An “electronic tongue” design for the qualitative analysis of natural waters

Ramón Martínez-Máñez a,∗, Juan Soto a,∗, Eduardo Garcia-Breijo b,∗,1, Luis Gil b, Javier Ibáñez b, Eduard Llobet c,∗

a GDDS, Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, 46021 Valencia, Spain
b Grupo de Microelectrónica Híbrida, Departamento de Ingeniería Electrónica, Universidad Politécnica de Valencia, Camino de Vera s/n, 46021 Valencia, Spain
c MINOS, Department of Electronic Engineering, University Rovira i Virgili, Avda. Països Catalans, 26, 43007 Tarragona, Spain

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Abstract

A new “electronic tongue” has been developed and used for the qualitative analysis of natural waters. Both wires and conducting surfaces in thick-film technology were used as potentiometric electrodes and the emf of each electrode in contact with a certain aqueous solution was used as input signal for a PCA analysis. An array containing the electrodes; RuO2 (with resistivities of 10 4Ω/sq and 1 MΩ/sq), C, Ag, Ni, Cu, Au, Pt, Al, Sn, Pb and C (graphite) were used in a first approach. To test this “electronic tongue” design, a family of different natural waters were studied. These include seven mineral waters, tap water and osmotised water. Additionally, a qualitative analysis of the different waters was performed using fuzzy ARTMAP neural networks. The final system was successfully employed for the differentiation of the above mentioned waters with a success rate higher than 93%.

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1. Introduction

In the last few years a great deal of work has been devoted to the development of “electronic noses”. This term refers to an array of non-specific gas sensors that combined with pattern-recognition techniques allow to get information from complex mixtures of gases [1]. More recently, and following a similar concept, the so called “electronic tongues” for the evaluation of liquids have been developed. Here the strategy relies on the use of a set of suitable “sensors” that respond rather unspecifically but in some way differentially toward a group of related chemical species [2]. In both “tongue” and “nose” strategies, the target idea is not to measure single chemical components but to get images of more general and usually “human” related attributes (such as taste, odour, ripeness, quality, etc.) common to intricate systems [3,4]. When comparing these two areas, more references are found in the field of electronic noses but it can be noticed an increasing interest in the development of electronic tongues or taste sensors. Such recent advances have been applied, for instance, for classifying food, drinks, water, etc. [5].

Basically two approaches in the design of electronic tongue devices have been followed by using either potentiometric or voltammetric sensor arrays. Voltammetry has been reported to show several advantages related with the versatility and robustness of the voltammetric methods [6]. Among different techniques, pulse voltammetry has been mainly used to get information from multi-component solutions [7]. Probably the main drawback in using voltammetric techniques is that those involve generally more complex procedures than simple potentiometric measurements. In potentiometry, the potential between two electrodes when there is no current flow is measured. Potentiometric techniques are also well-known versatile and simple methods in analytical chemistry and several examples of potentiometric electronic tongues have been reported [8] all of them having in common the use of membrane potentiometric sensors...
The membranes can be of different materials and they usually show certain selectivity towards particular chemical species. Thus, for instance, electrodes such as chalcogenide glass sensors [10], PVC-based or lipid/polymer membrane electrodes [11,12], Langmuir–Blodgett membranes [13,14], etc., have been used in the design of electronic tongues. These membrane-based sensors show sometimes large cross-sensitivities and their response, in combination with pattern-recognition algorithms, has been used for discriminating certain aqueous solutions such as foodstuffs [15] or different types of waters [16].

We were interested in further developing new electronic tongues by exploring a rather simple concept involving the use of certain surfaces as a set of un-specific potentiometric sensors. Although these surfaces are expected to display a very vague response we believed it could still be differentiable toward a group of chemical species. It is supposed that unspecific guest interactions with certain surfaces might open new perspectives in the design of electronic tongues. This design approach is very undemanding and might be easily tuneable. In order to test this approach we have selected a total of 12 “simple” electrodes and have studied their use to the differentiation of natural waters using potentiometric measurements combined with PCA algorithms and ARTMAP neural network [17]. A discussion about the more suitable combination of electrodes is also included.

