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Research Paper

Evaluation of an Array of Anions Selective Electrodes in a Continuous Flow Analysis System

Nayara Penoni[1], Gilmare Antônia da Silva[2], Clausius Duque Gonçalves Reis[3], Cherrine Kelce Pires[4], Gabriel Henrique Sperandio[5], Maria Isabel Cristina Batista Mayrink[6], Efraim Lázaro Reis[2,]*

[1] *(Federal Institute of Minas Gerais, Bambuí – MG – Brazil)*
[2] *(Department of Chemistry, Federal University of Viçosa, Viçosa – MG – Brazil)*
[3] *(Department of Informatics, Federal University of Paraná, Curitiba – PR – Brazil)*
[4] *(Federal University of Rio de Janeiro, Macaé – RJ – Brazil)*
[5] *(University College, Federal University of Viçosa, Viçosa – MG – Brazil)*
[6] *(Dinâmica do Vale do Piranga College, Ponte Nova – MG – Brazil)*
**Correponding Author: efraimreis@gmail.com*

ABSTRACT: *A potentiometric system was developed, composed of six ion-selective electrodes arranged in a continuous flow line. Solutions with varying concentrations of the corresponding ions were injected into the continuous flow line, passing through a flow cell where the electrodes were arranged sequentially. The system allows for complete automation of the analytical process, resulting in fast measurements with low reagent consumption. Electrode calibration was a fundamental step in the study, allowing the acquisition of analytical curves. For the supporting electrolyte used, which has a pH of 9.0, only the nitrite electrode has an operating range below this value. Despite this fact, all electrodes showed excellent linearity in their responses with good Nernstian behavior.*

KEYWORDS: *Ion-selective electrodes; Anions; Continuous flow analysis.*

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I. INTRODUCTION

Ion-selective electrodes (ISEs) are widely used in potentiometric determinations of various chemical species in diverse environments, such as aquatic environments. This is of paramount importance, as the need to maintain and even recover water quality, which is unfortunately increasingly contaminated by various types of pollutants, becomes more pronounced [1-4].

The use of these electrodes presents some advantages such as the reduced cost of the equipment and, in most cases, a short response time. In addition, since it is a non-destructive method, it is possible to perform in situ measurements [5-7].

Despite these advantages, the use of ion-selective electrodes remains restricted due to the interferences that generally occur in the measurements, especially in those where it is intended to obtain responses from a larger number of ions. However, these ion interferences can have their effects studied through multivariate analysis, which allows for a better understanding of the system. Thus, by employing an array of ion-selective electrodes, multivariate calibration techniques can eventually be applied, making it possible to separate the responses of various ions present in the medium in question and, consequently, obtain appropriate conditions for determining their concentrations. In this way, ion-selective electrodes can be used with greater effectiveness and precision, both in industrial processes and in environmental analyses [8].

In the system explored in this work, the solutions are injected into a continuous flow of carrier solution and pass through a flow cell, where the electrodes are arranged in sequence. This system allows for complete automation of the analytical process, resulting in fast measurements with low reagent consumption. The main advantage of the ion-selective electrode array is the ability to measure multiple ions in a single run, overcoming the limitation of a single electrode per analyte.

The use of flow cells helps ensure reproducible measurement conditions and can minimize contamination of the reference electrode junction and leaching of materials from the ISE membranes. Signals from multiple electrodes are recorded and can eventually be processed using chemometric methods to extract accurate information and correct cross-interference between ions [9].

In this work, an initial evaluation of an array of electrodes selective to chloride, bromide, iodide, nitrate, nitrite, and sulfide ions, integrated into a continuous flow analysis system, was carried out with the aim of investigating the linearity of responses in time and concentration, as a way to test the performance of the developed system.

II. MATERIAS AND METHODOLOGY

II.1. Solutions

For filling the electrodes, potassium nitrate (KNO_3) solutions at 1.00 mol L^{-1} were prepared for the outer chambers and solutions at 0.1 mol L^{-1}, respectively, of chloride, bromide, iodide, nitrate, nitrite, and sulfide for the inner chambers. To obtain the analytical curves for the electrodes, solutions for chloride, bromide, iodide, nitrate, nitrite, and sulfide ions were prepared at concentrations ranging from 0.0001 mol L^{-1} to 0.10 mol L^{-1}.

