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SIA system employing the transient response from a potentiometric sensor array—Correction of a saline matrix effect

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ABSTRACT

A Sequential Injection Analysis (SIA) system and an 8-potentiometric all-solid-state sensor array were coupled in a simple and automated electronic tongue device. The potentiometric sensors used were planar microfabricated structures with standard PVC membranes deposited onto a gold contact. The SIA system permitted the automated operation and generation of the calibration data, needed to build an Artificial Neural Network model, thanks to the precise dosing and mixing of volumes of stock solutions. The resolution of a four-ion mixture, i.e. ammonium, sodium, nitrate and chloride was the study case used for characterization of the system. Two different variants for signal acquisition, steady-state and transient recording, were arranged and compared. The dynamic treatment is shown to offer improved performance thanks to the benefits of the kinetic resolution. For this, it first extracts meaningful data from a FFT transform of each sensor's transient, which is then fed to an ANN model for estimation of each concentration in the four-ion mixture. While in a standard laboratory situation there was no difference between the two approaches, the dynamic treatment allowed the correction of a matrix effect in the case study, where an uncontrolled saline effect could be counterbalanced.

1. Introduction

A recent proposal in chemical sensing is the electronic tongue (ET) concept, a topic receiving special attention and which is systematically contributed by several laboratories in different countries. This novel analytical concept involves the use of a sensor array, normally with cross-response features among the different sensors used, plus a chemometric data processing tool to extract the complex response patterns [1]. This innovative intelligent system, bioinspired in nature's animal senses, allows a fast determination or identification of several compounds through a single stage that uses the cross-sensitivity of sensors plus an advanced data processing tool to interpret the signals' chemical meaning [1]. There are ETs described which employ sensors with potentiometric, voltammetric or impedimetric transduction, as the main variants. Ion-selective electrodes (ISEs) are widely used to form arrays for ETs [2,3]. For these sensors there are many formulations of membranes of varied selectivity allowing its use in several applications [4,5].

The Sequential Injection Analysis (SIA) technique has been proposed recently to add versatility and facilitate automation of calibration tasks when employing electronic tongue (ET) systems [6]. Over the last decade, more evolved techniques as multicommutated flow injection, multisyringe flow injection and sequential injection have increased the viability and capability of flow chemical analysis [7,8]. Especially, advanced treatment of samples is facilitated thanks to the versatility and high reproducibility offered by SIA systems. Recalling that one problem associated with the developing of ET is the large amount of calibration standards needed to generate an appropriate response model; it is therefore obvious that automated flow systems are highly valuable to generate the information necessary [9,10].

When ETs employ arrays of potentiometric sensors, the interference problem between the primary ions considered and closely related ionic interferences – of a very complex non-linear nature when the number of species increases– may then be tackled with the cross-response features very like as in the electronic tongue concept. Different chemometric treatments can then be employed, such as Partial Least Squares (PLS) and Artificial Neural Networks (ANNs) [11–13]. In our experience, we are in favour of the use of Artificial Neural Networks (ANNs), more suited to the high non-linearities present [9,14].

However, regardless of the method selected, a correct identification of signal characteristics is essential in order to build appropriate interpretation models. In this way, standard procedure is the use of SIA or FIA peak heights or also the steady-state poten-

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tials recorded after the injection [3]. But when the sensors are used within a FIA or a SIA system, a richer signal can be acquired, the transient response to a step or pulse profile of sample arriving to the sensor array. This richer signal, which entails the dynamic nature of the sensor's response, can be of high information content, either of primary ion activity or of possible interferences [15–17], which can be better discriminated thanks to the kinetic resolution added.

Although the potentiometric measurement process is relatively simple, recordings obtained according to the transient principle present increased complexity. Therefore, the choice of suitable pre-processing tools becomes critical in order to reduce data without loss of information. The transient can be subsequently reduced to significant features, for example through a Principal Component Analysis (PCA) [18,19], Legendre's polynomials [20,21], Fast Fourier Transform (FFT) [22] or Wavelet decomposition [23], while next, the reduced information may be taken as departure point for the ANN model.

The approach employing ETs and SIA has been successfully tested for alkaline ions mixtures [9], alkaline-earth [24], and also anions mixtures [21]. With use of dynamic treatment of signals, it has been used to resolve three [16] and four-cation mixtures [15]. In this communication, we present the SIA determination of both anions (nitrate, chloride) and cations (ammonium, potassium), employing the dynamic signals from a sensor array. The 8-sensor array was equipped with planar microfabricated structures with standard PVC membranes deposited onto a gold contact [25]. The chemometric treatment proposed to process the time transient firstly extracts meaningful data from a FFT transform of each sensor's recording, and feeds then an ANN model for quantitative estimation of each concentration of the quaternary mixture. Thanks to the automation capabilities of the used SIA system, all preparation of the ca. 100 standards used for the building of the response model, could be done easily and without special effort, demonstrating the versatility of the approach.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with doubly distilled water and the reagents used were of analytical grade. The measurements were performed using lithium acetate 0.05 M (Applichem, Germany) as a background salt in the carrier solution. Potassium acetate (Baker, Holland), ammonium acetate (Panreac, Spain), lithium nitrate (Fluka, Switzerland) and lithium chloride (Panreac, Spain) solutions were used as calibration species by dissolving the appropriate amount of salts in the above described background solution. It may be noticed that the counterion for each salt species considered was acetate or lithium to avoid any distortion in the measurements.

