Mapping of chemical functionality using an array of quartz crystal microbalances in conjunction with Kohonen self-organizing maps

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An optimized gas sensor array consisting of eight quartz microbalance sensors coated with different sorbent layers was used in conjunction with a Kohonen network to discriminate between different organic vapours. The sensing materials used in the array were chosen to promote the range of different solvation interactions possible with the sample test set. The feature extraction capabilities of the Kohonen network were realized in that Kohonen output patterns were more easily distinguished than the original sensor response patterns. The Kohonen network was also shown to preserve relationships in the data.

Introduction

Recent research in gas sensing with arrays has focused on both improvement of the transduction platform[1] and on alternative methods of pattern recognition to overcome limitations of the transduction platform. In particular artificial neural networks have become increasingly popular in some quarters as methods that accommodate sensors which drift and exhibit non-linear responses. Researchers have used back-propagation in conjunction with arrays of quartz crystals,[2–8] tin oxide devices,[9–14] surface acoustic wave devices[15–17] and pellistors.[18] Other workers have used self-organized maps such as the Kohonen network[19] in conjunction with an array of fuel cells for classification of organic vapour mixtures.[20] Gas sensing with arrays of tin oxide devices in conjunction with hybrid networks has proved promising by some researchers.[21] The network consisted of a generalized perceptron network and a self-organized map, with the former behaving as a feature extraction procedure and the latter performing classification and identification. In general, the Kohonen network alone has found wider application, for example, workers have used weight maps within a Kohonen network to map concentration values of fatty acids.[22] We have applied the Kohonen mapping method to the problem of using an array of chemical sensors to identify different chemical functionalities. The objective was to determine how the weight maps within a Kohonen network can be used to identify similar interactions of test compounds. The method was presented as an alternative to classical solvatochromic models.[23] The weight maps have been used to explain how the Kohonen network was trained and how test patterns were mapped onto an output grid. Outputs from the network generated from test patterns were presented in a single output grid layer and also as individual output patterns.

In a previous publication[24] we have demonstrated that when a limited number of sensor elements are available for inclusion in an array it is important to ensure that all chemical interactions of importance are represented. In the case of linear multivariate methods such as principal components analysis often the result is crucially dependent on matching the degree of variance contributed by the sensor. In this work a Kohonen network was employed to map chemical functionality in a non-linear fashion.

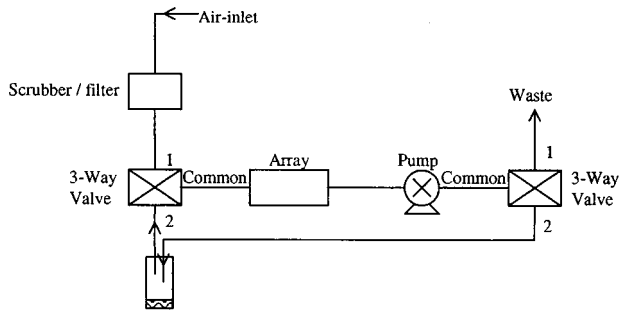

Fig. 1 Schematic diagram of the QTS-1 sensor array instrument. In the cleaning cycle the valve is in position 1. In the measurement cycle the valve is in position 2.

Experimental

Reagents and materials

The sample test panel comprised; hexane, ethanol, dichloromethane, nitromethane, chloroform, propan-1-ol, toluene, acetonitrile, ethyl acetate, 1,4-dioxane, butan-2-one and

Table 1 Pre-processing methods which have been employed for gas sensing with arrays ($F(t)_{ij}$ is the frequency of sensor i after t s exposure to gas j and $F_0(t)_{ij}$ is the initial frequency at $t = 0$ seconds, n is the number of sensors in the array, σ is the standard deviation, $\bar{x}$ is the mean of the fractional frequency responses of sensor i to all gases)

