In situ continuous monitoring of chloride, nitrate and ammonium in a temporary stream Comparison with standard methods

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Abstract

A multi-parameter probe was used for *in situ* chloride, nitrate and ammonium measurements in a temporary stream (Ribeira da Pardiela, in the South of Portugal). Comparison with standard analytical methods was performed for all elements. For chloride, the results of the probe depicted the same behaviour as that obtained with the standard method, although it is clear that the matrix effects were present. For nitrate, the results obtained with the probe were in agreement with the other standard methods used, except for samples collected during drought, when the stream water became brownish and exhaled an offensive smell, due to the decomposition of organic matter. For ammonium, surprisingly the probe show to be the best option, the phenate method being affected by matrix effects. The results still suggest an interference of the bicarbonate ion on nitrate determination, but standard additions approach was shown to minimize most of the matrix effects. Recoveries were reasonable to good for all the three anions under scrutiny.
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1. Introduction

Water quality monitoring is usually performed by sampling followed by storage, handling and analysis in the laboratory. This is a cumbersome process and often does not provide the required spatial discrimination and/or the large sets of data necessary to describe the temporal evolution of the parameters of interest. It is also known that during storage the integrity of the sample may not be preserved, due to a number of effects that include biological activity and matrix effects, even when correct sample handling protocols are strictly followed. An alternative approach consists in performing the measurements at the location of interest, i.e., *in situ*. This approach is likely to has a significant impact in the future on (i) our understanding of the ecosystem functioning, and (ii) our ability to monitor, model and therefore to efficiently protect these ecosystems [1]. As a

matter of fact *in situ* measurements is probably the best way to overcome a major problem facing aquatic analytical chemists, i.e., how to maintain the sample in its original state during sampling and handling, without stimulating any of the very dynamic chemical, biological and physical processes which may continue after sample collection. Indeed, in their natural environment, aquatic samples are not at thermodynamic equilibrium. In fact, at best, they may be in steady state conditions due to the continuous input (e.g., soil leaching, atmospheric inputs, cell growth) and output (e.g., coagulation/sedimentation, cell death) of colloids and microbes [2,3].

The major advantages of the *in situ* approach compared with laboratory analysis are the following [4]: (1) elimination of contaminants due to sample handling, i.e., no or minimum sample transformation; (2) minimization of the overall cost data collection (in particular, due to a reduction of time for collection, handling and analysis of the sample); (3) possibility of real-time analysis, allowing the rapid detection of pollutant inputs (e.g., monitoring of industrial wastes or water quality in water treatment plants); (4) ability to obtain detailed spatial and temporal

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data banks of complete ecosystems (lakes, aquifers, etc.); (5) possibility of performing measurements in locations which are difficult to access (deep lakes or oceans) and (6) possibility of measuring concentration gradients and fluxes at environmental interfaces (sediment water; air–water), at high (sub-mm) spatial resolution.

There has been an extensive effort to design chemical sensors and analysers that are capable of operating *in situ*. Much of this work has been summarized in a recent volume on chemical sensor systems for aquatic sciences, which describes a variety of continuous flow analysers, electrochemical sensors and optical sensors for *in situ* measurements of dissolved chemical species [1]. All of these systems are affected by interferences due to sample composition, i.e., matrix effects. In fact, even the standard methods when applied to real samples are subject to interferences [5].

Among the *in situ* chemical sensors, the ion selective electrodes (ISE) are able to continuously monitor a system, which is invaluable when it is necessary to use large sets of data to calibrate mathematical models capable to describe the behavior of complex ecosystems and when the sample matrix can be altered by sampling and storage and/or by inflow of nutrients or elements from various sources (as for example, wastewater and agriculture). In this work, we analyse chloride, nitrate and ammonium concentration using the corresponding ion selective electrodes placed *in situ* in a multi-parameter probe [6,7].

Chloride is one of the major inorganic anions in water and wastewater. A higher value of chloride may indicate the inflow of wastewater or industrial effluents into the river. The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common constituent of the diet and passes unchanged through the digestive system [8]. Nitrate and ammonium are important because they are the major forms of nitrogen which are directly assimilated by plants and organisms. Nitrate is one of the most common contaminants of groundwater, originating mainly from agricultural fertilizer application and release of sewage [8]. In fact, nitrogen dynamic plays a key role in determining the ecological status and health of lowland rivers, estuaries and coastal waters as limiting factor of primary production. Eutrophication is, indeed, a major concern in these ecosystems, and is strongly influenced by factors such as agricultural practices and demographic change, and its control requires intensive sampling, with high temporal and spatial collections in catchment areas [9].

