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A review of the use of the potentiometric electronic tongue in the monitoring of environmental systems

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ABSTRACT

This paper introduces electronic tongue systems for remote environmental monitoring applications. This new approach in the chemical sensor field consists of the use of an array of non-specific sensors coupled with a multivariate calibration tool which may form a node of a sensor network. In our work, the proposed arrays were made up of potentiometric sensors based on polymeric membranes, and the subsequent cross-response processing was based on a multilayer artificial neural network model. Two cases are described: the environmental monitoring of ammonium pollutant plus alkaline ions at different measuring sites in the states of Mexico and Hidalgo (Mexico), and the monitoring of heavy metals (Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+}) in open air waste streams and rivers heading down the Gulf of Mexico.

1. Introduction

Water is fundamental for all the Earth's life forms and a key issue in social and economical development. Nowadays, due to the increase in pollution, natural water sources have became insufficient to supply all the necessities. Access to potable water and the assessment of its environmental quality, normally through physicochemical monitoring, are emerging issues worldwide.

An important aspect in the monitoring of water quality is the identification of pollution events in order to determine the appropriate methodologies and to preserve public health and ecosystems.

Currently, the most often used strategy is performing off-line monitoring (Bonastre et al., 2005). This strategy starts with the sample collection and its subsequent chemical analysis employing conventional laboratory equipment (e.g., atomic spectroscopy, fluorometry or high-performance liquid chromatography) (Gentili et al., 2001), making it difficult for real-time monitoring applications. In any event, laboratory procedures are mandatory to reliably determine the chemical parameters and the presence of pollutants at very low concentrations. Off-line monitoring is suitable to monitor slight contamination events which could affect either the environment or the population exposed over long periods of time. In these cases, the time needed between the sample analysis and the reported results loses importance.

For real-time monitoring applications, in-line information about the current changes in water is required. In-line procedures are performed in situ, directly inside the process under study. For this reason, automatic analysis systems are highly valued. In this sense, recent use of chemical sensors has laid the groundwork to generate initial site-related information. Robustness, price, versatility and speed of response are just some of the attributes that sensors can offer for measuring the wide range of environmental elements at different sites in a locality (De Marco et al., 2007). Unfortunately, there are few optimally operating chemical sensors that may function without any interference or matrix effect.

In the past decade, a new concept in the field of sensors has appeared to facilitate different monitoring needs. Known as Electronic Tongues (ETs), these innovative systems employ an array of non-specific sensors plus data processing methods in order to interpret the overdetermined complex responses of the sensors and relate them with their analytical meaning (Vlasov et al., 2005).

The idea behind this concept is to use an appropriate sensor array that enables us to simultaneously determine a large number of species present in the sample as long as supplied data is rich enough; that is, cross-sensitivity of the different sensors to the different species exists, or co-linearity is absent. In addition,

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common problems such as drifts, non-idealities or interferences, often present in measurements with this kind of sensors (De Marco et al., 1997), can be corrected in the data processing stage. In this way, it is possible to conduct periodic recalibration checks to update the response model, as well as to apply a predefined ageing correction factor (Tønning et al., 2005). This procedure has been useful to correct electronic tongue environmental operation for unattended periods longer than one month (Gutiérrez et al., 2007a). The idea is to use calibration models robust enough to counteract sensors' ageing and temperature effects. Similarly, the data processing may offset any matrix or interference effect from the sample itself. With this methodology, it is possible to achieve a parallel determination of a large number of different species, while importantly any interference effect is solved using advanced chemometrics tools (Gutiérrez et al., 2007b).

Thus, by using ETs it is possible to provide multicomponent analytical information in real time with a direct, relatively simple measuring setup and low cost. In the same way, it is feasible to overcome the difficulties of analyzing the sensors' raw data by building calibration computer models. In theory, these models may be developed after careful training for specific chemical species as sensed by the system, or also for complex situations such as algal blooms (Marsili-Libelli, 2004); this situation is difficult to infer from a single chemical analysis but may be extracted through properly trained artificial intelligence tools fed with data from a multisensory system.

In the recent years, there have been published contributions on the use of ETs for environmental monitoring purposes. For example, an array of voltammetric sensors was developed and used to detect disturbances in the tap water quality; they were identified through the use of Principal Component Analysis (PCA) (Krantz-Rülcker et al., 2001), as a human expert would proceed. A similar approach was also used for the on-line monitoring of industrial processes (Winquist et al., 2005). Similar ETs have been developed employing arrays of chalcogenide glass sensors, which have been applied to monitor metal ions in river and ground waters (Legin et al., 1996; Di Natale et al., 1997). In our laboratory, we have gained some experience in a research line dealing with ETs. Qualitative and quantitative applications for different purposes have been developed, most of which are based on arrays of ion-selective electrodes (ISE) constructed using polyvinyl chloride (PVC) polymeric membranes. With these, Artificial Neural Networks (ANNs) have been used as the data processing tool to extract the sought information, solve the cross-response effects and offset the non-linearities present (Gallardo et al., 2003a,b, 2005; Gutiérrez et al., 2007a,b).