Pre-processing method	Formulae
Relative frequency	$F(t)_{ij}/F_0(t)_{ij}$
Frequency change	$F(t)_{ij} - F_0(t)_{ij}$
Log absolute frequency change	$\mathrm{Log} \mid F(t)_{ij} - F_0(t)_{ij} \mid$
Response integral	$\dfrac{1}{F_0(t)_{ij}} \sum_{i=1-n} F(t)_{ij} - F_0(t)_{ij}$
Fractional frequency change	$(F(t)_{ij} - F_0(t)_{ij})/F_0(t)_{ij}$
Normalized fractional change	$F(t)_{ij}\left(\dfrac{1}{n}\sum_i F(t)_{ij}\right)^{-1}$
Curve fitting	F = Constant + at + bt^2 + ct^3 + dt^4 + et^n
Autoscaling	$(F(t)_{ij} - \bar{x})/\sigma$
Min/max scaling	$\bar{x} - 2\sigma$, $\bar{x} + 2\sigma$

dimethylformamide. All were Analar grade reagents from Merck (Poole, Dorset, UK). The sample containers were 1.5 ml poly(propylene) vials (Sarstedt, Leicester, UK).

Instrumentation

The sensor response data was collected on a QTS-1 Sensor Array System (Quartz Technology Limited, Northwood, UK). An interchangeable array of eight piezoelectric quartz crystals coated with different sorbent layers was employed. The sorbent layers were chosen to give a balanced response to sample interactions; the method of optimization is detailed in an earlier publication.[24] Sensors 1–8 respectively were: poly(isobutylene) (PIB); poly(epichlorohydrin) (PECH) (all from Aldrich, Dorset, UK); poly(ethylenimine) (PEI); tris(cyanoethoxy)propane (TCEP) (all from Supelco Inc., Dorset, UK); cyano-substituted

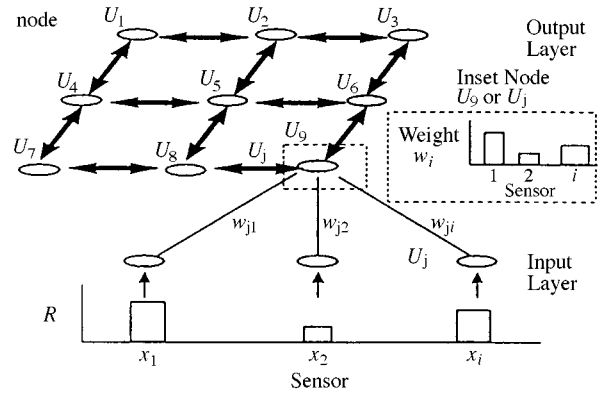

Fig. 3 A Kohonen network.