2.2. ISE array

The array used in the proposed ET was formed by eight ISEs (two sets of: potassium-, ammonium-, nitrate- and chloride-sensitive microelectrodes) with different cross-sensitivity features. The transducers, i.e. back-side contact Au microelectrodes were constructed employing a double side PCB layer as a base material. Details on the technology and procedures can be found in previous papers [25,26].

Different membrane cocktails were prepared, in order to be deposited on the surface of the back-side contact Au planar microelectrodes. Prior to membrane deposition, sensor's surfaces were cleaned with distilled water and methanol. After the membrane solvent evaporation, the sensors were mounted in flow-through cells. Planar Ag/AgCl microelectrodes, developed in silicon technology in the Institute of Electron Technology (Warsaw), have been applied as chloride-sensitive sensors. All the electrodes were conditioned 3 days before its first use in a 0.01 M solution of their primary ion. The detailed formulation of the membranes is summarized in Table 1. Provider of all the membrane components was Fluka (Switzerland).

2.3. Instrumentation

The developed SIA system had two clearly different parts: the first part was the fluid system formed by an automatic microburette, one holding coil, an 8-way Hamilton MVP multiport valve (Hamilton, Switzerland) and a 7-mL Perspex mixing cell with a magnetic stirrer. The multiport valve is connected to the burette with holding coil placed in between. The burette is fed through a carrier solution reservoir. By the time the common port may access any of the other ports which led to sample, standard stock solutions, mixing chamber or sensor array by an electrical rotation of the valve. All the elements were connected together using low-pressure liquid chromatography connectors. The second part was the measurement system, which is formed by the sensor array, the reference electrode (miniaturised silver/silver chloride electrode with a double junction) and an 8-channel signal conditioning circuit connected to the National Instruments Multifunction DAQ analogue inputs (Model NI6221, USA). The whole system was controlled by a PC using a virtual instrument developed in Labview [27].

2.4. Procedures

A first study stage consisted in the sensor characterization with single ion calibration measurements. The calibration consisted in recording the ISE potentials for different standard solutions of the primary ion (containing the background 0.05 M lithium acetate) prepared automatically by the SIA system by direct dosing or sequentially diluting a stock solution. The prepared mixture was

Table 1
Formulation of the ISEs forming the sensor array and initial characterization of their response towards single ions.

Sensor	PVC	Plasticizer	Ionophore	Sensitivity (mV/dec)[c]		τ (s)[d]
K^+	33%	Dioctylsebacate (65%)	Valinomycin (2%)[a]	K^+	53 ± 2	0.905
				NH_4^+	46 ± 7	0.976
NH_4^+	33%	Dioctylsebacate (66%)	Nonactin (1%)[b]	NH_4^+	53 ± 1	0.883
				K^+	50 ± 1	0.915
NO_3^-	33%	Nitrophenyloctylether (65%)	Tetradecyl ammonium bromide (2%)	NO_3^-	−45 ± 1	0.961
				Cl^-	−19 ± 2	0.998
Cl^-	2nd kind, Ag/AgCl electrode			Cl^-	−56 ± 1	0.881
				NO_3^-	–	–

[a] With the addition of x = (0.5, molar ratio towards ionophore) potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

[b] With the addition of x = (0.08 molar ratio towards ionophore) potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

[c] Uncertainty values correspond to standard deviation of 6 repeated calibration experiments.

[d] First-order time constants, fitted by non-linear regression to exponential rise (or decay for anions).

subsequently presented to the sensors with a step injection of sample. This stage was extended to binary mixtures of ions in order to characterize sensor's interference behaviour and determine their potentiometric selectivity coefficients; also, arbitrary quaternary mixtures could be prepared in a complete automated procedure for the ET training and operation [9].

2.4.1. Data generation

Building of the response model is required before the application. For this purpose, a set of mixtures with different concentrations of the four considered ions were prepared automatically with the SIA system. Prepared solutions also had the predefined background, lithium acetate 0.05 M, and were obtained through additions of microvolumes of stock solutions using the mixing cell.

