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Sequential injection system with higher dimensional electrochemical sensor signals

Part 2. Potentiometric e-tongue for the determination of alkaline ions

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Abstract

An intelligent, automatic system based on an array of non-specific-response chemical sensors was developed. As a great amount of information is required for its correct modelling, we propose a system generating it itself. The sequential injection analysis (SIA) technique was chosen as it enables the processes of training, calibration, validation and operation to be automated simply. Detection was carried out using an array of potentiometric sensors based on PVC membranes of different selectivity. The diluted standard solutions needed for system learning and response modelling are automatically prepared from more concentrated standards. The electrodes used were characterised with respect to one and two analytes, by means of high-dimensionality calibrations, and the response surface of each was represented; this characterisation enabled an interference study of great practical utility. The combined response was modelled by means of artificial neural networks (ANNs), and thus it was possible to obtain an automated electronic tongue based on SIA. In order to identify the ANN which provided the best model of the electrode responses, some of the network's parameters were optimised and its usefulness in determining NH_4^+, K^+ and Na^+ ions in synthetic samples was then tested. Finally, it was used to determine these ions in commercial fertilisers, the obtained results being compared with reference methods.

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1. Introduction

A recent advance in the field of sensors and biosensors has been the use of sensor arrays which enable researchers to determine different analytes simultaneously, determine species, correct for the presence of interferents, and build redundant systems [1,2].

An electronic tongue can be defined as an analytic instrument which includes an array of sensors with cross-sensitivity that is able to recognise quantitatively and qualitatively the composition of both simple and complex solutions [3–7]. For quantitative applications the sensor array must have at least as many sensors as the number of ions to be determined, and must also contain cross-sensitivity responses together with highly selective sensors [8]. As all the sensors respond to all the analytes a large amount of complex information is generated, and therefore one of the most important aspects of electronic tongues is the subsequent processing of data in order to obtain a coherent and useful response. This is achieved through the use of chemometric methods able to collect all the information obtained by the sensors, select that which is most important and interpret the complex signal.

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Some authors propose using artificial neural networks (ANNs) to process the data obtained from an array of potentiometric sensors [9,10]. Indeed, preliminary results have proved highly satisfactory, enabling application in both quantitative and qualitative analyses. Therefore, the use of ANNs for modelling the cross-sensitivity responses of sensors, due to the highly non-linear nature of the underlying model, would seem to be a feasible option.

In a typical application it is necessary to select a suitable array of sensors (capable of collecting the maximum amount of information about both analytes and interference), develop a set of standards that represents all the variability of the species in the sample (and in the concentration interval in which we wish to work), take the measurements, and train the ANN—the aim being that it becomes an intelligent system able to predict samples that have not been processed initially and then classify or quantify them, in much the same way as humans use the sense of taste. An ANN is not based on an explicit algebraic model, but rather on a set of activation units, known as neurons or nodes, which are connected to each other in the form of a network [11]. Feedforward multilayer perceptron neural networks were used for modelling the sensors, which structure consists of an input layer (which feeds the input signals to the succeeding layer), a hidden layer (that receives, processes and sends the filtered signals to the next layer), and an output layer, which links the ANN to the outside world and supplies the processed information. The information is processed through a transfer function in each neuron. In the hidden layer the function is usually sigmoidal, such as log-sigmoidal (*logsig*) or tan-sigmoidal (*tansig*), while in the input and output layers it is typically linear [12].

In order to train an ANN it is necessary to determine the magnitude of interaction (weights) between neurons, that is, to establish how changes among the weights of one layer lead to variations in those of the succeeding one. This is achieved using back-propagation techniques, which aim to find the weights that minimise the error function. The calculation can be performed using training algorithms, such as gradient descent with momentum (GDM) or Levenberg–Marquardt (LM).

One of the problems associated with the training of ANNs is what is known as overfitting: this occurs when the network models the training set very well but does not allow external points to be interpolated correctly. There are two ways of avoiding this problem: one is to use the Bayesian Regularisation (BR) algorithm [13] to simplify the network's structure, thus toning down the response and avoiding overfitting; the other method is what is known as early stopping, which consists in detecting the overfitting and then stopping the learning process. The latter is done by breaking the information down into three subsets—(1) training: used to evaluate the error and adjust the weight values; (2) validation: which detects the overfitting. The error of this subset is monitored during training and usually decreases at first, but when the network begins to overfit the error increases and training is stopped, returning to the weight values of the minimum calibration error; and (3) test: used to check the performance of a particular configuration of ANN [14].

Previous research [15–17] has clearly shown that a large amount of information is needed to train ANNs, where arrays of potentiometric sensors are used as tools for obtaining this information. However, thanks to the degree of automatisation provided by automated analysis systems, such as sequential injection analysis (SIA), this information can be obtained easily and quickly and without manual intervention [18]. Thus, an obvious alternative is to combine the two approaches—the use of potentiometric sensor arrays with automated systems—in order to overcome some of the above-mentioned limitations.