But, as a major streamline in the field, the information obtained through environmental surveillance sensor sites, or nodes, may be further coupled with data communication and electronics to develop a broader monitoring system, referred as sensor network (SN). A sensor network therefore represents the merging of measurements with communications intended to monitor and record the conditions at diverse locations in order to grasp the instant, global situation of a region or a system.

Up to now, the most easily networked parameters are those of a physical nature, e.g., temperature, humidity, pressure, wind direction and speed, illumination, etc., given that many sensors are available (Culler et al., 2004; Zhao and Guibas, 2004). Chemical information is also clearly demanded, though fewer solutions are available. Obviously, the supply of high-quality raw data with enough variety and sufficient detail can be one of the bottlenecks in obtaining reliable environmental models (Silberstein, 2006). Specifically, in water quality monitoring, SN try to focus on topics such as eutrophication, salinization, acidification, microbial outbreak and heavy metal pollution, among others, e.g., wherever a specific contamination problem is known to exist (Strobl and Robillard, 2008).

Given the fact that each node in SNs may be usually equipped with transducers, microcomputer, transceiver (which can be hard-wired or wireless) and power source, their underlying protocol may be highly compatible with electronic tongue systems, with the complex data processing both performed in-site (for example, using an embedded system) or done at a central control computer, where the different response models of the different nodes are run. In the end, the scenery envisaged may well be a smart environment to enable and enrich adaptive and dynamic interaction of human activities. But to succeed, cooperation between different field developers and researchers is needed in order to overcome the limitations and conceive improvements or common ground in current methodologies, as a means of developing profitable and feasible solutions.

The aim of this communication is to review the application of two different electronic tongue systems as potential nodes in sensor networks, amenable to developing in-site environmental monitoring tasks (Fig. 1). The proposed ETs were made using arrays

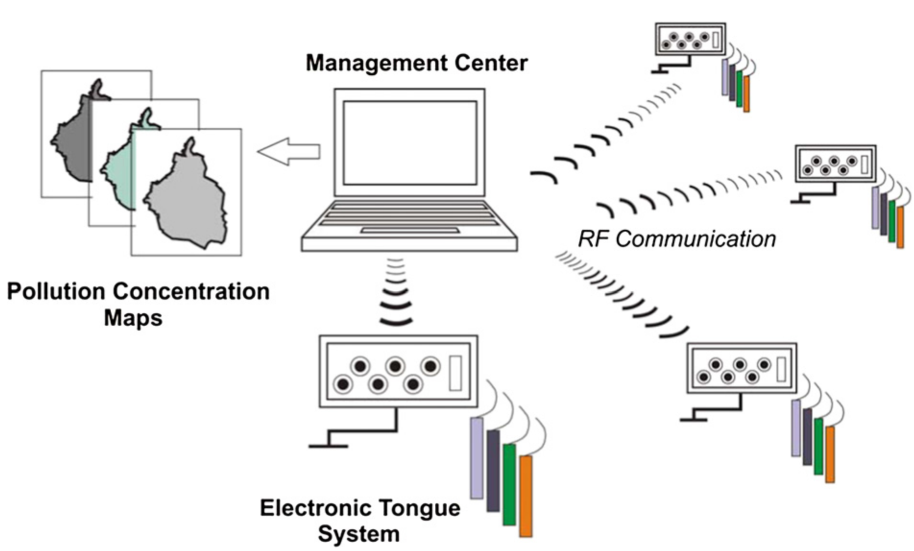

Fig. 1. Block diagram of a system for automatic remote measurements of a region combining electronic tongues technology and sensor networks.

of potentiometric sensors, in this case employing PVC membranes with common formulations. As the data processing stage, ANNs were used to build response models in order to predict concentrations of polluting species, departing from the cross-response signals from the array plus temperature perturbation to sensor operation. To demonstrate the functionality as an SN node, a digital radio link was established between the different monitoring locations and a personal computer as the central node where the data were processed and stored. As in the environmental applications carried out, two different situations were studied, one to quantify sodium, ammonium and potassium in the Rio Salado (Mexico) and the other to determine heavy metals (cadmium, copper, lead and zinc) in open air waste streams heading down the Gulf of Mexico.

2. Experimental

2.1. Reagents and solutions

For the first application case, the quantitative determination of ammonium, sodium and potassium, the ion-selective PVC membranes were prepared from high-molecular-weight PVC (Fluka, Buchs, Switzerland) and the plasticizers bis(1-butylpentyl) adipate (BBPA), dioctyl sebacate (DOS), 2-nitrophenyloctylether (NPOE) and dibutyl sebacate (DBS) (all from Fluka). 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 tri-N-dodecylamine (TDDA, hydrogen ionophore I, Fluka). Additionally, two generic response recognition elements were used: dibenzo-18-crown-6 and lasalocide, both for cations. All the components of the membranes were previously dissolved in tetrahydrofuran (THF, Fluka).