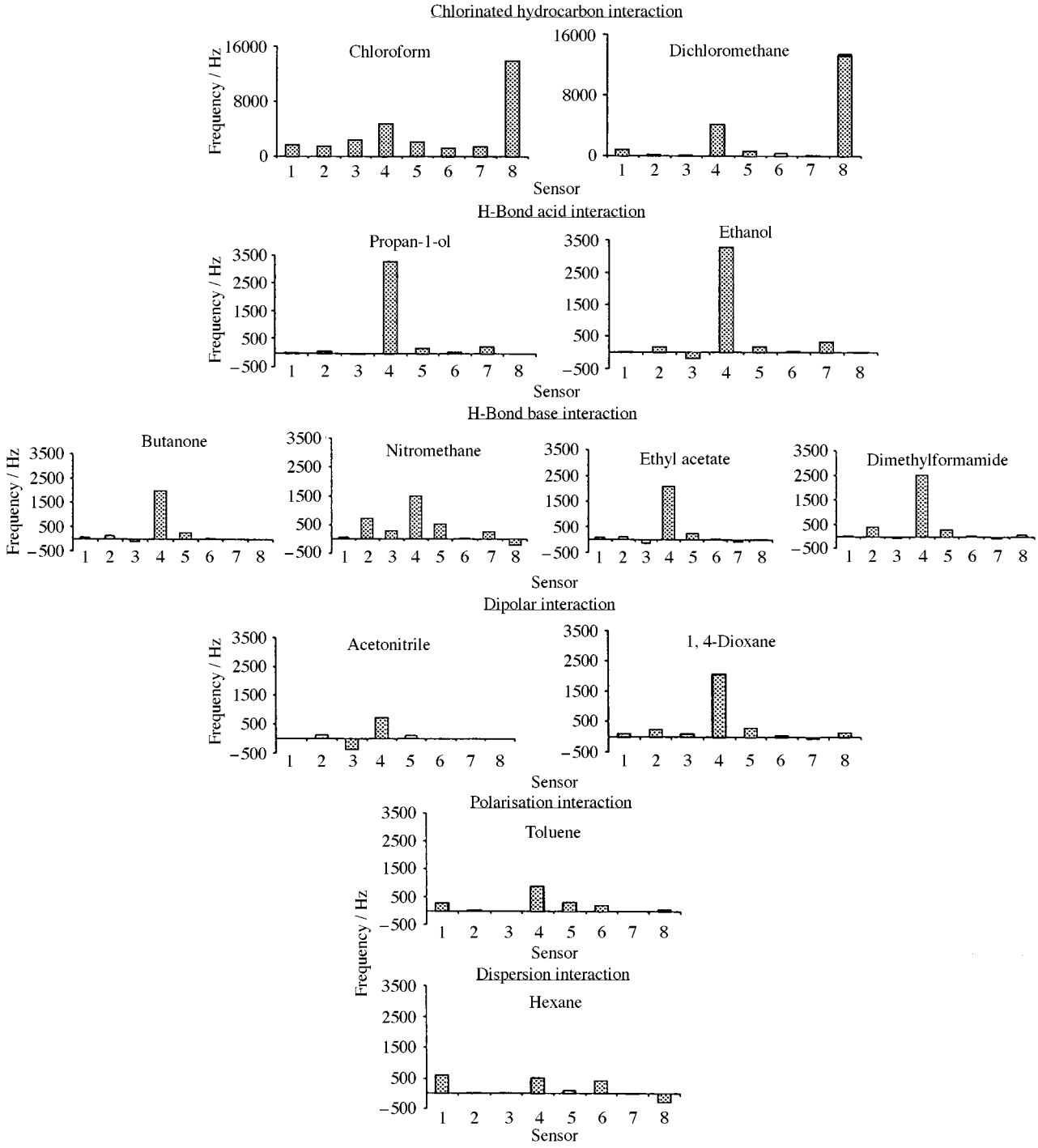

Fig. 2 Sensor responses for different organic vapours.

polysiloxane OV225 (Alltech, Lancashire, UK); poly(ethylene maleate) (PEM), 2,2-bis(4-alloxyphenyl)hexafluoropropane (Alloxy-Bis) and 2,2-bis(4-hydroxy-3-propylphenyl)hexafluoropropane (Pro-Bis) were synthesized as described in the literature.[24] The sensors were coated using an airbrush. Spray coating was found to be suitable for producing sensors with uniform coverage and controlled thickness coatings for certain materials.[24] The method is not universally applicable but worked adequately for the sensor coatings employed. The measurement protocol involved adding 0.5 ml of the sample to 1.5 ml poly(propylene) vials and sampling the headspace in a recirculating mode for 60 s followed by a 60 s clean-up cycle using scrubbed and filtered air. The entire procedure was repeated six times for each vapour to generate the sensor response data set. All measurements were performed in a controlled environment at 22.5 °C. A schematic diagram of the instrumentation is shown in Fig. 1. Comma separated variable (CSV) data files containing the frequency elements $[F(t)]_{s1}$–$[F(t)]_{s8}$ response of each individual sensor over the time course (t) of an experiment were collected. These data files were exported to Excel (Microsoft UK Ltd.) and Neuroshell 2 (Ward Systems Group, Inc., USA) for data analysis.