Sequential injection analysis, introduced by Ruzicka and Marshall in 1990 [19], is a development of the flow injection (FI) analysis technique. The main difference between the two techniques is that SIA, rather than use continuous flow, sequentially aspirates volumes of sample, carrier solution or reagents in a highly reproducible way; it then reverses the flow direction toward the detection system by means of a bi-directional propulsion system which is able to stop and reverse the flow direction in a controlled and automatic way [20]. The propulsion system has two combined functions: the accurate measurement of volumes of reagent and sample, and the propulsion/aspiration of solutions [21]. One way of facilitating the mixing of the sample and reagent areas is to incorporate a mixing chamber into the system, as demonstrated by McCormack and van Staden [22].

The present study demonstrates the use of an array of potentiometric sensors, with cross-response to alkaline ions, in conjunction with an SIA system in order to facilitate the training of ANNs and enable these species to be determined in a variety of different samples.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with doubly distilled water and reagents used were of analytical grade. Tris(hydroxymethyl)aminomethane (TRIS) (Merck), 0.01 M at pH 7.5, and the salts NH_4Cl, KCl (Panreac, Barcelona, Spain) and NaCl (Merck) were used as background and calibration species, respectively. Ammonium, potassium and sodium salts were prepared by dissolving the right amount of chloride salts in carrier solution.

Ion-selective electrode membranes were prepared dissolving the ionophore, the plasticiser and the polymeric matrix in an organic solvent. Ionophores employed were nonactin, valinomycin, lasalocid, dibenzo-18-crown-6 (Fluka, Switzerland) and 2,3:11,12-didecalino-16-crown-5 (Dojindo, Kumamoto, Japan). Plasticisers used were bis(1-butylpentyl) adipate (BPA), dioctyl sebacate (DOS) and dibutyl sebacate (DBS) (all from Fluka). The polymeric matrix was

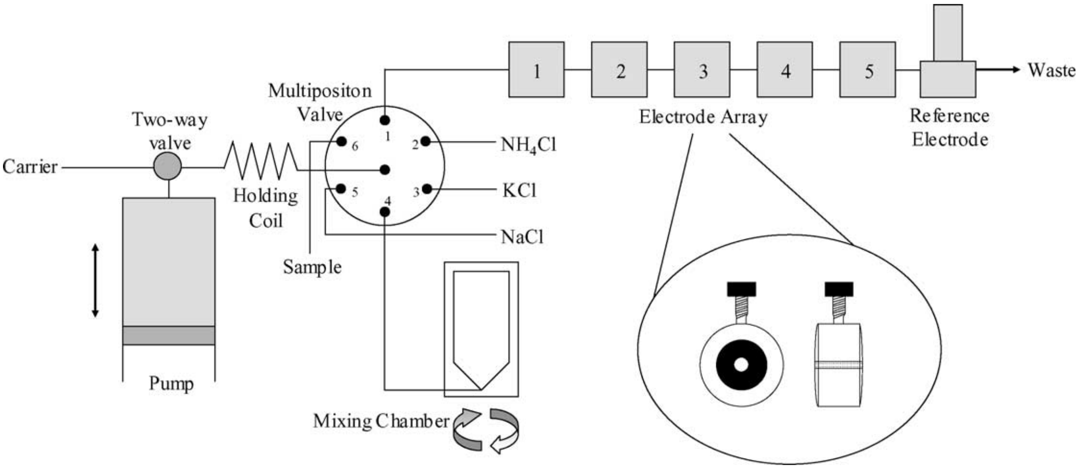

Fig. 1. Manifold of the SIA system employed in the study. The insert shows the design of a flow diagram of a flow-through tubular electrode.

poly(vinyl) chloride (PVC) (Fluka) and the volatile solvent was tetrahydrofuran (THF) (Merck, Germany).

Materials used for the preparation of the inner solid contact for the potentiometric sensors were the epoxy resin components Araldite M and HR hardener (Uneco, Barcelona, Spain), and graphite powder (50 μm, BDH Laboratory Supplies, UK) as the conducting filler.

2.2. Instrumentation

The SIA system developed (Fig. 1) comprised two clearly distinct parts: a fluid system and a measurement system. The fluid system consisted of a Crison 2030 automatic microburette (Crison Instruments, Alella, Spain), fitted with syringes of 2.5 and 5 ml (Hamilton, Switzerland) and controlled entirely by a PC; a Hamilton MVP valve (Hamilton, Switzerland) with six ports (Ref HVXM R36760), also controlled by computer; a 7 ml methacrylate mixing chamber with a conical base to aid emptying, used to homogenise the solutions; and a holding coil, formed by a PTFE tube (Bioblock, France) with an internal diameter of 1 mm and a total inner volume of 5 ml. The elements were connected together using low-pressure liquid chromatography connectors.

