A humid electronic nose based on pulse voltammetry; a proof-of-concept design.

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Abstract.

We report herein the design, manufacture and use of a “humid electronic nose” prototype based on voltammetric techniques. It consists in an array of four working electrodes (i.e., Au, Pt, Ir and Rh) housed inside a homemade stainless steel cylinder, in contact with a fabric mesh made of nylon damped with a NaCl aqueous solution, used as the supporting humid membrane. The “humid electronic nose” was tested for the discrimination of different samples displaying different volatile compounds. The samples chosen involve aqueous solutions of different simple volatile products (i.e., ammonia, acetone, acetic acid and 6-amino-1-hexanol) and different food samples (i.e., onion, coffee and Roquefort cheese). Under working conditions, the volatile compounds from the corresponding sample were generated in the measurement chamber and were partially dissolved in the damped nylon fabric, which was in contact with the set of electrodes. It was envisioned that provided different samples offer different vapours, the application of a suitable set of pulses to the electrodes will
differentiate the samples. This proof-of-concept study employed a Large Amplitude
Pulse Voltammetry (LAPV) wave form. The increment for the potential steps was of
200mV and potentials ranged from +1 to -1 V with each pulse applied for 50 ms. PCA
studies from the response obtained by the “humid electronic nose” discriminated the
different samples studied. The neural network Self Organized Map (SOM) was also
used to analyse the electrochemical data obtained from the “humid electronic nose”.

Keywords: Voltammetry; Wet electronic nose; PCA; ANN; SOM

1. Introduction.

Dodd and Persaud introduced the idea of an electronic nose as a device to mimic the
discrimination of the mammalian olfactory system for smells. [1] With this goal in mind,
the authors used three different metal oxide gas sensors and identified several
substances by employing the measured steady-state signals of these sensors. In this
particular area, one of the initial hopes was to instrumentally assess attributed
descriptors such as fruity, grassy, earthy, malty, etc. by relying on the results of
electronic nose measurements. The resulting receptor pattern, of biological inspiration,
pretends to determine an impression of the odour in an attempt to mimic the principles
of smelling. The sensor data are analysed to extract features, which can be evaluated
as a whole to eliminate redundancy and to obtain a description of the overall volatiles
mix. [2]

In most cases, classical electronic noses are built using metal oxide (MOX) sensors,
although new technologies have recently entered this field. For instance, the same
application has been found utilising other transducer principles, such as acoustic wave
(SAW, BAW) sensors, metal oxide semiconductor field effect transistors (MOSFETs),
conducting polymers (CP), optical sensors, gas chromatography, ion mobility
spectroscopy, infrared spectroscopy, etc. [3]

In the past two decades, the applicability of electronic noses has been tested in every
imaginable field where odours or odourless volatiles and gases are thought to play a
role. [4,5,6,7] For historical reasons, the main research fields for electronic nose
technologies are still related to those areas where the human olfaction system is
relevant. Typical examples have included the determination of the quality of complex
food products, such as coffee, tea, olive oil, or wine. [8, 9] In fact in recent years, many
efforts have been made in the field of foodstuff and beverages where, in addition to classification, time-dependent processes have been investigated. [7,8,9]

Moreover, several amperometric electrochemical sensors have been developed over the past five decades to measure target gases such as oxygen and carbon dioxide [10, 11,12,13,14,15]. These sensors have varied in their design, specifically in electrode dimension, electrode material, and choice of membrane, to improve performance, lifetime, and reliability, while reducing the cost and size [16]. The target gas permeates to the working electrode through the gas permeable membrane where it is detected. Recently, the use of ionic liquids as solvents for the electrochemical detection of oxygen, carbon dioxide, and ammonia was reported [17,18,19,20]. Signalling of other target gases such as hydrogen have also been reported [21]

As stated above, electronic noses commonly use resistive sensors in most cases, whose impedances vary in the presence of certain gases. However, these sensors work in a "non-humid" environment, therefore the measurement techniques that can be applied under these conditions can be somewhat limited. As an alternative, we were interested in designing a “humid electronic nose” as a substitute for the use of classical electronic noses based on metal oxides. One advantage of employing a “humid electronic nose” design to evaluate the presence of volatile compounds is the possibility of employing a wider range of electrochemical techniques. In fact this allows to use classical techniques used in electronic tongues (such as voltammetry) in the detection of volatile derivatives from liquid or solid samples.