Two different experiments were carried out in order to evaluate ET capabilities. The first experiment involved the simultaneous determination of four ions (K^+, NH_4^+, NO_3^- and Cl^-). The second experiment corresponds to the determination of K^+, NH_4^+ and NO_3^- in the presence of a variable concentration of NaCl as a perturbation event. For both experiments all the solutions were randomly generated considering the following concentration ranges: 0.4–10 mM for potassium, 0.1–4 mM for ammonium, 0.1–4 mM for nitrate, 0.3–10 mM for chloride in the first case and 0.01–0.2 M for sodium chloride in the second.

2.4.2. Multivariate modelling

ANNs were used in order to model the combined sensors' response obtained from standard solutions which contained the different ions studied. The corresponding programs and calculations were performed in MATLAB 7.1 (Mathworks, USA) using its Neural Network Toolbox Version 4.0.6 and Signal Processing Toolbox Version 6.4.

Conventionally, experimental SIA transient measurements contained hundreds of records and cannot be processed directly by an ANN due to its high data dimension. To solve this problem, ANN models are traditionally fed with steady-state signals, in this case it is common to use the mean values of measures from the last seconds of the sensors' dynamic records or simply the peak height. An alternative approach is to take advantage of the whole dynamic record; in this case the proposed pretreatment consists in calculating firstly the Fast Fourier Transform (FFT) coefficients of each signal and then feed the ANN model with some of the low frequency components [16].

In all cases, ANN models should be optimized by an iterative process in order to generate the best response model. To evaluate the model's performance, standard error of training and prediction were used. On the one hand, some combinations employing linear (*purelin*) and non-linear (*logsig* and *tansig*) transfer functions as well as different number of neurons (between 3 and 10) in the hidden layer were tested in order to assure the best performance. On the other hand, training algorithm Bayesian Regularization (BR), and training parameters as learning rate ($\alpha = 0.1$) and the momentum ($\beta = 0.4$) were set based on the previous group experience [28]. The appropriate number of ANN inputs, were chosen in the case of steady-state procedure using the mean of the last 15 s sensor's recording. In relation with ANN models fed by FFT coefficients, the use of different number (between 2 and 8) was tested in order to achieve optimal results.

3. Results and discussion

First of all, the sensors were characterized in their response towards single ion solutions and binary mixtures. Once the full characterization of the sensors had been made, the next step was to construct an ET with the purpose of determining simultaneously potassium, sodium, nitrate and chloride ions. In the same way, an additional application was performed, in order to determine potassium, sodium and nitrate ions simultaneously in the presence of uncontrolled saline medium.

Table 2
Summary of selectivity coefficients obtained from the selectivity study with two degrees of freedom.

Sensor and primary ion	Interfering ion	$\log K_{x,y}^{pot}$ [a]	$\log K_{x,y}^{pot}$ [b]
NH_4^+	K^+	−0.82 ± 0.04	−0.8[c]
K^+	NH_4^+	−1.8 ± 0.2	−1.9[d]
NO_3^-	Cl^-	−2.08 ± 0.2	−2.6[e]
Cl^-	NO_3^-	–	–

[a] Obtained values (two degrees of freedom) with flow conditions and Nikolskii–Eisenmann fit.
[b] Obtained values with static conditions and fixed interference method.
[c] Ref. [29].
[d] Ref. [30].
[e] Ref. [21].

3.1. Characterization of ISE sensors

In the characterization towards the primary ion, and taking advantage of the independent response between anions and cations, ammonium nitrate and potassium chloride were used as standard solutions to obtain two calibrations per run (the cation and the anion). In this sense, six calibration replicates were done with each standard to estimate repeatability of measurements. The sensitivities calculated from calibration curves of each sensor towards their primary ion are provided in Table 1. The values are not perfectly Nernstian, but we must consider they correspond to flow conditions. In the table were included also the first-order time constants (τ) of the sensors' dynamics of response. These were determined fitting the responses to a 3 parameters exponential rise to a maximum in the case of cations, and a 3 parameters exponential decay for anions. As it can be observed, time constants for primary ions are always smaller than their equivalent to the interfering ion, which may be used for better discriminating them.