For the second application, the quantitative determination of cadmium, copper, lead and zinc, the ion-selective PVC membranes were prepared from high-molecular-weight PVC (Fluka) and the plasticizers (10-Hydroxydecyl) butyrate (ETH 264), 2-nitrophenyloctylether (NPOE), bis(1-butylpentyl) adipate (BBPA), dibutylphtalate (DBP) and dibutyl(butyl) phosphonate (DBBP) (Fluka). The ionophores used were N,N,N′,N′-Tetrabutyl-3,6-dioxaoctanedi(thioamide) (Cadmium Ionophore I), *o*-Xylylenebis(N,N-diisobutyldithiocarbamate) (Copper(II) Ionophore I), S,S′-Methylenebis(N,N-diisobutyldithiocarbamate (Lead Ionophore II), *tert*-Butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) (Lead Ionophore IV), Tetrabutylthiuram disulfide (Zinc Ionophore I), 3,7,12,17-Tetramethyl-8,13-divinyl-2,18-porphinedipropionic acid disodium salt (Zinc Ionophore II) and tri-N-dodecylamine (TDDA, hydrogen ionophore I), all from Fluka. In addition, two generic response recognition elements were used: tetrabenzyl pyrophosphate (Fluka) and [2,2′]-Furildioxime monohydrate (Fluka).

The materials used to prepare the solid electrical contact were the epoxy resin components Araldite M and Hardener HR (both from Fluka) and graphite powder (50 μm, Merck) as a conducting filler. All other reagents used were of analytical grade, pro-analysis or the equivalent.

Both electronic tongues were used to predict the concentration of species of water samples studied from different sources. These samples were taken from different places of environmental concern in Mexico: Zumpango lake, a well, an irrigation channel (20°05′22.14′ N, 99°14′56.05″ W elevation; 2079 m) and Rio Salado (local name Hueypoxtla, 20°05′23,65″ N, 99°13′56.31″ W, 2069 m above sea level).

2.2. Sensor array

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 (Gallardo et al., 2003a; Alegret and Martinez-Fábregas, 1989). The PVC membranes were formed by solvent-casting the sensor cocktail dissolved in THF over the solid contact.

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

Sensor	PVC (%)	Plasticizer (%)	Ionophore (%)	Reference
NH_4^+	33	BPA (66)	Nonactin (1)	Davies et al. (1988)
K^+	30	DOS (66)	Valinomycin (3)[a]	Shen et al. (1998)
Na^+	22	NPOE (70)	CMDMM (6)[a]	Tamura et al. (1982)
H^+	32.8	DOS (65.6)	TDDA (1)[a]	Schulthess et al. 1981)
Generic 1	29	DOS (67)	Dibenzo-18-crown-6 (4)	Umezawa (1990)
Generic 2	27	DBS (70)	Lasalocide (3)	Suzuki et al. (1988)

[a] The formulation included potassium tetrakis(4-clorophenyl)borate as additive.

Table 2
Formulation of the ion-selective membranes employed in the construction of the potentiometric sensor array.

Sensor	PVC (%)	Plasticizer (%)	Ionophore (%)	Reference
Cd^{2+}	34	ETH 264 (65)	N,N′,N′-Tetrabutyl-3,6-dioxaoctanedi (thioamide) (1)[a]	Schneider et al. (1980)
Cu^{2+}	57.2	NPOE (34.3)	*o*-Xylylenebis(N,N-diisobutyldithiocarbamate) (6.9)[a]	Kamata et al. (1989)
Pb^{2+} (1)	37.2	NPOE (49.6)	S,S′-Methylenebis(N,N-diisobutyldithiocarbamate) (11.2)	Kamata and Onoyama (1991)
Pb^{2+} (2)	33	NPOE (65.65)	*tert*-Butylcalix[4]arene-tetrakis (N,N-dimethylthioacetamide) (1)[a]	Malinowska et al. (1994)
Zn^{2+} (1)	40.22	NPOE (53.62)	Tetrabutylthiuram disulfide (2.3)[a]	Kojiama and Kamata (1994)
Zn^{2+} (2)	55.25	DBBP (41.4)	3,7,12,17-Tetramethyl-8,13-divinyl-2,18-porphinedipropionic acid disodium salt (2.76)[b]	Gupta et al. (2003)
H^+	32.8	DOS (65.6)	tri-N-dodecylamine (1)[a]	Schulthess et al. (1981)
Generic 1	34.5	BPA (63.2)	Tetrabenzyl pyrophosphate (2.3)[a]	Xu and Katsu (2000)
Generic 2	34.5	DBP (62)	[2,2′]-Furildioxime monohydrate (4)[a]	Singh and Mehtab (2007)

[a] The formulation included potassium tetrakis(4-clorophenyl)borate as additive.
[b] The formulation included sodium tetra borate as additive.

For the first application the monitoring of alkaline species, the sensor array included a total of nine sensors: two replicate ion-selective electrodes for ammonium, two for sodium, two for potassium, one for hydrogen and two of a generic response to alkaline ions (one of each type), as optimized in preliminary studies (Gallardo et al., 2005). The formulations of the ion-selective membranes employed in the array are summarized in Table 1.

In the second application, for heavy metals, the sensor array was formed by 11 electrodes: two for cadmium, two for copper, two for lead (one of each type), two for zinc (one of each type), one for hydrogen ion and two of a generic response to metals (one of each type). The formulations of the ion-selective membranes employed in this array are summarized in Table 2.

