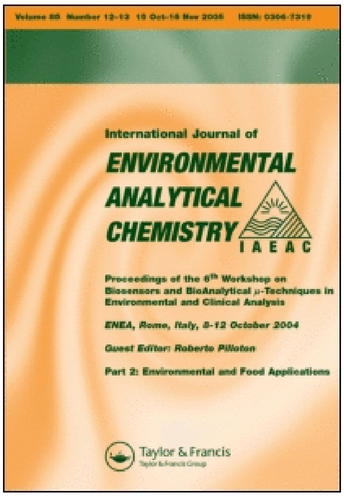

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Remote environmental monitoring employing a potentiometric electronic tongue

Manuel Gutiérrez[a]; Juan Manuel Gutiérrez[b]; Salvador Alegret[a]; Lorenzo Leija[b]; Pablo Rogelio Hernández[b]; Liliana Favari[c]; Roberto Muñoz[b]; Manuel Del Valle[a]
[a] Sensors & Biosensors Group, Department of Chemistry, Autonomous University of Barcelona, 08193 Bellaterra, Spain [b] Department of Electrical Engineering, CINVESTAV, 07360 Mexico D.F., Mexico [c] External Section of Pharmacology, CINVESTAV, 07000 Mexico D.F., Mexico

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Remote environmental monitoring employing a potentiometric electronic tongue

MANUEL GUTIÉRREZ†, JUAN MANUEL GUTIÉRREZ‡,
SALVADOR ALEGRET†, LORENZO LEIJA‡, PABLO
ROGELIO HERNÁNDEZ‡, LILIANA FAVARI§,
ROBERTO MUÑOZ‡ and MANUEL DEL VALLE*†

†Sensors & Biosensors Group, Department of Chemistry, Autonomous University
of Barcelona, 08193 Bellaterra, Spain
‡Department of Electrical Engineering, CINVESTAV,
07360 Mexico D.F., Mexico
§External Section of Pharmacology, CINVESTAV,
07000 Mexico D.F., Mexico

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This work investigates the use of electronic tongues for environmental monitoring. Electronic tongues were based on arrays of potentiometric sensors plus a complex data processing by artificial neural networks and data transmission by radiofrequency. A first application, intended for a system simulating real conditions in surface water, performed a simultaneous monitoring of ammonium, potassium, sodium, chloride, and nitrate ions. The proposed system allowed us to assess the effect of natural biodegradation stages for these species. A second application was used to monitor concentrations of ammonium, potassium, and sodium in the 'Ignacio Ramírez' dam (Mexico). The electronic tongue used here allowed us to determine the content of the three cations in real water samples, although a high matrix effect was encountered for sodium determination. The implemented radio transmission worked robustly during all the experiments, thus demonstrating the viability of the proposed systems for automated remote applications.

Keywords: Electronic tongue; Environmental monitoring; Sensor array; Potentiometric sensors; Artificial neural networks

1. Introduction

Environmental security and monitoring of natural water is a salient issue worldwide. Much attention has been focused on controlling the purity of natural waters, especially near possible contamination sites. Rapid determination of pollutants and other species penetrating into the environment is necessary for adequate measures to restrict

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*Corresponding author. Fax: +34-93-5812379. Email: manel.delvalle@uab.es

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environmental damages. Available laboratory methods for water analysis determine a wide range of components with a high precision, but most of them need complex sample pretreatments and are also rather expensive, e.g. ionic and high-performance liquid chromatography, spectroscopy, photometry, etc. [1–3]. To obtain on-line and real-time information about actual changes in water composition, automatic systems for on-site analysis are highly valuable. Besides, the measuring principles of these systems must be robust and sensitive enough, and with a broad selectivity. This is because target environmental sites, i.e. surface, ground, waste, and sewage water, etc., may present a broadly varied spectra of inorganic as well as organic compounds, microorganisms, etc.

One promising direction for natural water monitoring is the application of multisensor systems; these can be based on arrays of non-specific sensors combined with data processing of their complex signals using advanced chemometrical tools. This approach is named the electronic tongue [4]. The sensor array approach uses the advantages of chemical sensors such as speed of response, low cost of analysis, and on-site analysis possibility with a relatively simple measuring setup. Also, by using a sensor array, it is possible to enlarge the number of species that can be determined simultaneously [5]. In this field, electronic tongues based on voltammetric sensor arrays have been developed to detect annoyances in the quality of drinking water applying the principal-component analysis (PCA) [6] and to monitor on-line industrial processes [7]. In the same way, electronic tongues have been described based on arrays of chalcogenide glass potentiometric sensors plus conventional electrodes such as chloride-, sodium- and potassium-selective sensors that were combined with a pattern-recognition routine. The chalcogenide sensors showed cross-sensitivity applicable to the measurement of metal ions in river water and were suggested for environmental- and process-monitoring purposes [8, 9]. This type of potentiometric electronic tongue was also combined with sensors based on polyvinyl chloride (PVC) membranes for the measurement of different ionic species in model solutions of groundwater [10]. In our previous experience, all-solid-state potentiometric sensors based on polymeric membranes were used for the simultaneous quantification of alkaline ions in river and waste waters using a multilayer artificial neural network (ANN) model [11, 12].