2. Experimental

A total of six Spanish natural mineral waters (Bezoya, Lanjarón, Primavera, Liviana, Solán, Font-Vella), tap waters from the cities of Sagunto and Valencia and osmotised water have been selected as representative and have been studied by using the array of electrodes described below. The tap and mineral waters were settled into a vessel for some minutes before measurements. The names and concentrations (in mg/L) for the used mineral waters are listed in Table 1.

2.1. Measurement system

A wide range of different “surfaces” were selected in order to explore their differential response. Following this approach the following electrodes in thick-film technology were prepared: RuO₂ (with resistivities of 10Ω/sq and 1 MΩ/sq), C, Ag, Ni, Cu, Au, Pt and Al. We also used as electrodes small sticks of the elements Sn, Pb and C (graphite). This gave a set of 12 electrodes which were used as active system for potentiometric measurements. The “electronic tongue” was completed with the devices for acquisition, monitorisation and storage of the measured data, as well as the software for pattern-recognition studies.

The electrodes were on a board of alumina substrate RUBALIT 708S (supplied by Ceramic Tec) with an area of 2 in. × 1 in. and thickness of 0.635 mm. In order to prepare the above mentioned set of electrodes, three screens were made, corresponding to three layers: namely, the conductive layer working as a conductor of the signal, the active layer and the upper protection layer (see Fig. 1). The conductive paste used was Ag/Pd/Pt C4081T (supplied by HEREAUS). The layout of the tracks was made to join the board to a flat cable connector with a separation of 3 mm between terminals. The active pastes of RuO₂ of 10Ω/sq (model R8961) and 1 MΩ/sq (model R8961), Cu (model C7257), Ag (model C10755D), Pt (model C1076D) and Au (model C5755A) were supplied by HEREAUS whereas the pastes for Ni, Al and C were supplied by GEM. The protective paste was the IP9020 model supplied by HEREAUS.

Thick-film electrodes were made using serigraphic methods, using polyester screens with a density of 230 mesh (Saatilane Hitech 90/48 supplied by Saatilane) and films of 50μm thickness (Ulano CDF5 supplied by Ulano). The pastes were placed by a semiautomatic serigraphic machine.
5 min. Fig. 2 shows the final array of electrodes in thick-film technology. A final thickness of 30 µm after firing was achieved.

The conductive paste firing process was carried out at 850 °C in a cycle of 60 min with a peak of 10 min. The same cycle was used for RuO₂. A similar cycle but heating at 900 °C under inert atmosphere was used to prepare the electrodes of Cu, Ni, Ag, Pt, Al and C. The burning process for the protective paste was carried out at a temperature of 600 °C in a cycle of 30 min with a peak of 10 min. Fig. 2 shows the final array of electrodes in thick-film technology.

2.2. Measurements

Measurements were carried out using the operational amplifier OPA129P with high input impedance (10¹⁵ Ω) in buffer configuration and an active pass-bass filter to avoid interferences from the electrical network. An acquisition card ADLINK, model PCI9112 inserted into a personal computer, using a program developed using the VEE-Pro® software in which the amplifiers and filters were implemented, allowing flexible designs of different configurations and fabrication of large number of sensors at very low cost.

In a typical assay, the set of the 12 electrodes and the reference electrode were dipped in water at 25 °C containing 10 mL of 0.1 M NaCl, 10 mL of phosphate buffer pH 7, and 180 mL of distilled water (reference solution), and the potential for each electrode was measured. This was set as a zero reference value. Then the group of electrodes were immersed in the corresponding aqueous sample at 25 °C, and after a period of 5 min the potential of the electrodes was again measured for 5 min. Typical time to steady state was always less than 5 min. After each measurement, the electrodes were cleaned with distilled water.

The data for the posterior analysis was taken as the difference between the zero reference and the measured potential for each water sample. A total of five measurements corresponding to five different samples of each water type were used for the PCA analysis. The samples were measured in a random order. After each measurement, the set of electrodes was dipped in the “reference solution”. The set of electrodes used still was in use after several months and in general all of the electrodes have showed long term stability.

