An interference-tolerant nitrate smart sensor for Wireless Sensor Network applications

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Abstract

As a major contaminant in ground water, nitrate determination is a common practice in environmental analysis, especially the continuous and simultaneous monitoring of its concentration at many different points. For this task, sensor networks are a promising tool, although they require the use of sensors with special features, such as those of Ion Selective Electrodes (ISEs). Unfortunately, their measurements are – to a greater or lesser extent – affected by the presence of other coexisting (interfering) ions. A new methodology is then proposed in this work to deal with major interferences (chloride and bicarbonate in the case of nitrate determination), in such a way that the results obtained in the measurements of the content of NO\textsubscript{3} with a nitrate selective electrode can be considered as virtually error-free from these interferences. For this purpose, a new sensor node has been developed; it consists of three ISEs (NO\textsubscript{3}, Cl\textsuperscript{−}, and HCO\textsubscript{3}) coupled to a low-consumption, low-cost microcontroller (a small chip containing all the computer components), which receives and processes all signals coming from the electrodes. This information is suitably treated, as described in detail in this paper, to provide an accurate estimation of the true value of NO\textsubscript{3} concentration.

The application of this methodology results in an interference-tolerant nitrate smart sensor capable of being employed within a wireless sensor network in the continuous monitoring of nitrate concentration in aquifers and rivers.

Keywords: Smart sensor; Interference tolerance; Nitrate determination; Ion selective electrode; Interfering ion.
1 Introduction

Nitrate is one of the most common contaminants of ground water, originating mainly from agricultural fertilizer application and release of sewage. As the presence of this species in water presents a well-known risk to health, it seems obvious that the monitoring of nitrate concentration in aquifers and rivers may result fundamental. Several analytical techniques have been used for this purpose [1], ion-selective electrodes (ISEs) being perhaps the most suitable one; in this sense, the literature offers a great deal of references, from early work [2] [3] to recent contributions especially with a view of in-line monitoring [4] [5]. It is straightforward with advantages such as high selectivity, sensitivity, good precision, simplicity, portability, non-destructive analysis, and last but by no means least, low cost and power consumption. The latter makes this technique highly suitable for Wireless Sensor Network (WSN) applications.

However, it is a common feature of all analysis methods that when atoms or ions of a different species but with similar properties are also present, i.e. coexist with the atoms or ions of interest, they interfere with measurement. This is also true of analysis using ion selective electrodes, so that if ions similar to the target ions are present, they will – to a greater or lesser extent – affect measurement (when considered in contrast to the target ions, these ions are known as interfering ions). Therefore, when using the ion electrode method, care needs to be taken with regard to mutual interference within each of these groups [6].

In this sense, several attempts to deal with this problem have been carried out based on the joint consideration of several ISEs response. Some of these examples include the development of the so-called electronic tongues, arrays of potentiometric sensors (ISEs) coupled to pattern recognition tools. They have been applied to water quality monitoring [7][8], and their performances being compared to those of discrete conventional ion-selective electrodes [9]. On the other hand, recent efforts are focused on the development of artificial neural network (ANN) architectures; they have been applied to raw readings from a chemical sensor multi-probe (e-tongue), comprised of off-the-shelf ISEs, to estimate individual ion concentrations in solutions at environmentally relevant concentrations and containing environmentally representative ion mixtures [10]. Nevertheless, all these approaches –though successful-are sometimes
too complex (need of high-level computer resources) and time-consuming, and would not be adequate in case of WSN applications. That is why more simple developments, i.e. the utilization of discrete ISEs, are usually preferred.

No ion-selective electrodes are completely ion-specific [11]; all are sensitive to other ions having similar physical properties, to an extent which depends on the degree of similarity. Most of these interferences are weak enough to be ignored, but in some cases the electrode may actually be much more sensitive to the interfering ion than to the desired ion, requiring that the interfering ion be present only in relatively very low concentrations, or entirely absent. In practice, the relative sensitivities of each type of ion-specific electrode to various interfering ions is generally known and should be checked for each case; however the precise degree of interference depends on many factors, preventing precise correction of readings. Instead, the calculation of relative degree of interference from the concentration of interfering ions can only be used as a guide to determine whether the approximate extent of the interference will allow reliable measurements, or whether the experiment will need to be redesigned so as to reduce the effect of interfering ions.