In all analyses, the ionic strength of the solutions was controlled with sodium acid phosphate (Na_2HPO_4) solution at a concentration of 1.00 mol L^{-1}. In this way, the pH was maintained at approximately 9.0.

II.2. Electrode Arrangement and Potential Measurements

The system arrangement consisted of an Ag/AgCl reference electrode and ion-selective electrodes for chloride, iodeto, bromide, sulfide, nitrate and nitrite from Orion[10-15], positioned equidistant from each other (Figures 1 and 2) and pressed against the rubber separator by springs, as can be seen in Figure 2(a).

The potentials were measured at a temperature of 25 °C, with a maximum variation of 1°C. The electrodes were connected to a PROBER-PH8 multiplexer from Erlich Industrial Development (EID), which communicates with a microcomputer via a standard RS232C serial interface. This process handles all instrumental management and potentiometric data acquisition.

This instrument (Figure 2b) allows multiplexed measurement of potentiometric signals from up to eight electrodes sequentially, with a minimum reading time of 1 second for the electrodes.

A single flow channel was used for the standard solutions or samples and washing solution. The changeover to the washing solution was performed automatically by the system, through a Teflon solenoid valve, activated with a signal from the Centronic standard parallel output (Figure 1). The signal from this interface has a level compatible with digital circuit signals (TTL). The solenoid valve is activated with a potential difference of 12 volts, so it was necessary to boost the TTL signal from the parallel output with a circuit based on a power transistor.

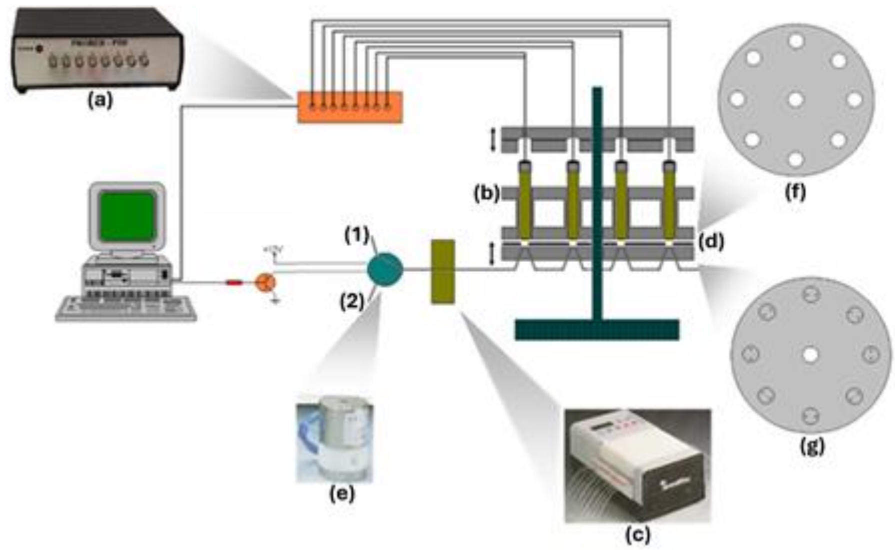


Figure 1: Continuous flow analysis system. (a) Potentiometric multiplexer; (b) Selective electrode assembly; (c) Peristaltic pump; (d) Silicone rubber spacer for sealing; (e) Three-way solenoid valve for washing solution (1) and sample (2) inlets; (f) Acrylic plates with holes for electrodes; (g) Acrylic plate with holes for solution inlet and outlet.

The liquids were conveyed through polyethylene tubes with an internal diameter of 0.8 mm, and an Ismatec peristaltic pump was used for pumping.

The potential readings for each of the prepared solutions are taken every second, and then the average is recorded for each set of 5 readings. This operation is repeated for a total time of 80 s. The final potential for constructing the analytical curve corresponds to the average of the potentials over this total time.

A commercial program in a Windows environment called Prober-PH8, developed by EID, was used to acquire the data. The program allows obtaining measurements in millivolt potential values, making it possible to choose the precision of the readings up to three decimal places and define the time interval with which the measurements obtained are to be recorded, with a minimum recording of one second between each reading of the six electrodes. The records are saved in a file in ASCII format. This standard file format for data storage allows for subsequent processing in other graphic or text programs.

For the control of the flow system and verification of the stabilization of potentiometric readings, a program was developed in the Delphi graphical language, called MULTIPLEX, which communicates in real time with the main program that acquires potentiometric data. This reads the file generated by the commercial program and creates an identical file, with a different name. The arithmetic averages of the signals are performed for all channels.