3. Results and discussion

As stated above, several approaches to potentiometric electronic tongues have been reported, all of them having in common the use of membrane potentiometric sensors. We were interested here to test the use of a somewhat different approach. The general concept is based on the idea that many types of surfaces might be polarised in aqueous environments due to either physisorption or chemisorption processes of a number of chemical species. This spontaneous polarisation (which is known to be very dependent on the chemical characteristics of the electrode surface), however, is a very unspecific process and this is why non-coated or non-modified conducting active surfaces are not usually used as selective sensors. Nevertheless, it is precisely this unspecificity, and therefore the large cross-sensitivity, that can be an appealing characteristic for the development of electronic tongues. The use of rather unspecific conducting surfaces might be a promising sensing approach due to the large number of available possibilities to tune the composition of the final sensor array which might turn in controlling the response to different complex liquid mixtures. Based on these concepts the following study was carried out using a design of electronic tongue built up with an array of electrodes containing the following surfaces RuO₂ (with resistivities of 10²Ω/sq (Ru10) and 1 MΩ/sq (Ru1M)), C, Ag, Ni, Cu, Au, Pt, Al, Sn, Pb and C (graphite). In a first approximation both metal wires and metallic surfaces in thick-film technology were used as potentiometric electrodes and the emf of each electrode in contact with a certain water samples was used as input signal for PCA analysis. Thick-film technology is an appropriate tool to solid-state manufacturing, allowing flexible designs of different configurations and the fabrication of large number of sensors at very low cost (see Fig. 1).

To test this “electronic tongue” design, a family of different natural waters were studied. These included seven mineral waters, tap water and osmotised water. In a typical assay, the electronic tongue containing the above mentioned array of electrodes was immersed in the corresponding aqueous sample and the potential of the electrodes versus a reference electrode was measured. Those measurements were compared for each electrode with the potential observed in a “standard or reference” solution (see Section 2). The data for the posterior analysis was taken as the difference between the potential of the standard solution and that measured for each water sample. A total of five trials corresponding to five different samples of each water type were considered. In order to analyse the possible existence of patterns in the emf variation, PCA algorithms were used and yielded the results summarised in Fig. 3, a two dimensional plot for the two components PC1 and PC2. As can
Fig. 3. Principal component analysis (PCA) score plot for different waters. Data show from five different trials. PC axes are calculated to lie along lines of diminishing levels of variance in the data set.

be deduced from the figure, recognition patterns can be identified for the waters analysed.

For the sake of comparison between the information obtained from the two-dimensional PCA plot and more classical parameters of water quality, the conductivity, the pH and the rH were also measured for the studied waters. Conductivity and rH data, together with averaged PC1 and PC2 values for each water type are shown in Table 2. A revision of these data shows that there is not a clear correlation between PC1 and PC2 values and typical, easy-to-measure, parameters in water such as conductivity, rH or pH. However, and despite that lack of correlation, the PCA analysis is capable of discriminating between waters with a close chemical composition (see Fig. 3). This is the case, for example, of Lanjaron and Font-Vella mineral waters or, for instance, the discrimination between osmotised and Lanjaron waters that, despite their very close value of conductivity, rH and pH, are clearly differentiated in the PCA plot.

Fig. 4 shows the loads of each electrodes in the PCA analysis. It can be observed that despite some electrodes which are far apart in the loads plot, many metallic electrodes show a strong correlation. Therefore it appeared advisable to make a thorough study using neuronal networks algorithms to look for a reduced set of electrodes.

A qualitative analysis of the different waters was performed using fuzzy ARTMAP neural networks. This consisted in a 9-category classification (nine different waters were tested). Prior to perform the analysis, the data matrix was normalised by subtracting its absolute minimum (e.g. a negative value) followed by the division by its absolute maximum. As a result of this process, every element in the normalised data matrix lay in [0, 1], which is a necessary condition to run the fuzzy ARTMAP network. Two different fuzzy ARTMAP models were built, which corresponded, either to the use of the 12 electrodes or to a restricted number of electrodes. Since each measurement was replicated 5 times, a total of 45 measurements were available to train and validate the networks. A leave-one-out cross-validation was implemented to estimate the performance of the neural networks. With the leave-one-out approach, the networks were trained 45 times using 44 measurements and tested against the measurement left out. The performance of a network was estimated as the average over the 45 tests. The results for the leave-one-out cross-validation were as follows.