The effects of coexisting ions can be predicted to some extent from the response membrane material, that is to say, the reactivity of the response membrane material to the coexisting ions. For example, a solid-state membrane electrode can be seriously affected by coexisting ions that form insoluble compounds or complex salts with the material of its response membrane; and a liquid membrane electrode can be affected by coexisting ions that form ionic associates with the components in its response membrane.

The intensity of the interference produced by an ion species is expressed by the selectivity coefficient (or by the maximum allowable coexistence factor, this roughly corresponding to the reciprocal of the selectivity coefficient). The Nicolsky-Eisenman equation (an extension to the Nernst equation) [12] defines the selectivity coefficient $k_{ij}$

$$E_i = E_i^0 + 2.303 \frac{RT}{n_i F} \log \left\{ a_i + \sum_j k_{ij} a_j^{(n_i/n_j)} \right\}$$

where $E$ is the emf, $E^0$ the standard electrode potential, $n$ the ionic valency including the sign, $a$ the activity, $i$ the ion of interest (target ion), $j$ the interfering ions and $k_{ij}$ is the selectivity coefficient. The smaller this value, the better the selectivity with respect to
the target ion, *i.e.* the less the interference by *j* [13]. Hence, in practice, the ratio of target ion to interfering ion concentration is very important. Higher concentrations of target ions result in the interfering ions having a smaller effect, and conversely, lower concentrations result in them having a larger effect. It is then logical that the ideal ISE should be interference-free, although up till now the objective of the major manufacturers of this type of devices consists of keeping these interferences to a minimum. Our aim is then to address cross-ion interferences in such a way that, although ISEs may be only partially selective for their target analyte, we can take advantage of their promising use in in-situ portable sensors.

Recent advances in the field of microelectronics and communications allow for the development of modern applications that require new sensors with different requirements from those of the traditional devices; additionally, and owing to their possibilities of data management, they permit to obtain more precise, robust, and powerful systems [14]. Following this line, in this paper we propose a nitrate smart sensor that is able to eliminate major interferences from other species, namely chloride and bicarbonate ions; moreover, it meets the necessary requirements to be utilized within an application based on WSN [15], with all its inherent benefits in the field of chemical analyses.

In the next sections, the procedure proposed for the rejection of major interferences in nitrate determination by ISEs will be described in detail, along with the results obtained after its application to discrete samples, with a view to use it in the future within a WSN for environmental analysis purposes.

## 2 Rejection of interferences

As mentioned above, one of the main drawbacks while measuring nitrate concentrations by means of ISEs is the interference caused by other similar species, since their presence may cause an incremental deviation on the results obtained. In case of the nitrate electrode [16], the following ions usually interfere (average selectivity coefficients, SC, in brackets): Chloride \(6.10^{-3}\), Bicarbonate \(5.10^{-3}\), Nitrite \(1.10^{-3}\), Acetate \(5.10^{-4}\), Fluoride \(1.10^{-4}\), Sulfate \(1.10^{-5}\). In this sense, the higher the value of SC, the more interference; therefore, in the present work we will consider those two
interferences with the highest SC values, i.e. chloride and bicarbonate. Nevertheless, the
procedure could easily be applied to other – though less important – potential interfering
anions. It should also be remarked that, in our case, the chloride and bicarbonate
concentrations have been chosen according to the range found in previous field sample
analysis. On the other hand, in the field of Electroanalytical Chemistry it is generally
accepted that, at low ionic strengths, (e.g. below 0.01M for monovalent ions and
0.001M for divalent ions) the difference between concentration and activity is really
small and the use of concentration units instead of activity for the measurements
(including calibration) should not cause a significant error in the determinations, even
without the use of ionic strength adjustment buffer (ISAB). In our case, all occurring
ions being monovalent, the ionic strength of the highest concentrated solution is 0.005,
what means that concentrations will be utilized instead of activities with no significant
error.
The correction system is then based on the evaluation of the accumulative error suffered
by the obtained measurement. This error has been found to depend on three factors,
namely: the concentrations of nitrate, bicarbonate, and chloride. Our initial hypothesis
was that it is possible to estimate, and then compensate, the interference error if [Cl\(^{-}\)]
and [HCO\(_3^{-}\)] are known. In this way, additional bicarbonate and chloride ISEs were
added to the nitrate ISE in order to measure all three concentrations. It must be
considered that the real concentrations are not available, as far as they have to be
determined by the measurements – probably affected by the interferences and perhaps
other instrumental errors – of these ISEs.
As described below, an exhaustive set of experiments (Table 2) has been carried out
under laboratory conditions. These experiments consisted of the application of the three
ISEs to mixtures prepared with known concentrations of all three anions. As expected,
measured nitrate concentrations suffered a relative error ranging from 15 % to 30 %
(easily determined as the difference between measured values and true values). For their
part, the errors of both bicarbonate and chloride measurements were under 2 % in all
instances.
In order to obtain reliable results, \(n\) replications have been performed for each
measurement, \(n\) being calculated as follows:
The results for each measurement have been considered as random variables \((X_1,\ X_2, \ldots, \ X_n)\) with a \(\mu\) mean value. \(n\) simulations have been repeated until an estimation of
\(\mu\) has been obtained with a 90 % confidence interval according to the expression:
\[ \bar{X}(n) \pm t_{n-1,0.95} \sqrt{S^2(n)/n} \]

