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

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15
16 **Abstract.**

17 We report herein the design, manufacture and use of a “humid electronic nose”
18 prototype based on voltammetric techniques. It consists in an array of four working
19 electrodes (i.e., Au, Pt, Ir and Rh) housed inside a homemade stainless steel cylinder,
20 in contact with a fabric mesh made of nylon damped with a NaCl aqueous solution,
21 used as the supporting humid membrane. The “humid electronic nose” was tested for
22 the discrimination of different samples displaying different volatile compounds. The
23 samples chosen involve aqueous solutions of different simple volatile products (i.e.,
24 ammonia, acetone, acetic acid and 6-amino-1-hexanol) and different food samples
25 (i.e., onion, coffee and Roquefort cheese). Under working conditions, the volatile
26 compounds from the corresponding sample were generated in the measurement
27 chamber and were partially dissolved in the damped nylon fabric, which was in contact
28 with the set of electrodes. It was envisioned that provided different samples offer
29 different vapours, the application of a suitable set of pulses to the electrodes will

30 differentiate the samples. This proof-of-concept study employed a Large Amplitude
31 Pulse Voltammetry (LAPV) wave form. The increment for the potential steps was of
32 200mV and potentials ranged from + 1 to -1 V with each pulse applied for 50 ms. PCA
33 studies from the response obtained by the “humid electronic nose” discriminated the
34 different samples studied. The neural network Self Organized Map (SOM) was also
35 used to analyse the electrochemical data obtained from the “humid electronic nose”.

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

37

38 1. Introduction.

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

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

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

62 efforts have been made in the field of foodstuff and beverages where, in addition to
63 classification, time-dependent processes have been investigated. [7,8,9]

64 Moreover, several amperometric electrochemical sensors have been developed over
65 the past five decades to measure target gases such as oxygen and carbon dioxide [10,
66 11,12,13,14,15]. These sensors have varied in their design, specifically in electrode
67 dimension, electrode material, and choice of membrane, to improve performance,
68 lifetime, and reliability, while reducing the cost and size [16]. The target gas permeates
69 to the working electrode through the gas permeable membrane where it is detected.
70 Recently, the use of ionic liquids as solvents for the electrochemical detection of
71 oxygen, carbon dioxide, and ammonia was reported [17,18,19,20]. Signalling of other
72 target gases such as hydrogen have also been reported [21]

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

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

89 Based on these previous concepts, our aim was to demonstrate that it is possible to
90 design a “humid electronic nose” using voltammetric techniques for the purpose of
91 discriminate some substances and complex products producing volatile compounds. In
92 particular, and partly given our interest in electronic tongues and noses,
93 [23,24,25,26,27] we report herein the design and application of a voltammetric “humid
94 electronic nose” that uses a simple set of metallic electrodes placed on a wet setting.
95 This proposed system detects volatile compounds that emanate from the sample and

96 which are apprehended by a moist environment when electrodes are included. The use
97 of such a “humid electronic nose” for the detection of volatile compounds is, as far as
98 we know, new and it allows the employment of classical electrochemical techniques
99 such as voltammetry, commonly used in electronic tongues, to analyse volatile
100 substances.

101

102 **2. Materials and Methods**

103 **2.1. Samples**

104 The response of the “humid electronic nose” was studied in the presence of seven
105 different samples: ammonia (1 mol dm⁻³, 20ml), acetic acid (1 mol dm⁻³, 20ml), acetone
106 (1 mol dm⁻³, 20ml), onion (chopped, 20 grams), 6-amino-1-hexanol (1 mol dm⁻³, 20ml),
107 coffee (ground, 20 grams) and Roquefort cheese (20 grams). The baseline current
108 (referred to as the control sample) was measured with the “humid electronic nose”
109 using an aqueous solution of NaCl (0.01 mol dm⁻³, 20ml) placed in the measuring
110 chamber. For all the samples, the membrane in contact with the electrodes in the
111 “humid electronic nose” was wet with an aqueous solution containing NaCl (0.01 mol
112 dm⁻³).

113 **2.2. Equipment**

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

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

123 The software application allows the setup of the pulse array parameters: number of
124 pulses, amplitude of each pulse, width of the pulses. A different pulse pattern can be
125 configured for each working electrode. Once the test has been configured, the
126 application sends this information to the electronic equipment, which generates and
127 applies the pulse array to the electrochemical cell, and also samples the voltage and

128 current signals. The system collects 1,000 current samples for each applied pulse
129 array. Finally, the equipment sends these samples to the PC where the data are
130 displayed and stored. This procedure is then repeated for the next working electrode of
131 the sequence.

