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Development and application of electronic tongue for detection and monitoring of nitrate, nitrite and ammonium levels in waters

Nuñez, L.[1,*]; Zanoni, M. V. B.[1], Cetó, X.[2], Pividori, M. I.[2], del Valle, M.[2]

[1] Departamento de Química Analítica, Universidade Estadual Paulista, Instituto de Química,
Araraquara, SP 14801-970, Brazil
[2] Sensors and Biosensors Group, Department of Chemistry,
Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

Abstract

This work present the first study and development of an electronic tongue analysis system for the monitoring of nitrogen stable species: nitrate, nitrite and ammonium in water. Electronic tongue was composed by an array of 15 potentiometric PVC membrane sensors sensitive to cations and anions plus an artificial neural network response model. The building of ANN model was performed in medium containing sodium, potassium, and chloride as interfering ions, simulating real environmental samples. Correlation coefficient in the cross-validation of nitrate, nitrite and ammonium was satisfactory, in the three cases with values higher than 0.92.

Corresponding autor: nunez.luciana@gmail.com

1. Introduction

Nitrate and nitrite presence in water above ppm levels can cause environmental problems of toxicity, mostly produced by the second. Their presence may set off serious problems to newborn babies and adults with enzymatic deficiency, namely the induction of metahemoglobinemia by reducing nitrate to nitrite, which subsequently combines with hemoglobin in the blood, disease known as the blue baby syndrome; nitrite may also the origin of certain cancers by formation of nitrosamide and nitrosamine compounds [1-3]. Sources of inorganic nitrogen species can be certain domestic, industrial, agricultural or farm activities, although they can also appear without human interference by natural processes [1,4,5]. Precise knowledge of the ratios for the different inorganic nitrogen species forms can be the basis to diagnose the status of an ecosystem or the fate of a dumping waste; that is why the simultaneous determination of ammonium, nitrite and nitrate has paramount significance in environmental chemistry [6].

There are available laboratory methods for water analysis that can be used for the speciation of inorganic nitrogen with a high precision, but some of them need complex sample pretreatments and are also time consuming or rather expensive, e.g. ionic and high-performance liquid chromatography, spectroscopy or photometry [7, 8].

Very few laboratory procedures are available for the simultaneous determination of ammonium, nitrite and nitrate. There can be listed the methods employing liquid chromatography, with conductivity detection for the anions and postcolumn derivatization to indophenol blue and spectrophotometric detection for ammonium [9] or other ionic chromatography variants [10]. The second group is related to flow injection systems that may employ redox conversion of species, like the one with reduction of nitrate to nitrite thanks to a Cd metal column, plus the oxidation of ammonium to nitrite, both coupled with the Griess reaction and spectrophotometric detection [11]. A further example can be the flow injection system with gas difussion of ammonia generated by alkalinization and detected with a conductivity unit, plus spectrophotometric determination of nitrite/nitrate after its conversion with a reducing Zn column [12].

But one desirable feature for environmental monitoring is the unattended, autonomous operation, a condition mainly achieved when (bio)chemical sensors are used; their deployment is the convenient way to get automatic, on-line and real time information about actual changes in surface waters [13]. In this way, one promising direction for the monitoring of natural waters is the application of multisensory systems [14, 15]; these can be based on arrays of non-specific sensors combined with data processing of their complex signals using advanced chemometric tools. This approach is named the electronic tongue [16, 17], and it has been a topic with intensive research in the last decade [18]. 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 [19].

The determination of ammonium ion has been tackled with the electronic tongue approach [20], where the known interference of existing ammonium sensors by alkaline ions sodium and potassium were counterbalanced thanks to the multiple sensor information available [21]. Equivalent treatment received the determination of nitrate, in this case to correct the interfering effect presented by chloride [22]. The conjunction of these principles permitted to develop monitoring systems for ammonium pollution episodes [23], or, equivalently, for the monitoring of nutrient species in greenhouse facilities [24, 25], or nitrogen species (nitrate and ammonium) in fish farms [26]. On the other hand, an electronic tongue developed with the voltammetric technique [14] made possible the determination organic content (as the chemical oxygen demand, COD) in wastewater [27], or COD plus ammonium [28]. A unique antecedent in the simultaneous determination of nitrate and nitrite was proposed by using a similar voltammetric electronic tongue system, in this study applied to brines and minced meat [29].