Next, the sensor responses were characterized for binary mixtures using the versatility shown by the automated SIA system. In there, both the concentrations of the primary ion and the interfering ion were allowed to vary simultaneously, in contrast to the fixed interference method, where only one ion is varied. This characterization represents a very useful interference study because the values of the potentiometric selectivity coefficients in the Nikolskii–Eisenmann equation ($K_{x,y}^{pot}$), are obtained with two degrees of freedom. The logarithms of the corresponding potentiometric selectivity coefficients are reported in Table 2, together with their reference value from the literature, normally calculated from fixed interference method. Fig. 1A shows the obtained response surface for the ammonium selective electrode (steady-state potentials), where ammonium is considered to be the primary ion and potassium the interfering one. The figure illustrates the experimental points prepared automatically with the SIA system, as well as the three-dimensional response surface which is obtained from the Nikolskii–Eisenmann equation fitted with Levenberg–Marquardt algorithm, as available in Sigmaplot 8.0 (SPSS Inc., Chicago, IL). It can be clearly seen how, with low concentrations of the primary ion, the curvature gets steeper as the concentration of the interferent increases. The same behaviour was observed for potassium sensors, but in this case the primary ion was potassium and ammonium the interfering ion. With regard to anion interferences, they just affected the nitrate sensors (Fig. 1B), for this also the curvature gets steeper when the concentration of chloride increases. Again, this very special study was feasible thanks to the versatility of the SIA system, which permitted the effortless automated preparation of 42 binary mixtures for each combination of cations or anions.

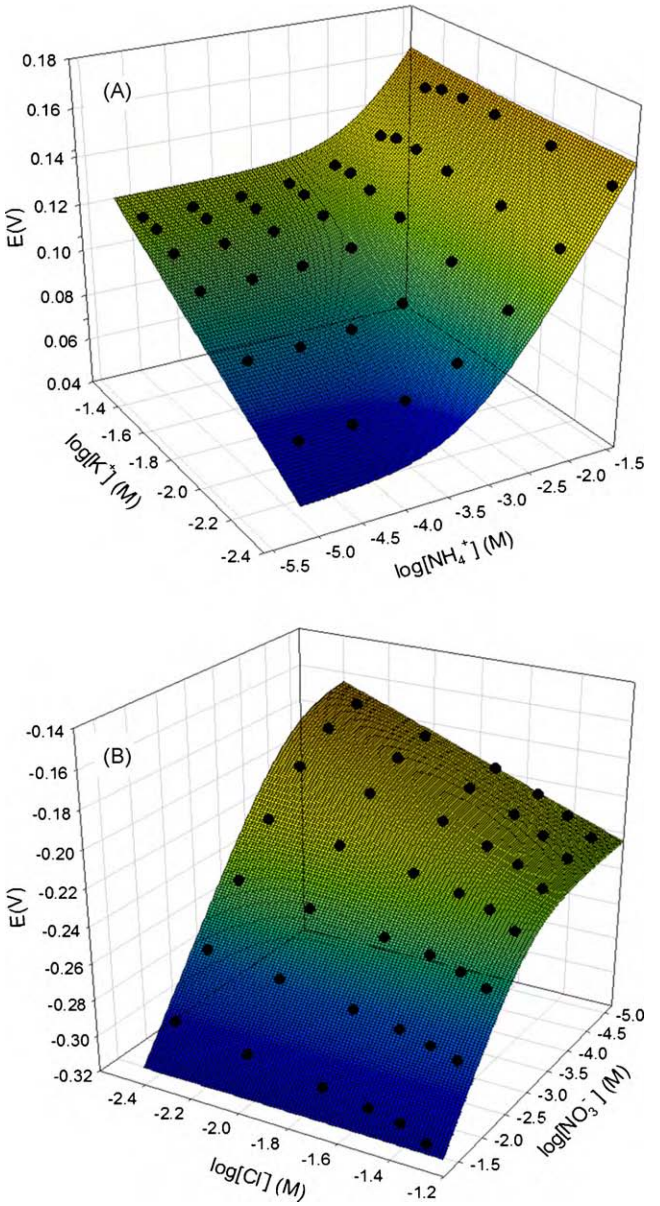

Fig. 1. Response surface plots corresponding to selectivity experiments of two of the sensors employed in the array, showing their cross-response features: (A) NH_4^+ sensor and (B) NO_3^- sensor.

3.2. *First study case: simultaneous determination of potassium, ammonium, nitrate and chloride*

The SIA electronic tongue approach was attempted for the determination of the four considered ions. The sensor array used was composed by NH_4^+-ISE, K^+-ISE, NO_3^--ISE and an Ag/AgCl second kind electrode, all duplicated. The automated SIA system permitted the effortless generation of the samples needed; a total amount of 100 samples were measured in order to generate the response model. These samples were divided in two sets, 70 samples for the training step and 30 for the test set. A total of 600 potential values per sample were measured for each ISE (60 s of transient recording and 0.1 s between readings). In order to build different models and to compare their performance, both steady-state and dynamic signal pretreatments were used.

After checking ca. 20 different ANN configurations following the optimization procedure described in Section 2.4.2, the best results were obtained with a model generated by an ANN with an 8-4-4 architecture for steady-state signals and 32-4-4 for ANN-FFT (four coefficients per sensor). Both models were trained employing the BR algorithm, and used a *logsig* and *purelin* transfer functions for the hidden and output layer, respectively, as the optimal arrangement. Comparison graphs of predicted vs. expected concentrations for the four species under study were built to check the prediction ability of the ANN. For the selection of the best configuration, we considered the Root Mean Squared Error (RMSE) of the fit and the slope, intercept and correlation coefficient of the comparison graphs (ideal values close to 0, 1, 0, and 1, respectively) (Fig. 2).

