



# Development and application of an electronic tongue for detection and monitoring of nitrate, nitrite and ammonium levels in waters <sup>☆</sup>



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## ARTICLE INFO

### Article history:

Received 15 January 2013  
Received in revised form 11 April 2013  
Accepted 25 April 2013  
Available online 7 May 2013

### Keywords:

Electronic tongue  
Sensor array  
Ammonium  
Nitrate  
Nitrite  
Speciation

## ABSTRACT

This work presents the first study and development of an electronic tongue analysis system for the monitoring of nitrogen stable species: nitrate, nitrite and ammonium in water. The electronic tongue was composed of an array of 15 potentiometric poly(vinyl chloride) membrane sensors sensitive to cations and anions plus an artificial neural network (ANN) response model. The building of the ANN model was performed in a medium containing sodium, potassium, and chloride as interfering ions, thus simulating real environmental samples. The correlation coefficient in the cross-validation of nitrate, nitrite and ammonium was satisfactory in the three cases with values higher than 0.92. Finally, the utility of the proposed system is shown in the monitoring of the photoelectrocatalytic treatment of nitrate.

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## 1. Introduction

The presence of nitrate and nitrite in water above ppm levels can cause environmental problems of toxicity, mostly produced by the latter. Their presence may set off serious problems to newborn babies and adults with enzymatic deficiencies leading to the induction of methemoglobinemia. This disease is known as the blue baby syndrome and occurs by reduction of nitrate to nitrite, which subsequently combines with hemoglobin in the blood. Nitrite may also be the origin of certain cancers through the formation of nitrosamide and nitrosamine compounds [1–3]. There are natural sources of inorganic nitrogen species, but they can also originate from domestic, industrial, agricultural or farm activities [1,4,5]. The speciation or precise knowledge of the ratios for the different forms of inorganic nitrogen species can be used as the basis to diagnose the status of an ecosystem or to predict the fate of a waste product. Therefore, 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 high precision. However, some of them require complex sample pre-treatments and are also time consuming or rather expensive, e.g. ionic and high-performance liquid chromatography, spectroscopy or photometry [7,8].

Analytical methods for simultaneous determination of ammonium, nitrite and nitrate are scarce. The usual methods employ, for example, liquid chromatography with conductivity detection for anions and use of post-column derivatization to form indophenol blue, with subsequent spectrophotometric detection for ammonium [9]; other ionic chromatographic variants are also listed [10]. Apart from this, there are other methods based on flow injection systems that may employ redox conversion of species. For instance, the reduction of nitrate to nitrite using a Cd metal column, plus the oxidation of ammonium to nitrite, both coupled with the Griess reaction and spectrophotometric detection [11]. A further example is the flow injection system using gas diffusion of ammonia, formed by alkalization, and conductivity detection coupled to photometric determination of nitrite/nitrate after conversion with a reducing Zn column [12].

However, autonomous operation and on-line and real time information about actual changes in surface waters are desirable features for environmental monitoring sometimes neglected [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, known as the electronic tongue (ET) [16,17], has received much research attention 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].

<sup>☆</sup> Paper presented at 5th Ibero-American Congress of Analytical Chemistry 2012.

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The determination of ammonium ions has been tackled with the electronic tongue approach [20], where the known interference of existing ammonium sensors by alkaline ions sodium and potassium was counterbalanced using the multiple sensor information available [21]. Equivalent treatment led to the determination of nitrate, in this case by correcting the interfering effect presented by chloride [22]. The conjunction of these principles permitted the development of monitoring systems for ammonium pollution episodes [23], equivalently, for the monitoring of nutrient species in greenhouse facilities [24,25], or even nitrogen species (nitrate and ammonium) in fish farms [26]. On the other hand, an electronic tongue developed by using voltammetric technique [14] allowed the determination of 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 the 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 poly(vinyl chloride) (PVC) membranes. These use literature formulations, with known ionophores for ammonium, nitrite and nitrate. However, other ISEs sensitive to potential interfering species such as sodium, potassium and chloride plus sensors with generic response to the different cations or anions are also considered. The overall response generated is processed with an artificial neural network (ANN) response model [15,17,18], constructed from an appropriate set of calibration solutions, and devised to decode the cross-response among sensors and the interfering effects among ions. In this field, this is the first time an electronic tongue system based on potentiometric sensors is reported to perform the speciation of inorganic nitrogen compounds, which can be promising devices for environmental monitoring.