2.3. Apparatus

Potentiometric measurements were performed with an electronic system developed in our laboratory (Gutiérrez et al., 2007a). Each channel had

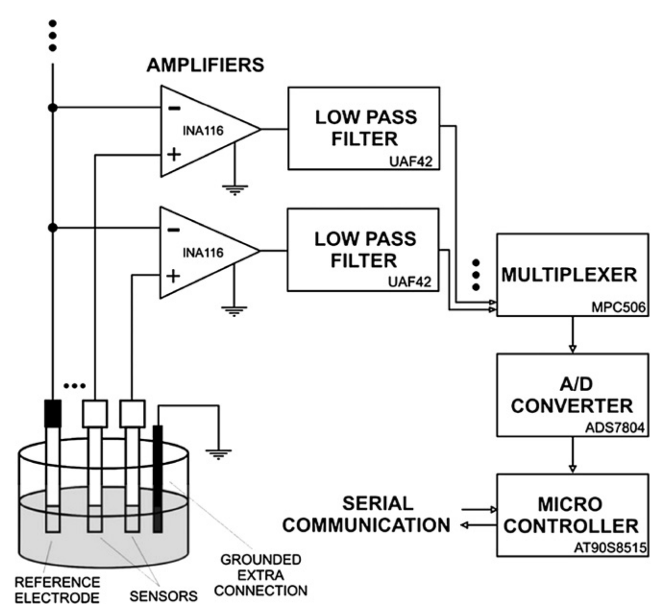

Fig. 2. Block diagram of the interconnections of the electronic system used.

Table 3
Ranges of variation in the concentration of the analytes in the solutions used for the training process in the first application.

Ion	Concentration ranges (M)
$[Na^{+}]$	3.4×10^{-3}–1.5×10^{-2}
$[NH_4^{+}]$	7.3×10^{-6}–9.7×10^{-4}
$[K^{+}]$	3.8×10^{-4}–1.5×10^{-3}

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 an MPC506 (Texas Instruments) 16-channel analogue multiplexer. Digitalization was performed by an ADS7804 (Texas Instruments) 12-bit 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 from 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 of both control and data. The time involved in accessing the multiplexer channels, performing the analogue-digital conversion and subsequent transmission was 15.5 μs. In standby mode, the system consumes about 100 mW. Fig. 2 depicts these interconnections in detail. For telemetry tests, the physical communication channel was replaced by a pair of wireless radio modems (Data-Linc Group, Bellevue, WA), model SRM6100, operating in a 2.4–2.4835 GHz licence-free band employing advanced spectrum 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 and a maximum power consumption of 500 mW according to the manufacturer.

2.4. Training and measurement procedure

The ANN response model had to be built before the application. The objective of this step is to determine the ANN configuration that best describes the response of the system. For this purpose, measurements were taken employing standard solutions with a defined background that have to match the real samples analyzed in order to counterbalance any matrix effect. Due to the difficulty of reproducing the background of an environmental sample, we decided to employ a 1/3 dilution (v/v) of a natural water sample taken from the Rio Salado in Milli-Q water (Millipore, Billerica, MA). The next step was to prepare a set of mixtures of the different ions considered. These were carried out through additions of a standard solution over the previously defined background.

The training of the first electronic tongue was performed from the measures of a sensor array corresponding to a set of samples defined from a Factorial Design (FD). The use of FDs allows several levels of variables to be studied, as well as the relationships between them, to be distinguished with a minimum experimental effort (Montgomery, 2000). In this way, 27 solutions were defined from a complete factorial design with three levels of concentration and three factors (the three ions considered, 3^3). The analytes variation ranges in these solutions are summarized in Table 3. The ranges were in accordance with the expected levels on the natural samples. Apart from this set of solutions defining the training space, 10 additional synthetic samples were prepared for a test subset in order to evaluate the performance of the electronic tongue. These additional samples did not participate in the training process and their concentration ranges were distributed randomly inside the training space. In order to correct possible drifts, the inputs to the neural network of each sensor were periodically checked against a background solution.

For the second case studied, that of heavy metals, 27 solutions were defined from a fractional factorial design with three levels of concentration and the four ions considered (3^{4-1}) (Gutiérrez et al., 2007b). The ranges of variation of the concentration for the analytes in these solutions are summarized in Table 4. In this case, 10 additional synthetic samples were also included in a test subset. As before, these were distributed randomly inside the training space.

Table 4
Ranges of variation in the concentration of the analytes in the solutions used for the training process in the second application.

Ion	Concentration ranges (M)
$[Cd^{2+}]$	5.2×10^{-8}–2×10^{-6}
$[Cu^{2+}]$	5.2×10^{-7}–2×10^{-5}
$[Pb^{2+}]$	5.2×10^{-8}–2×10^{-6}
$[Zn^{2+}]$	5.2×10^{-7}–2×10^{-5}

2.5. Software

The ANNs tested were trained and evaluated using the routines available to the Neural Network Toolbox v. 4.0.6, which are optional add-ons in the Matlab v.7.1 (Math Works, Inc., Natick, MA) environment. Sensor readings were acquired on the PC using custom software written in Visual Basic (Microsoft, Seattle, WA). Information about the developed software is available by contacting the authors.