The aim of the present work has been the development, application, and testing of different electronic tongues, based on potentiometric sensors and ANN models, for environmental monitoring purposes. The used sensors are based on PVC membranes that provide a cross-response to various species in solution. The ANN is a multivariate calibration tool that can extract analytical data to quantify target analytes contained on these cross-signals. Two different applications have been considered. In the former, a Continuous Stirred-Tank Reactor (CSTR) with a simulated surface water background was inoculated with natural microorganisms to imitate natural biodegradation conditions. The purpose was the simultaneous monitoring of ammonium, potassium, sodium, chloride, and nitrate when a perturbation occurred; in this case, the addition of a concentrated liquid fertilizer. In the latter, an electronic tongue was optimized for on-site determination of ammonium, potassium, and sodium in the 'Ignacio Ramírez' dam (Mexico). Special attention was paid in compensating for temperature effects and response drifts. In all cases, the possibility of a wireless connection has been explored. A digital radio link was used between the monitoring site and the PC, where the data were processed and stored. Both applications were useful for examining the applicability of an electronic tongue as an automatic remote measurement system that is currently under development.

2. Experimental

2.1 *Reagents and solutions*

The ion-selective PVC membranes were prepared from high-molecular-weight PVC (Fluka, Buchs, Switzerland), using bis(1-butylpentyl) adipate (BPA), dioctyl sebacate (DOS), 2-nitrophenyloctylether (NPOE), dibutyl phtalate (DBP), and dibutyl sebacate (DBS) (all from Fluka) as plasticizers. The recognition elements employed to formulate the potentiometric membranes were the ionophores nonactin (nonactin from Streptomyces, Fluka), valinomycin (potassium ionophore I, Fluka), bis[(12-crown-4)methyl]-2-dodecyl-2-methylmalonate (CMDMM, Dojindo Laboratories, Kumamoto, Japan) and tetradodecylamine (TDDA, hydrogen ionophore I, Fluka) plus the charged carrier tetraoctylammonium nitrate (TOAN, Fluka). Additionally, three recognition elements with generic response were used: dibenzo-18-crown-6 and lasalocide both for cations, and tetraoctylammonium bromide (TOAB) for anions (all from Fluka). All the components of the membrane were dissolved in tetrahydrofuran (THF, Fluka). Ag (Aldrich, Milwaukee, WI) of 99.9% purity and 0.5 mm thick was used to prepare an Ag/AgCl-based sensor for chloride.

The materials used to prepare the solid electrical contact were the epoxy resin components Araldite M and Hardener HR (both from Uneco, Barcelona, Spain), and graphite powder (50 μm, BDH Laboratory Supplies, Poole, UK) as a conducting filler. All other used reagents were of high purity, analytical grade, pro-analysis, or equivalent.

For the first application, a sample of water was taken from the Nespres stream, which lies in the 'Sant Llorenç del Munt' Natural Park in Barcelona (Spain). The sample was taken at 'Mura' town 450 m above sea level. During this application, a liquid fertilizer with guano (Compo, Barcelona, Spain) was also used.

For the second application, real sample waters were obtained from 'Ignacio Ramírez' dam, a eutrophic reservoir that lies in the 'Lerma-Chapala' system in Mexico at 99° 46′ 25″ W, 19° 27′ 35″, 2548 m above sea level. These samples were taken at five different points of the dam.

2.2 *Sensor arrays*

The sensors used were all-solid-state ion-selective electrodes (ISEs) with a solid electrical contact made from a conductive epoxy composite. This is the usual configuration in our laboratories [11, 13]. The PVC membranes were formed by solvent-casting the sensor cocktail dissolved in THF. The formulation of the different membranes used is outlined in table 1.

In the first application, the sensor array used comprised 11 sensors altogether: two ion-selective electrodes for ammonium, two for potassium, two for sodium, two of a generic response to alkaline ions (one of each type: Generic 1 and Generic 2), one for nitrate, and one of a generic response to anions employing TOAB (Generic 3). One chloride electrode based on Ag/AgCl was included to complete the array.

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

Sensor	PVC (%)	Plasticizer (%)	Recognition element (%)	Reference
NH_4^+	33	BPA (66)	Nonactin (1)	[14]
K^+	30	DOS (66)	Valinomycin (3)[a]	[15]
Na^+	22	NPOE (70)	CMDMM (6)[a]	[16]
H^+	32.8	DOS (65.6)	TDDA (1)[a]	[17]
NO_3^-	30	DBP (67)	TOAN (3)	[18]
Generic 1	29	DOS (67)	Dibenzo-18-crown-6 (4)	[19]
Generic 2	27	DBS (70)	Lasalocide (3)	[20]
Generic 3	29	DBP (65)	TOAB (4)	[21]

[a] The formulation includes potassium tetrakis(4-chlorophenyl)borate as additive.

This chloride sensor was formed by AgCl electrodeposition on a disc of Ag, 5 mm in diameter. To obtain a homogeneous deposition, 0.1 mA was passed through the hydrolysis cell containing 0.1 M NaCl, for 1 h, using an Autolab PGSTAT (Eco Chemie, Utrecht, The Netherlands). The sensors for anions could not be duplicated because the data acquisition system had 11 channels.

The sensor array in the second application was a simplification of the previous one, in which only cations were considered. Therefore, the sensor array used comprised two sensors for each cation: ammonium, potassium, and sodium, plus two generic membrane formulations based on dibenzo-18-crown-6 and one additional ion-selective electrode for hydrogen ion, making nine sensors altogether.