where \( t_{n-1,0.95} \) represents the upper limit of the Student’s t-distribution on \( n-1 \) degrees of freedom, and \( \bar{X}(n) \) and \( S^2(n) \) are the mean and the variance of the results obtained in the different experiments. In general, 5-12 replications were carried out for each measurement.

We have evaluated different techniques that relate the interferences of chloride and bicarbonate on nitrate measurements, from simple, fixed (predetermined) corrections to more complex techniques. From the corresponding essays, it could be noticed that the former did not prove to be useful in all cases. More complex solutions yielded good results, but their high requirements of computing resources make them unsuitable for WSN. Instead, the proposed methodology brings together simplicity and highly satisfactory results [17]. It assumes that there is some relationship between the concentration of interferents and the error committed in the determination. Bearing this in mind, several experiments were carried out using standard solutions; then, with the results obtained as well as the corresponding true values, different mathematical procedures were evaluated to determine the error committed. Least squares linear regression was chosen since it provided negligible errors in the estimation. According to this procedure, the values provided by the three ISEs used are plotted against (correlated with) the errors in nitrate measurements (true values are known), the corresponding regression line coefficients being shown in Table 1. Linear regression has proved to be satisfactory (\( R^2 = 0.9607 \)). This accuracy is better, for example, than the measurement error. This method also deals with cross-ion interferences, since the regression line is based on measured ISE concentrations, rather than on true concentrations. Thus, the mutual interferences have also been considered. Thereafter, an estimation program was implemented; it applied the previously defined error estimation procedure to the obtained measurements. The estimated error is then subtracted to the nitrate concentration measured to obtain the corrected value. Once the latter has been achieved, the error turns out to be under 5 % in all studied cases.
3 System description

The application of the technique described in the previous section results in the development of a smart sensor node formed by three ISE-type transducers for the determination of nitrate, chloride, and bicarbonate, respectively. The core of the system consists of a low-consumption, low-cost microcontroller; its capacity is nevertheless more than sufficient to carry out all the operations required to apply the developed techniques. This microcontroller is a small integrated circuit that contains all the computer components (CPU, memory, and necessary I/O subsystems), and therefore offers the possibility to implement complete applications using only one chip [18]. The device chosen (ARM Cortex M0) is a 32-bit microcontroller with a high energy efficiency (12.5 μW / MHz) and performance; it has 2 KB RAM memory and 8 KB flash memory, as well as three timers (16 and 32 bits) and an A/D converter (10-bit resolution and 8 channels). Incoming signals from ISEs are adapted/amplified by means of an AD524 Instrumentation Amplifier (Analog Devices).

The capture of the information in the sensor node begins in the transducers (nitrate-ISE, chloride-ISE, and bicarbonate-ISE). The analogical signals from these ISEs are conveniently processed and amplified by means of analogical circuits, as shown in Figure 1. The output of this circuit is received by the A/D converters of the microcontroller (Input/Output subsystems) to be discretized. After the suitable conversion, a digital information of each ISE measurement is available and, therefore, able to be processed. From this moment, the error estimation procedure evaluates the interference influence, and the measured nitrate concentration is then corrected by using the proposed method, as described in Section 2.

Once the corrected measurement has been calculated, it is transmitted through the communication subsystem, be it periodically, upon request, or in an automatic way when certain conditions are met [19].