In fact in a recent work, we have shown the conceptual basis of how we can design a “humid electronic nose”. [22] This electronic nose was constructed using an array of potentiometric metal wire electrodes fitted to a wet nylon membrane. The “humid electronic nose” was used to detect the volatile compounds generated during the microbiological spoilage of wines and, together with an electronic tongue, it was employed to evaluate the time evolution of wine samples.

Based on these previous concepts, our aim was to demonstrate that it is possible to design a “humid electronic nose” using voltammetric techniques for the purpose of discriminate some substances and complex products producing volatile compounds. In particular, and partly given our interest in electronic tongues and noses, [23,24,25,26,27] we report herein the design and application of a voltammetric “humid electronic nose” that uses a simple set of metallic electrodes placed on a wet setting. This proposed system detects volatile compounds that emanate from the sample and
which are apprehended by a moist environment when electrodes are included. The use
of such a “humid electronic nose” for the detection of volatile compounds is, as far as
we know, new and it allows the employment of classical electrochemical techniques
such as voltammetry, commonly used in electronic tongues, to analyse volatile
substances.

2. Materials and Methods

2.1. Samples

The response of the “humid electronic nose” was studied in the presence of seven
different samples: ammonia (1 mol dm$^{-3}$, 20ml), acetic acid (1 mol dm$^{-3}$, 20ml), acetone
(1 mol dm$^{-3}$, 20ml), onion (chopped, 20 grams), 6-amino-1-hexanol (1 mol dm$^{-3}$, 20ml),
coffee (ground, 20 grams) and Roquefort cheese (20 grams). The baseline current
(referred to as the control sample) was measured with the “humid electronic nose”
using an aqueous solution of NaCl (0.01 mol dm$^{-3}$, 20ml) placed in the measuring
chamber. For all the samples, the membrane in contact with the electrodes in the
“humid electronic nose” was wet with an aqueous solution containing NaCl (0.01 mol
dm$^{-3}$).

2.2. Equipment

A system for pulse voltammetry implementation was designed in the Centro de
Reconocimiento Molecular y Desarrollo Tecnológico (IDM) at the Universidad
Politécnica de Valencia (UPV - Spain). The system consists of a software application
that runs on a PC and electronic equipment. [26,28]

The equipment generates a sequence of up to 50 pulses with an amplitude in the range
of [-2V to +2V]. The width of the pulses can also be configured: [1 ms to 800 ms]. The
equipment includes a potentiostat, which applies the voltage to the counter electrode of
the electrochemical cell and measures the voltage at the reference electrode and the
current at the working electrodes (up to 8).

The software application allows the setup of the pulse array parameters: number of
pulses, amplitude of each pulse, width of the pulses. A different pulse pattern can be
configured for each working electrode. Once the test has been configured, the
application sends this information to the electronic equipment, which generates and
applies the pulse array to the electrochemical cell, and also samples the voltage and
current signals. The system collects 1,000 current samples for each applied pulse array. Finally, the equipment sends these samples to the PC where the data are displayed and stored. This procedure is then repeated for the next working electrode of the sequence.

The electronic equipment includes a 16-bit microcontroller (PIC24FJ256), a 12-bit Digital-to-Analogue converter (DAC), two 12-bit Analogue-to-Digital converters (ADC) and a potentiostat that incorporates a current measurement circuit, a working electrode multiplexing block and a stabilization circuit.

2.3. Measurement procedure

The measuring chamber (Figure 1.b) consists of a sealed glass cell (750 ml) with a top cover with five inlets. The cell has been designed to avoid gas leaks. One inlet was for the “humid electronic nose”, one for the reference electrode, two for the argon line (inlet and outlet) and one for sample addition. The cell was thermostated with a commercial circulating temperature controller. This glass reactor was used as the measuring chamber in which a given sample was directly introduced.

The “humid electronic nose” device (Item 1 in Figure 1.a) consists of an array of four working electrodes (i.e., Au, Pt, Ir and Rh) with 99.9% purity and 1-mm diameter from ALDRICH which were housed inside a homemade stainless steel cylinder used as the electronic nose body. The different wire electrodes were fixed inside the cylinder using an epoxy RS 199-1468 polymer. Before use, the electrode surface was prepared by mechanically polishing with emery paper and was rinsed with distilled water. Then it was polished on a felt pad with 0.05 µm alumina polish from BAS, washed with distilled water and polished again on a nylon pad with 15, 3 and 1 µm diamond polishes to produce a smooth, mirror-like electrode surface. Later during the development of series of measurements, only one simple diamond polishing was performed.