After the stabilization of the measurements of the eight electrodes, verified by the variance of five consecutive measurements with five-second intervals, the Multiplex program saves the averages of the potentiometric data of each of the electrodes and activates the solenoid valve to wash the system. Data acquisitions were made over time for each selective electrode, which allowed verification through the potential values of the repeatability of the measurements.

These data were used to construct individual analytical curves and, from the values of the angular coefficients obtained, it was possible to highlight the Nernstian behavior of the electrodes.

(a) (b)

Figure 2: (a) Selective electrode array and (b) Complete continuous flow analysis system.

III. RESULTS AND DISCUSSION

The electrodes for chloride, iodide, bromide, sulfide, and nitrate respond well at the pH established by the ionic strength regulator, which is a sodium acid phosphate (Na_2HPO_4) solution at a concentration of 1.00 mol L^{-1}, whose pH is maintained at 9.0. The nitrite electrode, according to the instruction catalog, responds in the pH range between 4 and 7, a narrower range. of the values at which the other electrodes operate without problems (Figure 3), however this electrode maintained linearity of response and exhibited a Nerstian response.

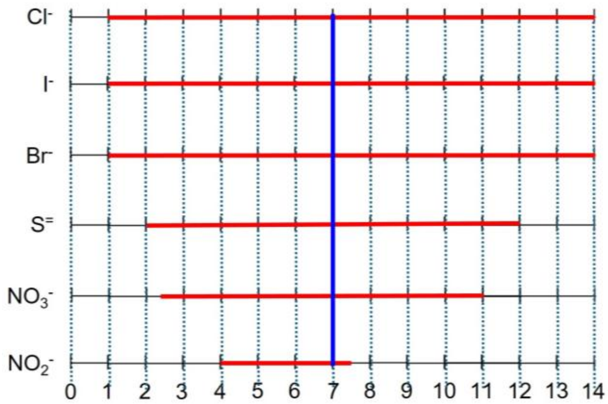


Figure 3: pH range of the electrodes.

Figure 4 shows the home page of the Prober-PH8 commercial program. Clicking the OK button advances the program to the screen shown in Figure 5, which displays the eight data acquisition channels, with the possibility of also measuring temperatures.

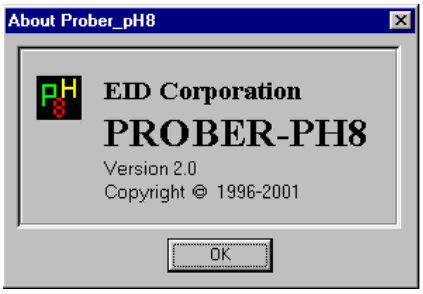


Figure 4. Opening page of the data acquisition software.

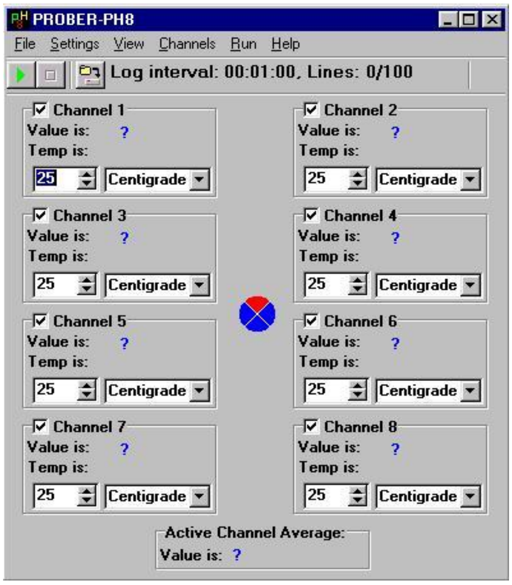


Figure 5: Software page, showing the 8 possible channels for data acquisition.

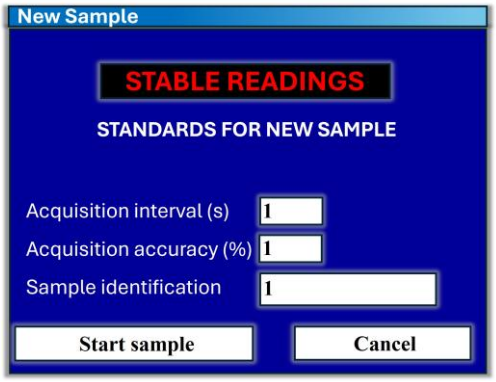


Figure 6: Auxiliary software page.