2.6. Determining natural water samples

Once we had trained and tested the ET system using synthetic solutions, the next step was to apply them in natural water samples from different sources. Several water samples were collected from different areas of the state of Hidalgo (Mexico). All samples were filtered before use and no other pretreatment was performed except in the case of the heavy metals; in this case buffering conditions have to be ensured. For these samples, the pH was adjusted at 4.5 using acetic/acetate buffer. The measurements were carried out off-line, employing the same methodology that we had previously used with the synthetic samples.

2.7. Environmental networked monitoring

Simultaneous monitoring of ammonium, potassium and sodium was carried out in the Rio Salado also called Hueypoxtla (Hidalgo, Mexico), a river fed by the runoff water in the rainy periods. The river crosses different inhabited nuclei and continues heading northwards to the Tula River, from which it becomes an indirect tributary. The monitoring site was situated near the village of Doxey. At that point, the river may contain polluting species coming from the waste waters of villages and industries and runoffs from the crop fields.

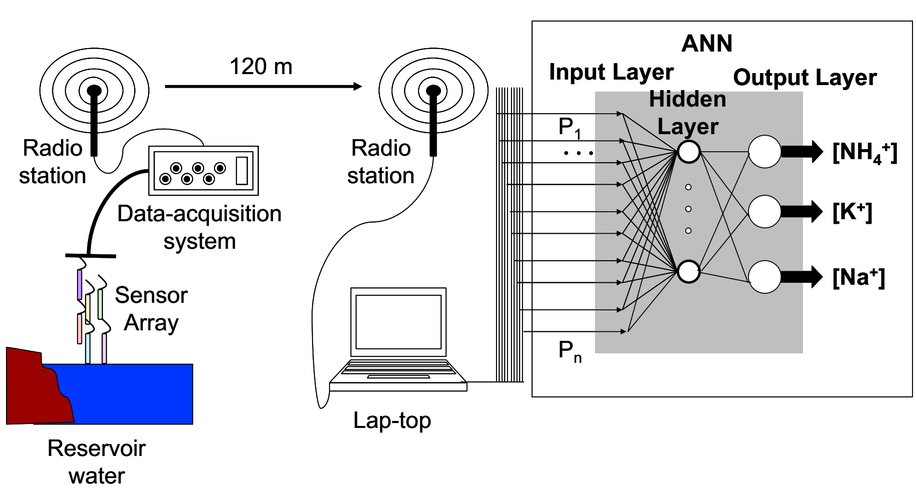

Fig. 3. Block diagram of the proposed manifold for monitoring the concentration of ammonium, potassium and sodium in the Rio Salado.

For the monitoring process, the ISE array was deployed into the river, while the data acquisition system maintained a radio frequency link with a laptop located 120 m from the checkpoint (Fig. 3). The sensor readings were taken every minute for 8 h. In order to correct possible deviations in the readings, a blank measurement was taken every 30 min.

3. Results and discussion

3.1. Building the ANN models

The first task for operating with an electronic tongue is to build up its response model. If this model uses ANNs, significant effort is needed to optimize the configuration details that determine its operation. Normally, this is a trial-and-error process, where several parameters (training algorithms, number of hidden layers, transfer functions, etc.) are fine-tuned in order to find the best configuration to optimize the performance of neural network model.

In the monitoring applications, the ANN architectures were exhaustively studied, as our group had previously done (Gallardo et al., 2003b). The algorithm selected for the learning process was Bayesian Regularization due to its solid capacity for training and prediction in comparison to other training strategies such as Levenberg–Marquardt or Gradient Descent; the latter in particular suffers from a slow convergence of training, and its predictive power is often poor. In addition to these benefits, the Bayesian Regularization training algorithm does not need an internal validation data set to minimize overfitting, as it accomplishes this objective through other means; this requires less experimental effort, as only two data subsets (training and external test) are needed (Demuth and Beale, 1992).

Similarly, the choice of the number of hidden layers as well as the number of neurons was optimized in order to find the smallest topology with better performance. Just one hidden layer was necessary to achieve good results. Different numbers of neurons (from 3 to 20) and the combination of transfer function in hidden and output layers were also studied. Considering the non-linear behaviour of the sensors, two different non-linear functions were considered for the hidden layer, a sigma-shaped function named the *tansig* function (Freeman and Skapura, 1991) and a logarithm function represented by the *logsig* function.

Other parameters for the configuration for ANN models were initially fixed: the learning rate was set at a value of 0.1 and the momentum to a value of 0.4 (Gutiérrez et al., 2007b). The modelling capacity of the ANN was examined in terms of the Root Mean Squared Error (RMSE), plus the linear regression analysis of the comparison graphs between obtained and expected concentration values for the different analytes.