The fabric mesh (Item 2 in Figure 1.a) was used as the supporting humid membrane where vapours were trapped. The humid membrane came in contact with the electronic tongue. The fabric of the membrane was nylon with a fibre thickness of 350 microns separated by about 150 microns. The membrane was damped with a NaCl aqueous
solution (0.01 mol dm\(^{-3}\)). The role of the moistened fabric was to perform the absorption of the volatile compounds from the sample and to provide a conductive vehicle to the electrode interface. Before a new measurement was taken, the membrane was rinsed with distilled water, dried and then moistened again with salt solution. The reference electrode was a Saturated Calomel Electrode (SCE), which was connected to the damped fabric with a curved low-density polyethylene (LDPE) tube with cotton at the end (Item 3 in Figure 1.a). The set of electrodes, the nylon fabric and the LDPE tube were held together with a PVC connector which has two pieces (Items 5a and 5b in Figure 1.a). The nylon membrane was trapped between these two pieces and was held still with a nylon screw (Item 4 in Figure 1.a). The LDPE tube was connected to the nylon membrane through a hole on the edge of the outer PVC piece, which allowed contact between the damp nylon fabric in contact with the working electrodes and the reference electrode. The measuring chamber was thermostated at 37\(^\circ\)C. All the measurements were made under argon. Prior to the sample addition the argon atmosphere was created by displacing the air for 10 minutes with argon. The argon flow was stopped and then the sample was directly introduced into the measuring chamber and left for at least 5 min before the measurement was taken. This time period was established after studying the absorption processes of volatile substances (NH\(_3\), HCl, etc.) in the nylon fabric membrane. After these 5 min had passed, the measurement was taken: i.e., the pulse pattern was applied and the current response of each electrode was measured and stored in the PC.

This study employed a Large Amplitude Pulse Voltammetry (LAPV) wave form. [29,30] Figure 2a shows the applied pulse pattern which consists of 40 pulses in a configuration similar to a staircase voltammetry, but the potential was set to 0 after each increment. In particular, the pulse sequence was: 0, 200, 0, 400, 0, 600, 0, 800, 0, 1000, 0, 800, 0, 600, 0, 400, 0, 200, 0, -200, 0, -400, 0, -600, 0, -800, 0, -600, 0, -400, 0, -200, 0, 0, 0, 0, 0 (mV). Each pulse was applied for 50 ms. The increment for the potential steps was 200mV, and the maximum and minimum potentials were chosen in order to avoid water electrolysis phenomena. Figure 2b illustrates the intensity/time diagram for an acetic acid 0.001 mol dm\(^{-3}\) solution using iridium as the working electrode, which overlapped the control sample response.

2.4. Data analysis
In order to show the different responses of the “humid electronic nose” to the different samples, the voltammetric electrochemical response data were combined to form ensembles for pattern recognition in an attempt to discriminate samples. Hence, a multivariate data analysis (MVDA) was used for this purpose. A principal components analysis (PCA) proves an efficient approach for reducing the dimension of a data set. [31] In addition, Artificial neural networks analyses have also been carried out to extend the statistical study of the resulting data.

The test settings in the software application were configured to measure five consecutive iterations; that is, the pulse pattern was applied to the four working electrodes (in this order: Ir, Rh, Pt and Au) and the test was run five times before the sealed measuring environment had to be opened to discard the sample and to prepare a new one. The resulting data contains 1,000 current values for each applied pulse array, this is: 1,000 current values x 4 electrodes x 5 iterations = 20,000 current values for each measurement. Three replicates were measured for each of the eight samples, so this sums up: 20,000 current values x 8 samples x 3 replicates = 480,000 current values. Having this amount of data proved highly valuable to be able to discard erratic data due to electric noise. These data were then preprocessed by calculating the mean of iterations in order to obtain a favourable signal-to-noise ratio, so the data set was reduced by 5 (480,000 current values / 5 iterations = 96,000) [26,28]. The last data preprocessing step was to subtract the baseline. The baseline was calculated in the same way as the rest of the samples, the same preprocessing steps were done and the mean of three baseline samples was calculated so that a single data set was used to be subtracted from the rest of the samples. The baseline samples were named control samples and they underwent no subtraction. The measurements were made on different days and for a given day the samples were measured randomly. No replicates were measured on the same day. Only the control sample (NaCl 0.01 mol dm$^{-3}$) was measured at the starting of the experiments each day.