Concerning the obtained results, reported in Table 3, the evaluation parameters extracted from the comparison graph of the test set (Fig. 2) are close to the ideal values for all ions under study. Moreover these quite ideal performances were obtained independently of the two proposed pretreatments.

Furthermore, 10 additional synthetic samples were measured following the same procedure as before. In order to evaluate the benefits related to the ANN processing these samples were processed also employing a linear Nernstian model with direct interpolation of steady-state potential. A Student's paired samples *t*-test was performed between both series of data, while the obtained results are reported in Table 4. From these *t*-test results it could be extracted that the ANN data treatment is required to quantify correctly all the ions, except for chloride for which the Nernstian linear model is enough. This is a predictable observation, as the 2nd kind Ag/AgCl electrode does not present any interference by the cations or anions tested. When comparing steady-state and FFT pretreatments for the other ions, no differences could be discerned between the obtained results, but as a conclusion, both ANN treatments solved successfully the interference problem of cations as much as anions.

3.3. *Second study case: simultaneous determination of potassium, ammonium and nitrate in the presence of uncontrolled saline medium*

Once the ET capabilities were checked achieving the simultaneous determination of the quaternary ion mixture, a second experiment was performed including a variable perturbation of high arbitrary concentrations (up to 0.2 M) of NaCl in the training (and external test) samples. The goal is to check if the proposed system could overcome this situation of strong interference of sodium and chloride, which is common in field analysis in waters from estuaries, deltas, wells close to the sea, etc.

In order to generate the response model, 80 sample standards were used, a smaller dataset, given it only modelled a trinary mixture. Later these samples were divided in two subsets; 50 were assigned to the training step and 30 for the external test set. The subsequent pretreatment consisted in extracting the FFT coefficients and the steady-state values, as in the first case, in order to feed the ANN with them and generate the response model.

As in the previous case, at least 20 different architectures were programmed in order to optimize the best ANN configuration. Final ANN architectures had the following structure: an 8-3-3 architecture for steady-state case and 40-3-3 for ANN-FFT (five Fourier coefficients per sensor). Both models were trained employing the BR algorithm, and showed better results when using a *logsig* and *purelin* transfer functions for the hidden and output layer, respectively.

Comparison graphs of predicted vs. expected concentrations for the three species under study were again built to check the prediction ability of the ANN (Fig. 3). Related to the evaluation parameters of the obtained results, reported in Table 5, several observations can be made. This time, distinct behaviours could be appreciated depending on the choice of data pretreatment. On the one hand, the comparison graphs for the external test set and synthetic samples employing the dynamic FFT approach are close to the ideal