After the start of reading the potentiometric data from the electrode array, the auxiliary program, as shown in Figure 6, developed in the Delphi language, begins. This auxiliary program reads the data being acquired and performs statistical analysis to verify the stability of the responses. After stabilization, the data is saved in ASCII format.

Every 5 seconds, the potential values are collected from the commercial program and automatically passed to the Multiplex program, where they appear sequentially on the microcomputer screen (Figure 7). On this screen, it is possible to view the exact moment of acquisition and the potential values of the channels enabled with the electrodes.

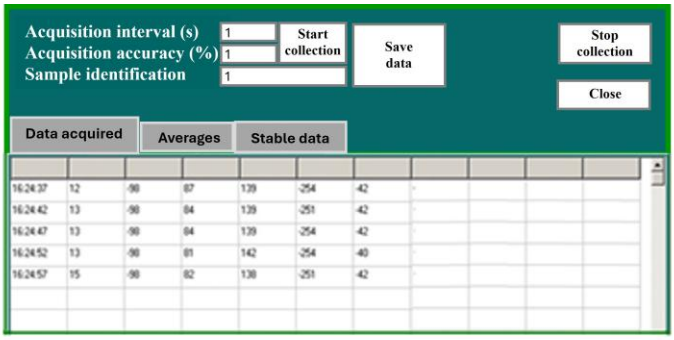
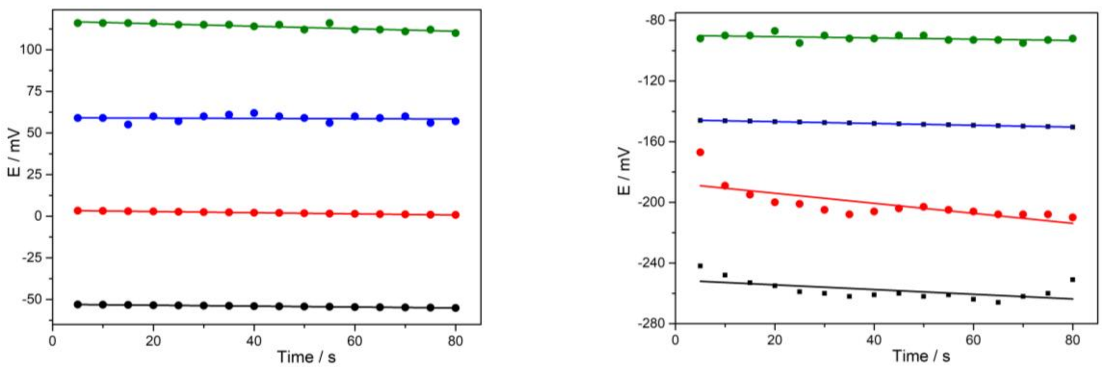


Figure 7: Example of the auxiliary software page with acquisition data.

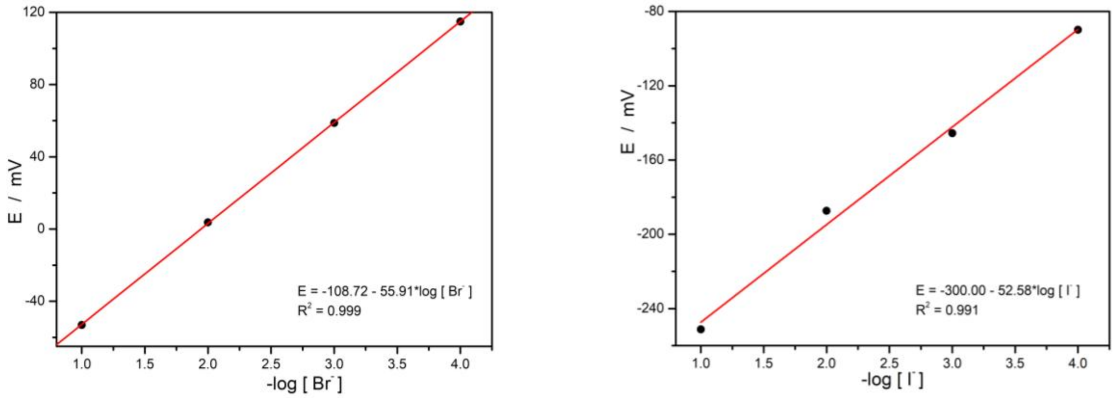
Readings are continuous until they become stable, according to the chosen precision. As soon as these measurements stabilize, the program itself stops the readings.