The measurement system comprised the detection system (sensor array incorporated into the system in series), a Ag/AgCl double-junction reference electrode (Orion 900200), a Crison 2002 potentiometer and a multiplexor built in our laboratories, enabling up to eight electrodes to be controlled and which was itself controlled by computer, the latter picking up the signal of the potentiometer.

Indicator electrodes, shown in the insert in Fig. 1, were all-solid-state, tubular, flow-through electrodes of normal use in our laboratories [23]. Their particular design facilitates their placement in series in the flow system. For proper functioning, the inner wall of the axial hole drilled through the inner solid contact is carefully covered with a PVC membrane cocktail. Once formed, membranes were conditioned in a solution of their primary ion for 24 h. Table 1 summarises the formulation of the different membranes. Generic formulations were included with the aim of obtaining global response for alkaline ions. As all potentiometric measurements were performed with equivalent ionic media, activity coefficients were taken to be constant.

Communication between the computer (PC Pentium at 166 MHz) and the various apparatus of the SIA system was achieved by means of protocol RS-232. To this end a program written in Quick BASIC (Microsoft, USA) was used. By way of example, Table 2 shows the steps required to carry out a dilution with the SIA system used in the present study.

2.3. Procedure

ANNs were used in order to model the combined response of the three ions studied (NH_4^+, K^+ and Na^+) and calculations were made by developing the corresponding programs in MATLAB (MATLAB 6.0, Mathworks, USA) and through

Table 1
Formulation of the ion-selective membranes employed in the construction of the potentiometric sensor array

Selective membrane to:	PVC (%)	Plasticiser	Ionophore	Ref.
Ammonium	33	BBPA (66%)	Nonactin (1%)	[24]
Potassium	30	DOS (67%)	Valinomycin (3%)	[25]
Sodium	29.1	BBPA (67.9%)	2,3:11,12-Didecalino-16-crown-5 (3%)	[26]
Generic I	29	DOS (67%)	Dibenzo-18-crown-6 (4%)	[27]
Generic II	27	DBS (70%)	Lasalocid (3%)	[28]

Table 2
Analytical sequence to perform a sample dilution and a measurement with the sensor array

Analytical sequence	Open port	Pump position	Pumping direction
Draw up sample to holding coil	3	Input	Reversal
Draw up carrier to holding coil	–	Input	Reversal
Pump sample and carrier to the mixing chamber	4	Output	Direct
Homogenisation	–		
Draw up solution to holding coil	4	Input	Reversal
Pump solution to detector	1	Output	Direct

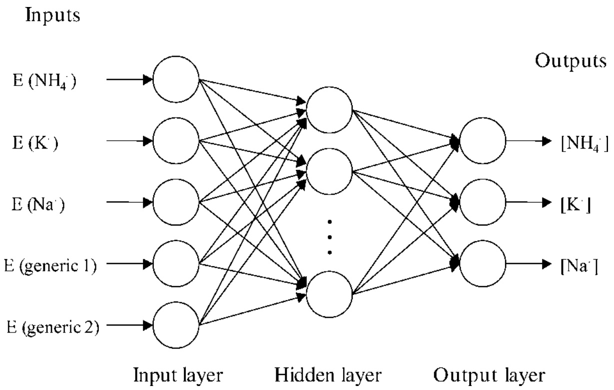

Fig. 2. Structure of ANNs used in the present study: five neurons for the input layer, one for each potentiometric sensor; three neurons for the output layer, one for each concentration value, NH_4^+, K^+ and Na^+.

use of its Neural Network Toolbox (Neural Network Toolbox 4.0.2, Mathworks, USA). In all cases, the ANNs used were feedforward (see Fig. 2), and were trained employing backpropagation algorithms, viz. Gradient Descent with Momentum (GDM), Levenberg–Marquardt (LM) and Bayesian Regularisation (BR) [14].

In generating calibration samples it is first necessary to establish the range of concentrations to be worked within. A decision then has to be made regarding the number of samples to be produced, and finally, the desired concentration of each ion in each sample has to be defined randomly. The SIA system enables easy preparation of solutions with a given concentration of each ion.

Once the calibration samples have been measured the complete set must be divided into three subsets—(1) training: which serves to determine the model's parameters; (2) validation: which enables overfitting in the model to be detected; and (3) test: which enables the model's predictive ability to be evaluated. In the present study a training algorithm known as Bayesian Regularisation [13], which does not require the validation subset to be used, was also employed.

3. Results and discussion

3.1. Characterisation of the sensors used in the study

The electrodes used in the array were characterised by means of high-dimensionality calibrations with respect to two analytes. For each one the characterisation was performed following Nikolskii–Eisenman [29], and through representation of the corresponding response surface. This characterisation enabled an interference study of great practical utility to be carried out, the value of the potentiometric selectivity coefficients in the Nikolskii–Eisenman equation (k^{pot}) being obtained with two degrees of freedom. A much more real meaning can thus be attached to the potentiometric selectivity coefficients obtained from modelling the surfaces compared with what would be obtained through classical methods (fixed interference method [30]).