The present work reports a new approach for speciation of inorganic nitrogen (nitrite, nitrate and ammonium) in this case by the use of an electronic tongue system formed by 15 ion selective electrodes (ISEs) made with polymeric PVC membranes. These use literature formulations, basically with ionophores for ammonium, nitrite and nitrate, but also, other ISEs sensitive to potentially interfering species (sodium, potassium or chloride) or sensors with generic response to the different cations or anions considered. The overall response generated was processed with an artificial neural network (ANN) response model [15,17,18], constructed from an appropiate set of calibration solutions, and devised to decode the cross-response among sensors and the interfering effects among ions. In this field, an electronic tongue system based on potentiometric sensors to perform the speciation of inorganic nitrogen compounds can be a promising environmental monitoring device, studied by the first time in this report.

2. Experimental

2.1 Reagents and solutions

All the chemicals used were analytical grade or higher quality. Solutions were prepared using Milli-Q distilled water. For preparing the membrane cocktails, there were used the plasticizers: bis(1-butylpentyl) adipate (BPA), dioctyl sebacate (DOS), 2-nitrophenyloctylether (NPOE) and dibutyl phtalate (DBP), 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 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). Components of the membrane, together with high-molecular-weight polyvinyl chloride (PVC, Fluka) were dissolved in tetrahydrofuran (THF, Fluka) in order to satisfy the relation of 100 mg of PVC in 2.5 mL of THF, according to table 1.

2.2 Sensor arrays

The sensors array were comprised of 8 kinds of sensors, divided into two groups which were those sensitive to anions and cations. With the exception of the chloride sensor, which was a solid state Ag/AgCl sensor prepared previously [25] and available in the lab, the other sensors were of polymeric PVC selective membrane type, and were newly prepared as following: a membrane cocktail formulated with specific composition (table 1) and containing a specific recognition element (ionophore) for certain ion was drop over a solid contact electrode, made from a graphite-epoxy composite [37]. Each ion selective PVC membrane was formed by depositing two drops of PVC cocktail every 30 minutes to evaporate the THF, the procedure was repeated until eight layers were deposited. Then the membrane was air dried for 24 hours and conditioned in a solution mol.L^{-1} of their ion for 24 hours and then stored at the sensor has been dried.

The graphite-epoxy resin was prepared by adding the components of the epoxy resin in proportions of 24% Araldite M (Fluka), 24% Araldite Hardener 964 M (Fluka), 2% Araldite M Accelerator 960 (Fluka) at 50% graphite carbon (Merck). The electrodes were manufactered and cured well before deposition of the membranes.

Manufacturing process of ion-selective electrodes occurred in basically three steps: the body of the electrode assembly, deposition of conductive graphite-epoxy resin and formation of the selective membrane, and has been previously described in the literature [20, 24, 37].

2.3 Apparatus

The emf measurements were performed with a laboratory made data acquisition system consisting of 32 input channels made with differential instrumentation amplifiers (INA116, Burr-Brown, USA) that adapted the impedance for each sensor . Emf measurements were performed against a double junction Ag/AgCl reference electrode (model 90-02 -00, Thermo Electron, Waltham, MA), with 0.1 M lithium acetate in the outer bridge. Each channel was noise-shielded with its signal guard. The output of each amplified channel was filtered with a second order low pass active filter centred at a 2 Hz frequency and connected to an Advantech PC-Lab 813 A/D conversion card installed in a PC. Readings were acquired by using custom software developed in Microsoft QuickBasic Version 4.5.

2.4 Sensor characterization

For characterization of the sensors prepared calibration procedures were performed prior to construction of the model response of the electronic tongue (ET), whose processes include steps involved known as training and testing.

The characterization of the sensor was carried out by performing calibration of the analytical curve. To build the model response, standard solutions of each ion were prepared at concentrations of 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} mol L^{-1}. Microvolumes of these standards were added successively to the calibration vessel containing 25 ml of Milli-Q water. After each addition of a pattern of potential reading was performed. This calibration procedure was performed on different days, in triplicate each day to verify the repeatability of the response. In these, there were determined the limit of detection and sensitivity by curve fitting to the Nernst equation.