In the Mediterranean region, the dominant types of streams are the temporary [8]. The hydrologic and biogeochemical processes that occur during the wetting and drying periods, in this type of stream, are far from being well understood [10–13]. Ribeira da Pardiela is a temporary stream on the right shore of the Degebe river which is one of the main tributaries of the Guadiana river (in the South of Portugal).

The aim of this work was to compare the *in situ* determination of chloride, nitrate and ammonium with well-established laboratory procedures, in a temporary stream (Ribeira da Pardiela).

2. Experimental

2.1. Instrumentation

A multi-parameter probe (Yellow Spring–YSI 6600) was used to *in situ* monitor parameters such as depth, temperature, conductivity, pH, oxidation–reduction potential, dissolved oxygen, chlorophyll, turbidity, chloride, ammonium/ammonia and nitrate. Chloride, ammonium and nitrate were measured using three ion selective electrodes (ISE) incorporated in the probe. The probe chloride ISE employs a solid state membrane attached to a conductive wire. When the probe is immersed in water, a potential is established across the membrane that depends on the relative amounts of chloride in the medium. This potential is read relative to the reference pH electrode of the probe. The probe ammonium ISE employs a silver/silver chloride (Ag/AgCl) wire electrode in a custom filling solution. Nonactin membrane separates the internal solution from the sample medium and this membrane selectively interacts with ammonium ions. When the probe is immersed in water, a potential is established across the membrane that depends on the relative amounts of ammonium in the sample and the internal filling solution. This potential is also read relative to the reference pH electrode of the probe. The probe nitrate ISE consists of a silver/silver chloride wire electrode in a custom filling solution. The internal solution is separated from the sample medium by a polymer membrane, which selectively interacts with nitrate ions. When the probe is immersed in water, a potential is established across the membrane that depends on the relative amounts of nitrate in the sample and the internal filling solution. This potential is read relative to the pH reference electrode of the probe [6].

A Unicam UV/vis spectrophotometer was used for all measurements of nitrate and ammonium with the cadmium reduction method and the phenate method, respectively [5]. An Inolab WTW potentiostat with a nitrate selective electrode (Methrom 6.1241.050) and a reference Ag/AgCl electrode (Methrom 6.0726.100) was used for the nitrate electrode method [5], which was compared with the probe nitrate ISE.

2.2. Reagents and standards solutions

All solutions were prepared from analytical reagent grade chemicals using distilled and deionised water from a Milli-Q water purification system. The deionised water had a specific conductivity less than $0.1\,\mu S\,cm^{-1}$.

Chloride standard solutions (YSI) of 10 and $1000\,mg\,l^{-1}$, nitrate standard solutions (YSI) of 1 and $100\,mg\,l^{-1}$, and ammonium standard solutions (YSI) of 1 and $100\,mg\,l^{-1}$ were used for probe calibration. A two-point calibration was performed for all elements.

3. Analytical procedure

3.1. Sampling and storage

Water samples were regularly collected at the study site between 9 and 10 a.m., maintained at $4\,^{\circ}C$ during transporta-

tion and filtered through 0.47 μm glass fibre filters (Schleicher & Schuell) immediately at the arrival in the laboratory. Sample conservation was done as specified in [5].

3.2. Probe procedure

The probe was cleaned with distilled water (and soft paper) and calibrated for all parameters before being placed in the field, inside a metal structure for security reasons. This metal structure was partially immersed in Ribeira da Pardiela at the following coordinates: latitude 41°10′45″N, Longitude 8°36′23″W and altitude 178 m.

3.3. Methods

The methods used for comparison, in the laboratory, were the argentometric method for chloride (4500-Cl$^-$ B), the phenate method for ammonium (4500-NH$_3$ F), and the cadmium reduction (4500-NO$_3^-$ E) and the nitrate electrode methods (4500-NO$_3^-$ D) for nitrate [5]. The argentometric method is based on the precipitation of the silver chloride, which is indicated by the formation of the red silver chromate. The phenate method consists in the formation of indophenol, an intensely blue compound, that results from the reaction of ammonia, hypochlorite and phenol, which is catalyzed by sodium nitroprusside. For the cadmium reduction method, nitrate is reduced almost quantitatively to nitrite in the presence of cadmium treated with copper sulfate and packed in a glass column. The nitrite thus produced is determined by diazotizing with sulfanilamide and coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured colorimetrically. A correction may be made for any nitrite present in the sample by analysing without the reduction step. The nitrate electrode method consists in using an ion selective electrode. This nitrate ion electrode is a selective sensor that develops a potential across a thin, porous and inert membrane. A solution of ammonium sulphate 1 M (1:1) was added to standard solutions and samples in order to keep constant the ionic strength and the pH during measurements. Replicates were done for all the methods.