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

136 **2.3. Measurement procedure**

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

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

153

154  Insert here Figure 1

155

156 The fabric mesh (Item 2 in Figure 1.a) was used as the supporting humid membrane
157 where vapours were trapped. The humid membrane came in contact with the electronic
158 tongue. The fabric of the membrane was nylon with a fibre thickness of 350 microns
159 separated by about 150 microns. The membrane was damped with a NaCl aqueous

160 solution (0.01 mol dm^{-3}). The role of the moistened fabric was to perform the absorption
161 of the volatile compounds from the sample and to provide a conductive vehicle to the
162 electrode interface. Before a new measurement was taken, the membrane was rinsed
163 with distilled water, dried and then moistened again with salt solution. The reference
164 electrode was a Saturated Calomel Electrode (SCE), which was connected to the
165 damped fabric with a curved low-density polyethylene (LDPE) tube with cotton at the
166 end (Item 3 in Figure 1.a). The set of electrodes, the nylon fabric and the LDPE tube
167 were held together with a PVC connector which has two pieces (Items 5a and 5b in
168 Figure 1.a). The nylon membrane was trapped between these two pieces and was held
169 still with a nylon screw (Item 4 in Figure 1.a). The LDPE tube was connected to the
170 nylon membrane through a hole on the edge of the outer PVC piece, which allowed
171 contact between the damp nylon fabric in contact with the working electrodes and the
172 reference electrode. The measuring chamber was thermostated at 37°C . All the
173 measurements were made under argon. Prior to the sample addition the argon
174 atmosphere was created by displacing the air for 10 minutes with argon. The argon
175 flow was stopped and then the sample was directly introduced into the measuring
176 chamber and left for at least 5 min before the measurement was taken. This time
177 period was established after studying the absorption processes of volatile substances
178 (NH_3 , HCl , etc.) in the nylon fabric membrane. After these 5 min had passed, the
179 measurement was taken: i.e., the pulse pattern was applied and the current response
180 of each electrode was measured and stored in the PC.

181 Insert here Figure 2

182 This study employed a Large Amplitude Pulse Voltammetry (LAPV) wave form. [29,30]
183 Figure 2a shows the applied pulse pattern which consists of 40 pulses in a
184 configuration similar to a staircase voltammetry, but the potential was set to 0 after
185 each increment. In particular, the pulse sequence was: 0, 200, 0, 400, 0, 600, 0, 800, 0,
186 1000, 0, 800, 0, 600, 0, 400, 0, 200, 0, -200, 0, -400, 0, -600, 0, -, 800, 0, -1000, 0, -
187 800, 0, -600, 0, -400, 0, -200, 0, 0, 0, 0 (mV). Each pulse was applied for 50 ms. The
188 increment for the potential steps was 200mV, and the maximum and minimum
189 potentials were chosen in order to avoid water electrolysis phenomena. Figure 2b
190 illustrates the intensity/time diagram for an acetic acid $0.001 \text{ mol dm}^{-3}$ solution using
191 iridium as the working electrode, which overlapped the control sample response.

192 2.4. Data analysis

193 In order to show the different responses of the “humid electronic nose” to the different
194 samples, the voltammetric electrochemical response data were combined to form
195 ensembles for pattern recognition in an attempt to discriminate samples. Hence, a
196 multivariate data analysis (MVDA) was used for this purpose. A principal components
197 analysis (PCA) proves an efficient approach for reducing the dimension of a data set.
198 [31] In addition, Artificial neural networks analyses have also been carried out to extend
199 the statistical study of the resulting data.

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

220 Principal Components Analysis (PCA)

221 Typically, a PCA decomposes the primary data matrix by projecting the
222 multidimensional data set onto a new coordinate base, formed by the orthogonal
223 directions with maximum data variance. The eigenvectors of the data matrix are called
224 principal components and they are not intercorrelated because they are orthogonal.
225 The principal components (PCs) are ordered so that PC1 displays the greatest amount
226 of variance, followed by the next greatest PC2, and so on. The main PCA features are
227 the coordinates of the data in the new base (scores plot) and the contribution of the

228 sensors to each component (loading plot). [32] In addition, in order to minimize effects
229 that can derive from employing the electrodes (non-specific chemisorption or
230 physisorption), after each voltammetric sequence, the electrodes surface was polished
231 to provide a clean metal surface for the next measurement. Having done all the
232 preprocessing, the PCA was calculated. All the statistical analyses were performed
233 with the Solo application software (version 6.5, Eigenvector Research, Inc.).