2.5 Training and evaluation

For the obtaining of the ANN response model, weights forming the ANN were iteratively obtained by optimizing obtained response vs. expected values for a subset of samples (the training subset) [38, 39]. This subset was formed by 37 sample standards, each one with its concentration of specified ions previously defined. The concentrations of these standards were determined by fractional factorial design with three levels of concentration and six factors (the six considered ions, 3^{6-2}). The potential values from the sensor array are the input information, while the concentrations of the six ions is the final information sought. The next step, the verification of the goodness of fit of the response function provided by the ANN model was done by checking predicted concentrations of a separate subset of 15 additional samples, with concentrations of the six ions defined randomly (cross-validation).

2.6 Software

The ANNs tested were trained and evaluated using MATLAB 7.0 (Mathworks, Natick, MA, USA), using its Neural Network Toolbox (v. 3.0).

3. Results and discussion

3.1 Characterization of the sensors

The first stage of the work done after making each sensor was its calibration. Each sensor was calibrated in triplicate on different days to assess the repeatability of the response with respect to the detection limit and sensitivity [37]. Only the sensors that showed no significant variations in the measurements of these parameters were used for making the electronic tongue. Thus, two sensors were used for each ion, except for the sensor to the chloride ion which was used a Ag/AgCl solid state sensor as already mentioned at experimental section.

The data obtained from the calibrations can be plotted on a graph of the logarithm of ion concentration measured by the potential (data not show). From those calibration curves were determined the parameters of sensibility and quantification limit which characterize the sensor made, shown in Table 2. The lower sensitivity was observed respected to nitrite sensors, however, this can be compensated by the better regression coefficient and stability of response along the time.

3.1 Building of the ANN models

The response model of artificial neural network (ANN) had to be built prior to application. The purpose of this step is to determine the configuration of the ANN that best describes the response of the system. Commonly, this is a trial-and- error process, where some parameters shoud be evaluated: number of neuron at hidden layer, number of hidden layers, transfer functions, between others computer parameters determinate at the neural network modeling.

Once established these parameters of modeling, there was prepared two sets of samples for a internal (training) and external (testing) standard calibration, which concentrations were determinate by a fractional factorial of 37 samples for training and 15 for testing. For the construction of model ANN's response to the ET potentiometric measures of this samples were taken from all standards containing species at concentrations above the detection limit determined for each analyte. The minimum and maximum concentrations of each ion are shown in Table 3.

Once obtained the values of potential of the stages of training and testing, the followed stage was the building the model response. Due to the difficulty of predicting the best configuration of the RNA, this step is usually performed by trial and error [18, 21]. In order to facilitate this is carried out a measure of the error associated with each function provided for the transfer and the number of neurons which may be used, this error was calculated by measuring the Normalized Root Mean Squared Error - NRMSE [21, 40]. The NRMSE calculated is expressed through a graphical representation of NRMSE versus the number of neurons for each transfer function studied. In this work we study the functions *pureline, logsig* and *tansig*, and assessed the number of neurons 1-12. The construction of the response of the ANN template requires more than simple measure NRMSE [15, 21, 25]. Figure 1 shows the results for NRMSE calculated, the smallest error conditions are always the most desirable application, and are those which deserve special attention to evaluate the efficiency of the adjustment function.

Based on NRMSE values, Figure 1, determining the best set of transfer functions were performed analyzing the following conditions:

- 4 hidden nodes, with the transfer function G between the input layer and the hidden layer and P between the hidden layer and output layer (LP4).
- 4 hidden nodes, with the transfer function T between the input layer and the hidden layer and P between the hidden layer and output layer (TP4).
- 8 hidden nodes, with the transfer function T between the input layer and the hidden layer and T between the hidden layer and output layer (TT8).

Considering the three conditions of lower associated error, choose the best configuration of the RNA takes into account the training data and test of LE. The results obtained in these steps were evaluated in terms of the correlation between the expected concentrations obtained for the different analytes.