4. Results and discussion

4.1. Analysis of simple and real samples with the probe and the respective standard methods

To establish the validity of our procedure, before using the multi-parametric probe in real samples we compare the ISE results with the standard methods [5], using standard solutions.

Fig. 1 shows that the values obtained for chloride using a standard solution of 121 mg l^{-1} Cl$^-$, were the same for the probe ISE and for the argentometric method, within the experimental errors. Nevertheless when the chloride concentration was determined in real samples the probe ISE results were higher than those obtained with the argentometric method, both for filtrated and non-filtrated samples. Filtration does not seem to influence the chloride measurement by the two methods (Fig. 1).

The results obtained with the probe and the phenate method on standard ammonium solutions (0.16, 0.39 and 0.78 mg l^{-1}
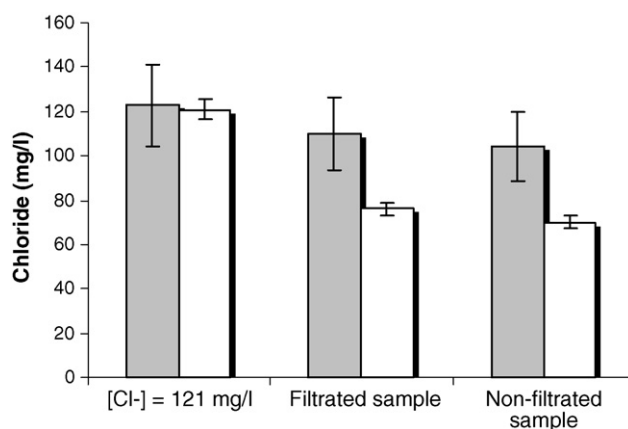

Fig. 1. An example of chloride determinations in standard and field samples, using the probe (■) and the argentometric method (□). *Note*: The errors presented are not due to replicates but to the uncertainty of the method used.

NH$_4^+$-N) agreed, within experimental error (Fig. 2). On the other hand, in real samples, the values obtained with the probe ISE were higher than the values obtained with the phenate method. Moreover the ammonium concentrations determined in non-filtrated samples were higher than in filtrated samples, and these differences are not within the experimental errors. A likely explanation is that ammonium ions adsorb on the suspended particles, and therefore non-filtrated samples present an higher ammonium concentration [8].

For nitrate, the probe ISE was compared with two standard laboratory methods, one of them also an ion selective electrode (ISE), the nitrate electrode method, and the other the cadmium reduction method. Fig. 3 depicts the results obtained with these methods in a standard solution and in filtrated and non-filtrated real samples. It can be seen that in a solution with a known concentration of nitrate (1.4 mg l^{-1} NO$_3^-$-N) the values obtained are in close agreement for all the three methods, considering the experimental errors associated with each method. For real samples, similar results were obtained with the probe and the nitrate electrode method [5]. However the values obtained with the cadmium reduction method showed to be lower.

For filtrated and non-filtrated real samples the results were again within the experimental errors for each method used. How-
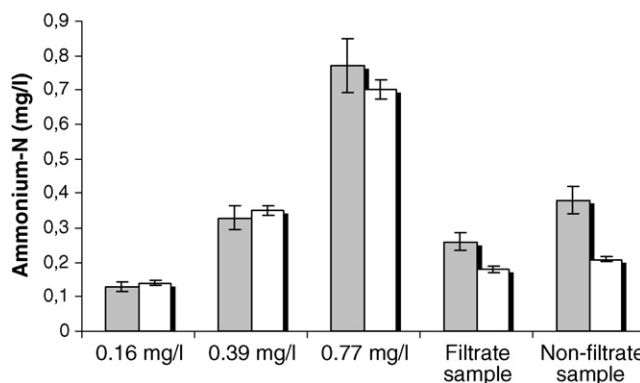