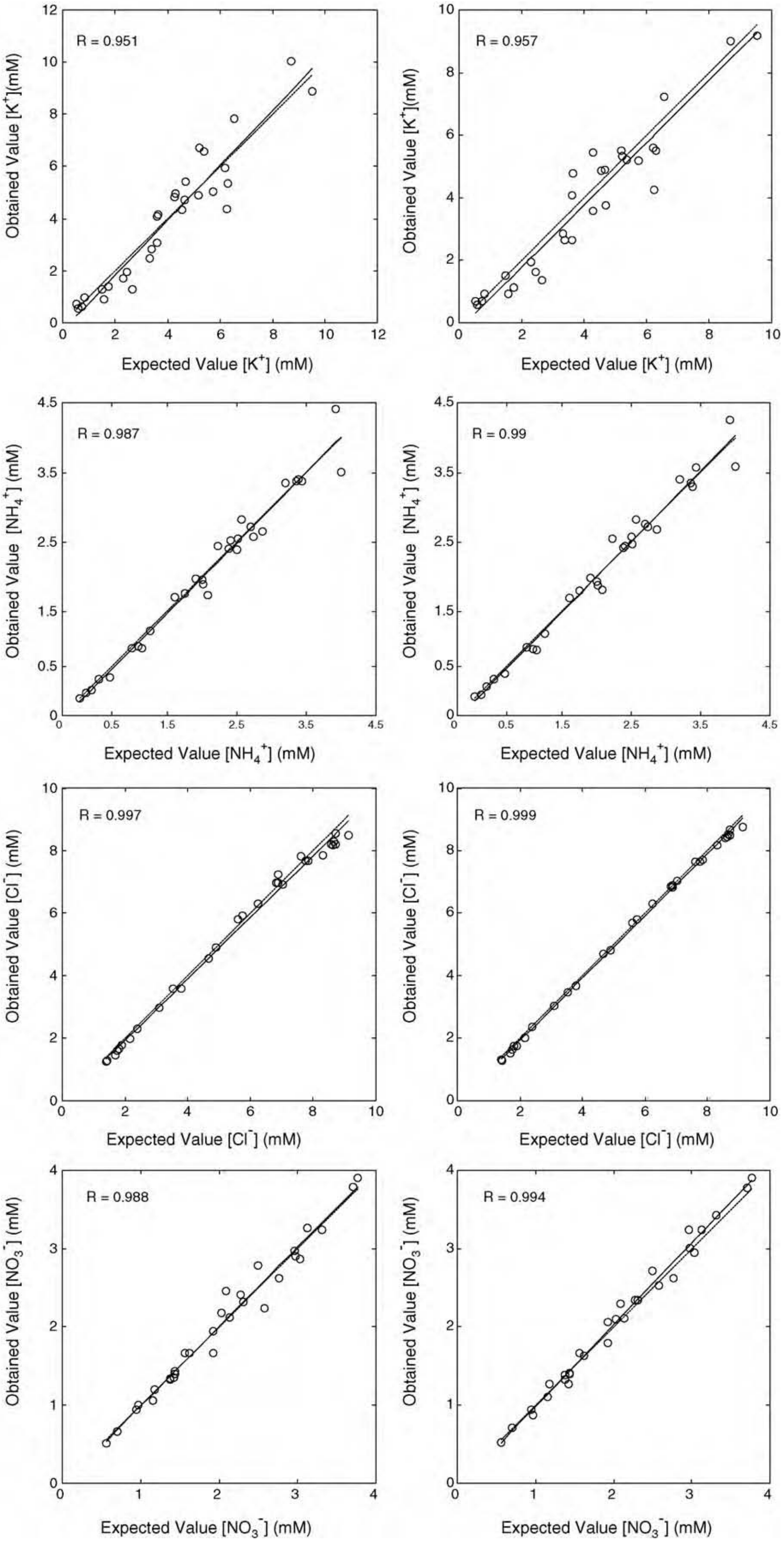

Fig. 2. Comparison of obtained vs. expected concentrations for samples in the external test subset: potassium, ammonium, nitrate and chloride ions. Graphs on the left correspond to steady-state signal, and on the right to FFT preprocessing.

Table 3
Results of the regression lines obtained in comparison between obtained vs. expected concentrations, for the determination of the four species and considering the steady-state approach and the FFT pretreatment (uncertainty intervals calculated at the 95% confidence level).

Ion	Steady-state signal				FFT pretreatment			
	Correlation	Slope	Intercept (mM)	RMSE (mM)	Correlation	Slope	Intercept (mM)	RMSE (mM)
External test subset								
K^+	0.957	0.99 ± 0.1	−0.2 ± 0.5	0.7	0.951	1.05 ± 0.1	−0.2 ± 0.6	0.8
NH_4^+	0.99	1.02 ± 0.06	0 ± 0.1	0.2	0.987	1.02 ± 0.06	−0.1 ± 0.1	0.2
NO_3^-	0.994	1.04 ± 0.04	−0.6 ± 0.1	0.1	0.988	1.01 ± 0.06	0 ± 0.1	0.1
Cl^-	0.999	1.00 ± 0.01	−0.07 ± 0.09	0.1	0.997	0.98 ± 0.03	0 ± 0.2	0.1
Synthetic samples								
K^+	0.993	1.1 ± 0.1	0 ± 0.5	0.2	0.935	0.99 ± 0.3	0.3 ± 1	0.5
NH_4^+	0.987	1.1 ± 0.1	−0.1 ± 0.1	0.08	0.982	1.1 ± 0.2	−0.1 ± 0.2	0.1
NO_3^-	0.999	0.96 ± 0.03	0.1 ± 0.2	0.07	0.993	1.00 ± 0.1	0 ± 0.2	0.08
Cl^-	0.996	0.97 ± 0.07	0.1 ± 0.2	0.06	0.998	0.96 ± 0.05	0.1 ± 0.2	0.1