3.1.1. Electronic tongue to determine alkaline ions

For this case, the ANN model had 10 input neurons (nine sensors from the array plus the temperature sensor) and three output neurons (one for each analyte modelled: ammonium, sodium and potassium). After a systematic evaluation of topologies, the best training results were obtained employing a *tansig* function and 10 neurons in the hidden layer, and a *purelin* function in the output layer. Fig. 4 summarizes the comparison results corresponding to the external test, displaying predicted versus expected concentrations for ammonium, sodium and potassium. Furthermore, the linear regression analysis is depicted, one per analyte. The ideal behaviour is that which offers unity slopes and zero intercepts; in addition, the correlation coefficient has to be close to one. The ANN model's generalization capability is evidenced from the accuracy of the concentration values obtained from the external test, as these samples did not take part in the training process. The correlation coefficients obtained are good for ammonium and sodium ($R > 0.9$) and worse for potassium, as its correlation coefficient is lower

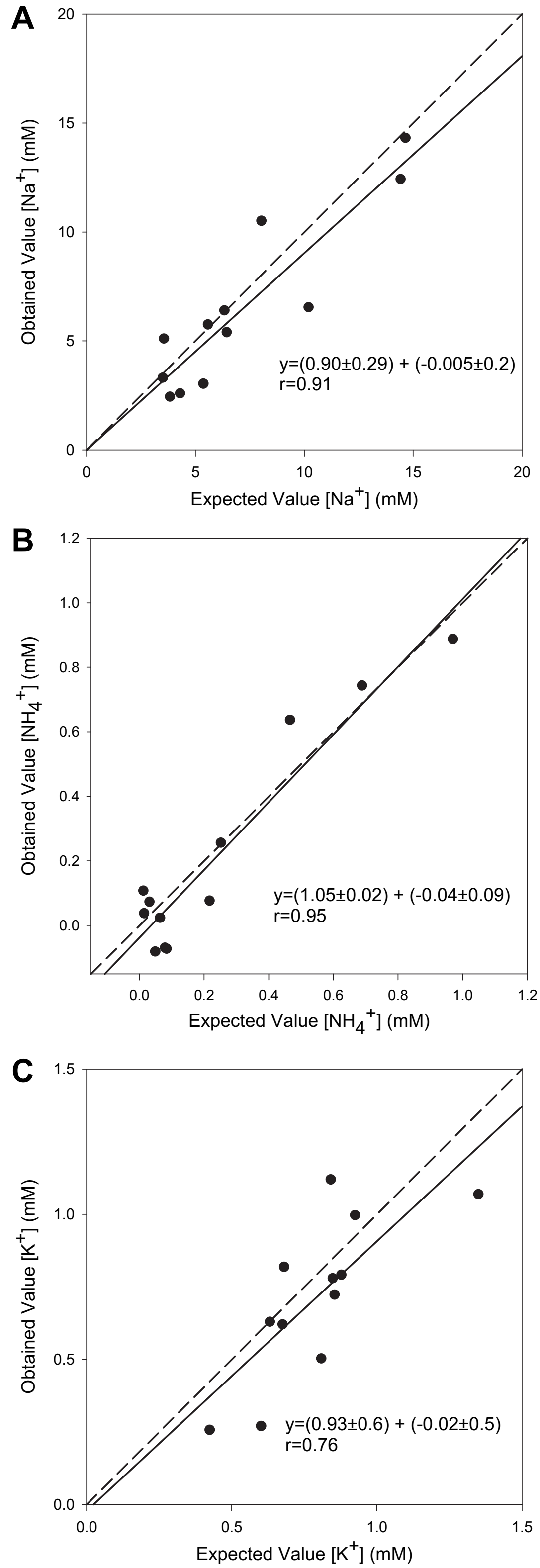

Fig. 4. Modelling performance achieved for the optimized ANN with samples from the external test set: (A) sodium, (B) ammonium and (C) potassium for the Rio Salado application monitoring. The dashed line corresponds to ideality, and the solid line is the regression of the comparison data. Uncertainty intervals calculated at the 95% confidence level.