234 Artificial Neural Networks

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

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

245  Insert here Figure 3

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

254

255 **3. Results and discussion**

256 As stated above, due to our interest in designing electronic tongues and noses for
257 different applications, we attempted to test the possible use of a voltammetric “humid
258 electronic nose” for the discrimination of different samples. In our humid nose detection
259 is based on the changes in the electrochemical properties that occur when a gas or

260 vapour is dissolved by a conductive membrane. The absorption processes of gases
261 and vapours follow Henry's law, which states:

$$262 \quad (A) = k_H \cdot f_A$$

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

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

292 **3.1. PCA**

293 The different electrochemical responses of each sample, using the “humid electronic
294 nose”, were analysed by a PCA. This is a powerful linear unsupervised pattern
295 recognition method. PCA is an efficient approach to diminish the dimensionality of a
296 dataset. A PCA study of the full set of patterns revealed a medium degree of dispersion
297 among the independent dimensions created by the linear combinations of the
298 electrochemical responses of the four electrodes used in the array. The first PC
299 contained 67.87% of the variance of the data, whereas the first two components
300 represented 86.24% of total variance, while five PCs were needed to account for
301 96.06% of variance. This relatively large number of independent dimensions to account
302 for most of the variance may be due to the different composition of the samples used,
303 which generate very different volatile compounds during the experiments. Although a
304 relatively large number of dimensions are required to explain total variance, PCA
305 captured 86.23% of the variance observed in the experiment in the first two PCs. The
306 plot of these two PCs on the x and y axes is shown in Figure 4, which displays the
307 resulting PCA for eight samples (three replicates) when using the response of all four
308 electrodes in the “humid electronic nose”. As observed, it was possible to discriminate
309 among the samples studied. Moreover, when the control data were introduced into the
310 PCA analysis, all the data were situated around the same place, which is in agreement
311 with the systems’ capacity to differentiate the control from the rest of the samples.
312 Moreover, as the control solutions were measured on different days, the results
313 suggest a high degree of repeatability in the electrodes’ response. Clearer
314 differentiation in the PCA plot was observed for the aqueous samples containing
315 ammonia, acetic acid and for the Roquefort cheese. A second PCA plot in which these
316 samples were omitted is shown in Figure 5. In this new plot, the first PC contained
317 69.69% of the variance of the data, whereas the first two PCs represented 81.31% of
318 total variance. The figure depicts a relatively clear discrimination among the remaining
319 samples.

320 From the plot, it is apparent that the “humid electronic nose” is able to differentiate not
321 only samples containing simple compounds such as ammonium, acetone, acetic acid
322 and 6-amino-1-hexanol, but also more complex samples with a number of volatile
323 compounds that define their characteristic aroma such as Roquefort cheese, coffee
324 and onion. In fact it has been reported that, for instance, in French blue cheeses, an
325 important amount of methyl ketones was present in the flavour profile and a significant
326 number of secondary alcohols and esters were also present.[34] In coffee, more than
327 one thousand compounds, including furans, ketones, pyrazines, alcohols, aldehydes,
328 esters, etc., are characteristic of their typical aroma [35,36], whereas in chopped onion,

329 a number of volatile oxygen derivatives (especially carbonyl compounds) and saturated
330 and unsaturated disulphides have been found in the headspace.[37] Despite the
331 presence of some of these compounds at a relatively low concentration, the “humid
332 electronic nose” is able to show an electrochemical fingerprint response that
333 characterizes the aroma of these specific foods.

334 Insert here Figures 4 and 5

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

353 Insert here Figure 6

354

355 **3.2. Classification with Self-Organized Maps**

356 Apart from the study carried out with PCA analysis, the neural network Self-Organized
357 Maps (SOM) has also been used to analyse the electrochemical data obtained from the
358 “humid electronic nose”. Studies with the SOM neural network were carried out using
359 the software application SOMmine 5 by Viscovery. The number of nodes used in all
360 cases was 1,000. The programme calculates a neighbourhood of at least 50 nodes
361 with a linear neighbourhood weight function. Viscovery SOMine divides a map into

362 regions, called clusters. The nodes of a cluster are similar in that that they are
363 neighbours in the data space. For this study, in order to reduce the number of data, the
364 value for each pulse was calculated as the corresponding area enclosed by the current
365 signal, so a single value is used for each pulse.