2.3 *Apparatus*

Potentiometric measurements were performed with an electronic system developed in the laboratory. Each channel had a conditioning stage using an INA116 (Texas Instruments, Dallas, TX) instrumentation amplifier for adapting the impedance of each sensor. Measurements were differential *versus* the reference electrode (double junction Ag/AgCl electrode, Orion Model 90-02-00 Waltham, MA) and grounded with an extra connection in contact with the solution through a stainless steel wire. All channels were noise-shielded with their signal guard, and the outputs of each amplifier were filtered with a second-order active low-pass filter with −3 dB, 2-Hz cutoff frequency, using a UAF42 (Texas Instruments) universal filter. These filtered outputs were connected to a MPC506 (Texas Instruments) 16-channel analogue multiplexer. Digitalization was performed by an ADS7804 (Texas Instruments) analogue-to-digital converter. The complete data-acquisition system was controlled using an AT90S8515 (Atmel, San José, CA) microcontroller which also supplied the RS-232-C serial communication. This microcontroller was programmed making use of the interface ImageCraft Development Tools that employed language C. The program's main task was the multiplexer's control that selects each channel, the data acquisition with the analogue-to-digital converter and the transmission/reception of words as much of control as of data. Figure 1 depicts these interconnections in detail.

For telemetry tests, the physical communication channel was replaced with a pair of wireless radio modems (Data-Linc Group, Bellewe, WA), model SRM6100, operating in a 2.4–2.4835 GHz licence-free band employing advanced spectrum

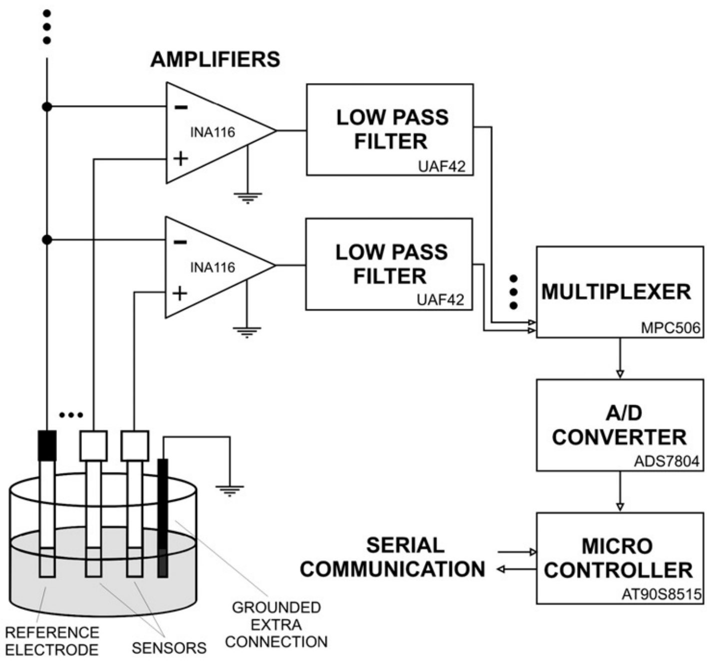

Figure 1. Block diagram of the interconnections of the used electronic system.

frequency hopping and error-detection technology. To obtain the best communication performance, a data transmission rate of 57,600 bauds was used. This speed of transmission allowed a distance of up to 15 miles to be reached under optimal conditions with line-of-sight between radios, according to the manufacturer. A peristaltic pump (Gilson Minipuls 2, Villiers-le-Bel, France) of four channels was used for the first application.

2.4 *Training and measurement procedure*

Before any application, the response of the system had to be assessed employing an ANN model. Measurements for training were done with solutions with a defined background. In order to compensate for the matrix effect, the background has to be as similar as possible to the real matrix, and so a different training process was done for each application of the electronic tongue. For the CSTR application, the background was a solution prepared in the laboratory with controlled amounts of each considered ion in water. For the second application, we used a 1/3 (v/v) mixture of water from 'Ignacio Ramírez' dam and Milli-Q water (Millipore, Billerica, MA) instead of generating it in the laboratory because of the complexity of the environmental samples.

Once the background was defined, different mixtures were prepared by additions of standard solutions of the different considered ions according to a statistical experimental design [22]. For the first application, 27 solutions were defined from a fractional factorial design with three levels of concentration and five factors (the five considered ions, 3^{5-2}). For the second application, 27 solutions were also defined from a complete factorial design with three levels of concentration and three factors

Table 2. Ranges of variation of the concentration of the analytes in the solutions used for the training process.

Species	First application (M)	Second application (M)
Ammonium	$5.3 \times 10^{-4} - 0.015$	$7.3 \times 10^{-6} - 9.7 \times 10^{-4}$
Potassium	$2.0 \times 10^{-3} - 0.015$	$3.8 \times 10^{-4} - 1.5 \times 10^{-3}$
Sodium	$5.0 \times 10^{-4} - 0.015$	$3.4 \times 10^{-3} - 0.015$
Chloride	$6.0 \times 10^{-4} - 0.015$	–
Nitrate	$2.7 \times 10^{-3} - 0.015$	–

(the three considered ions, 3^3). The ranges of variation of the concentration for the analytes in these solutions are summarized in table 2. For both applications, the different levels of ion concentration were defined taking into consideration the variability of the real samples in each case and the complexity of the training space. For the first application, these ranges of variation were chosen arbitrarily but taking into account that the concentrations could increase in several decades for some ions, since the fertilizer is highly concentrated. For the second application, the concentrations of ammonium, potassium, and sodium ions in the studied dam and their variations defined the different levels of concentration in the experimental design [23].