**Principal Components Analysis (PCA)**

Typically, a PCA decomposes the primary data matrix by projecting the multidimensional data set onto a new coordinate base, formed by the orthogonal directions with maximum data variance. The eigenvectors of the data matrix are called principal components and they are not intercorrelated because they are orthogonal. The principal components (PCs) are ordered so that PC1 displays the greatest amount of variance, followed by the next greatest PC2, and so on. The main PCA features are the coordinates of the data in the new base (scores plot) and the contribution of the
sensors to each component (loading plot). [32] In addition, in order to minimize effects
that can derive from employing the electrodes (non-specific chemisorption or
physisorption), after each voltammetric sequence, the electrodes surface was polished
to provide a clean metal surface for the next measurement. Having done all the
preprocessing, the PCA was calculated. All the statistical analyses were performed
with the Solo application software (version 6.5, Eigenvector Research, Inc.).

Artificial Neural Networks

Neural networks constitute simple components that operate in parallel; these
components are based on biological nervous systems. As in nature, the connections
between components largely determine the network function. A neural network can be
trained to perform a particular function by adjusting the values of the connections
between elements. Neural networks have been trained to perform complex functions in
various fields, including pattern recognition, identification or classification.

Data matrices generated by electronic tongue systems are generally considerable in
size and neural networks tools are needed to process them. Among several types of
neural networks, the following has been used in this work: Self-Organized Maps (SOM)
as unsupervised network.

The Self-Organizing Map (SOM), also known as the Kohonen Map, is an unsupervised
neural model of widespread use in areas such as pattern recognition. The SOM is a
neural network model that projects a high dimensional input space, usually onto one or
two dimensional output space(s) by using unsupervised training. Given its typical two-
dimensional shape, it is also easy to visualize. This architecture is similar to that of a
competitive network, except no bias is used (Figure 3). The competitive transfer
function produces 1 for output element $a^1_i$, the winning neuron. All the other output
elements in $a^1$ are 0. [33]

3. Results and discussion

As stated above, due to our interest in designing electronic tongues and noses for
different applications, we attempted to test the possible use of a voltammetric “humid
electronic nose” for the discrimination of different samples. In our humid nose detection
is based on the changes in the electrochemical properties that occur when a gas or
vapour is dissolved by a conductive membrane. The absorption processes of gases and vapours follow Henry’s law, which states:

\[ \text{(A)} = k_H \cdot f_A \]

where \( \text{(A)} \) is the activity of the absorbed substance in the liquid phase, \( k_H \) is the Henry’s law constant which is dependent on the working temperature and composition of the liquid and \( f_A \) is the fugacity of the gas. As stated above this procedure allows using a wide range of electrochemical techniques (e.g. voltammetry) which could not be employed in classical electronic noses. Moreover the use of humid noses may attain additional advantages. For instance it is known that \( k_H \) for vapors in a liquid usually decreases when the temperature increases and this could be used as a preconcentration method for instance via heating up the sample while the temperature of the membrane in the humid nose is reduced. Moreover it is known that gas solubility in liquids depends on the chemical affinity between the liquid and the gas and could be used to modulate the selectivity of the ‘humid electronic nose’ towards different gases by using a particular solvent or a mixture of solvents in the membrane.

In this proof-of-concept design of a humid electronic nose based on pulse voltammetry we have used a static headspace technique for the volatile generation following similar procedures to those used for classical electronic noses. The samples chosen in this study involve aqueous solutions of different simple volatile compounds (i.e., ammonia, acetone, acetic acid and 6-amino-1-hexanol) and different food samples (i.e., onion, coffee and Roquefort cheese). These systems, showing very different natures, were chosen in order to gain a wide variety of samples which may provide a realistic view of the potential use of this electronic nose format. All the measurements were strictly taken under the same conditions: 37°C, argon atmosphere and polishing the surface of working electrodes before each new measurement. It was envisioned that, as long as different samples provide different vapours, the application of a suitable set of pulses to the electrodes will allow differentiating the samples. In this proof-of-concept study, a Large Amplitude Pulse Voltammetry (LAPV) wave form was used. The increment for the potential steps was of 200mV and potentials ranged from +1 to -1 V, with each pulse applied for 50 ms. Samples were measured three times following a random sequence. Moreover, pure water containing NaCl was used as a control solution to determine the stability and repeatability of the system versus time.