Results and discussion

The sample test panel was designed to cover important interactions[24] and consisted of: hexane, ethanol, dichloromethane, nitromethane, chloroform, propan-1-ol, toluene, acetonitrile, ethyl acetate, 1,4-dioxane, butan-2-one and dimethylformamide. The characteristics of the sensor elements within the array included: a sensor coated with PIB (polymeric hydrocarbon) for promoting hydrophobic interactions, PEM (polymeric ester) and PEI (polyethylenimine) coated sensors for H-bonding base interactions, Pro-Bis (fluorinated aromatic alcohol) for H-bonding acid interactions,[25] OV225 (cyano-substituted silicon oil) and TCEP (nitrile) for dipolar interactions and PECH[26] (chlorinated polymer) and Alloxy-Bis (substituted aromatic ether) for polarization interactions. The sensor responses (frequency changes after 30 s exposure) to different classes of analytes are shown in Fig. 2. The anomalous negative response values may be due to viscoelastic changes in the sensor coating material but are usually small and therefore are unlikely to significantly influence the pattern recognition process.

Data pre-processing

Since the efficiency of pattern recognition methods relies on samples having different response patterns it is crucial to maximize these differences using the most appropriate pre-processing algorithm. The pre-processing methods which have been employed for gas sensing with arrays[27–30] are listed in Table 1 with formulae applying to signals obtained from an array of quartz crystal microbalances.

In this work frequency changes ($F(t)_{ij} - F_0(t)_{ij}$) were used as input where t = 30 s. Suspected outliers were detected by comparing the difference between the suspect value and the

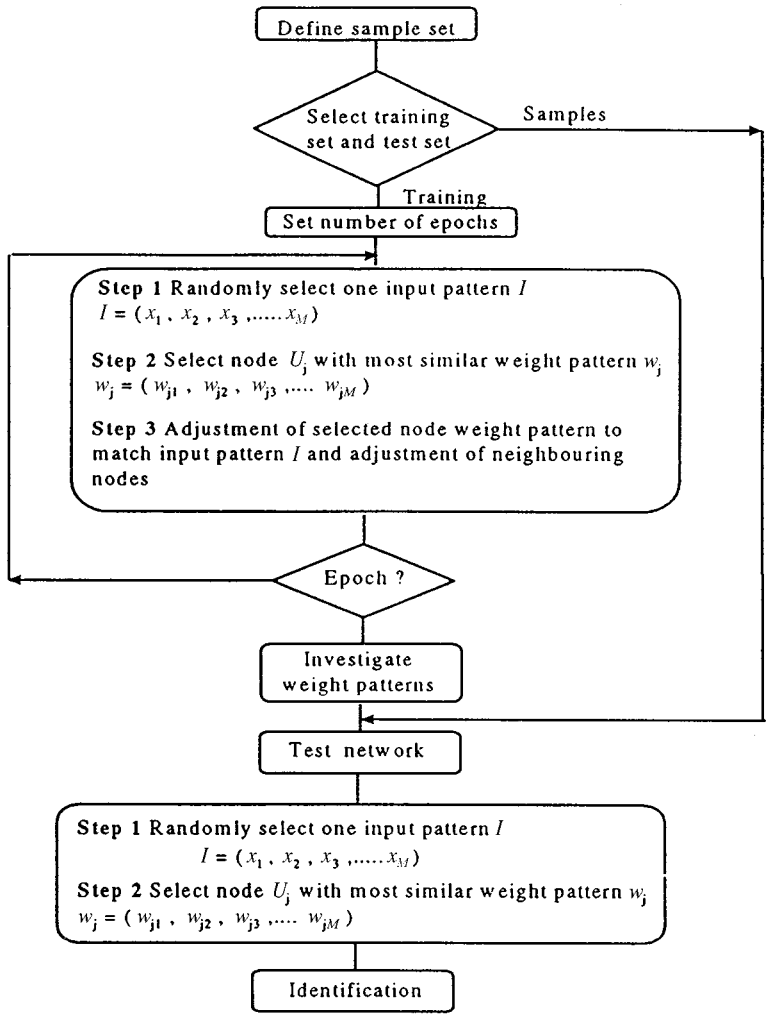

Fig. 4 Steps involved in training and testing a Kohonen network.