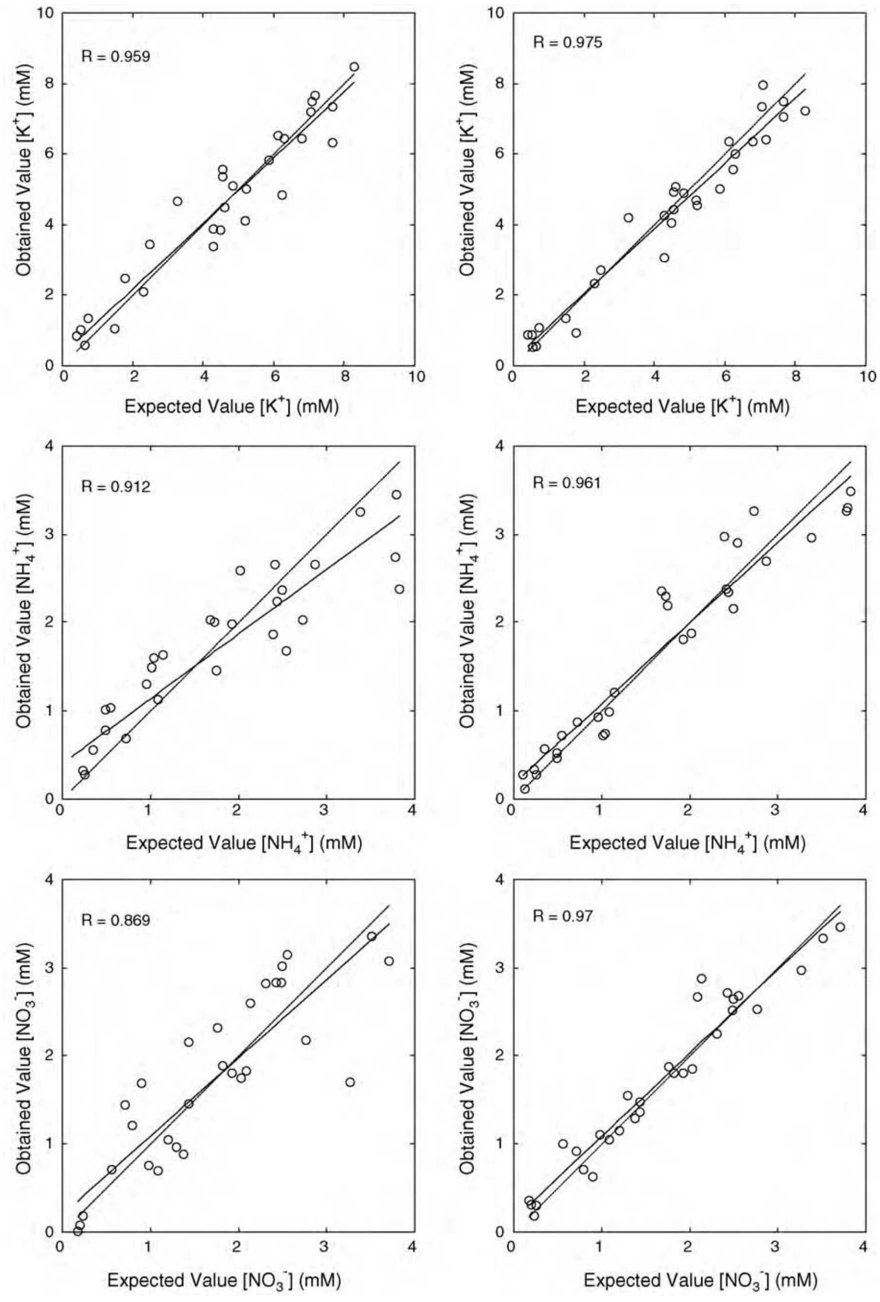

Fig. 3. Comparison of obtained vs. expected concentrations for samples in the external test subset (study case with uncontrolled saline background): potassium, ammonium and nitrate ions. Graphs on the left correspond to steady-state signal, and on the right to FFT preprocessing.

Table 4
Comparison series of theoretical, classical Nernst model, proposed FFT-ANN and ANN-ST (steady-state signal) model according to Student's paired samples *t*-test.

Analyte	Expected vs. Nernst	Nernst vs. ANN-FFT	Expected vs. ANN-FFT[a]	ANN-FFT vs. ANN-ST
NH_4^+	2.987	2.973	0.046	1.110
K^+	2.42	2.444	1.134	0.116
NO_3^-	3.206	3.208	0.091	0.390
Cl^-	0.136	0.126	0.324	0.690

[a] Critical tabulated *t* value (95% confidence level, 9 degrees of freedom), $t^* = 2.26$.

Table 5
Results of the regression lines obtained in comparison between obtained vs. expected concentrations, for the determination of three species in saline background and considering the steady-state approach and the FFT pretreatment (uncertainty intervals calculated at the 95% confidence level).

