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New Sensor System for Environmental Monitoring: the Potentiometric Electronic Tongue

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Abstract: The use of electronic tongues is proposed for two different environmental monitoring applications. This approach in chemical analysis consists of an array of nonspecific sensors coupled with a multivariate calibration tool. In this case, the proposed arrays were formed by potentiometric sensors based on polymeric membranes (PVC) and the subsequent cross-response processing was based on a multilayer artificial neural network (ANN) model. Special attention was paid in compensating temperature effects and response drifts in the sensors. In addition, in order to demonstrate the viability of the proposed systems for automated remote applications, the use of data transmission by radiofrequency has been tested.

Keywords: Sensor Array; Ion Selective Electrodes; Artificial Neural Networks; Electronic Tongue; Environmental Monitoring.

1. INTRODUCTION

Environmental monitoring and surveillance of surface waters is a major issue worldwide. Particular attention is dedicated to assess the integrity of natural waters, especially near potential pollution sites. The quick determination of contaminants and other species entering into the environment is necessary for taking control measures to confine any environmental damage. There are laboratory methods available for analysis of the different substances in water, featuring high precision and confidence, however, most of them need complex sample pretreatment and/or sophisticated equipment, e.g. high performance liquid chromatography, atomic spectroscopy, fluorimetry, etc. To get on-line and real time information about actual changes of the water composition, automatic systems for on-site analysis are highly desirable. The measuring principles employed within these systems must be robust, sensitive enough and of wide applicability. These requirements are needed because the monitoring sites may present differences in sample nature, i.e. surface, ground, waste, and sewage water, etc. and may present a broad scope of inorganic as well as organic target compounds, microorganisms, etc.

The use of chemical sensors for natural water monitoring has been successful in certain cases; a progress of the use of a single sensor is the use of multisensor systems; these can be based on arrays of non-specific sensors combined with advanced data processing of their complex signals, in the approach called electronic tongue [Vlasov et al., 2005]. The sensor array takes profit of the advantages of using chemical sensors such as speed of response, low cost of analysis and on-site determination with a relatively simple measuring setup. Also, the use of a sensor array permits to widen the number of species that can be determined simultaneously, while any interference effect can be solved employing
chemometric tools as data processing element. In this field, electronic tongues employing voltammetric sensors and Principal Component Analysis (PCA) [Krantz-Rülcker et al., 2001] have been applied to detect annoyances in drinking water quality and to monitor online industrial processes [Winquist et al., 2005]. In the same way, electronic tongues using an array of potentiometric sensors, specifically made of chalcogenide glasses, and combined with a pattern recognition routine, were used to detect heavy metals in river water, and were suggested for environmental- and process-monitoring purposes [Legin et al., 1996]. When this type of potentiometric sensors were combined with others based on poly(vinyl chloride) (PVC) membranes, heavy metals, alkali- and alkali-earth cations plus inorganic anions could be quantified in model solutions of groundwater [Rudnitskaya et al., 2001]. In our own experience, all-solid-state potentiometric sensors based on polymeric membranes were successfully applied for the simultaneous quantification of alkaline ions in river and waste waters using a multilayer artificial neural network (ANN) model where the different crossed interference effects could be solved [Gallardo et al., 2003; Gallardo et al., 2005].

This communication describes the development, application and testing of specifically designed electronic tongues, which employs potentiometric sensors and ANN models to develop environmental monitoring systems.

2. EXPERIMENTAL SECTION

The used sensors were based on PVC membranes and provided cross response to various species in solution. The ANNs were the multivariate calibration tools used to process the original complex data, being able to quantify the target analytes for which their cross-response interference effects had to be compensated. Two different applications were developed.

2.1 First Application in the CSTR

Firstly, a Continuous Stirred-Tank Reactor (CSTR) with a simulated surface water background was inoculated with natural microorganisms in order to imitate natural biodegradation conditions. While in operation, the simultaneous monitoring of ammonium, potassium, sodium, chloride and nitrate was accomplished during a perturbation lasting for several days, in this case, the addition of a concentrated liquid fertiliser to the whole, simulating a wastewater spillage. Figure 1 shows the whole proposed manifold for this first application.

![Figure 1. Block diagram of the proposed system for monitoring the concentration of ammonium, potassium, sodium, chloride and nitrate in the CSTR.](image-url)
2.2 Second Application in the “Ignacio Ramírez” Dam

Secondly, an electronic tongue was optimised for on-site determination of ammonium, potassium and sodium ions in the “Ignacio Ramírez” dam (Mexico). Before this on-site application, the system was validated with a set of real water samples collected from four different points of the dam. Once filtered, different dilutions of these samples with Milli-Q water were processed by the electronic tongue. Results were compared with those provided by reference methods: ammonium was determined by the Nessler reaction, and potassium and sodium, by atomic absorption spectroscopy.

Figure 2 shows the whole proposed manifold for this second application. In both cases, special attention was paid in order to compensate temperature effects and sensor drifts. Apart, the possibility of wireless connection has been explored to demonstrate remote, unattended operation. A digital radio link was used between the monitoring site and the PC, where the data were processed employing a previously trained ANN model.

3. RESULTS AND DISCUSSION

3.1 First Application in the CSTR

With the optimised ANN, we estimated the performance of the proposed system as the Relative Standard Deviation (% RSD) for a measurement interpolated in the training curve. The obtained values were 6.5% for ammonium determination, 15.2% for potassium, 9.4% for sodium, 2.3% for chloride and 2.4% for nitrate. In all cases, except for potassium, the RSD is lower than 10%, and specially good results were obtained for the determination of the two anions, chloride and nitrate.