After the settings of the studied RNA's model response to the three lower associated error conditions, the best fit was obtained for the configuration TP4, whose results are shown in Figure 2 and 3. In Figure 2 it appears that all are good correlation coefficients R> 0.9. It is also known that adjustment of the model has greater deviations for the analytes potassium and ammonium, with slopes less than 0.9. This greater difficulty in adjusting for the analytes of potassium and ammonium is also observed in the test samples (Fig. 3), with correlation coefficients and slope less than 0.9, showing that there is discrepancy between the calculated and real. However, considering that the amount of potassium is not part of the objectives of this work and that among the species of inorganic nitrogen stable in aqueous ammonium is less toxic, and there are no other studies in the literature on ET for simultaneous detection of these forms of nitrogen, this work contributes greatly to the development of these devices for the monitoring of such species.

Thus, the ET for the detection of species of nitrogen-N, nitrate, nitrite, and ammonia had characteristics as 15 input neurons (15 sensors used), a core layer containing neurons 4 and 6 neurons in the output layer, corresponding to 6 analytes. Using the transfer function T between the input layer and the hidden layer and P as the transfer function between the hidden layer and output layer.

3.2 Application to the monitoring of a photoelectrodegradation process

In order to evaluate the efficiency of application of the electronic tongue in aqueous solution containing the analytes was performed by the monitoring of kinetics of remotion of nitrate by photoelectrocatalytical process, similar as related at literature [23].

The photoelectrocatalytic reduction experiment were performed in a becker with capacity of 500 mL as a reactor, there was positioned a working electrode of Ti/TiO_2-CuO, a Ag/AgCl reference electrode and a Pt gauze electrode as counter electrode. The electrode Ti/TiO_2-CuO with composition of 75:25 of TiO_2:CuO was prepared according to the literature [24], with a photoactive area of 25 cm^2 and was illuminated with a UV light source (315-400 nm) of pressure mercury lamp of 20 W (I_0 = 0.27 $mW.cm^{-2}$ at the becker glass surface). The nitrate solution (100 $x10^{-3}$ $mol.L^{-1}$ of nitrate in 7 $x10^{-3}$ $mol.L^{-1}$ of NaCl) was placed in the reactor and the photoelectrochemical process was performed for 90 minutes by applying a bias voltage of -0.2V as on literature [23] under irradiation of lamp. Nitrate and nitrite amounts were monitored by taking aliquots from the photoelectrochemical reactor after different time intervals and submitted to analysis by electronic tongue made. The observed results are show at the Figure 4. There is observed a gradual decrease of nitrate concentration along the time, while occurred a increase of ammonium concentration as product of the nitrate reduction according the global reaction

$$NO_3^- + 4H_2O + 4e^-_{bc} \rightarrow NH_3 + 5OH^-$$

where nitrate reacts with water and the photoexcited electrons on the valence band of semiconductor [23] forming ammonia and hydroxyl groups. There was also observed no variation of nitrite concentration (concentration below lower concentration detected, data not shown).

This application demonstrates that the electronic tongue made can be a useful choose for monitoring solutions with variable concentrations of inorganic species of nitrogen in presence of interferents of chloride, sodium and potassium ions. We believe that in future research this electronic tongue can be better study for environmental monitoring of rivers and lakes containing levels of inorganic species of nitrogen.

4. Conclusions

The present work correspond to the first building of ANN model for quantified N species of environmental interesting: nitrate, nitrite and ammonium. The sensors prepared for this application present high detection limit between 10^{-5} to 10^{-8} $mol.L^{-1}$. It was demonstrated that the electronic tongue made allows the quantification of nitrate, nitrite, and ammonia in an aqueous medium in presence of interfering sodium, potassium and chloride ions. Using this system it was possible to distinguish between species nitrate and nitrite in a satisfactory manner, however with larger deviations for ammonia cation. We believe that the produced device is promising for analysis of environmental samples containing nitrate, nitrite and ammonium.

Simple use – just immersion of the sensors … complexity on the software side

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Table 1: Formulation of ion selective membranes employed in the construction of the potentiometric sensors.