In order to correct the possible drifts, the inputs in the neural network were relative measurements of each sensor with respect to a reference solution periodically checked. We also included as inputs the solution temperature in order to compensate any influence in the response of these potentiometric sensors. A laboratory-made temperature probe based on an LM35 integrated circuit (National Semiconductor, Santa Clara, CA) was employed together with the array of electrodes.

For the proper verification of the electronic tongue performance, a set of solutions was used, the test set, which does not participate in the training process. The test set was formed by 10 synthetic solutions prepared in the same way but with concentrations generated randomly inside the training space.

These 37 prepared solutions, 27 for training and 10 for testing, were measured in three turns for the CSTR application; one with all the solutions at room temperature (around 24°C), another with half of the solutions at lower temperature (around 10°C) and the third with the other half at a higher temperature (around 35°C). For the second application, all the solutions were measured at these three levels of temperature.

2.5 *Software*

The ANNs tested were trained and evaluated using the routines available to the Neural Network Toolbox v. 4.0, which are optional add-ons in the Matlab v.6.1 (Maths Works, Inc. Natick, MA) environment. Sensor readings were acquired on the PC using custom software written in Visual Basic (Microsoft, Seattle, WA). The experimental data were fitted to a negative exponential function, used in the first application, with Sigmaplot 8.0 (SPSS Inc. Chicago, IL).

2.6 *First application: the CSTR*

The first application of the electronic tongue involved monitoring a CSTR by modelling the concentration of ammonium, potassium, sodium, chloride, and nitrate,

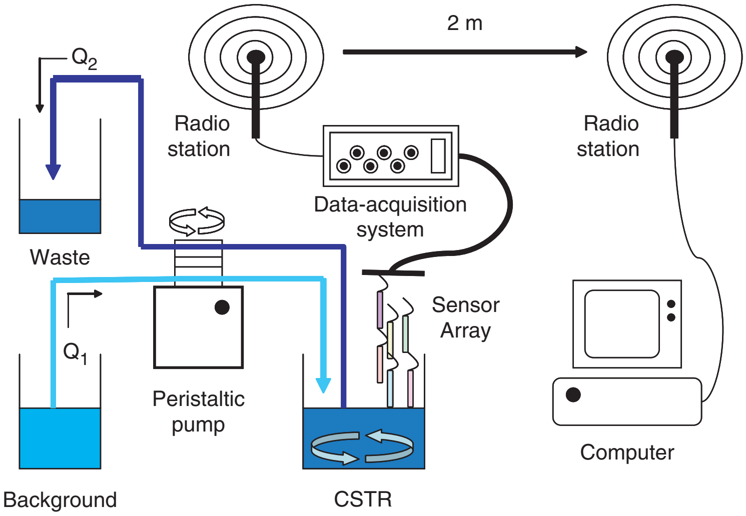

Figure 2. Block diagram of the proposed manifold for monitoring the concentration of ammonium, potassium, sodium, chloride, and nitrate in a CSTR.

when a volume of concentrated guano fertilizer was added to a controlled background. Figure 2 depicts the whole system.

The selected steady-state working conditions used an input flow rate (Q_1) equal to the output flow rate (Q_2), and consequently the volume of the tank did not change. With these conditions, the equation that relates the concentration of the species inside the reactor to time is a negative exponential function (equation (1)):

$$C(t) = C_0 \exp\left(-\frac{Q}{V}t\right), \tag{1}$$

where $C(t)$ is the concentration in time t, C_0 is the initial concentration, Q is the flow rate, and V is the volume of the tank. $\tau = V/Q$ is the time constant for the system. Under the assumption of perfect mixing, this time constant is the mean residence time.

In the proposed system, the volume of the tank was 1.5 L, and it was full of background solution at the beginning. The flow rate was controlled by a peristaltic pump and was fixed to 1.0 mL min^{-1}, each channel. Consequently, the residence time for this CSTR (τ) was 1.04 days. The tank was inoculated with 10 mL of water from the Nespres stream to imitate the real biodegradation conditions in a surface water. When it passed 1 h, approximately, 15 mL of the liquid fertilizer was added into the tank, and one measurement per sensor was done every 20 min. These readings, once amplified and filtered, were transmitted to the computer using the radio link. The system was left in continuous operation for more than 3 days, which served to validate the different parts of the monitoring system.

2.7 *Second application: 'Ignacio Ramírez' dam*

The second application of the electronic tongue involved the simultaneous monitoring of the concentration of ammonium, potassium, and sodium in the

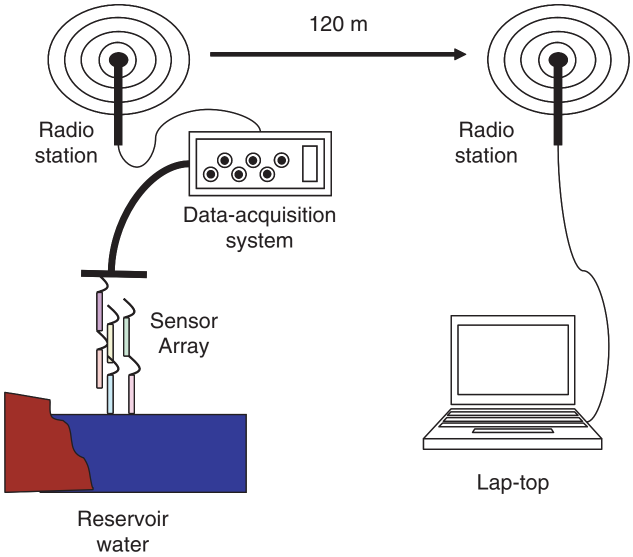

Figure 3. Block diagram of the proposed manifold for monitoring the concentration of ammonium, potassium, and sodium in 'Ignacio Ramírez' reservoir.