Fig. 2. An example of ammonium determinations in standard and field samples, using the probe (■) and the phenate method (□). *Note*: The errors presented are not due to replicates but to the uncertainty of the method used.
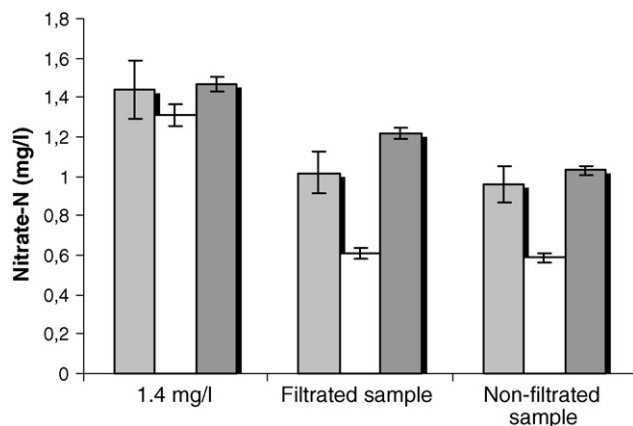
Fig. 3. An example of nitrate (NO_3^--N) determinations in standard and field samples, using the probe (▨), the cadmium reduction method (□) and nitrate electrode method (▩). *Note*: The errors presented are not due to replicates but to the uncertainty of the method used.

ever, the values obtained for nitrate by the three methods with filtered samples appear to be higher than those obtained for non-filtered samples. The filters were therefore tested for nitrate contamination, passing ultra pure Millipore water through them, and analysing the resulting operational blanks, but no contamination could be detected.

4.2. Analysis of real samples with the standard additions method

The standard additions method is known to overcome most of matrix effects, i.e., interferences due to sample composition. It consists in adding known concentrations of the analyte to the sample, and to compute its concentration by extrapolation and interception with the *x*-axis, after a linear correlation. All the readings are taken in the same sample matrix, which avoids or minimizes matrix effects [14].

In order to avoid sample matrix effects, we used the standard additions approach and compared the results obtained with the probe ISEs and the reference methods adopted for comparison for each species (chloride, ammonium and nitrate), using samples collected in the field.

The results obtained for chloride showed that, when the standard additions approach was applied with the argentometric method, no matrix effects could be detected, i.e., the results obtained with standard additions ($107 \pm 4\%$ mg l^{-1} Cl$^-$) and without standard additions ($106 \pm 4\%$ mg l^{-1} Cl$^-$) were the same, within the experimental errors. When measuring chloride with the probe ISE, matrix effects were present, as expected, the standard additions approach considerably reducing their interference in most of the samples, though not always.

As can be seen in Fig. 4, the behaviour of chloride concentrations along time, with considerably varying discharge, depicted by the results obtained with the probe ISE is essentially the same as that obtained with the argentometric method determinations, even being affected by sample composition. The initial higher values corresponding to the dry season, decrease abruptly with the onset of the wet season, and rise again with drought until attaining the values of the next dry season. As a matter of fact the
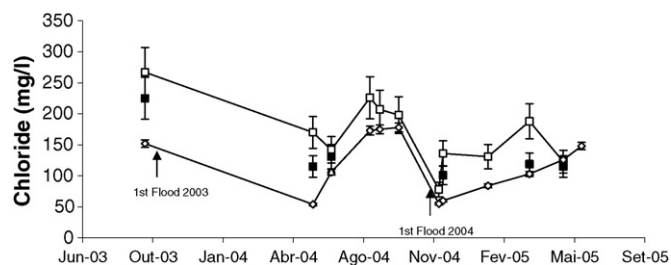

Fig. 4. Chloride determinations vs. time (months) with the probe (□), the probe with standard addition approach (■) and with the argentometric method (◇). *Note*: the values were connected only to demonstrate that the probe behaviour was the same as obtained with the argentometric method. The errors presented are not due to replicates but to the uncertainty of the method used.

first values of Fig. 4, were determined just before the wet season began with the flood of the 30 September 2003. The chloride concentration decreased considerably then and it began to increase in May attaining a maximum value at the end of the summer of 2004 (389 mg l^{-1} Cl$^-$ probe, 27 October 2004; 9–10 a.m.) just before the flood of the 27 October 2004 (1.15–1.30 p.m.). It attained the lowest measured value at the time (28 mg l^{-1} Cl$^-$ probe; 28 October 2004; 9–10 a.m.) and began to rise in November (44 mg l^{-1} Cl$^-$ probe; 06 November 2004; 9–10 a.m.) along the dry season of 2005 until the beginning of the next wet season. The dry season began exceptionally early this year, concentrating chloride earlier. In Fig. 4 the values were connected only to show that the behaviour depicted by the results obtained with probe ISE is essentially the same as the behaviour that follows from the results obtained with the argentometric method.