Ion	Steady-state signal				FFT pretreatment			
	Correlation	Slope	Intercept (mM)	RMSE (mM)	Correlation	Slope	Intercept (mM)	RMSE (mM)
External test subset								
K^+	0.959	0.93 ± 0.10	0.3 ± 0.5	0.7	0.975	0.93 ± 0.08	0.2 ± 0.2	0.5
NH_4^+	0.912	0.73 ± 0.10	0.4 ± 0.3	0.4	0.961	0.91 ± 0.10	0.2 ± 0.2	0.3
NO_3^-	0.869	0.89 ± 0.20	0.2 ± 0.3	0.5	0.970	0.95 ± 0.09	0.1 ± 0.2	0.2
Synthetic samples								
K^+	0.96	0.97 ± 0.23	0 ± 1	0.5	0.957	0.98 ± 0.2	0 ± 1	0.4
NH_4^+	0.865	0.70 ± 0.3	0.3 ± 0.9	0.2	0.983	1.1 ± 0.2	0 ± 0.3	0.1
NO_3^-	0.943	0.85 ± 0.20	0 ± 0.7	0.2	0.987	0.94 ± 0.20	0.1 ± 0.4	0.1

values for all the species under study. In this sense, the correlation coefficients, slopes, intercepts and also RMSE indicate that this procedure was able to avoid the distortion in the determination of the analytes even in the presence of uncontrolled saline media. These results clearly show the correction of a matrix effect through the use of a multi-way data, a feature normally faced with spectroscopic or chromatographic techniques, and firstly demonstrated here with an electronic tongue system.

Considering the steady-state pretreatment, it achieved satisfactory results only towards potassium determination, probably because the selectivity of the used sensor is high enough to minimize the saline effect. Concerning ammonium and nitrate ions, the model fitting degrees, the correlation coefficients of the comparison graphs as well as their slopes were clearly worse when compared with the FFT approach. From the inspection of Fig. 3, the higher scatter of comparison values for the steady-state approach is clearly seen, demonstrating a worse overall performance than with the dynamic data treatment.

In order to compare the different pretreatments in more realistic way, from 8 samples the relative errors of the predicted concentrations were calculated. Table 6 summarizes this information. In it, it may be observed for each ion (specially for ammonium and

Table 6
Relative errors obtained for the predicted concentrations of 10 samples applying the two pretreatments (Fast Fourier Transform, Steady-State) and compared to a direct Nernstian interpolation for the respective sensor.

	Sample (mM)	Rel. error FFT[a]	Rel. error SS[b]	Rel. error DI[c]
K^+	5.18	9.6	20.7	69.2
	4.5	10.2	14.5	38.6
	6.14	3.8	6.5	68.3
	4.85	1.1	5.3	73.9
	8.3	13.0	2.3	81.1
	3.25	28.9	43.7	58.8
	6.8	6.4	5.1	92.1
	1.76	47.2	40.8	193.6
NH_4^+	2.87	5.9	7.5	132.2
	0.715	21.7	4.6	1037.8
	2.54	14.4	34.0	55.0
	3.83	8.8	37.9	103.4
	1.03	27.7	55.0	203.7
	2.02	7.3	28.4	825.5
	0.49	5.4	106.5	318.0
	0.95	2.0	37.1	2941.9
NO_3^-	1.43	4.8	1.5	436.7
	0.225	19.8	21.7	7339.2
	1.08	2.7	35.7	1731.8
	1.38	5.9	35.7	1262.9
	1.43	3.1	50.5	873.0
	2.49	1.3	13.7	606.7
	0.71	29.3	103.6	2791.0
	1.29	20.4	25.1	1564.1
Average relative error (%)	K+	15.0	17.4	84.4
	NH_4^+	11.7	38.9	702.2
	NO_3^-	10.9	35.9	2075.7

[a] Fast Fourier Transform.
[b] Steady-state.
[c] Direct interpolation.

nitrate) that the FFT achieves more accurate predictions than the steady-state treatment. On the one hand, it is possible to confirm the importance of using the kinetic resolution of potentiometric signals; on the other hand, the requirement of applying the Artificial Neural Network to process the potentiometric data is irrefutable, as in a situation without controlling the interfering species, performance with direct interpolation in the Nernstian equations fitted for each sensor reaches uncontrolled errors.

4. Conclusions

A simple, automated analytical device – potentiometric electronic tongue – based on all-solid-state sensor array, SIA system and multidimensional sensor signal analysis has been developed. By coupling the ET with the SIA system the required experimental effort diminished and enabled to perform the large amount of measurements needed; additionally, the richer dynamic signal could be recorded with high reproducibility. Quantitative determination of a quaternary mixture was performed to evaluate the reliability of the system in normal conditions and with the saline background.

In the first study case potassium, ammonium, nitrate and chloride ions were determined obtaining accurate predictions independently of the pretreatment chosen, steady-state or dynamic. In this sense, the steady-state procedure, which is the simpler, seems to be the best option. In contrast, under a perturbation situation as it is the presence of an uncontrolled saline matrix, the ANN-FFT processing offers more accurate predictions than just using the steady-state values. These results demonstrate that the dynamic characteristics of the ISEs furnish extra information about the sample composition, helping to better discriminate components in the sample, and counterbalancing a matrix effect. In this way, this is the first time an electronic tongue system demonstrates the so-called "second-order advantage" [31], i.e. it succeeds in predicting the concentrations of the analytes of interest in the presence of a highly interfering sample matrix.

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