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

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

391  Insert here Figure 7 and 8

392 **4. Conclusions**

393 We report herein the design, manufacture and use of a “humid electronic nose”
394 prototype. This new system entails innovation in the electronic noses field, and it relies
395 on the use of a wet environment to perform pulse voltammetry experiments on an array

396 of four working electrodes (i.e., Au, Pt, Ir and Rh) which were in contact with a fabric
397 mesh made of nylon damped with a NaCl aqueous solution. As a proof-of-concept, the
398 “humid electronic nose” was able to “sense” the presence of aqueous solutions of
399 different simple volatile compounds (i.e., ammonia, acetone, acetic acid and 6-amino-
400 1-hexanol) and different food samples (i.e., onion, coffee and Roquefort cheese). PCA
401 and SOM studies were performed. The neural network SOM allowed us to determine
402 that good classification results were obtained when using all four electrodes and a set
403 of only six pulses. From our point of view this opens new applications and allows to
404 develop electronic noses following classical electronic tongue designs which can be
405 applied to both liquid or solid samples (via the detection of volatile compounds). This
406 preliminary study led us to believe that this “humid electronic nose” may be applied to a
407 wide range of situations, in the food industry (e.g. inspection of food quality control,
408 monitoring fermentation processes, checking rancidity and spoilage, flavor control, etc.)
409 and in environmental monitoring (e.g. for testing ground water for odors, identification
410 of toxic wastes, air quality monitoring, monitoring factory emissions, etc.). Moreover,
411 although we have used in this this proof-of-concept design a static headspace
412 technique for the volatile generation other configurations will be studied in due course.

413 **Acknowledgement**

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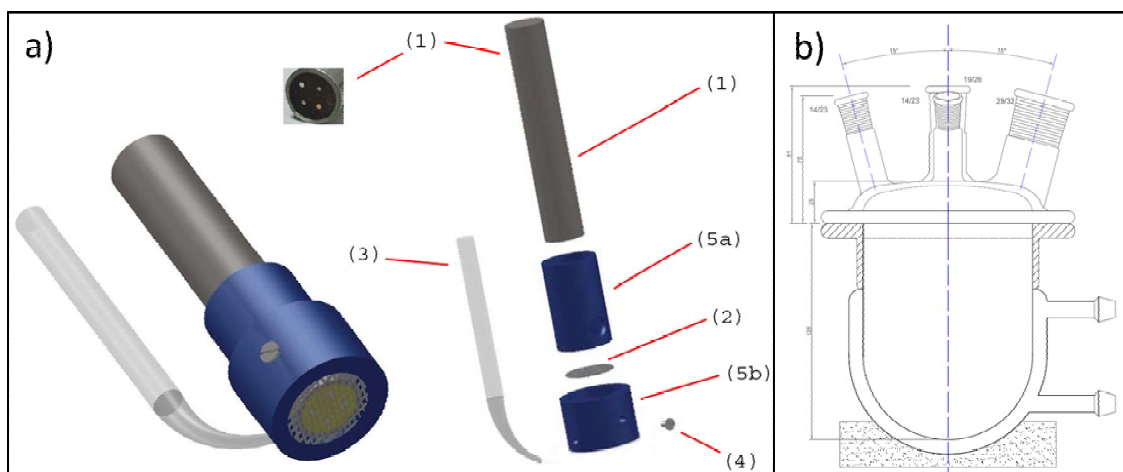
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581 Figure 1: Humid Electronic Nose sketch. Description of parts: a) (1) "humid electronic
 582 tongue"; (2) humid membrane; (3) reference electrode and LDPE adapter; (4) nylon
 583 screw; (5) PVC adapters. b) measuring chamber.