When the responses of the 12 electrodes were input to the network a 91.1% success rate in the identification of the different waters was reached. The four misclassified samples corresponded to Liviana and Solán waters (two samples) and Solán and Font-Vella (two samples). This result is in perfect agreement with PCA results since misclassified samples correspond to the waters that appear in close regions of the score plot (see Fig. 3).

Since the loadings plot of the PCA (see Fig. 4) shows that some colinearity exists between the 12 electrodes, i.e. different electrodes have similar loadings, a fuzzy ARTMAP based classification was attempted using a restricted set of
Table 3
Confusion matrices for the two fuzzy ARTMAP classifiers built to discriminate between different waters

<table>
<thead>
<tr>
<th>Actual water</th>
<th>Primavera</th>
<th>Bezoya</th>
<th>Lanjarón</th>
<th>Liviana</th>
<th>Solán</th>
<th>Font-Vella</th>
<th>Tap Valencia</th>
<th>Tap Sagunto</th>
<th>Osmotised</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primavera</td>
<td>5</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Bezoya</td>
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<td>5</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Lanjarón</td>
<td>5</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Liviana</td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solán</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Font-Vella</td>
<td>1</td>
<td>4</td>
<td>5</td>
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<tr>
<td>Tap Valencia</td>
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<tr>
<td>Tap Sagunto</td>
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<td>Osmotised</td>
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</table>

Classification success rates are 91.1 and 93.3% for the models using the responses of 12 and 7 electrodes, respectively.

4. Conclusions

In conclusion, a new design of electronic tongue using a rather simple concept involving the use of no coated surfaces as unspecific sensors has been envisioned and successfully employed for the differentiation of rather similar water samples (e.g. identification success rate is higher than 93%). The design approach we used is very simple and might be in principle easily tuneable by the simple combination of different suitable active surfaces. It is believed that the interplay of rather unspecific surface-ions interactions such as physisorption and chemisorption phenomena onto certain surfaces can open new perspectives for the future design of electronic tongues. We are currently using a similar simple design for their application to even more complex aqueous mixtures.

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References

Biographies

Eduardo Garcia-Breijo was graduated in electronic engineering from the Universitat de València (Spain) in 1997, and received his PhD in 2004 from the Universidad Politécnica de Valencia (UPV). His thesis was focused on the development of multisensor for water quality parameters in thick-film technology. He is assistant professor of Electronic Technology in the Electronic Engineering Department of the UPV. He is a member of the Hybrid Microelectronics Laboratory at the UPV.

Luis Gil was graduated in electronic engineering from the Universitat de València (Spain) in 1989. He is assistant professor of Electronic Technology in the Electronic Engineering Department of the Universidad Politécnica de Valencia (UPV). He is a member of the Hybrid Microelectronics Laboratory of UPV. His main areas of interest are the chemical sensors, instrumentation systems and pattern recognition for electronic tongues.

Ramon Martínez-Máñez was graduated in Chemistry from the Universitat de València (Spain) in 1986 and received his PhD in 1988 in the same University. After a postdoctoral period at Cambridge (UK), he joined the Department of Chemistry at the Universidad Politécnica de Valencia. He became full professor in 2002. His research interest comprises the development of new electrochemical, fluorogenic or chromogenic chemosensors and molecular probes for anions, cations and neutral chemical species.

Juan Soto Carnizo was graduated in Chemistry from the Universitat de València in 1981 and received his PhD in 1986 in the same University. He is currently associate professor in the Department of Chemistry at the Universitat Politécnica de Valencia. His main areas of interest are the development of chemical chemosensors and probes, especially those based on electrochemical processes.