### 3.1. PCA
The different electrochemical responses of each sample, using the “humid electronic nose”, were analysed by a PCA. This is a powerful linear unsupervised pattern recognition method. PCA is an efficient approach to diminish the dimensionality of a dataset. A PCA study of the full set of patterns revealed a medium degree of dispersion among the independent dimensions created by the linear combinations of the electrochemical responses of the four electrodes used in the array. The first PC contained 67.87% of the variance of the data, whereas the first two components represented 86.24% of total variance, while five PCs were needed to account for 96.06% of variance. This relatively large number of independent dimensions to account for most of the variance may be due to the different composition of the samples used, which generate very different volatile compounds during the experiments. Although a relatively large number of dimensions are required to explain total variance, PCA captured 86.23% of the variance observed in the experiment in the first two PCs. The plot of these two PCs on the x and y axes is shown in Figure 4, which displays the resulting PCA for eight samples (three replicates) when using the response of all four electrodes in the “humid electronic nose”. As observed, it was possible to discriminate among the samples studied. Moreover, when the control data were introduced into the PCA analysis, all the data were situated around the same place, which is in agreement with the systems’ capacity to differentiate the control from the rest of the samples. Moreover, as the control solutions were measured on different days, the results suggest a high degree of repeatability in the electrodes’ response. Clearer differentiation in the PCA plot was observed for the aqueous samples containing ammonia, acetic acid and for the Roquefort cheese. A second PCA plot in which these samples were omitted is shown in Figure 5. In this new plot, the first PC contained 69.69% of the variance of the data, whereas the first two PCs represented 81.31% of total variance. The figure depicts a relatively clear discrimination among the remaining samples.

From the plot, it is apparent that the “humid electronic nose” is able to differentiate not only samples containing simple compounds such as ammonium, acetone, acetic acid and 6-amino-1-hexanol, but also more complex samples with a number of volatile compounds that define their characteristic aroma such as Roquefort cheese, coffee and onion. In fact it has been reported that, for instance, in French blue cheeses, an important amount of methyl ketones was present in the flavour profile and a significant number of secondary alcohols and esters were also present.[34] In coffee, more than one thousand compounds, including furans, ketones, pyrazines, alcohols, aldehydes, esters, etc., are characteristic of their typical aroma [35,36], whereas in chopped onion,
a number of volatile oxygen derivatives (especially carbonyl compounds) and saturated
and unsaturated disulphides have been found in the headspace.[37] Despite the
presence of some of these compounds at a relatively low concentration, the “humid
electronic nose” is able to show an electrochemical fingerprint response that
characterizes the aroma of these specific foods.

In order to help identify the signals response of each electrode for the discrimination
observed in the current pattern, a loading analysis was carried out. As the data set
included a large number of data, the amount of points was reduced to make a loading
plot viable, and only one of every 10 data points was used to construct the following
plot figure. Most electrode responses are represented in the first two PCs (plot not
shown), suggesting that the response of all four electrodes are captured by both PC1
and PC2. Besides when PC1, PC3 and PC4 are considered, the response of the Au
electrode (triangles in Figure 6) forms a plane which is orthogonal to the plane of the
data from the Ir and Pt electrodes (squares and circles in Figure 6), whereas the Rh
electrode response (crosses in Figure 6) forms a third new plane which is almost
orthogonal to the Au and Ir-Pt planes. Accordingly with the figure the responses of Ir
and Pt electrodes appear to be highly correlated. Based in this concept we carried out
additional classification studies removing the data from Ir or Pt electrodes. Discarding
the data from Ir or Pt sensor results in a very similar classification than when all the
electrodes were used, however the systems needs more latent variables to achieve the
same performance, which leads us to maintain data from all the electrodes in the
dataset. These results make us think that the set of all four electrodes provides
valuable and complementary information to help discriminate samples.

3.2. Classification with Self-Organized Maps

Apart from the study carried out with PCA analysis, the neural network Self-Organized
Maps (SOM) has also been used to analyse the electrochemical data obtained from the
“humid electronic nose”. Studies with the SOM neural network were carried out using
the software application SOMmine 5 by Viscovery. The number of nodes used in all
cases was 1,000. The programme calculates a neighbourhood of at least 50 nodes
with a linear neighbourhood weight function. Viscovery SOMine divides a map into
regions, called clusters. The nodes of a cluster are similar in that that they are neighbours in the data space. For this study, in order to reduce the number of data, the value for each pulse was calculated as the corresponding area enclosed by the current signal, so a single value is used for each pulse.