Since one of the goals was that this interference-tolerant nitrate smart sensor node could be employed in future WSN applications (and thus within the future Internet of Things), both its consumption and maintenance must reach a minimum value [20]. Therefore, low consumption components (the ISEs and the microcontroller) have been utilized; furthermore, the sensor node has been equipped with an energy harvesting subsystem that is able to keep it on over long periods of time [2].
4. Experimental

All standard and reagent solutions were prepared from analytical reagent grade chemicals (KNO$_3$ for nitrate, NaHCO$_3$ for bicarbonate, and KCl for chloride) using distilled and deionized water from a Milli-Q water purification system. The deionized water had a specific conductivity less than 0.1 µS cm$^{-1}$.

Nitrate, bicarbonate, and chloride concentrations are measured using three different homemade ISEs. When the ISE is immersed in an aqueous solution, a potential is established across the membrane that depends on the relative amounts of analyte in the medium, this potential being read relative to a double-junction reference electrode of the probe. Our ISEs were prepared and conditioned following some of the guidelines provided by the literature [21].

In case of nitrate, the ISE employs a silver/silver chloride wire electrode in a custom filling solution. The internal solution is separated from the sample medium by a polyvinylchloride (PVC) membrane, which selectively interacts with NO$_3^-$ ions. To prepare this membrane, a mixture of 45 mg tridodecylammonium nitrate, 370 mg dibutylphthalate as plasticizer and 160 mg PVC is thoroughly dissolved in 7 mL tetrahydrofuran. The solution obtained is then poured into small glass rings and the organic solvent is evaporated, thus achieving homogeneous membrane layers with a thickness ranging between 450 and 500 µm. The resulting electrode has the following characteristics: a Nernstian slope of 54 ± 5 mV per decade change in activity, a limit of detection of 0.05 mg L$^{-1}$ of NO$_3^-$, a response time of less than 10 seconds, a selectivity coefficient for nitrate against chloride ($k_{NO3^-,Cl^-}$) of 5 × 10$^{-3}$, and a selectivity coefficient for nitrate against bicarbonate ($k_{NO3^-,HCO3^-}$) of 4 × 10$^{-3}$.

The nitrate-ISE was then calibrated with potassium nitrate standard solutions maintained at 25°C and constantly stirred. Figure 2 shows a calibration curve for this anion. All measurements (including calibration) were carried out with 100 mL of test solution in a suitable Pyrex beaker. All glassware was decontaminated, washed several times with double-distilled water and dried in an oven at 150°C overnight prior to use. The validation of the results obtained by the nitrate-ISE was achieved using an official standard method [22] and showed excellent correlation between the two techniques ($R^2= 0.9948$) over a large range from 0.1 to 20 mg L$^{-1}$ nitrate-N with no systematic errors. On the other hand, the drift of the electrode contacting a 9.9 mM nitrate solution
is less than 0.4 mV h⁻¹, measured at constant temperature and with ISE and reference electrode continually immersed.

As regards bicarbonate, the ISE consists of a polyvinyl chloride tube covered with a thin (10-25 µm) HCO₃⁻-selective membrane made from a mixture containing polyvinyl chloride, di-(2-ethylhexyl) sebacate, trioctyl tin chloride and an H⁺ interference-removing trifluoroacetophenone (trifluoroacetyldecylbenzene), a liquid solution containing 50 mM phosphate buffer and 0.01 M sodium chloride in the tube, and a lead wire connected to a Ag/AgCl reference electrode positioned in the tube. This ISE has then the following features: a Nernstian slope of 55 ± 5 mV per decade change in activity, a limit of detection of 1.5 mg L⁻¹ of HCO₃⁻, and a response time of less than 20 seconds.

The bicarbonate-ISE was calibrated with sodium bicarbonate standard solutions maintained at 25°C and constantly stirred. Figure 2 shows a calibration curve for this anion. All measurements (including calibration) were carried out with 100 mL of test solution in a suitable Pyrex beaker. All glassware was decontaminated, washed several times with double-distilled water and dried in an oven at 150°C overnight prior to use.

The validation of the results obtained by the bicarbonate-ISE was performed using an official standard method [22] and showed excellent correlation between the two techniques (R²= 0.9936) over a large range from 10 to 250 mg L⁻¹ bicarbonate with no systematic errors. It should also be noted that the drift of the electrode contacting a 11.9 mM bicarbonate solution is less than 0.5 mV h⁻¹, measured at constant temperature and with ISE and reference electrode continually immersed.