'Ignacio Ramírez' dam. This reservoir is about 500 km^2 area with fluctuating water levels. The dam was built in 1964 on 'La Gavia' river, State of Mexico. It is located in a rural, livestock, and agricultural zone. The rates of soil erosion are high and excessive sediments run off into the water. In addition, the climate is temperate and subhumid, with summer rains from July to September [23].

The electronic tongue system was validated before the on-site application with a set of real water samples collected from five different points of the dam. Once filtered, different dilutions of these samples with Milli-Q water were processed by the system. Results were compared with their composition determined by reference methods of widespread use: ammonium was determined by the Nessler reaction, and potassium and sodium were quantified by atomic absorption spectroscopy. Once the applicability of the system in real samples was demonstrated, the on-site monitoring was done, as depicted in figure 3. Sensor readings were taken every minute for 2 h. The laptop computer was sited 120 m from the point of monitoring, and the data were transmitted by the radio link.

3. Results and discussion

3.1 *Building of the ANN models*

Selecting the topology of an ANN is a first obstacle, because of the difficulty in predicting an optimum configuration in advance. The ANN structure for the best modelling of a sensor array is obtained by a trial-and-error procedure. This process includes a combination of the number of neurons of the hidden layer and the transference function used within. These characteristics will define the specific combination leading to the best modelling ability [24].

We initially fixed the following parameters, which were common for the two optimized ANNs models: a linear transfer function of the output layer (*purelin*) and a single hidden layer of neurons; these selections are based on previous experience with electronic tongues using potentiometric sensors [25]. The learning strategy used was Bayesian Regularization and employed for its internal parameters, a learning rate of 0.1 and a momentum of 0.4 selected from preliminary tests. The modelling capacity of the ANN was examined in terms of the root mean squared error (RMSE).

When compared with others, the strategy selected for the learning process (Bayesian Regularization) provided a better RMSE value, a greater consistency between the predicted and obtained values for the training, and a higher significance for the external test set. Besides, an internal validation subset of samples was not necessary, as it avoids overfitting by other means [26]. Considering the non-linear behaviour of the sensors, two different non-linear transfer functions were considered for the hidden layer, a sigma-shaped function named the *tansig* function [27] and a logistic function represented by the *logsig* function.

3.1.1 ANN model for the CSTR. For this case, the ANN model had 12 input neurons (11 sensors from the array plus the temperature) and five output neurons (the five modelled analytes). After the systematic evaluation of configurations, the best training results were obtained with the *tansig* function and five neurons in the hidden layer; these conditions provided a RMSE value of 0.00575 M for the external test set, those samples not intervening in training. Figure 4 illustrates the global behaviour of the modelling system for the external test set, displaying the obtained values for ammonium, potassium, sodium, chloride, and nitrate ions. The figure compares predicted *versus* expected concentrations. Predictions were good for the individual ions and for their mixtures. The figure also shows the linear regression results for the five individual species. The accuracy of the obtained response approached ideality, with unity slopes and zero intercepts, in the external test set (all confidence intervals were calculated at the 95% confidence level). For chloride, the confidence interval of the slope did not include unity, but a good regression coefficient was obtained as well as a zero intercept. Especially good results were obtained for ammonium and sodium ions, with experimental lines practically superimposed on the theoretical ones.

3.1.2 ANN model for the 'Ignacio Ramírez' dam. For the ANN model in this case, the number of input neurons was 10 (nine sensors from the array plus the temperature), and the number of output neurons was three (the three considered cations). Again, among the different configurations, the best results were obtained with the *tansig* function and nine neurons in the hidden layer, which provided RMSE = 0.0014 M for the test set. Figure 5 shows the behaviour of the optimized model for the external test set ammonium, potassium, and sodium concentrations. The linear regression results between predicted and expected values for the test set are also shown. All confidence