Sensor	**PVC (%)**	**Plasticizer (%)**	**Recognition element (%)**	**Reference**
NH_4^+	33	BPA (66)	Nonactine (1)*	30
K^+	30	DOS (66)	Valinomicine (3)*	31
Na^+	22	NPOE (70)	CMDMM (6) *	32
Generic (cations)	29	DOS (67)	Dibenzo-18-crown-6 (4)	33
NO_3^-	30	DBP(67)	TOAN(3)**	34
NO_2^-	33	DBP(66)	Ionophore 1 (1) **	35
Generic (anions)	29	DBP(65)	TOAB(4)	36

*Formulation includes potassium tetrakis(4-clorophenyl) borate as additive, 1:0.5 mol ratio in recognition element: additive.

** The formulation includes TOAB as an additive in 1:0.5 mol ratio of component recognition: additive.

Table 2: Response parameters observed for the sensors.

Sensor	**Sensitivity (mV)**	**Limit of Detection (mol.L^{-1})**	**Regression Coefficient**
Sodium	59.3	6.4x10^{-7}	>0.999
Potassium	63.0	7.3 x10^{-8}	>0.999
Ammonium	58.3	1.0 x10^{-7}	>0.999
Chloride	-50.0	7.9 x10^{-5}	0.996
Nitrate	-68.2	4.6 x10^{-6}	0.994
Nitrite	-40.8	3.4 x10^{-5}	0.999

Table 3: Ranges of variation of the concentration of analytes in the solutions used for training and testing of LE.

Specie	**Concentration range (mol.L^{-1})**
Sodium	2.0 x10^{-4} - 2.0 x10^{-2}
Potassium	1.0 x10^{-5} - 1.0 x10^{-3}
Amonium	1.0 x10^{-5} - 1.0 x10^{-3}
Chloride	2.0 x10^{-4} - 2.0 x10^{-2}
Nitrate	1.0 x10^{-5} - 1.0 x10^{-3}
Nitrite	5.0 x10^{-5} - 5.0 x10^{-3}

CAPTIONS FOR FIGURES

Figure 1: Calculation of NRMSE for optimization of the function and number of neurons

Figure 2: Learning results for the electronic tongue in terms of the correlation of expected and obtained concentration-x10-3mol.L-1 one of the samples.

Figure 3: Test results for the electronic tongue in terms of the correlation of expected and obtained concentration-x10-3mol.L-1 one of the samples.