The results obtained for ammonium showed that the phenate method was affected by sample composition, i.e., the results obtained with standard additions ($0.27 \pm 4\%$ mg l^{-1} NH$_4^+$-N) and without standard additions ($0.18 \pm 4\%$ mg l^{-1} NH$_4^+$-N) were significantly different. In this case, the probe ISE seemed to be unaffected by sample composition, i.e., the results obtained with standard additions ($0.26 \pm 10\%$ mg l^{-1} NH$_4^+$-N) and without standard additions ($0.26 \pm 10\%$ mg l^{-1} NH$_4^+$-N) converge within experimental error. However, comparing the ammonium values obtained with the standard additions approach when applied to the probe ($0.26 \pm 10\%$ mg l^{-1} NH$_4^+$-N) and to the phenate method ($0.27 \pm 4\%$ mg l^{-1} NH$_4^+$-N) there is close agreement, within the experimental errors. In this case, we observed that the standard addition approach is important for the phenate method, since it is affected by matrix effects.

As can be seen in Table 1, the results obtained for nitrate showed that, when the standard additions approach was applied to the cadmium reduction method, no matrix effects could be observed, i.e., the results obtained with standard additions (e.g., $0.48 \pm 4\%$ mg l^{-1} NO$_3^-$-N) and without standard additions (e.g., $0.50 \pm 4\%$ mg l^{-1} NO$_3^-$-N) were the same, within the experimental errors. However, matrix effects could be observed when using the probe ISE and the nitrate electrode method, particularly when dealing with samples colleted during the summer drought. The standard additions approach considerably reduces this effect. For example in the sample collected the 12 May 2005 (Table 1), without standard additions, the values obtained

Table 1
Nitrate (NO_3^--N) determinations in filtrated samples with and without standard additions approach, for all the methods used

Date	Probe NO_3^--N (mg l^{-1}) (%)	Probe with standard addition NO_3^--N (mg l^{-1}) (%)	Cadmium reduction method[a] NO_3^--N (mg l^{-1}) (%)	Cadmium reduction method with standard addition NO_3^--N (mg l^{-1}) (%)	Nitrate electrode method NO_3^--N (mg l^{-1}) (%)	Nitrate electrode method with standard addition NO_3^--N (mg l^{-1}) (%)
25 September 2003	2.21 ± 10	–	0.47 ± 4	–	–	–
16 November 2004	0.61 ± 10	–	0.42 ± 4	–	–	–
24 November 2004	0.51 ± 10	–	0.31 ± 4	–	–	–
25 January 2005	0.45 ± 10	0.42 ± 10	0.30 ± 4	0.48 ± 4	–	–
25 March 2005	0.49 ± 10	0.43 ± 10	0.50 ± 4	0.48 ± 4	–	–
12 May 2005	1.87 ± 10	0.60 ± 10	0.44 ± 4	0.40 ± 4	1.79 ± 2.5	0.83 ± 2.5

Note: The errors presented are not due to replicates but to the uncertainty of the method used.

[a] Nitrite concentration in samples was negligible.

with the probe ISE and the nitrate electrode method were 1.87 and 1.79 ± 2.5% mg l^{-1}, respectively, whereas with standard additions these results lowered to 0.60 and 0.83 ± 2.5% mg l^{-1}, respectively.

In fact, the major discrepancies were observed for the dry season samples. This is probably due to the high concentration of decomposing organic matter in the water, that may interfere with the functioning of the nitrate electrode. The water of the drying pools, that were sampled at the time, was deep brown, of oleaginous consistency and exhaled an offensive smell. It seems clear that the conditions were not ideal for accurate chemical determinations and that the chemistry of drying waters poses a considerable analytical challenge. In 2005, as the dry season began exceptionally early, discrepancies were evident in May, which were expected to be observed only in the August and September samples (Table 1).

However some samples collected during the wet season, and therefore less prone to matrix effects, still showed a difference of almost 0.2 mg l^{-1} NO_3^--N between the results obtained with the probe and the cadmium reduction methods, when applied without standard additions (e.g., samples of 16 and 24 November 2004). It is also known that if the conductivity in the sample was all due to sodium bicarbonate, the sensor output would indicate 0.2 mg l^{-1} of non-existent nitrate due only to the bicarbonate interference [6]. The values obtained in Table 1 suggest that, in these field samples, the predominant anion could be the bicarbonate. In fact, the bicarbonate concentration, in these samples, was about 100 mg l^{-1}, whereas the chloride concentration is on the range of 50 mg l^{-1}.