In this first application, the concentrations levels of ammonium, potassium, sodium, chloride and nitrate, once the fertiliser was added, were continuously monitored for more than 3 days, from which the first 24 h were analysed in more detail. Figure 3 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. At the beginning of the experiment, the tank was inoculated with natural microorganisms from a stream to imitate real biodegradation conditions in a surface water. After 1 hour, the liquid fertilizer was added into the tank, and one measurement per sensor was done every 20 min.

The results demonstrated that the electronic tongue corrected the temperature effect, as observed by the smooth variation of concentrations. The Figure shows that ammonium

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**Figure 2.** Block diagram of the proposed manifold for monitoring the concentration of ammonium, potassium and sodium in the “Ignacio Ramírez” dam.
disappeared more quickly than the other species, that displayed equivalent behaviour. This fact suggested that a biochemical reaction was occurring inside the CSTR depleting ammonium. Considering that ammonium ion is the unique monitored substance that can be oxidized, this behaviour can be consequence of the natural biodegradation by the environmental microorganisms that were introduced in the tank.

**Figure 3.** 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 of continuous monitoring. The variation of temperature according to the cycle of day and night is also observed.

3.2 Second Application in the “Ignacio Ramírez” Dam

With the optimised ANN, we estimated the performance of the proposed system as before. The obtained RSD were 4.2% for ammonium determination, 2.8% for potassium and 3.1% for sodium. These values are comparable to those obtained for the used reference methods, which were between 0.8 and 1.3% for ammonium, and between 0.2 and 1.5% for potassium and sodium.

The proposed system was first applied to real samples from the dam. The predicted relative errors of the logarithm of the concentration of the three considered ions are summarized in Table 1. The errors are in specific cases higher than 10%, although lower on average. For example, the mean relative error was 3.2% in the determination of potassium. All the obtained errors for sodium and potassium were negative because of the influence of the sample matrix, which is highly saline and specially complex in this reservoir. The matrix effect is a special type of interference that caused a decrease or increase of the sensor response due to the presence of other species in solution. This effect specially affects the determination of sodium, the more concentrated ion, since a mean relative error of 8.4% was obtained.
Table 1. Obtained relative errors of the logarithm of the concentration of the three ions in real water samples from “Ignacio Ramírez” dam.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dilution</th>
<th>Relative Error (%) NH₄⁺</th>
<th>Relative Error (%) K⁺</th>
<th>Relative Error (%) Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real 1</td>
<td>3:2</td>
<td>-1.6</td>
<td>-7.9</td>
<td>-10.7</td>
</tr>
<tr>
<td>Real 2</td>
<td>2:3</td>
<td>0.2</td>
<td>-2.6</td>
<td>-8.5</td>
</tr>
<tr>
<td>Real 3</td>
<td>2:3</td>
<td>-2.2</td>
<td>-2.0</td>
<td>-11.2</td>
</tr>
<tr>
<td>Real 4</td>
<td>2:3</td>
<td>-1.4</td>
<td>-1.2</td>
<td>-3.5</td>
</tr>
<tr>
<td>Real 1</td>
<td>3:2</td>
<td>12.9</td>
<td>-4.7</td>
<td>-9.7</td>
</tr>
<tr>
<td>Real 2</td>
<td>2:3</td>
<td>-2.2</td>
<td>-2.1</td>
<td>-7.9</td>
</tr>
<tr>
<td>Real 3</td>
<td>2:3</td>
<td>7.3</td>
<td>-1.1</td>
<td>-12.0</td>
</tr>
<tr>
<td>Real 4</td>
<td>2:3</td>
<td>11.9</td>
<td>-0.4</td>
<td>-3.6</td>
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<td>-11.4</td>
</tr>
<tr>
<td>Real 4</td>
<td>2:3</td>
<td>-5.9</td>
<td>-2.3</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

Mean Relative Error (%)

- NH₄⁺: 4.3
- K⁺: 3.2
- Na⁺: 8.4

Once the system was validated, the concentration of ammonium, potassium and sodium was continuously monitored on-site for 2 h, approximately. Figure 4 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 graphs, were caused by the periodically measurement of the reference solution, that was at 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 light trend toward decreasing, while the ammonium concentration was between $1.5 \times 10^{-5}$ and $4 \times 10^{-5}$ M. The predictions of the ammonium and potassium contents were close to the concentrations determined by reference techniques for the real samples. However, the sodium concentration determined by the electronic tongue was lower. As we explained before, the matrix effect was specially strong for sodium, although its presence was correctly counterbalanced for the determination of ammonium and potassium employing the ANN model.

4. CONCLUSIONS

Two different electronic tongue systems have been developed and optimised 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 one, 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 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 to monitor the content of ammonium, potassium and sodium in real dam water, but the calculated concentration of sodium is lower than the obtained by reference methods due to the high matrix effect. To improve the response towards this cation, an alternative would be to increase the number of sensors used in the array, incorporating new species not considered here to the model. It is important also to establish the training space before designing the electronic tongue in order to cover the variability and the complexity of the real conditions. Therefore, the calibration medium needs a exhaustive study to match better the real samples.
In any case, the two systems are able to compensate 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 [Gutiérrez et al., 2007]. The used radio link demonstrated a robust operation, so we can conclude that systems of the studied type can be applied to automatic wireless monitoring for environmental applications.

![Graph](image)

**Figure 4.** 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 monitorized water temperature is also represented.

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