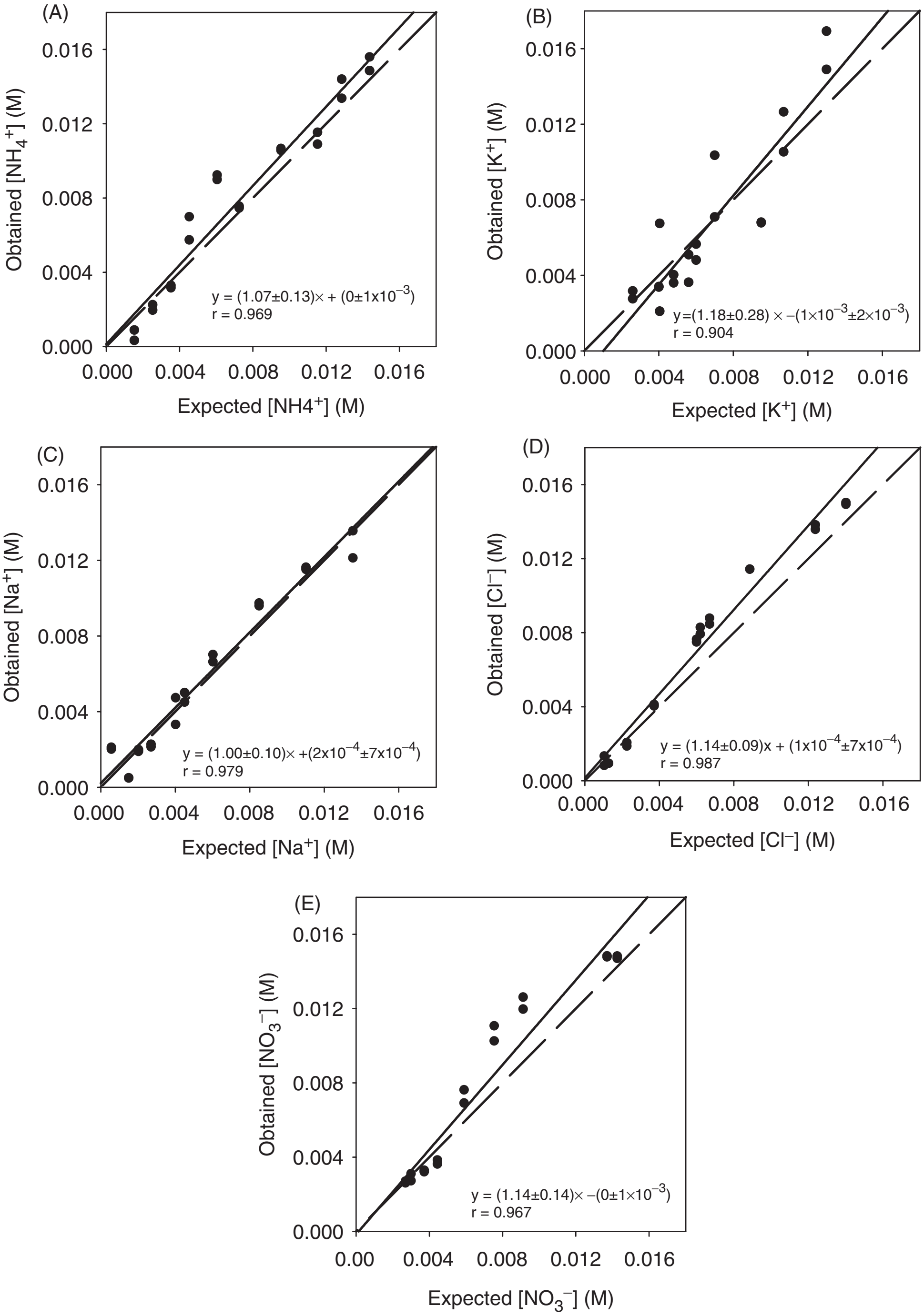

Figure 4. Modelling performance achieved for the optimized ANN with the samples of the external test set: (A) ammonium, (B) potassium, (C) sodium, (D) chloride, and (E) nitrate, for the CSTR application. The dashed line corresponds to ideality, and the solid line is the regression of the comparison data. Each sample was processed twice at three different temperatures.