Figure 1

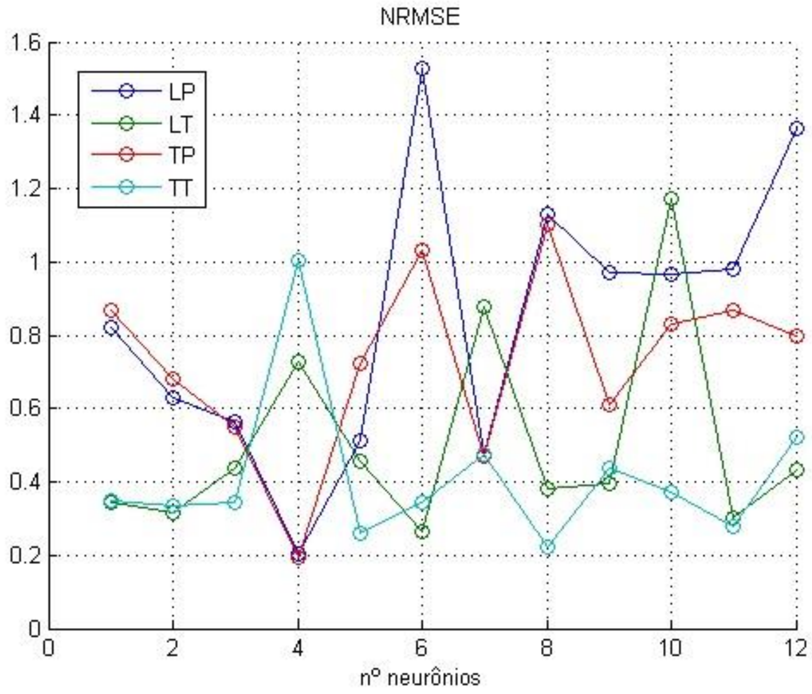


Figure 2

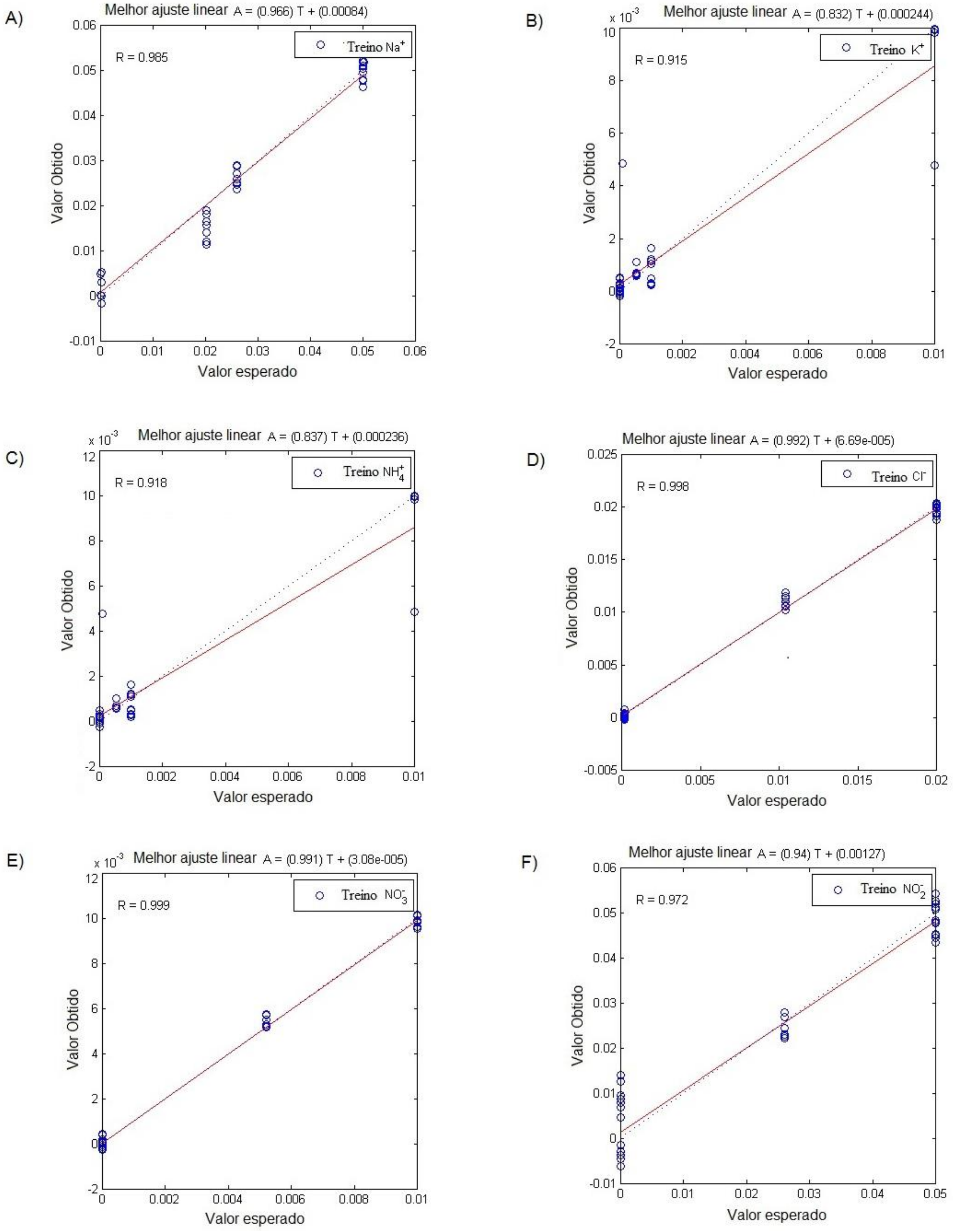
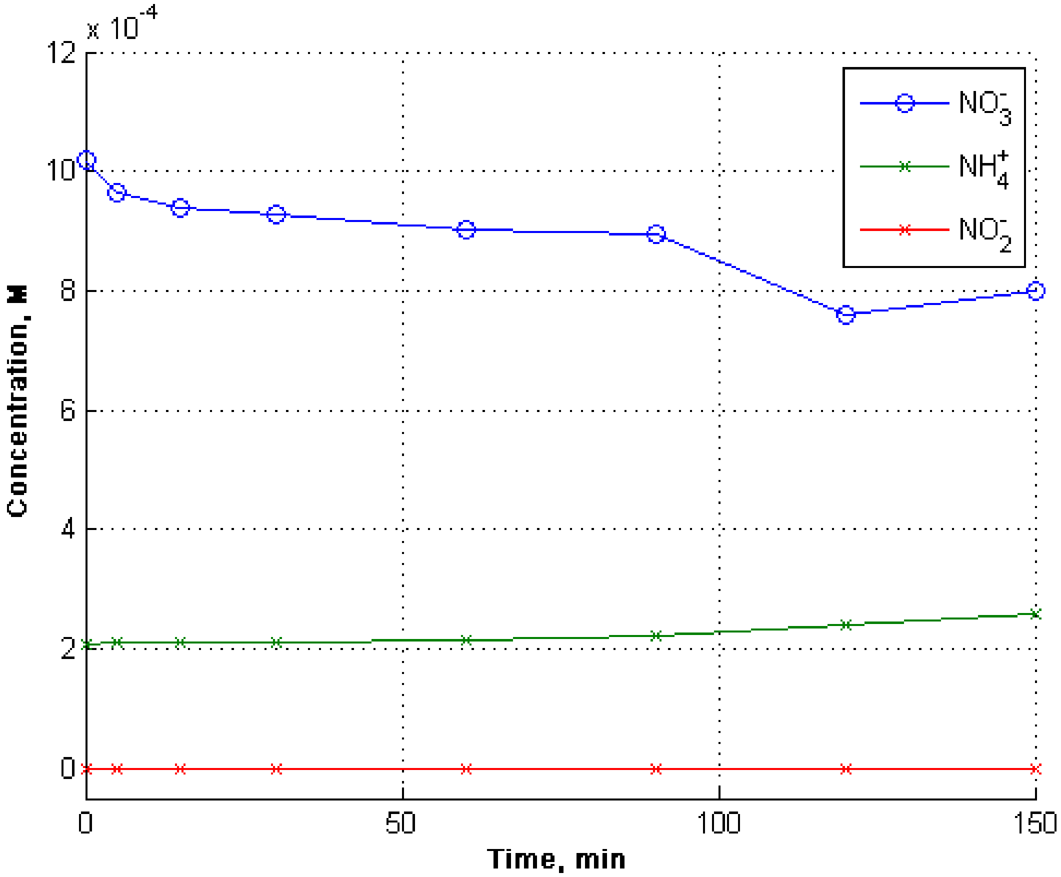