The Multiplex program verifies the stabilization of the data from the enabled channels, takes the averages of the readings, and activates the solenoid valve, and the entire system is flushed. After the flushing stage, the solution to be analyzed is changed to restart the entire process.

Figure 8 shows the variation in the potentials of bromide and iodide electrodes over time at different concentrations. For the analytical curves of these two anions, it was possible to verify Nernstian behavior.



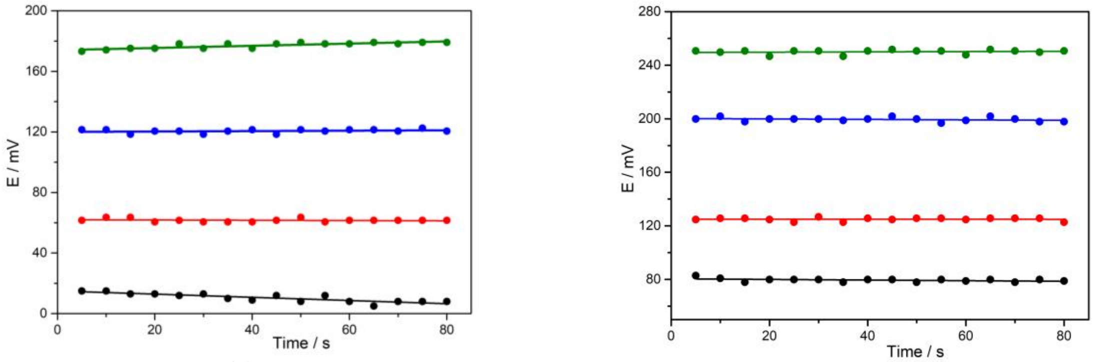
(a) (b)



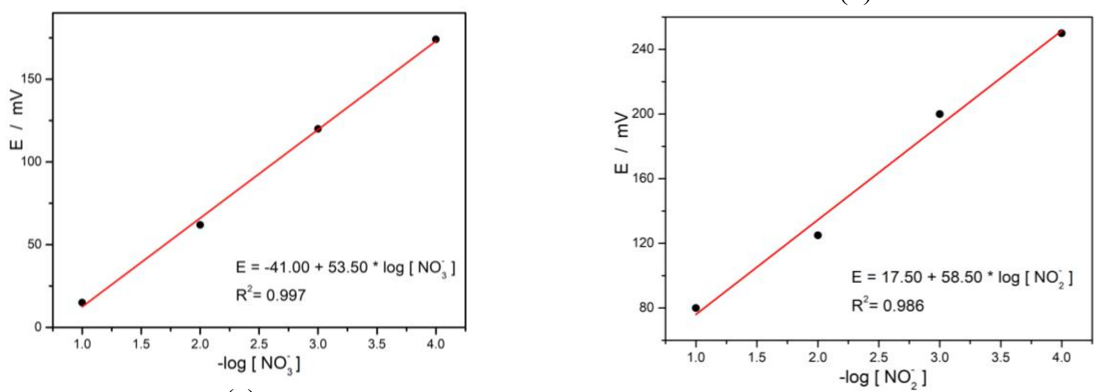
(c) (d)

Figure 8: Variations in the potential of bromide (a) and iodide (b) solutions at different concentrations as a function of time; Analytical curves for bromide (c) and iodide (d) ions as a function of concentrations versus the average potential of flow readings.

Similarly, Figure 9 shows the variation in the potentials of nitrate and nitrite electrodes over time at different concentrations. And in this case, it was also found that the analytical curves of these two anions also follow a Nernstian pattern.omportamento Nernstian.



(a) (b)



(c) (d)

Figure 9. Variations in the potential of nitrate (a) and nitrite (b) solutions at different concentrations as a function of time. Analytical curves for the nitrate ion (c) and nitrite (d) ions as a function of concentrations versus the average potential of flow readings.

The electrode response is considered Nernstian when the constant 2.303·RT/n·F, from the Nernst equation, for n=1 is equal to 59.1 at 25 ºC. However, values between 55.0 and 60.0 are considered Nernstian depending on the analysis conditions. The terms sub-Nernstian and super-Nernstian are used when the value of this constant is below 55.0 or above 60.0, respectively.