nearest measurement value, with the difference between the highest and lowest measurements. The ratio of these differences is known as Dixon's Q where

$$Q = |\text{suspect value} - \text{nearest value}|/(\text{largest value} - \text{smallest value})$$

If the calculated value of Q exceeded the critical value for $P = 0.05$ the suspect value was rejected.[31] When the pre-processed data were fed into the Kohonen network it were necessary to define the target values onto which the input data were mapped. In this work the minimum value was set to the mean minus two times the standard deviation ($\bar{x} - 2\sigma$). The maximum was set to the mean plus two times the standard deviation ($\bar{x} + 2\sigma$).

The Kohonen algorithm

Kohonen networks have two layers, a standard input layer and an output layer known as the competitive Kohonen layer as shown in Fig. 3.

For a network with M inputs the weight values for a Kohonen layer node, U_j, are denoted by

$$w_j = (w_{j1}, w_{j2}, \ldots w_{jM})$$

and the Euclidean distance D_j for each of the Kohonen nodes is given by

$$D_j = [(x_1 - w_{j1})^2 + (x_2 - w_{j2})^2 \ldots + (x_M - w_{jM})^2]^{1/2}$$

where x_i are the sensor inputs (i = 1–8 in this case).

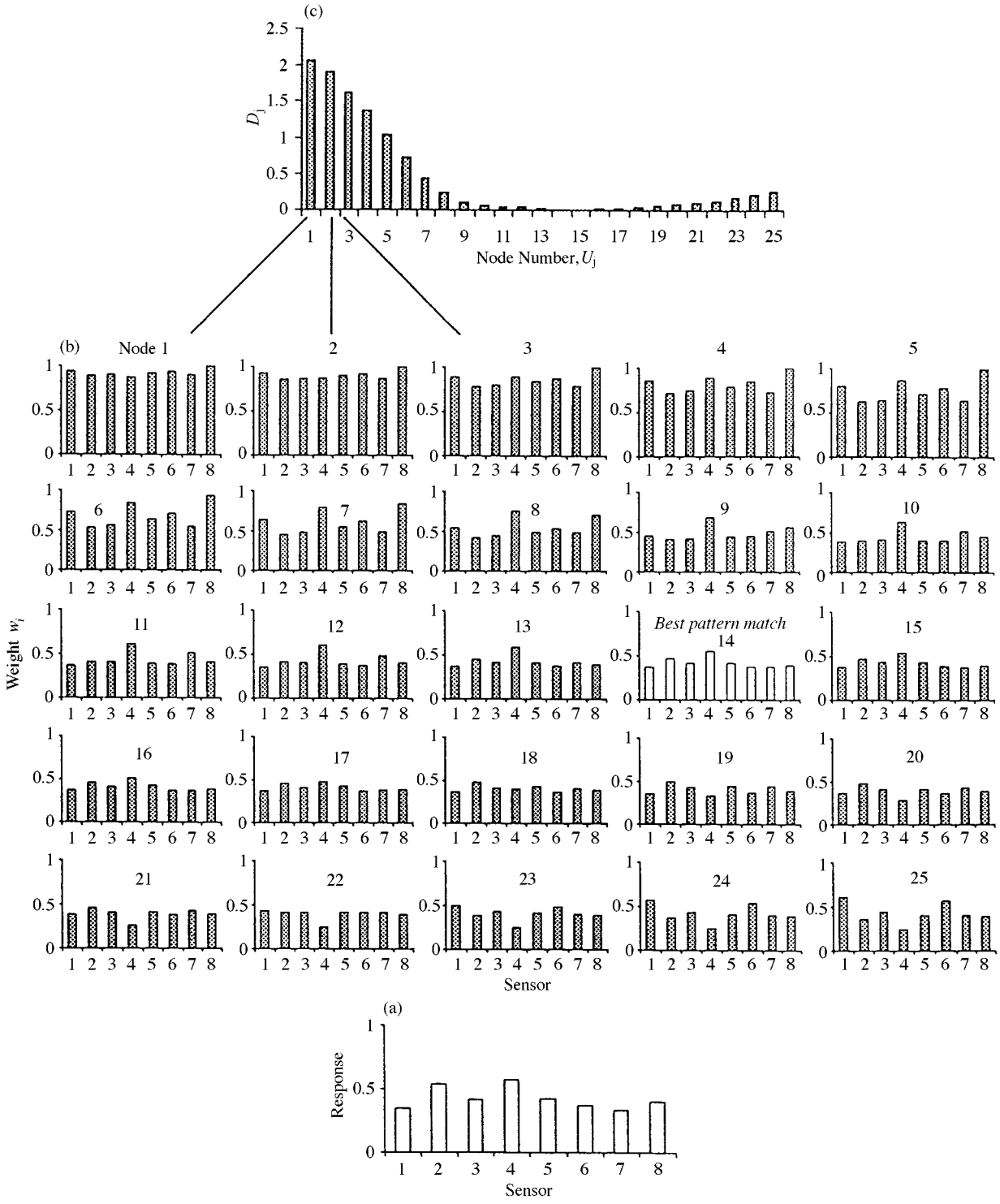

Fig. 5 (a) Input pattern obtained from dimethylformamide; (b) weight maps generated in training from complete solvent vapour set; (c) output pattern for dimethylformamide.

Once the node with the smallest distance is selected, the weight adaptation for this winning node and neighbouring nodes occurs. The formula for adjusting the weights of node U_j is

$$w_{ji\,\mathrm{new}} = w_{ji\,\mathrm{old}} + \alpha\,(x_j - w_{ji\,\mathrm{old}})$$

where α is a learning coefficient which is a function of both time and distance from the winning node. The steps involved in training and testing a Kohonen network are summarized in Fig. 4. Steps 1–3 are termed an epoch or cycle.

The Kohonen network employed for classification of the 12 organic vapours consisted of 8 inputs and an output layer consisting of 25 nodes. The number of nodes (grid size) in the Kohonen output layer was chosen on the basis of the number of groups to be distinguished. The data collected were divided into a training set (36 patterns) and a test set (24 patterns). The learning rate was set to 0.5 and initial weight settings were confined to −0.5–0.5. The network was trained for 100 epochs with patterns selected randomly as opposed to sequentially. Software authors suggest this selection method may provide