In order to achieve the response surfaces of the electrodes and obtain the values of the potentiometric selectivity coefficients, the SIA system was used to prepare five measurement sequences, varying the concentration of both the analyte and the interferent. In each sequence the concentration of the interferent ion was maintained constant but different to its magnitude in the other sequences.

This study was extended to all combinations of two ions (among the three studied) for each electrode. A total of 30 different cases (three combinations of two ions for five electrodes) were therefore studied. Given the availability of an automated system the work involved here is more than manageable.

Fig. 3 shows the response surface for the ammonium-selective electrode, where ammonium is considered to be the principal analyte and potassium the interferent. The figure illustrates the experimental points prepared automatically with the SIA system, as well as the three-dimensional response surface which corresponds to the Nikolskii–Eisenman expression, fitted with non-linear regression methods [31]. It can be clearly seen how, with low concentrations of the principal ion, the curvature gets steeper as the concentration of the interferent ion increases.

Table 3 presents the logarithmic values of the potentiometric selectivity coefficients as determined from the modelling of the different response surfaces of the three sensors with the highest selectivity among those used in the array.

The response surfaces of the generic electrodes were also developed, and the different potentiometric selectivity coefficients were calculated. However, in this case, as the primary ion is not predefined, rather than assuming a principal species the different combinations of ions were studied. From these studies, the generic I electrode was observed to be more se-

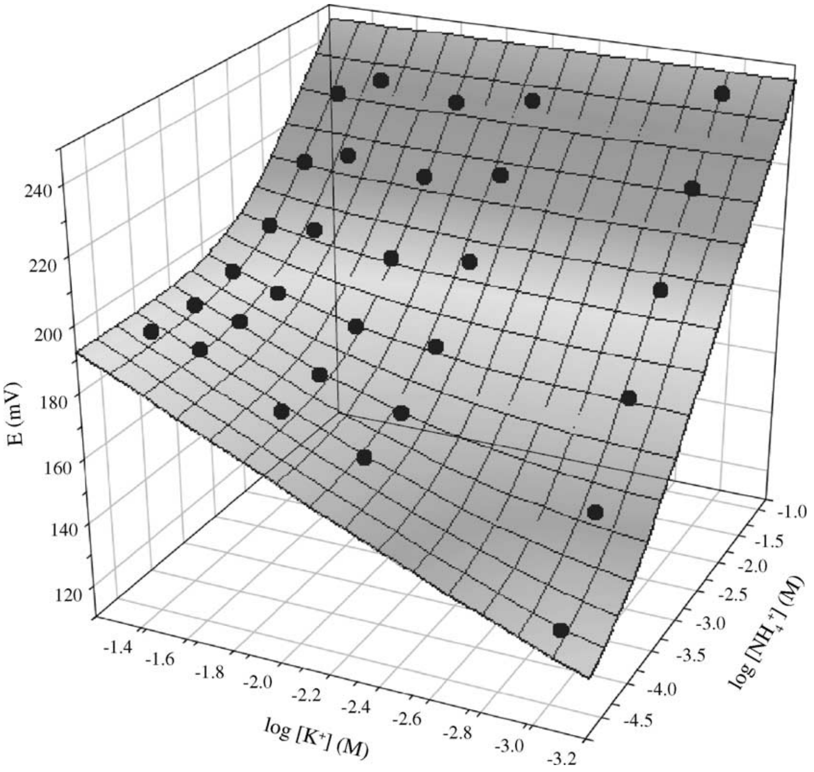

Fig. 3. Response surface for the ammonium-selective electrode with potassium interference.

lective to K^+ than to the other two ions, while generic II electrodes showed no Nernstian response.

3.2. Electronic tongue

3.2.1. Automated generation of information for training

The training subset was generated by varying the concentrations of the three ions considered. It is very important that this subset covers the whole range of expected compositions for each sample, and that there are sufficient examples of possible interactions among them. The aim is that once the ANN has been trained the concentration of species in a sample that was not included in training, but which remains within the concentration range studied, can be predicted.

A decision was made to use a training set comprising 60 randomly chosen points, prepared automatically by the SIA system, with concentrations of ammonium, potassium and sodium covering, approximately, the range 0.002–0.05 M in each of the species studied. The values are shown in Fig. 4, and no non-random trend is revealed. It should be pointed out that the range of concentrations studied was not any wider due to the limits imposed by the minimum volume able to be used in the automatic burette—and having decided against serial dilutions.

The points obtained were randomly assigned to each subset (viz. training, validation and external test), the exception being the extreme values which were reserved for the training subset. Without the latter precaution the adjusted ANN would have to extrapolate these points in the obtained model. In our case the training subset comprised 32 points, the validation subset 15, and the test subset 13 (ca. 50, 25 and 25%, respectively, of the total amount). When using the Bayesian Regularisation training algorithm, 46 points were assigned to the training subset and 14 to the test subset (ca. 75 and 25%, respectively).