The other results obtained, for samples collected during the wet season, are in good agreement, comparing the probe with the column reduction method, with or without standard additions approach. It should be noticed that at this time of year the water is cleaner, presenting a low solid suspended particle concentration, and posing fewer matrix problems (Table 1).

4.3. The study of interferences

The effect of potential interfering ions normally found in association with chloride and nitrate was studied. A given ion was considered to significantly interfere with the determination

when a mean change was observed in the results that reached at least 5%.

4.3.1. Bicarbonate interference

In order to study the possible interference of the bicarbonate ion on the determination of nitrate we measured nitrate, by the three methods under scrutiny, using standard solutions of 1 mg l^{-1} (NO_3^--N) in the absence and in the presence of bicarbonate ion, with known concentrations (100 and 200 mg l^{-1}). These bicarbonate ion concentrations were chosen according to the range found in previous field sample analysis.

For the cadmium reduction method the changes observed were lower than 5%. However, the bicarbonate ion contributed to increase the values given for the concentration of nitrate when using the probe ISE and the nitrate electrode method, by a relative change of 100% and 27%, respectively. Moreover the probe ISE measurements were more affected by the increase in the bicarbonate concentration.

In order to study the influence of bicarbonate ion on the determination of chloride we determined chloride using standard solutions with 70 mg l^{-1} (Cl$^-$) in the absence and presence of bicarbonate ions in two concentrations (100 and 200 mg l^{-1}). The bicarbonate ion does not interfere with the determination of chloride, the relative error associated being lower than 2%, both for the probe or the argentometric methods.

4.3.2. Chloride interference

To test the influence of chloride in the determination of nitrate we measured nitrate using standard solutions of 1 mg l^{-1} (NO_3^--N) in the absence and presence of several chloride concentrations (50, 100, 150, 200, 250 and 300 mg l^{-1} Cl$^-$). These concentrations were chosen according to the range of concentrations likely to be expected from our previous knowledge of chloride measurements in the *Pardiela* samples. It was observed that the presence of chloride in such concentrations enhances the nitrate measured values by about 10%, for all the three methods used. It can be concluded that chloride indeed interferes with the measurement of nitrate by such methods, but because such interference goes in the same sense and is of the same range for all the methods used, it may be not particularly relevant if our goal is the determination of trends or the understanding the gen-

eral biogeochemical behaviour of the river, more than absolute quantitation.

4.4. Recovery analysis with probe and standard methods

We have studied the response of the probe and of the adopted standard methods using field samples. For chloride the recovery obtained in real samples was 100% ($n = 3$; R.S.D. = 4%) using the probe and 97% ($n = 3$; R.S.D. = 0.3%) using the argentometric method. For ammonium the values obtained were 73% ($n = 3$; R.S.D. = 0.4%) with the probe and 98% ($n = 3$; R.S.D. = 2%) with the phenate method. For nitrate the values obtained with the probe were 105% ($n = 3$; R.S.D. = 4%), with the cadmium reduction method they were 97% ($n = 3$; R.S.D. = 3%) and with the nitrate electrode method they were 109% ($n = 3$; R.S.D. = 8%). The recoveries obtained were therefore good, with the exception of the recovery obtained for ammonium determined with the probe, which can only be considered as reasonable.

5. Conclusions

Although great emphasis is given in this work to the study of matrix effects, the results obtained supports the idea that, most of the time, the field monitoring of chloride, nitrate and ammonium, can be performed with ion selective electrodes, with all the advantages of *in situ* determinations. The probe is quite stable and robust, and provides very important information, that would be unavailable otherwise, particularly in what concerns the chemical response of the river to the first flood in the beginning of the wet season. The study of such response with the probe was in fact, the initial goal of this work, and this was accomplished. During dry season the conditions were adverse for all probe ion selective electrodes considered, particularly for the nitrate and the chloride electrodes.

It can also be concluded that a background correction is necessary, especially in the summer due to the complex and largely unknown matrix, if acceptable results are to be obtained. This can be done by regularly comparing the values obtained with the probe and the respective standard methods in the laboratory.

Although not being always effective for chloride, the standard additions approach considerably reduces the matrix effects. Particularly when applied to nitrate, the results obtained with the probe and the cadmium reduction method shows a reasonable good agreement.

Acknowledgements

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