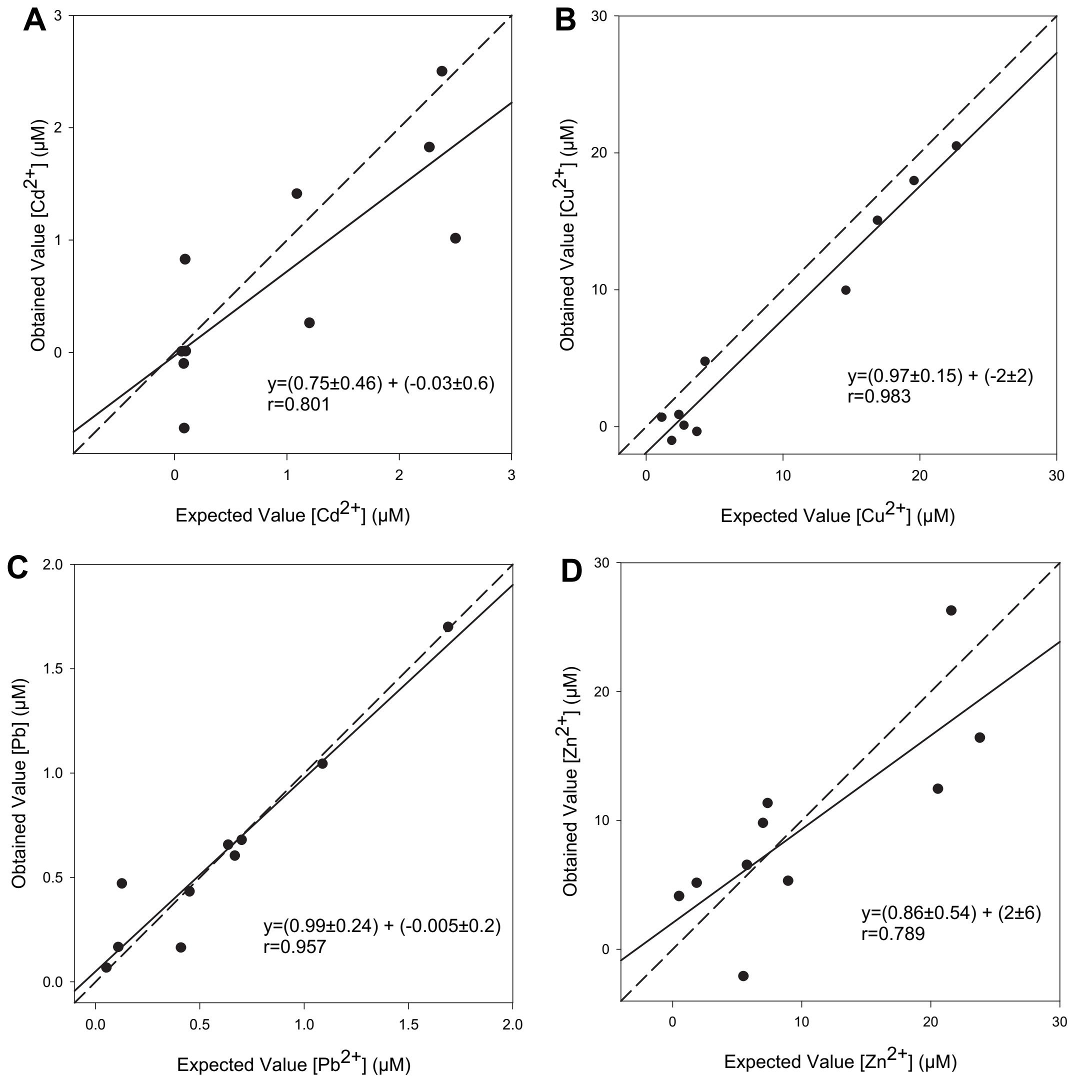

Fig. 5. Modelling performance achieved for the optimized ANN with samples from the external test set: (A) cadmium, (B) copper, (C) lead and (C) zinc for the natural water samples' application analyses. The dashed line corresponds to ideality, and the solid line is the regression of the comparison data. Uncertainty intervals calculated at the 95% confidence level.

($R = 0.756$); in any case, the confidence intervals for intercept and slope are in agreement with the ideal situation.

3.1.2. *Electronic tongue to determine heavy metals*

The characteristics of the ANN model used in this case could be summarized as follows: there were 12 input neurons (11 sensors from the array plus the temperature) and four output neurons (the four concentrations considered, Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+}). Once the ANN optimization was completed, the best results were obtained with six neurons in the hidden layer, and with the *tansig* and *purelin* transfer functions (in the hidden and output layers, respectively).

The behaviour of the optimized model for the external test set, defined for quaternary mixtures of the four species, is shown in Fig. 5. The linear regression of the comparison results between predicted and expected values for the external test set is also shown. All regression results include unity slopes and zero intercepts at a 95% confidence level for the four ions considered.

3.2. *First application – natural water samples*

The training process of the electronic tongues was conducted with a diluted natural water background. To ensure the ET capabilities, several measurements of natural water samples coming from different sources were carried out. Table 5 summarizes the

Table 5
Ammonium, potassium and sodium concentrations in real samples analyzed by the electronic tongue.

Sample	Ion		
	$[Na^+]$ (M)	$[NH_4^+]$ (M)	$[K^+]$ (M)
Well	9.70×10^{-3}	7.10×10^{-4}	8.70×10^{-4}
Irrigation channel	1.15×10^{-2}	6.84×10^{-4}	8.30×10^{-4}
Rio Salado	1.02×10^{-2}	6.10×10^{-4}	7.60×10^{-4}
Zatopenco Lake	1.05×10^{-3}	8.12×10^{-4}	9.10×10^{-4}

Table 6
Heavy metal concentrations in real samples analyzed by the electronic tongue.

Sample	Ion			
	$[Cd^{2+}]$ (M)	$[Cu^{2+}]$ (M)	$[Pb^{2+}]$ (M)	$[Zn^{2+}]$ (M)
Well	1.6×10^{-7}	6.1×10^{-6}	1.6×10^{-7}	6.2×10^{-6}
Irrigation channel	1.5×10^{-7}	6.3×10^{-6}	1.1×10^{-7}	7.7×10^{-6}
Rio Salado	1.5×10^{-7}	5.7×10^{-6}	1.2×10^{-7}	7.3×10^{-6}
Zatopenco Lake	1.4×10^{-7}	6.1×10^{-6}	1.8×10^{-7}	8.7×10^{-6}

concentration values for ammonium, sodium and potassium in the individual samples tested. It is clear that there are no clear differences between the results obtained from different samples. The catchment was a limited area, so this could be the reason for the similarity.