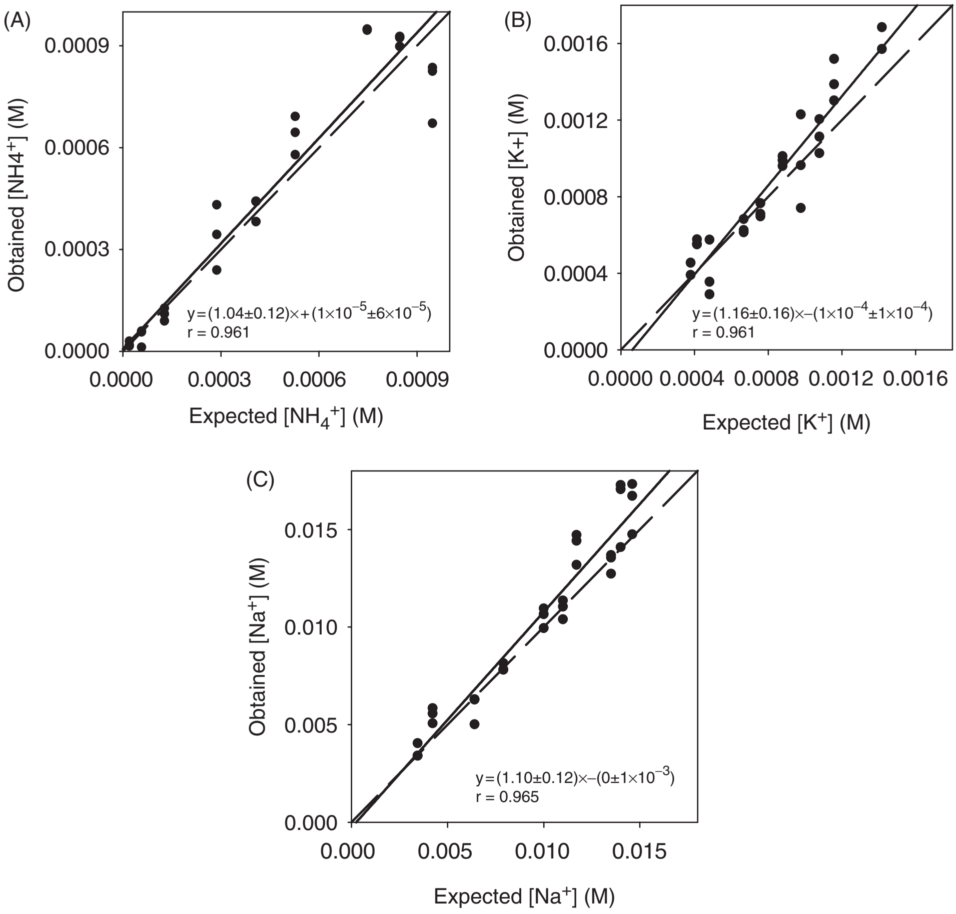

Figure 5. Modelling performance achieved for the optimized ANN with the samples of the external test set: (A) ammonium, (B) potassium, and (C) sodium, for the dam application. The dashed line corresponds to ideality, and the solid line is the regression of the comparison data. Each sample was processed three times at three different temperatures.

intervals included unity slopes and zero intercepts at the 95% confidence level for the three considered ions.

3.2 *First application: the CSTR*

With the previously optimized ANN, the primary data were turned into analytical information. The concentrations of ammonium, potassium, sodium, chloride and nitrate, once the fertilizer was added, were continuously monitored for more than 3 days, from which the first 24 h were analysed in more detail. Figure 6 represents this detailed period of the experiment, where the concentrations of the considered ions predicted by the electronic tongue, together with the solution temperature, are shown.

The results demonstrate that the electronic tongue corrected the temperature effect, as observed by the smooth variation of concentrations. The figure shows that ammonium, more affected by biodegradation, disappears more quickly than the other

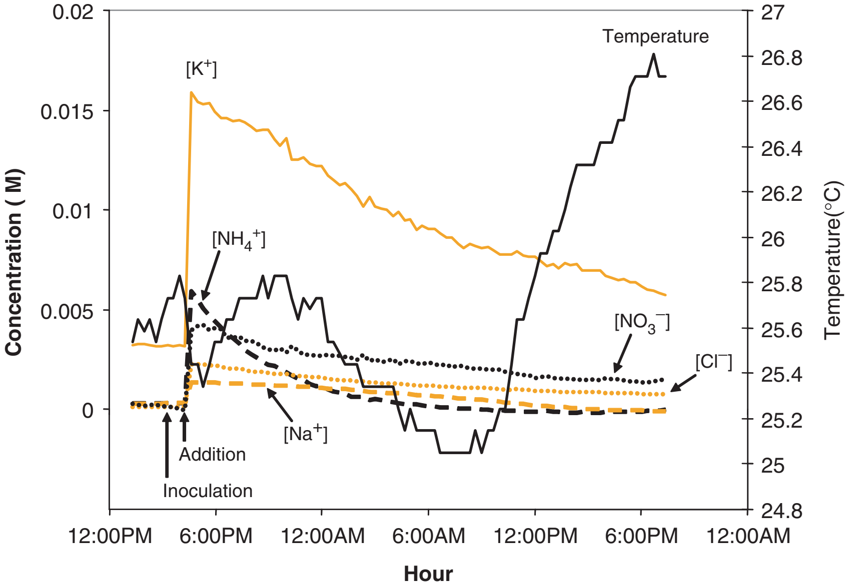

Figure 6. Representation of the concentration values predicted by the electronic tongue for the considered ions: ammonium, potassium, sodium, chloride, and nitrate, in the CSTR during 24 h continuous monitoring. The variation of temperature according to the cycle of day and night is observed (experiment carried out in the summer).

Table 3. Residence time values for the five considered ions obtained from the fitting of the experimental data at the 95% confidence level.

Analyte	Residence time (days)	Regression coefficient
Ammonium	0.170 ± 0.004	0.999
Potassium	1.08 ± 0.03	0.994
Sodium	0.62 ± 0.05	0.935
Chloride	0.99 ± 0.02	0.995
Nitrate	1.02 ± 0.02	0.984

species that display equivalent behaviour. In fact, the fitting of these experimental curves to equation (1) yielded the residence time values summarized on table 3.

For chloride, nitrate, and potassium, their τ is indistinguishable from the fixed residence time of the system (1.04 days), demonstrating that these ions experience only the typical dilution of the CSTR. Sodium has a lower residence time, a worse regression coefficient, and a worse error. This effect can be caused by loss or adsorption of sodium ions on the glass walls of the tank or by the fact that the sodium concentration is the lowest during all the experiment, and it is considerably affected by determination uncertainty. Ammonium has a clear diminished time constant, demonstrating that a biochemical reaction is occurring inside the CSTR depleting ammonium. Considering that ammonium is the unique controlled substance that can be oxidized, this behaviour can be a consequence of the natural biodegradation by the environmental microorganisms that were introduced in the tank.

Table 4. Relative errors obtained of the logarithm of the concentration of the three ions in real water samples from 'Ignacio Ramírez' dam[a].