Table 3
Summary of the selectivity coefficients found for the different sensors using two degrees of freedom

Sensor, *x*	Interfering ion, *y*	$\log K_{x,y}^{\mathrm{pot}}$	Values from the literature
NH_4^+	K^+	-1.17 ± 0.02	-0.8[a]
	Na^+	<-3	-2.9[a]
K^+	NH_4^+	-2.8 ± 0.2	-1.9[b]
	Na^+	-2.87 ± 0.04	-3.7[b]
Na^+	NH_4^+	-2.96 ± 0.15	-3.3[c]
	K^+	-2.54 ± 0.04	-2.9[c]

Uncertainties are the standard errors estimated by the non-linear fitting procedure [31].
[a] Ref. [24].
[b] Ref. [25].
[c] Ref. [26].

3.2.2. Construction of the model based on ANNs

For each point generated by the automatic system the corresponding measures for the array of five potentiometric sensors were taken. The response model was built from an ANN

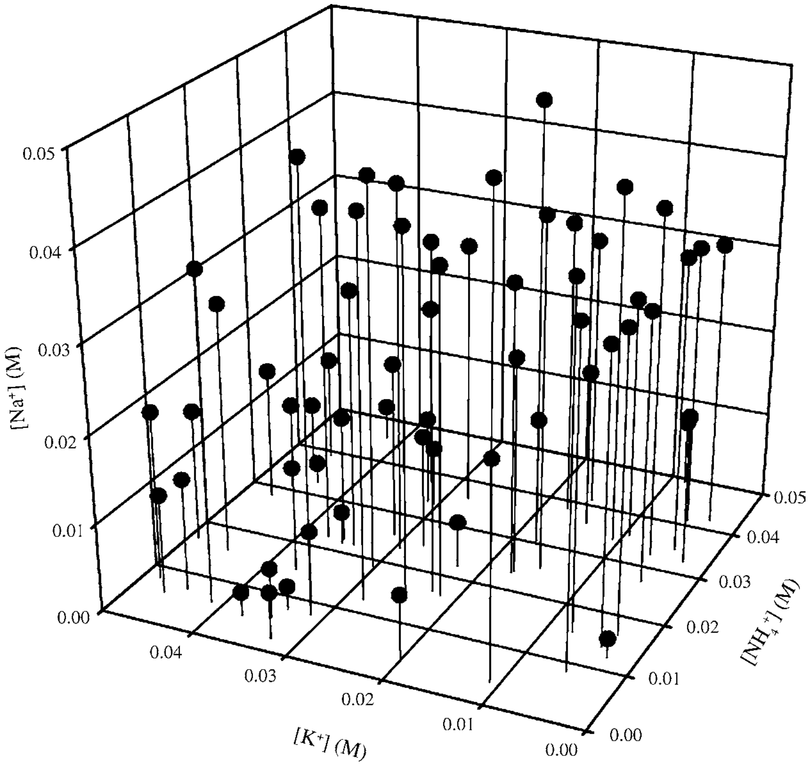

Fig. 4. Graphic plot of the complete net of points prepared employing the SIA system for the training of the electronic tongue.

with five neurons in the input layer, one per sensor. Although the generic II electrode showed no Nernstian response, it was decided to use the information it provided, as by taking it into account it was possible to obtain better models, capable of satisfactorily predicting the concentrations of each of the species considered. The output layer was also defined a priori: it required three neurons, one for each species to be quantified (ammonium, potassium and sodium). Only structures with a single hidden layer were assayed, as research suggests that the results obtained are as good as those produced with two layers [32].

On the basis of previous experience, and as a first factor to bear in mind, the data were range-scaled prior to training so that they had a value between −1 and 1, having demonstrated [15] that this pre-processing facilitates the modelling process. The internal parameters of the learning algorithms were then set in order to update the weights, these being, for the gradient algorithm, the learning rate ($\alpha = 0.1$) and the momentum ($\beta = 0.4$). The transfer functions used in the input and output layers were also set to be always linear.

3.2.3. Optimisation of the ANN configuration

Table 4 summarises the ANN parameters considered in the optimisation. It should be pointed out that, of the factors studied, fits were made for all the possible combinations, this resulting in a systematic comparative study of over 30 combinations of ANN.

All possible combinations of algorithms, transfer functions and number of neurons in the hidden layer (with absolute and relative measures) were tested, and the root mean square error (RMSE) values [8] were recorded for the test subset, broken down according to each ion considered and the total value. The regression lines obtained by representing the expected values against those predicted by the ANN in the test subset were also recorded for each ion. A good ANN configuration should give small RMSEs and, for each ion, comparative lines with a good correlation and slope equal to 1 with zero intercept.

First, the nature of the readings was assessed: the fits obtained with the absolute readings of potential were compared with those from relative measures (versus a 0.01 M TRIS solution), the former proving to be better as the obtained RMSEs were better.

