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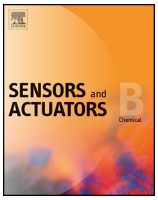

An interference-tolerant nitrate smart sensor for Wireless Sensor Network applications

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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_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_3^-, Cl^-, and HCO_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_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.

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

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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}

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

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.

Table 1
Coefficients obtained in the regression analysis (concentrations in mg L^{-1}).

Coefficient	Value
Intercept	−0.108336504
$[NO_3^-]$	0.123178928
$[Cl^-]$	0.000920765
$[HCO_3^-]$	0.000386705

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 0.01 M for monovalent ions and 0.001 M 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