The SOM neural network allows to carry out a study of the contribution that the different pulses make on the response of a selected electrode and the weight that a certain electrode has in the overall response obtained in the electronic nose in terms of the classification of different substances. In relation to the first issue, it was found that the pulses corresponding to a potential of 0V (i.e., P1, P3, P5, P7, etc.) provided practically no information, except for pulse 1 (P1). Moreover, it was observed that the pulses with the same potential value (i.e., P2 and P18, P4 and P16, P6 and P14 and P8 and P12) displayed similar information. The SOM analysis was also repeated for the negative pulses (P21 to P40). The maps reveal that the resemblance between pulses is not so obvious. Certain similarities in terms of response were observed in pulses P28, P26 and P30, but not for the rest of the pulses, and not even the same pulses in different metals were similar, as found for the positive pulses. Nevertheless, additional studies confirmed that negative pulses were not necessary to obtain a good classification as this was achieved using only the above-mentioned positive pulses. The study suggested that for this particular application, the use of pulses P1, P2, P4, P6, P8 and P10 sufficed to achieve a good classification (see Figure 7). As an example Figure 8 shows the SOM map of pulse 4 for the Ir electrode. As it can be observed this pulse has a large contribution to the detection of ammonia, but a medium-low contribution to the rest of samples.

Having studied the set of pulses, the contribution of different electrodes to the “humid electronic nose” response was also carried out. Several combinations of electrodes were tested, but it was generally established that a suitable response in terms of the correct classification of the different samples was observed when all four metal electrodes were in use. Based on these data, further studies were performed using all four metal electrodes and pulses P1, P2, P4, P6, P8 and P10.

4. Conclusions

We report herein the design, manufacture and use of a “humid electronic nose” prototype. This new system entails innovation in the electronic noses field, and it relies on the use of a wet environment to perform pulse voltammetry experiments on an array
of four working electrodes (i.e., Au, Pt, Ir and Rh) which were in contact with a fabric
mesh made of nylon damped with a NaCl aqueous solution. As a proof-of-concept, the
“humid electronic nose” was able to “sense” the presence of aqueous solutions of
different simple volatile compounds (i.e., ammonia, acetone, acetic acid and 6-amino-
1-hexanol) and different food samples (i.e., onion, coffee and Roquefort cheese). PCA
and SOM studies were performed. The neural network SOM allowed us to determine
that good classification results were obtained when using all four electrodes and a set
of only six pulses. From our point of view this opens new applications and allows to
develop electronic noses following classical electronic tongue designs which can be
applied to both liquid or solid samples (via the detection of volatile compounds). This
preliminary study led us to believe that this “humid electronic nose” may be applied to a
wide range of situations, in the food industry (e.g. inspection of food quality control,
monitoring fermentation processes, checking rancidity and spoilage, flavor control, etc.)
and in environmental monitoring (e.g. for testing ground water for odors, identification
of toxic wastes, air quality monitoring, monitoring factory emissions, etc.). Moreover,
although we have used in this this proof-of-concept design a static headspace
technique for the volatile generation other configurations will be studied in due course.

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Figure 1: Humid Electronic Nose sketch. Description of parts: a) (1) “humid electronic tongue”; (2) humid membrane; (3) reference electrode and LDPE adapter; (4) nylon screw; (5) PVC adapters. b) measuring chamber.
Figure 2: a) applied voltammetric pulse pattern; b) response for control and AcOH (0.001 mol dm$^{-3}$) samples using an Ir electrode.
Figure 3 Self-Organizing Map Architecture.
Figure 4: A PCA plot for the complete sample array.
Figure 5: A PCA plot excluding \( \text{NH}_3 \), \( \text{AcOH} \) and Roquefort cheese samples.
Figure 6: A plot of the loading factors for PC1, PC3 and PC4 using a reduced data set.
Figure 7.- Classification with Self-Organised Maps (SOM) using pulses P1, P2, P4, P6, P8 and P10.
Figure 8.- Contribution of pulse P4 from the Ir electrode to the complete SOM classification.