Sample	Relative error (%) NH_4^+	Relative error (%) K^+	Relative error (%) Na^+
1	−1.6	−7.9	−10.7
2	0.2	−2.6	−8.5
3	−2.2	−2.0	−11.2
4	−1.4	−1.2	−3.5
5	12.9	−4.7	−9.7
6	−2.2	−2.1	−7.9
7	7.3	−1.1	−12.0
8	11.9	−0.4	−3.6
9	1.2	−8.9	−11.0
10	−2.2	−2.6	−8.1
11	−2.2	−3.2	−11.4
12	−5.9	−2.3	−3.3
Mean relative error (%)	4.3	3.2	8.4

[a] The RSD obtained for the determination of the reference value of ammonium was between 0.8 and 1.25%, and for potassium and sodium, between 0.2 and 1.5%.

3.3 *Second application: 'Ignacio Ramírez' dam*

In this second application, the proposed system was first applied to real samples from the 'Ignacio Ramírez' dam. The predicted relative errors of the logarithm of the concentration of the three ions are summarized on table 4 and show that the errors are in specific cases higher than 10%, although lower on average. For example, we obtained a mean relative error of 3.2% in the determination of potassium. All the obtained errors for sodium and potassium were negative because of the influence of the matrix, which is highly saline and specially complex in this reservoir. The concentrations predicted by the electronic tongue were slightly lower than those obtained by reference methods. This effect especially affects the determination of sodium, the more concentrated species, since a mean relative error of 8.4% was obtained.

Once the system was validated with real samples, the concentration of ammonium, potassium, and sodium was continuously monitored on-site for 2 h approximately. Figure 7 shows the concentration of the considered ions that was predicted by the electronic tongue, together with the recorded dam water temperature.

Sudden changes in temperature, observed in the graphics, were caused by the periodic measurement of the reference solution, which was at a higher temperature. Nevertheless, the system is able to correct the effect of these temperature changes, given that alterations in the calculated concentrations of the three ions were not observed. The predicted concentration of sodium was around 0.006 M; for potassium, the obtained concentration was around 0.001 M with a slight trend to decrease, while the ammonium concentration was between 1.5×10^{-5} and 4×10^{-5} M. The predictions of the content in ammonium and potassium were close to the concentrations determined by reference techniques for the real samples. However, the concentration for sodium determined by the electronic tongue was lower. As we have explained before, the matrix effect was especially strong for sodium, although its presence was correctly counterbalanced for the calculation of ammonium and potassium employing the ANN model.

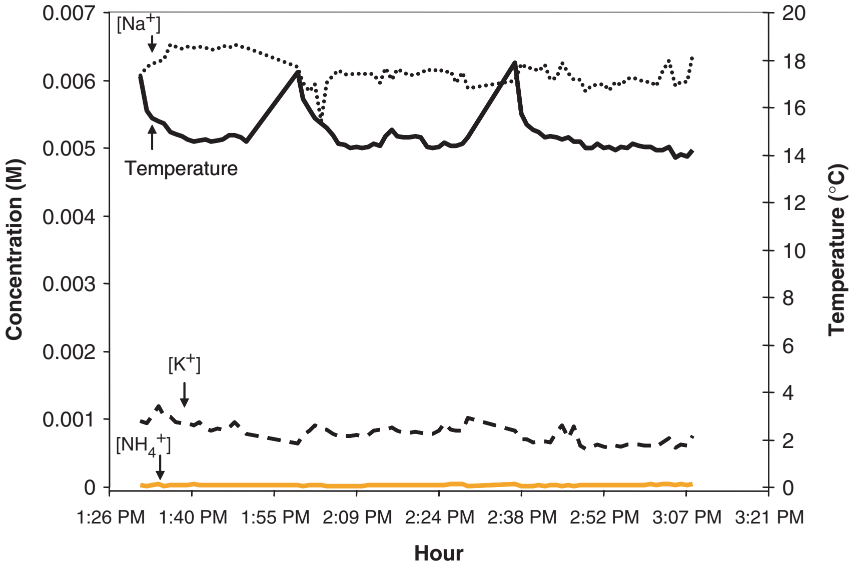

Figure 7. Representation of the concentration values predicted by the electronic tongue for the cations considered: ammonium, potassium, and sodium, during the application in the 'Ignacio Ramírez' dam. The water temperature is also represented.

4. Conclusions

Two different electronic tongue systems have been developed and optimized for environmental monitoring applications using potentiometric sensors and ANN models: one, to monitor the concentration of ammonium, potassium, sodium, chloride, and nitrate inside a CSTR that imitates real biodegradation conditions in surface waters; the second to monitor the concentration of ammonium, potassium, and sodium in the 'Ignacio Ramírez' dam (Mexico). For the first application, it has been demonstrated that the electronic tongue approach allows us to monitor accurately the dilution of the five considered ions, as well as the effect of the natural biodegradation. For the second application, the results show that the proposed electronic tongue allows us to determine the content of ammonium, potassium, and sodium in real water samples from the studied dam, but the calculated concentration of sodium is lower than that obtained by reference methods because of the high matrix effect. One alternative to correct this effect would be to increase the number of sensors used in the array, incorporating new species not considered until now. In any case, the two systems are able to compensate for natural temperature variations by incorporating the solution temperature as input in the ANN model. Although the two considered experiments show a measuring time of several hours, in previous works we have checked that the applicability of the numerical model, in terms of aging of the electrodes, for a system like this is longer than one month [28]. The radio link used here demonstrated a robust operation, so we can conclude that systems such as that studied here can be applied to automatic wireless monitoring for environmental applications.

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