The next step in choosing the best ANN was to select the best combination of learning algorithm and transfer function used in the hidden layer. For each learning algorithm the RMSEs (total and for each ion) and correlation coefficients of the regression line of each ion were represented against the number of neurons in the hidden layer, this being performed for each transfer function. The best combinations were found to

Table 4
Parameters optimised in the search towards an ANN model with a correct prediction capability

Input reading	Absolute, relative
Learning algorithms	GDM, LM, BR
Transfer function (hidden layer)	*tansig*, *logsig*
Number of neurons (hidden layer)	Between 3 and 12

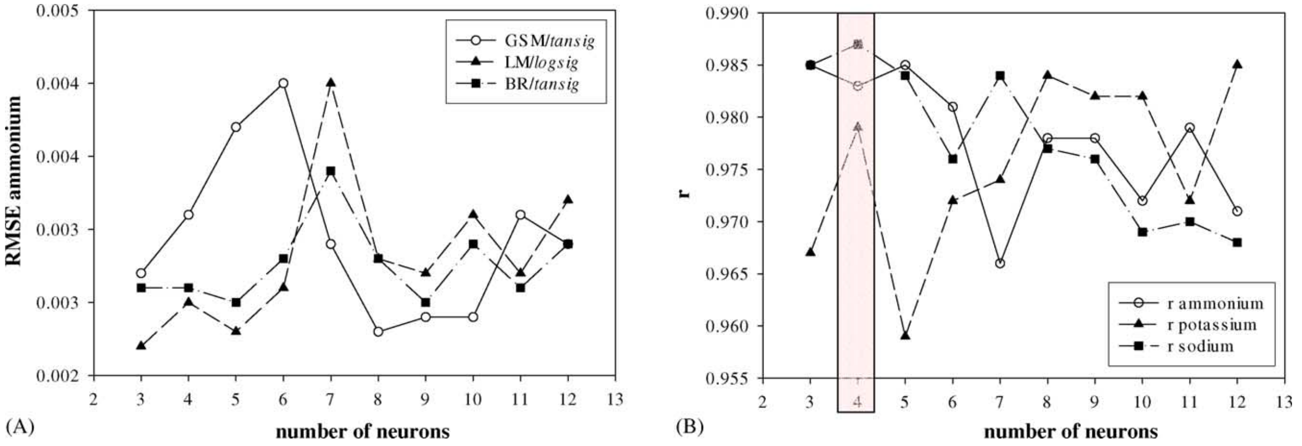

Fig. 5. Selection of the configuration of the final ANN model. (A) Total RMSE values obtained for different number of neurons in the hidden layer and three combinations of training algorithms/transference function in the hidden layer. (B) Correlation coefficients for the three considered ions vs. number of neurons in the hidden layer for the LM/*logsig* ANN.

be the GDM algorithm with the *tansig* transfer function, the LM with the *logsig* and the BR with the *tansig*. Having selected these three, they were then compared with each other; Fig. 5A shows the RMSEs for ammonium ion in the test set with respect to the number of neurons. The best combination was found to be LM/*logsig* and a reduced number of neurons. And finally, the number of neurons in the hidden layer was chosen using the selected algorithm and transfer function. It can be seen in Fig. 5B that the configuration which gives the most significant correlation coefficients is four neurons in the hidden layer. Therefore, the selected ANN which best models the set of initial data uses the Levenberg–Marquardt training algorithm, has four neurons in the hidden layer and uses the *logsig* transfer function.

The correct modelling was then visualised using these optimum conditions, the predicted values being represented with respect to those expected from the external test subset. In this way it is possible to check the degree of generalisation of the ANN, that is, its ability to represent information which did not form part of the training. Fig. 6 shows the comparisons for the goodness of fit of the test subset, while Table 5 presents the parameters of the regression lines corresponding to these fits, the correlation coefficients always being close to 1. It can be seen that for the three ions there is a trend line indistinguishable from ideality, with zero intercept, and whose slope is equal to 1. Therefore, there is a clear correspondence between the values obtained using the network and the expected values for the three ions.

Table 5
Summary of the goodness of fit obtained for the three ions with the external test set ($n = 13$)

	Slope	Intercept (M)
NH_4^+, $r = 0.983$	0.95 ± 0.12	0.001 ± 0.003
K^+, $r = 0.979$	1.03 ± 0.14	0.000 ± 0.004
Na^+, $r = 0.987$	1.02 ± 0.11	0.001 ± 0.003

r is the correlation coefficient. Confidence intervals calculated at the 95% confidence level.

In order to ensure that the results obtained did not correspond to local minimums a supplementary check was carried out, in which the weight values were reinitialised at random and the ANN retrained to see if the model showed convergence in similar situations or whether it reached local minima. This was done by repeating the network's learning through resetting the weight values five times and then evaluating the results obtained. The product of this operation was verified by checking graphically an equivalent distribution of the residuals of the external test subset. As is shown in Table 6 the overall values for these residuals (RMSEs and correlation coefficients of the test subset) also showed equivalent results, thus giving validity to the finally obtained model.