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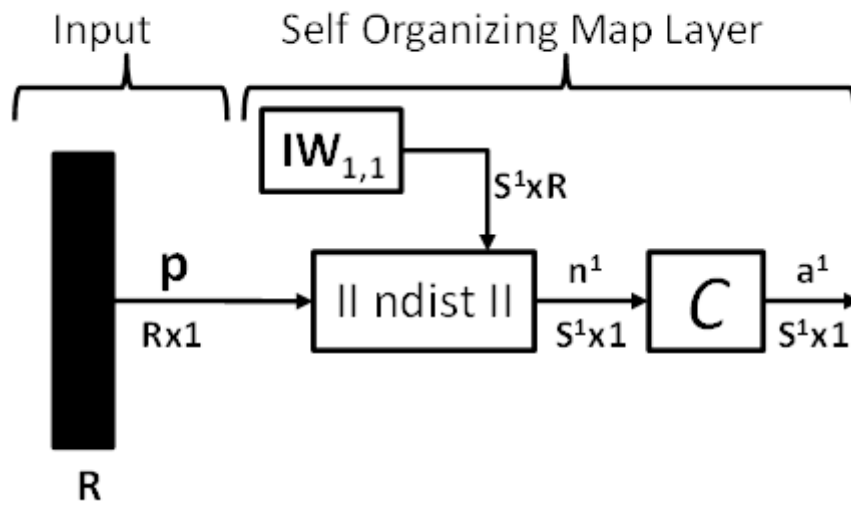
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586 Figure 2: a) applied voltammetric pulse pattern; b) response for control and AcOH
587 (0.001 mol dm⁻³) samples using an Ir electrode.

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Figure 3 Self-Organizing Map Architecture.

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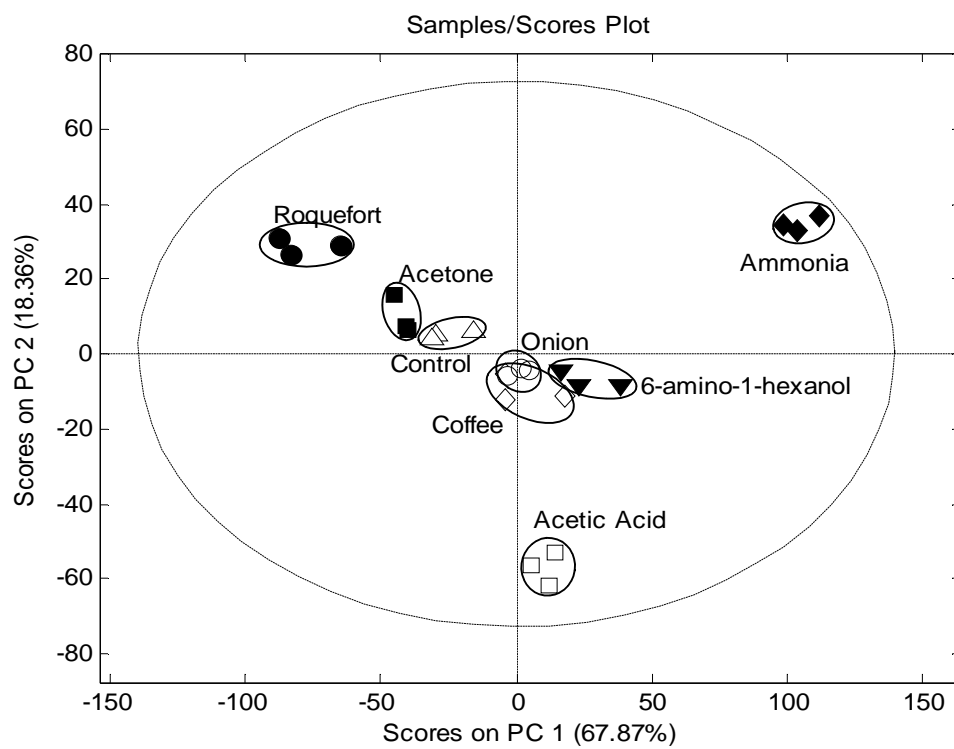
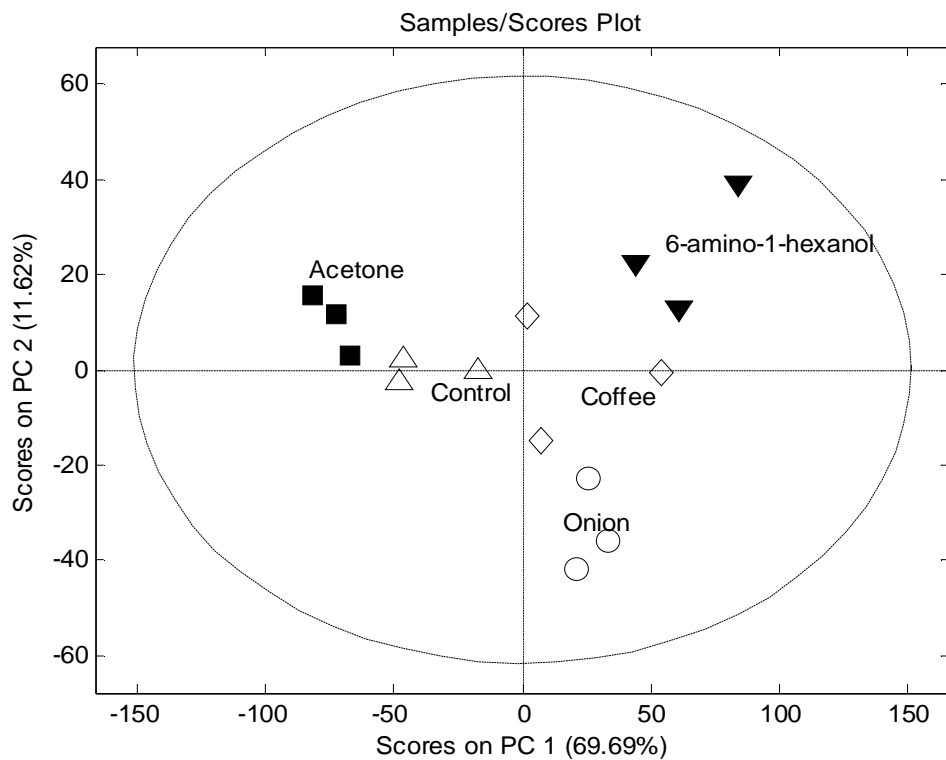