## 2. Experimental

### 2.1. Reagents and solutions

All the chemicals used in the present work were of analytical grade or higher quality. Solutions were prepared using Milli-Q distilled water. For preparing the membrane cocktails, the following were used as plasticizers: bis(1-butylpentyl)adipate (BPA), dioctyl sebacate (DOS), 2-nitrophenyloctylether (NPOE) and dibutyl phthalate (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), dibenzo-18-crown-6 (Acros), tetraoctylammonium nitrate (TOAN, Fluka), aquo-cyano-cobyrinic acid-heptakis-(2-phenylethylester) (nitrite ionophore I, Fluka) and tetraoctylammonium bromide (TOAB, Fluka). Additionally, two lipophilic additives were used when needed: potassium tetrakis(4-chlorophenyl)borate (Sigma Aldrich) for cationic, and TOAB for anionic membranes.

### 2.2. Sensor arrays

The sensor array was composed of 8 kinds of sensors, divided into two sub-groups, anions and cations. With the exception of the chloride sensor, which was a solid state Ag/AgCl sensor prepared previously [25], the other sensors were of polymeric PVC selective membrane type. These 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

**Table 1**

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

Sensor	PVC (%)	Plasticizer (%)	Recognition element (%)	Reference
NH <sub>4</sub> <sup>+</sup>	33	BPA (66)	Nonactin (1) <sup>a</sup>	[30]
K <sup>+</sup>	30	DOS (66)	Valinomycin (3) <sup>a</sup>	[31]
Na <sup>+</sup>	22	NPOE (70)	CMDMM (6) <sup>a</sup>	[32]
Generic (cations)	29	DOS (67)	Dibenzo-18-crown-6 (4)	[33]
NO <sub>3</sub> <sup>-</sup>	30	DBP (67)	TOAN (3) <sup>b</sup>	[34]
NO <sub>2</sub> <sup>-</sup>	33	DBP (66)	NO <sub>2</sub> <sup>-</sup> ionophore I (1) <sup>b</sup>	[35]
Generic (anions)	29	DBP (65)	TOAB (4)	[36]

<sup>a</sup> Formulation includes potassium tetrakis(4-chlorophenyl)borate as additive, at a ratio of 1:0.5 mol (recognition element:additive).

<sup>b</sup> The formulation includes TOAB as an additive, at a ratio of 1:0.5 mol (recognition element:additive).

PVC cocktail every 30 min and by evaporating the dissolvent; the procedure was repeated until eight layers were deposited. Then, each membrane was air dried for 24 h and conditioned in a solution 0.01 mol L<sup>-1</sup> of its primary ion for 24 h and finally stored. Table 1 presents the composition of each electrode with the respective ratio of each component. 100 mg of poly(vinyl chloride) (PVC, Fluka) was used as a departure amount and mixed with the appropriate amounts of plasticizer and ionophore, in a formulation to obtain the specific ratio of each component described in Table 1. The cocktail was obtained after dissolution of these mixtures in 2.5 mL of tetrahydrofuran dissolvent (THF, Fluka).

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

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

### 2.3. Apparatus

The electromotive force (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 mol L<sup>-1</sup> 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 centered at a 2 Hz frequency and connected to an Advantech PC-Lab 813 A/D conversion card installed in a Pentium PC computer. Readings were acquired by using custom software developed in Microsoft QuickBasic Version 4.5.

### 2.4. Sensor characterization

Prior to the construction of the electronic tongue (ET) response model, calibration procedures for all analytes of interest were performed. Characterization of the sensors was carried out by performing analytical calibration curves for each analyte using accumulated microadditions from 0 to 0.01 mol L<sup>-1</sup> (18 measurements). From these, the IUPAC limit of detection and sensitivity values were established by curve fitting to the Nernst equation.

### 2.5. Training and evaluation

To obtain the ANN response model, sensor responses were first normalized and then different weights for each sensor were given for the ANN model initialization. The weights were then iteratively optimized (employing backpropagation algorithm) by minimization of the sum

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