3.2.4. Application to synthetic samples

In order to further demonstrate the correct modelling of the electronic tongue, it was applied for determining alkaline ions in synthetic samples, in which a number of laboratory samples with a known concentration of each of the ions studied (within the concentration range considered) were prepared and measured using the SIA system. These samples were prepared with the same ionic medium used during training, 0.01 M TRIS at pH 7.5, in order to ensure equivalent conditions to those of the initial data. The measures obtained with these samples were processed with the previously trained

Table 6
Obtained fittings after five successive reinitialisations of the ANN with optimal configuration

Assay	RMSE (M)				*r*		
	NH_4^+	K^+	Na^+	Total	NH_4^+	K^+	Na^+
1	0.0025	0.0030	0.0029	0.0049	0.983	0.979	0.987
2	0.0024	0.0030	0.0029	0.0048	0.983	0.978	0.990
3	0.0024	0.0029	0.0028	0.0047	0.983	0.979	0.988
4	0.0030	0.0026	0.0030	0.0050	0.977	0.984	0.985
5	0.0024	0.0029	0.0029	0.0048	0.983	0.979	0.991

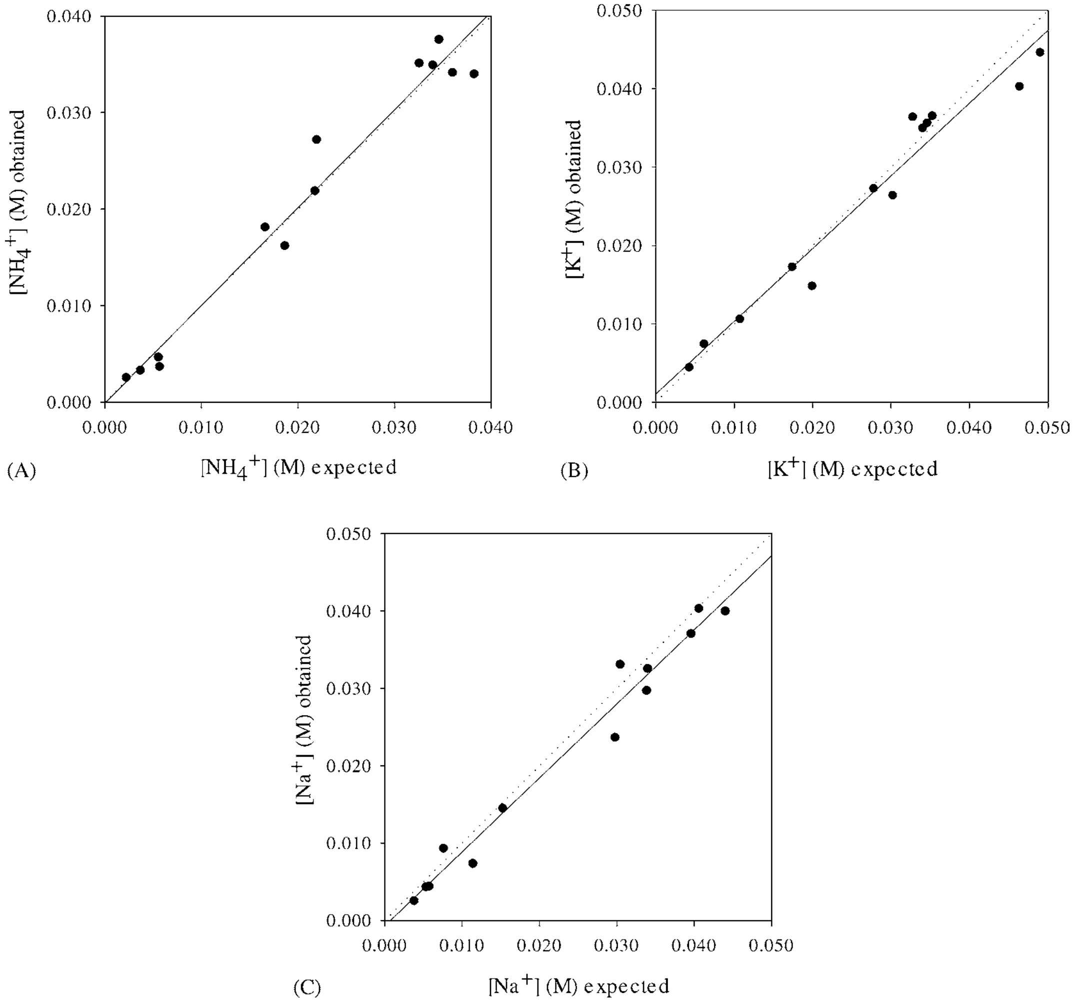

Fig. 6. Correlation between expected and obtained concentration for ammonium (A), potassium (B) and sodium (C) ions, pertaining to the external test set. The dotted line represents the theoretical comparison line $y = x$.