Although values slightly below those considered Nernstian were obtained for some of the electrodes in this arrangement, such as the sulfide electrode (Figure 10), for example, the linearity of the analytical curves was observed and, therefore, they can be used for subsequent analyses of these anions.

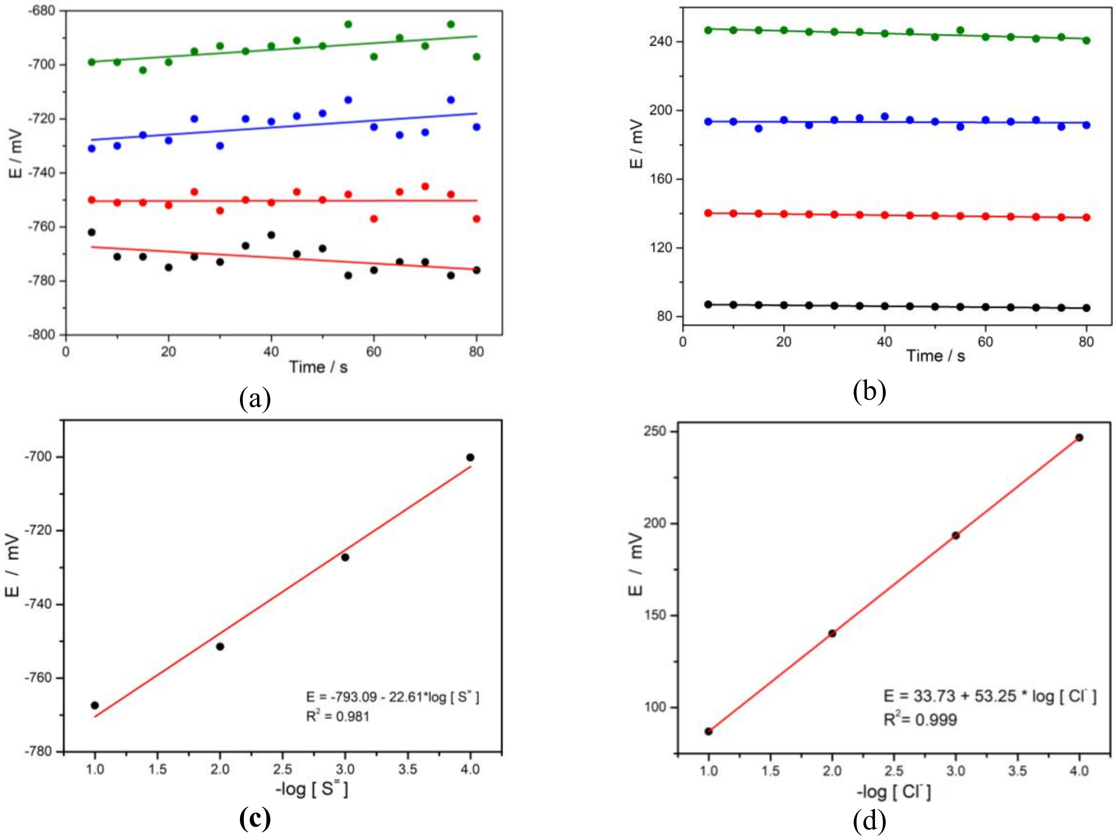


Figure 10. Variations in the potential of sulfide (a) and chloride (b) solutions at different concentrations as a function of time. Analytical curves for the sulfide (c) and chloride (d) ions as a function of concentrations versus the average potential of flow readings.

IV. CONCLUSIONS

The implemented potentiometric automation enabled the development of new experimental approaches with selective electrodes. One of the main advantages of arranging the electrodes in a continuous flow system was the significant reduction in reagent consumption compared to discrete assembly.

In data acquisition, the high efficiency of the management program was evident, allowing a large amount of potentiometric data to be acquired in a relatively short time and with simultaneous control of instrumental parameters. The system is simple to operate, and the potentiometric multiplexer can be used for up to eight selective electrodes simultaneously.

The electrode calibration process was an important step in the work. With the procedures described in the experimental part, it was possible to construct the analytical curves, and it was found that the electrodes responded according to the Nernst equation. Although the ideal operating range of nitrite (pH 4 to 7) is lower than the pH 9.0 of the supporting electrolyte, this electrode showed surprising robustness, maintaining linearity and Nernstian response like all other electrodes.

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