The results of the electronic tongue for heavy metals are shown in Table 6. In this case there are no differences to remark upon, except for the low concentration values attained, which is the desirable situation. With the exception of an anthropic cause, the heavy metal concentrations in natural waters are closely related to the geomorphic characteristics of the zone. The small size of the area under study seems to be the reason for these similar results.

3.3. Second application: Rio Salado monitoring

In the first application, the proposed system was trained using diluted natural water, and then the electronic tongue was applied to individual samples. The second application consisted of simultaneous unattended monitoring of ammonium, sodium and potassium concentrations in the Rio Salado. For approximately 8 h, these analytes were continuously monitored, as initially attempted in a previous study (Gutiérrez et al., 2007a), but this time exploring a different catchment for a longer period of time.

Fig. 6 shows the concentration values for the ions predicted by the electronic tongue, which had been previously trained in the laboratory. Analogously, the figure also displays the corresponding river water temperature. The monitoring day (December 18th, 2008), was warm and sunny, and the water temperature variation was approximately 2 °C during the monitoring time.

Our previous attempt carried out in the Ignacio Ramirez dam (Gutiérrez et al., 2007a) reported an important matrix effect in the case of sodium determination. In this study, the same fact was confirmed because the determinations of sodium concentrations were lower than those obtained by reference methods. This is the main reason a further study should be conducted in order to identify the adequate capabilities of the electronic tongue needed to resolve this. It is worthwhile to mention that although sodium was the most difficult chemical to track, the most significant species in terms of environmental significance, ammonium, could be correctly predicted. Moreover, the interference shown by sodium and potassium in their individual sensor was correctly counterbalanced, an achievement that is impossible to attain using an ammonium sensor alone. Lastly, the robust operation exhibited by the radio link reveals the feasibility of developing an environmental sensor network for monitoring surface waters employing this analytical system.

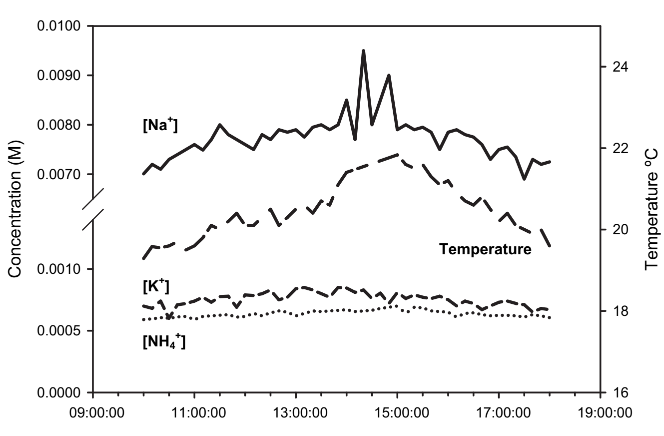

Fig. 6. Representation of the concentration values predicted by the electronic tongue for the ions considered: ammonium, potassium and sodium in the Rio Salado monitoring. The water temperature is also represented.

4. Conclusions

Two different electronic tongue systems have been proposed and optimized for the environmental monitoring of various pollutants using similar procedures and equipment. This is a proof of concept for the versatility of the proposed system. The complex response obtained from the sensor array could be successfully processed employing a multilayer ANN; this tool has proved to be especially suited for building response models for highly non-linear cases, such as the potentiometric sensors considered. With this approach, a quantitative multidetermination of a number of chemical species is easily attainable with rather simple equipment, shifting the complexity from the sensors to the software side.

The first case studied showed the monitoring of ammonium, sodium and potassium in natural water samples. In order to demonstrate the viability of the proposed system for automated remote applications, it was further combined with a radio link for real-time monitoring during an 8-h period. The electronic tongue used here made it possible to determine the content of the three cations in real water samples, although a high matrix effect was encountered for sodium determination, basically caused by the high salinity in the samples. This matrix effect has to be further studied and offset. One alternative to correct this effect would be to increase the number of sensors used in the array, incorporating additional sensors for new species. The second electronic tongue system was used to monitor heavy metals (copper, lead, zinc and cadmium) and was applied on natural water samples from open air waste streams heading down the Gulf of Mexico. Although the ANN had some difficulties in modelling the cadmium and zinc concentrations because of the low levels involved, the natural samples' analyses carried out employing the electronic tongue are in concordance with the reference method determinations.

Overall, it has been demonstrated that the electronic tongue approach can be a viable option to monitor several analytes on-site, with the added advantages of simplicity, the low cost of both the system and the analysis, speed of response, versatility, simple measuring setup, etc. Furthermore, radio transmission can be easily incorporated for easy and robust communication, thus demonstrating the feasibility of the proposed system for automated remote applications and their integration into sensor network technologies.

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