A)
Melhor ajuste linear A = (0.966) T + (0.00084)
R = 0.985
Treino Na^+
Valor Obtido
Valor esperado
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
0
0.01
0.02
0.03
0.04
0.05
0.06
B)
x 10^{-3}
Melhor ajuste linear A = (0.832) T + (0.000244)
R = 0.915
Treino K^+
Valor Obtido
Valor esperado
10
8
6
4
2
0
-2
0
0.002
0.004
0.006
0.008
0.01
C)
x 10^{-3}
Melhor ajuste linear A = (0.837) T + (0.000236)
R = 0.918
Treino NH_4^+
Valor Obtido
Valor esperado
12
10
8
6
4
2
0
-2
0
0.002
0.004
0.006
0.008
0.01
D)
Melhor ajuste linear A = (0.992) T + (6.69e-005)
R = 0.998
Treino Cl^-
Valor Obtido
Valor esperado
0.025
0.02
0.015
0.01
0.005
0
-0.005
0
0.005
0.01
0.015
0.02
E)
x 10^{-3}
Melhor ajuste linear A = (0.991) T + (3.08e-005)
R = 0.999
Treino NO_3^-
Valor Obtido
Valor esperado
12
10
8
6
4
2
0
-2
0
0.002
0.004
0.006
0.008
0.01
F)
Melhor ajuste linear A = (0.94) T + (0.00127)
R = 0.972
Treino NO_2^-
Valor Obtido
Valor esperado
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
0
0.01
0.02
0.03
0.04
0.05

Figure 3


x 10^{-4}
12
10
8
6
4
2
0
Concentration, M
0
50
100
150
Time, min
NO_3^-
NH_4^+
NO_2^-