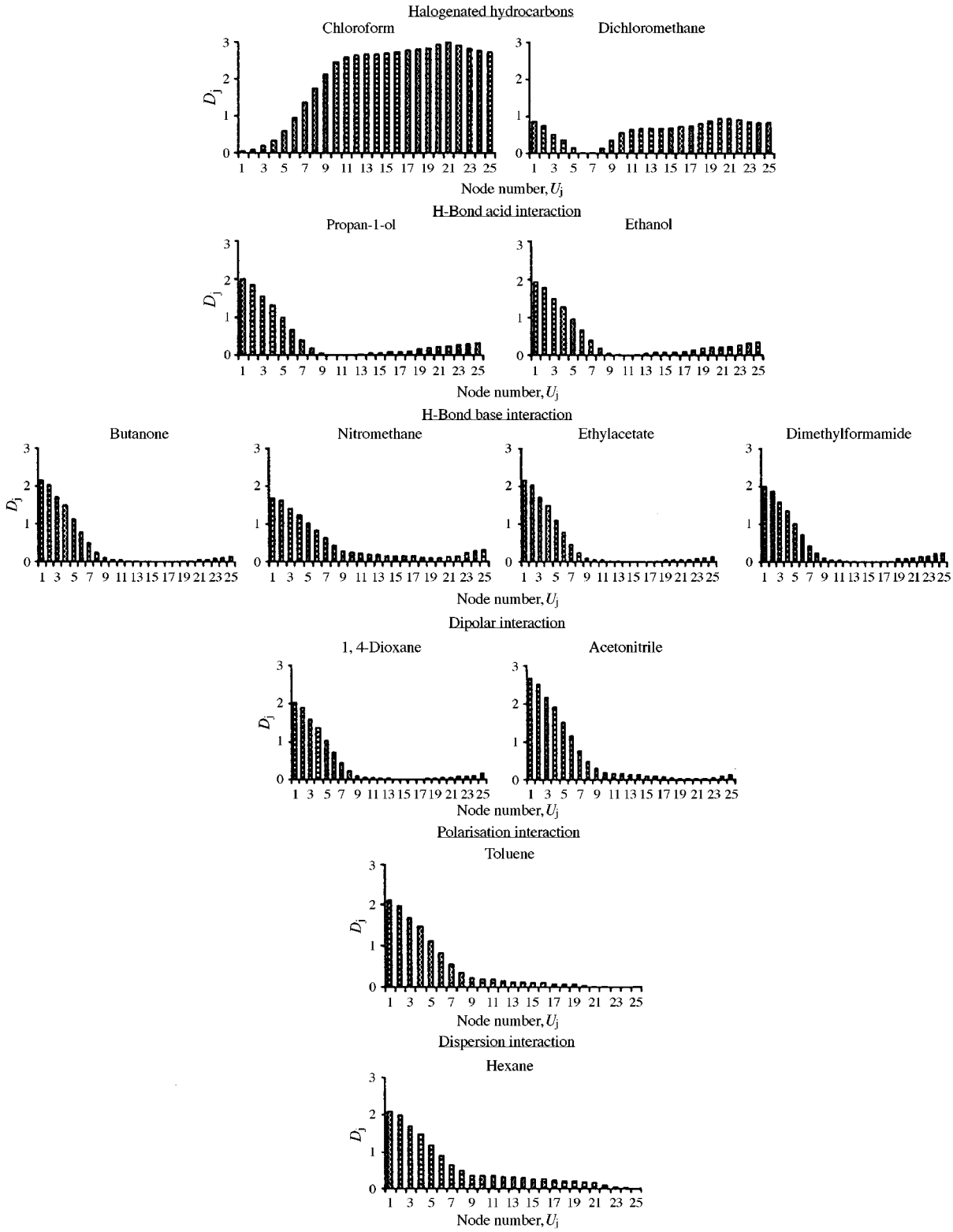

Fig. 6 Output patterns generated by the Kohonen network for different organic vapours.