Figure 4: A PCA plot for the complete sample array.



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Figure 5: A PCA plot excluding NH_3 , AcOH and Roquefort cheese samples.

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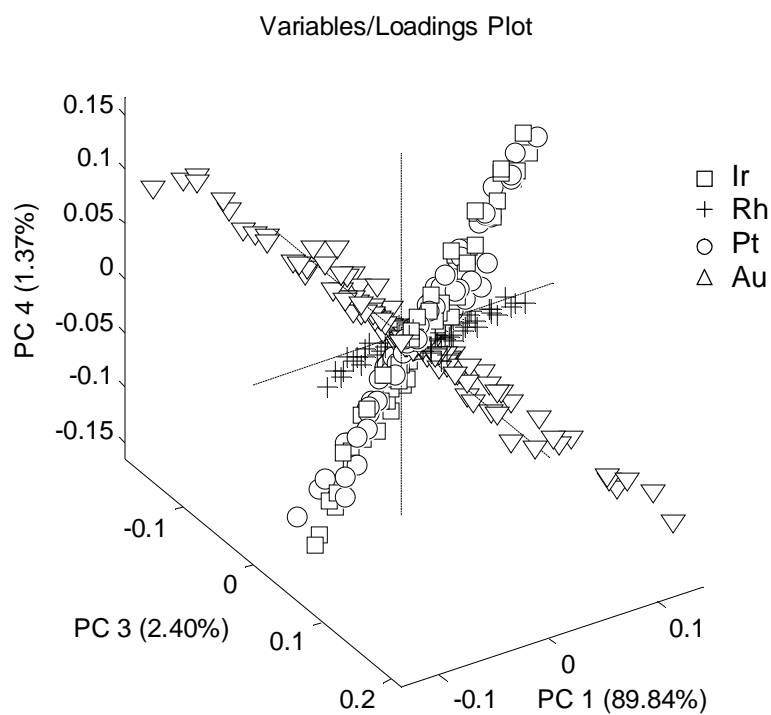
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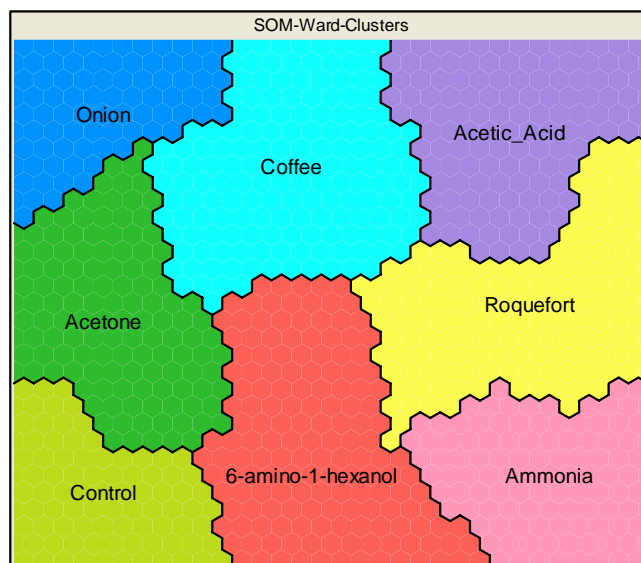
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623 Figure 6: A plot of the loading factors for PC1, PC3 and PC4 using a reduced data set.