Finally, in the case of the chloride-ISE, the membrane is made from a combination of ([γ-[4,5-dimethyl-3,6-bis(octyloxy)-1,2-phenylene]bis(trifluoroacetato-O)dimercury), tridodecylmethylammonium chloride, bis(2-ethylhexyl)sebacate, and polyvinylchloride, a reference solution containing 0.1 M potassium chloride, and a wire connected to a Ag/AgCl reference electrode. The ISE so constituted is characterized by a Nernstian slope of 54 ± 5 mV per decade change in activity, a limit of detection of 1 mg L⁻¹ of Cl⁻, and a response time of less than 10 seconds.

The chloride-ISE was calibrated with potassium chloride standard solutions kept at 25°C and constantly stirred. Figure 2 shows a calibration curve for this anion. All measurements (including calibration) were carried out with 100 mL of test solution in a suitable Pyrex beaker. All glassware was decontaminated, washed several times with double-distilled water and dried in an oven at 150°C overnight prior to use.
The validation of the results obtained by the chloride-ISE was performed using an official standard method [22] and showed excellent correlation between the two techniques ($R^2=0.9963$) over an approximate range between 1 and 300 mg L$^{-1}$ chloride with no systematic errors. And last but not least, the drift of the electrode contacting a 13.4 mM chloride solution is less than 0.4 mV h$^{-1}$, measured at constant temperature and with ISE and reference electrode continually immersed.

Stock solutions of KNO$_3$ (for nitrate), NaHCO$_3$ (for bicarbonate), and KCl (for chloride) were prepared by dissolving the appropriate amount of reagent in distilled-deionized water. In order to carry out the measurements, the three aforementioned ISEs were then simultaneously immersed in solutions obtained by suitable mixtures of the stock solutions, in such a way that the following concentrations were selected: (a) 0.0, 0.5, 1.0, 1.5, and 2.0 mg L$^{-1}$ of nitrate, (b) 0, 125, 150, 175, and 200 mg L$^{-1}$ of bicarbonate, and (c) 0, 50, 100, 150, and 200 mg L$^{-1}$ of chloride. The contents of the three analytes were then measured in combinations of these solutions in threes (Table 2).

5 Results and discussion

The results achieved are summarized in Figures 3 and 4. Figure 3 shows the values obtained without applying the proposed methodology. The horizontal axis represents the true values of [NO$_3^-$] (solutions were prepared by us following the procedure described in the previous section, and are therefore known values), whereas the vertical axis represents the measured concentrations, i.e. the experimental values provided by the ISEs. Needless to say that an ideal nitrate sensor should give rise to a 45-degree line to which the red line of the figure approximates a lot. This line reflects the results obtained with the nitrate-ISE after its calibration and in the absence of interferences (i.e. immersed in a standard nitrate solution). On the other hand, when the interfering anions (chloride and bicarbonate) are added at known concentrations, the measured values start to distance themselves from real concentrations owing to the interferences. Consequently, an uncertainty area appears depending on the concentration of the interfering species. For the concentration ranges of the interferents (see section 4), this uncertainty area is the one between the upper and lower lines.

As it can be inferred from our study, and on the basis of a known nitrate concentration...
(i.e. any point at the horizontal axis), the response of nitrate-ISE may vary – as a function of the concentration of interferents – in the range resulting from the intersection of the vertical line at this point with the uncertainty area. As an example, for a known value of $[\text{NO}_3^-] = 2 \text{ mg L}^{-1}$ the results that could be obtained by measuring with the corresponding ISE would lie between 2.04 mg L$^{-1}$ (no interferences) and 2.52 mg L$^{-1}$ (corresponding to $[\text{Cl}^-] = 200 \text{ mg L}^{-1}$ and $[\text{HCO}_3^-] = 200 \text{ mg L}^{-1}$). It can be noticed that – depending on the concentrations of interferents – the error obtained can be significant, up to 26 %.

On the other hand, attention should also be paid to the real case of the need to determine (using a NO$_3^-$-ISE) the concentration of nitrate in the presence of an unknown amount of chloride and bicarbonate. In these circumstances, the starting point is the vertical axis (measured values of nitrate-ISE); true nitrate concentrations in the sample may be anyone corresponding to the intersection of a horizontal line passing at this point with the uncertainty area. For instance, for a measured concentration of 2 mg L$^{-1}$, true values of $[\text{NO}_3^-]$ in the analyzed sample may be in the range between 1.56 mg L$^{-1}$ (highest concentration of interferents) and 1.96 mg L$^{-1}$ (no interferences). The measurement uncertainty is again really high.