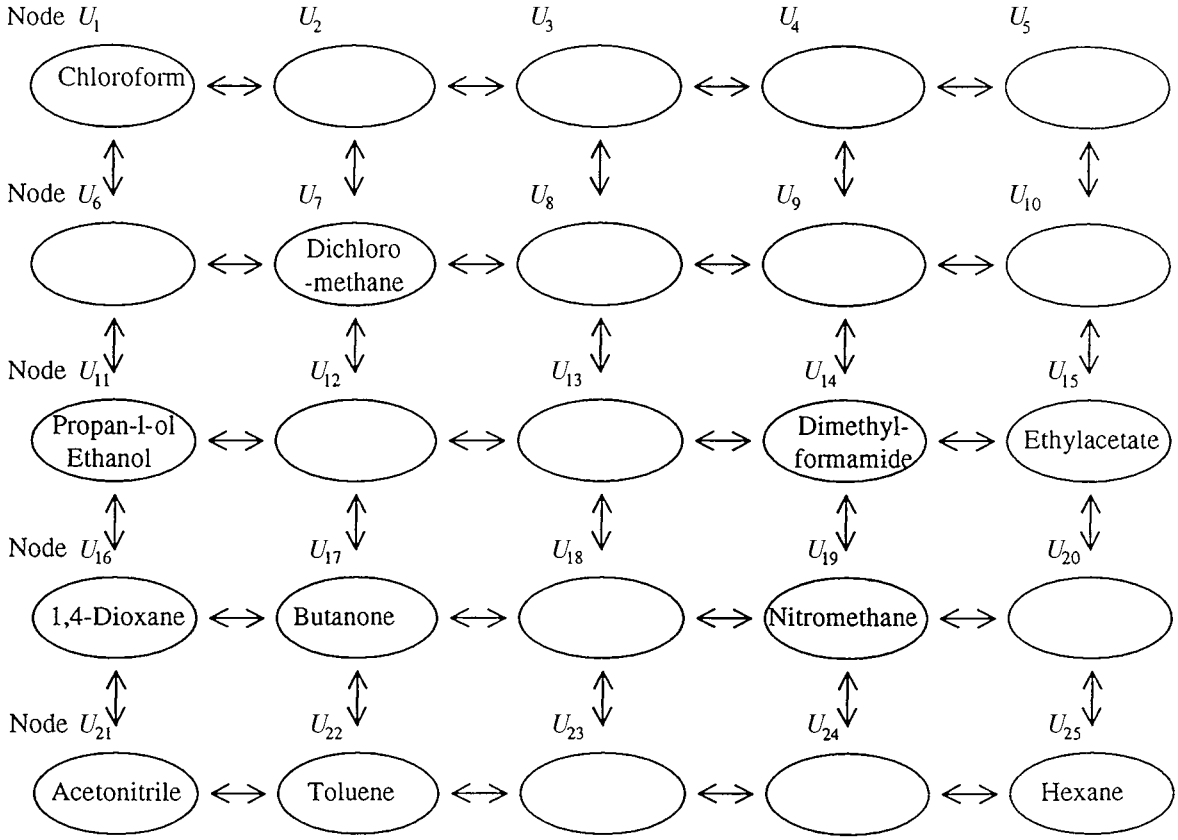

Fig. 7 Mapping of chemical functionality using a Kohonen network.

better results due to greater oscillations of weight links during training.[32]

The input pattern, node weight patterns and the output pattern generated by the Kohonen network for dimethylformamide are shown in Fig. 5(a), (b) and (c) respectively. The output pattern generated by the network is essentially the difference (D_j) between the input pattern and the weight patterns. The input pattern is compared with each weight pattern in each of the 25 nodes which have been established during training. Node U_{14} had a weight pattern most similar to the input pattern for dimethylformamide and therefore this node was deemed the 'winner'. The output patterns generated by the Kohonen network for different vapours are shown in Fig. 6. A comparison of the actual sensor responses (Fig. 2) with the Kohonen output patterns generated for different organic vapours (Fig. 6) shows that the Kohonen patterns are more easily distinguished than the original sensor response patterns for similar types of interactions. The results also demonstrate that the method usefully preserves relationships within the data set unlike data reduction techniques such as factor or canonical function analysis. Chemically similar organic vapours were found to generate similar output patterns or 'fingerprints', for example, ethanol and propan-1-ol. The winning node for each vapour has the smallest difference D_j. For example, dichloromethane has the lowest score D_j for node 7 and occupies this node in the final output grid shown in Fig. 7.

The Kohonen output layer shown in Fig. 7 provided the basis of a chemical interaction profiling method. Hexane was found to 'win' node U_{25}, ethanol and propan-1-ol U_{11}, chloroform U_1, nitromethane U_{19} and so on. The relative strength of interaction decreased with increasing node number as shown in Fig. 7.

The Kohonen interaction profiling method could be considered as an alternative to other classification schemes.[23] Existing models may provide more rigorous classification schemes; however, the Kohonen network has an advantage in that it does not rely on gas chromatography data.

Conclusions

The Kohonen network was shown to provide patterns which were more easily distinguished than the original sensor response patterns for similar types of interactions. This provided the basis of an effective feature extraction method in that distance values generated by the network allowed better discrimination of 'fingerprints'.

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