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626 Figure 7.- Classification with Self-Organised Maps (SOM) using pulses P1, P2, P4, P6,
627 P8 and P10.

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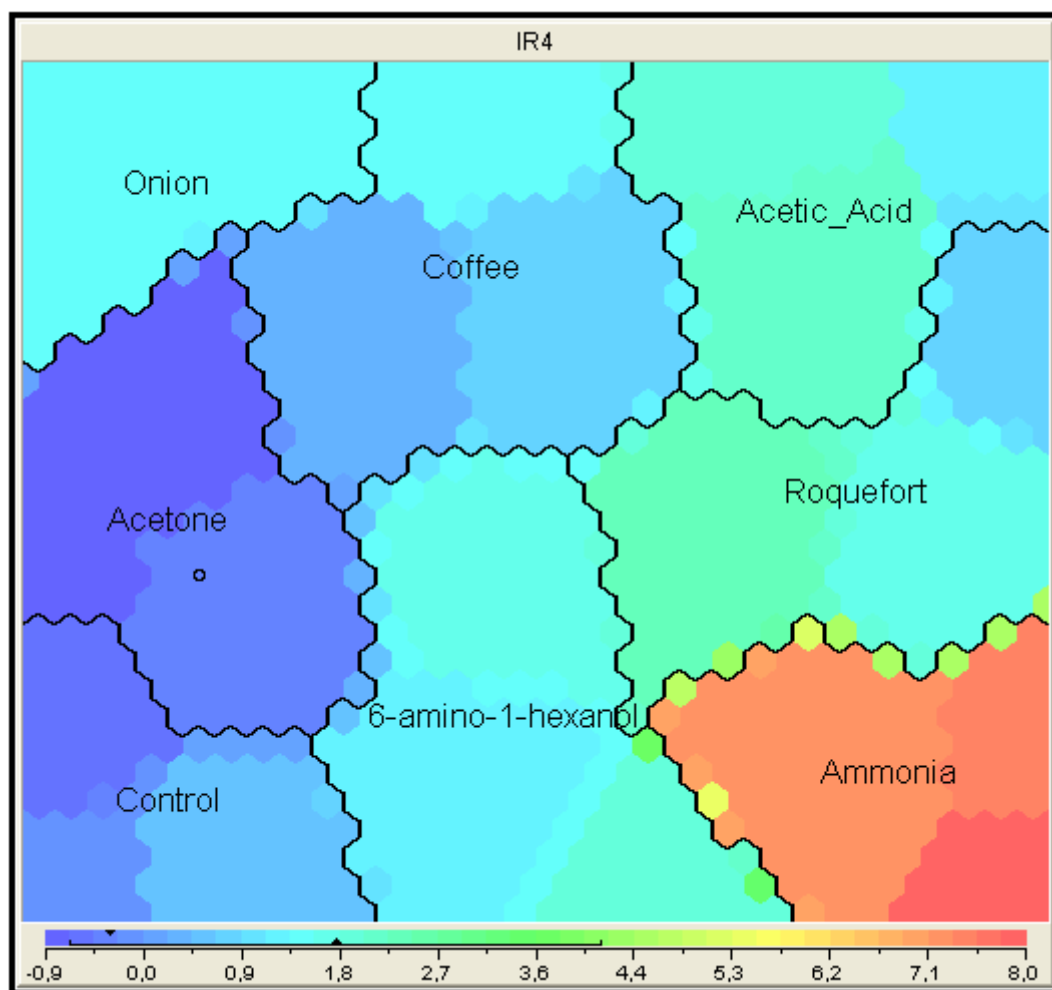
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645 Figure 8.- Contribution of pulse P4 from the Ir electrode to the complete SOM
646 classification.

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