Figure 4 shows the results obtained after the data treatment of previous measurements with the method described in section 2. The values yielded by a node using this procedure would also generate (as described above for Figure 3) an uncertainty area, although in this case it is significantly smaller. This fact makes the measurements from this node to be virtually free from the effects of the interferences, unlike in case this methodology would not be used. Indeed, if a given value of $[\text{NO}_3^-]$ is now considered and a vertical line is drawn through this point, its intersection with the uncertainty area yields a much lower dispersion of values. In case of the above mentioned example ($[\text{NO}_3^-] = 2.00 \text{ mg L}^{-1}$), the values obtained vary between 1.99 mg L$^{-1}$ (for 100 mg L$^{-1}$ chloride and 125 mg L$^{-1}$ bicarbonate) and 2.07 mg L$^{-1}$ (for 150 mg L$^{-1}$ chloride and 200 mg L$^{-1}$ bicarbonate), that is to say, with a maximum error of 3.5 %, far from the aforementioned 26 %.

Again, we return to the real case of the need to determine (using a NO$_3^-$-ISE) the concentration of nitrate in the presence of an unknown amount of chloride and bicarbonate. A point is taken at the vertical axis (the value corresponding to the measurement obtained using the proposed methodology), for instance 2.00 mg L$^{-1}$ nitrate; when a horizontal line is drawn through this point, it intersects with the
uncertainty area at values ranging from 1.93 mg L$^{-1}$ (for 200 mg L$^{-1}$ chloride and 175 mg L$^{-1}$ bicarbonate) to 1.99 mg L$^{-1}$ (for 50 mg L$^{-1}$ chloride and 125 mg L$^{-1}$ bicarbonate). This demonstrates that the resulting nitrate concentration is very close to the true value, the error being thus considerably reduced.

6. Conclusions

This work presents a new methodology to develop smart sensors with interference tolerance based on simple Ion Selective Electrodes (ISE). For this purpose, a correction mechanism based on interferent concentration measurement, error estimation, and a correction procedure has been added. This method permits to “reject” the mutual contributions to the analytical signals of ISEs due to the presence of interfering species in the analyzed samples. Basically, it consists of applying statistical techniques –linear regression of experimental data- to adjust the linear coefficients of each interferent on the basis of the experiments observed.

This has been incorporated into the design and implementation of a nitrate smart sensor for WSN applications that is able to overcome the problem associated with interfering anions in ground waters, namely, chloride and bicarbonate. The procedure has been applied to the measurements obtained from a nitrate-ISE in the presence of those two anions by means of a microcontroller. The smart sensor node is then composed of the three ISEs used (NO$_3^-$, Cl$^-$, HCO$_3^-$) along with a low-cost, low-consumption microcontroller. All three ISE’s are simultaneously immersed in a water sample; the corresponding measurements obtained are then conveniently received and processed by the microcontroller. The final result after applying the proposed method is that the nitrate measurements performed by this smart sensor turn out to be virtually interference-free.

Finally, the significance of this proposal lies in the application of automatic procedures implemented in microcontrollers in order to compensate physical deficiencies, such as the impact of interferences, in measurement processes. This proposal may be extended to increase the smartness of sensor nodes in order to enhance their features.

New-generation smart sensors applying these principles may be suitable for integration in Wireless Sensor Networks, on which Internet of Things and Ambient Intelligence will be based.
Acknowledgements

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References


Legends of figures

Figure 1.- Structure of a nitrate smart sensor node. A = signal amplifier & conditioner.

Figure 2.- Calibration plots for the determination of nitrate, bicarbonate, and chloride using the corresponding ion-selective electrodes. Activities are expressed in mol L\(^{-1}\).

Figure 3.- Experimental results obtained in the presence of interferences. Values between parenthesis on the right side of the figure denote the following: ([HCO\(_3\)]\(^-\),[Cl\(^-\)]) All concentrations are expressed in mg L\(^{-1}\).

Figure 4.- Experimental results obtained with interference tolerance. Values between parenthesis on the right side of the figure denote the following: ([HCO\(_3\)]\(^-\),[Cl\(^-\)]) All concentrations are expressed in mg L\(^{-1}\).
Table 1.- Coefficients obtained in the regression analysis (concentrations in mg L\(^{-1}\))

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<td>([\text{Cl}^-])</td>
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<td>([\text{HCO}_3^-])</td>
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Table 2.- Initial concentration data set

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<th>[Cl⁻], mg L⁻¹</th>
<th>[HCO₃⁻], mg L⁻¹</th>
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64 experiments