ANN, and the comparative graphs of obtained value vs. expected value were produced.

Table 7 shows the parameters of the regression lines corresponding to these fits. In each of the three cases an ideal situation can be observed, that is, lines with a slope equal to 1 and zero intercept; unfortunately, in the case of potassium ions, the errors were excessive. A Student's t-test for paired samples was applied to check that there were no significant differences between the obtained and expected values, significance being set at 95%. There were no significant differences for ammonium ($t = 2.59$) and potassium ions ($t = 0.39$), as $t < t_{tab}$ ($t_{95\%} = 3.18$); however, due to a systematic error there were significant differences in the case of sodium ions ($t = 6.84$).

Table 7
Results obtained in the determination of ammonium, potassium and sodium ions in a set of synthetic samples ($n = 4$) employing the proposed methodology

	Slope	Intercept (M)
NH_4^+, $r = 0.990$	0.97 ± 0.34	-0.0008 ± 0.0051
K^+, $r = 0.853$	1.01 ± 1.88	-0.001 ± 0.028
Na^+, $r = 0.984$	1.10 ± 0.61	0.006 ± 0.013

Confidence intervals calculated at the 95% confidence level.

3.2.5. *Application to real samples*

Once the satisfactory modelling of the electronic tongue for determining NH_4^+ and K^+ ions in synthetic samples had been checked, it was decided to apply the system to the determination of these species in complex real samples such as fertilisers.

Four liquid fertilisers and one solid fertiliser were analysed. The liquid fertilisers were first filtered and then diluted at 10:100 with 0.01 M TRIS at pH 7.5 (to obtain similar conditions to those used in training the ANN). In order to analyse the solid fertiliser, a 5 g sample was left for 1 h in 100 ml of 0.01 M TRIS at pH 7.5, the soluble part then being taken.

The sensor measurements were processed with the trained ANN in the same way as with the synthetic samples. The results obtained were then compared with reference methods. The ammonium reference values were obtained by means of an ammonia electrode [33], while the reference values for

Table 8
Results obtained in the determination of ammonium ion in fertiliser samples employing the reference method and the proposed methodology

Fertiliser name	$[NH_4^+]$ (M), reference value	$[NH_4^+]$ (M), found value	Relative error (%)
Universal liquid fertiliser (brand#1)	0.0891	0.0832	+6.6
Geranium’s fertiliser (brand#1)	0.0874	0.0814	+6.9
Liquid fertiliser with guano (brand#2)	0.0884	0.0827	+6.4
Geranium’s fertiliser (brand#2)	0.0823	0.0827	−0.5
Flowerpot’s fertiliser (brand#2)	0.0725	0.0754	−4.0

sodium and potassium were obtained by means of inductively coupled plasma optical emission spectroscopy (ICP-OES) [34].

Results for the ammonium ion are shown in Table 8, where the absolute errors can be seen to be always less than 7%. In the case of potassium and sodium the distribution of obtained values did not allow significant conclusions to be drawn. Although the proposed values for the potassium ion approach reference values, they are significantly dispersed. While the sodium ion shows good concordance, the determination of Na^+ in fertilisers is of no relevance. It is likely that there are matrix effects for the chosen real samples. A Student’s *t*-test for paired samples was again applied and revealed no significant differences between the obtained and expected ammonium values, significance being set at 95%; $t < t_{95\%}$ ($t = 1.52$, $t_{95\%} = 2.78$). For the potassium ion, confirming which the exact situation is would require the complete characterisation of the samples studied.

4. Conclusions

An automated electronic tongue was built by coupling an SIA system to an array of potentiometric sensors. This system enabled the automated, simultaneous characterisation of the sensors used with respect to two ions, and the coefficients of potentiometric selectivity coefficients were able to be calculated with two degrees of freedom. This kind of study constitutes an advance on the usual characterisation of potentiometric sensors as the system was used for two-dimensional characterisations.

The SIA system was able to generate automatically, and with a high degree of randomness, the information necessary for training the ANNs; this enabled us to work with a relatively low number of points, and what would have required weeks of experimental work if performed manually [14] was achieved in a matter of hours. The response of the sensor array was modelled using ANNs. Of the many parameters which make up an ANN the present study evaluated training algorithms, transfer functions and topology (number of neurons in the hidden layer). Of the different combinations of algorithm/transfer function assayed the best fit was achieved with LM/*logsig*. The structure providing the best modelling was a single hidden layer containing four neurons. The electronic tongue developed was then applied to the determination of ammonium, potassium and sodium ions in synthetic samples. While ammonium and potassium were able to be determined, a systematic error was observed in the case of sodium. The electronic tongue was also able to determine ammonium ions in commercial fertilisers without interfering species being eliminated; however, potassium and sodium ions could not be fully determined in this case. Although certain ions did not show correct results for given sample matrices, it was nevertheless possible to correct for their interference. Research now in progress aims to add new sensors to the array in order to correct some of the drawbacks observed in the present study.

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