C. Pearce, J. W. Gardner, S. Friel, P. N. Bartlett and N. Blair, Analyst, 118 (1993) 371.
6 J. W. Gardner, E. L. Hines and H. C. Tang, Sens. Act. B, 9 (1992) 9.
7 T. Sarkodie-Gyan, C. W. Lam and A. W. Campbell, IEEE/ASME Trans. on Mechatronics, 2 (1997) 2.
8 T. Sarkodie-Gyan, C. W. Lam and A. W. Campbell, Int. Journal of Mechatronics, 7 (1997) 185.
9 C. Barnes, Sensors and Actuators A., 29 (1991) 59.
10 H. Ishibuchi, IEEE Trans. on Fuzzy System, 1 (1993) 85.
11 M. M. Gupta, Fuzzy Sets and Systems, 61 (1994) 1.