USE OF THE SANDWICH TECHNIQUE IN FLOW INJECTION SYSTEMS FOR EXTENDING THE RANGE OF AN ANALYTICAL METHOD. APPLICATION TO CHLORIDE DETERMINATION IN WATERS

A. N. Araújo, J. L. F. C. Lima[1], A. O. S. S. Rangel[2] and M. T. M. Teixeira

Department of Physical-Chemistry, Faculty of Pharmacy, University of Porto, 4000 Porto, Portugal

ABSTRACT

In this paper we describe the extension of the range of an analytical method using a sandwich technique in a flow injection system. This was demonstrated by the colorimetric determination of chlorides in natural and residual water. The manifold which incorporated a 6-way injection valve, permits determinations in concentrations ranging from 0.1 to 1000 mg/L, with a coefficient of variation less than 1% and at a rate of 60 determinations/hour. The FIA results for water samples are in good agreement with those of the reference method, there being no deviations greater than 4%.

KEY WORDS: Sandwich technique, flow injection analysis, natural and wastewater chloride determination, colorimetric thiocyanate method.

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1   To whom correspondence should be addressed.
2   Permanent address: College of Biotechnology, Portuguese Catholic University, 4200 Porto, Portugal.

INTRODUCTION

In the development of flow injection systems devoted to routine analysis, namely in environmental control, difficulties often arise due to wide analyte concentration ranges in samples. This situation is particularly critical when spectroscopic detection systems are used, due to their narrow working range.

In these circumstances, one of the major difficulties to overcome, especially when sample pre-treatment is to be avoided, is implementing large dilutions inside the FIA manifold without significantly decreasing sensitivity and sampling rate.

Zone sampling, asynchronous merging zones and electronic dilution modes [1] were ingenious approaches for overcoming the aforementioned problem, although they imply a sensitivity decrease if the operating settings are unmodified during a set of determinations.

One way of obtaining a manifold able to respond according to the analyte concentration level in the test solution was proposed by Ruzicka et al. [2], and was based on the reproducible sample plug splitting, after injection, between two channels where different dilution extents occur. The two resulting sample plugs are merged into a single channel and measured sequentially.

In this paper the usefulness of the sandwich technique performed with the 8-port, 6-way injection valve (commercially available), in extending the range of the concentrations is demonstrated by implementing a FIA manifold to create two different degrees of dilution at the head and the tail of the sample plug.

The versatility of this valve was previously shown in the sequential determination of two species [3, 4], in saving expensive reagents [5], and in continuous monitoring to avoid the necessity of periodically interrupting the process to calibrate the system [6].

The possibility of performing determinations at two different analyte concentration ranges, with the 8-port injection valve, was evaluated using the colorimetric determination of chlorides in natural and residual waters which may contain a large range of concentrations of this ion. This determination was chosen because it already has been used for assessing other approaches concerning the handling of large concentration ranges [2, 7]. In effect, this situation is also recognized by the reference method [8] which recommends the use of more than one calibration curve.

EXPERIMENTAL

Reagents and Solutions

Analytical reagent grade chemicals and double-deionized water (specific conductivity less than 0.1 μS/cm) were used for the preparation of the solutions.

The carrier solution was prepared in a volumetric flask by taking 0.626 g of mercury (II) thiocyanate, 30.3 g of iron (III) nitrate, 3.4 mL of concentrated nitric acid, 150 mL of methanol, and filling it up to 1 L with water. This solution was filtered and degassed before use to eliminate any solid particle residue and to avoid the appearance of air bubbles in the system [9].

The standard chloride solutions, ranging from 10 mg/L to 1000 mg/L, were prepared from previously dried solid sodium chloride.

Sandwich Technique Flow Injection System

The propulsion of the solutions in the FIA manifold (Fig. 1) was effected by a Gilson Model Minipuls-2 peristaltic pump using flow tubes of the same brand (ref. 617939).

Test solutions and the color reagent were introduced into the reactor by acting an 8-port Hamilton HVLX 8-7 injection valve.

Omnifit teflon flow tubes (0.5 mm inner diameter), Gilson end-fittings and connectors were used to connect the different components of the manifold.

A Hitachi Model U 2000 spectrophotometer equipped with an 8 μL Hellma type 178.713 flow cell was used as detection system.
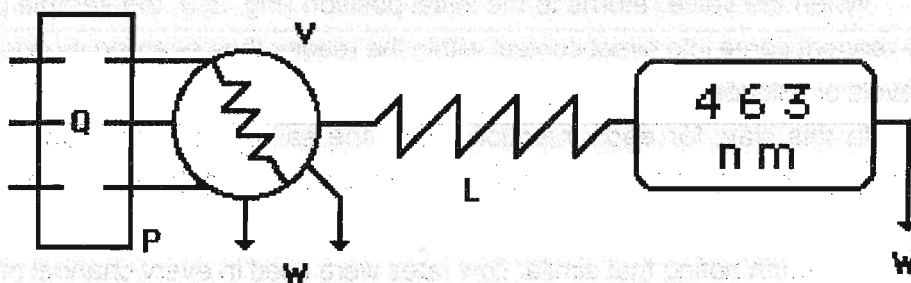

FIG. 1 - FIA manifold used for determination of chlorides in water and wastewater samples. P - peristaltic pump; Q - flow rate in the three channels; V - 8-port rotatory injection valve; L - reactor (0.5 inner diameter); W - waste.

Reference Procedure

The method B (argentometric titration) [8] suggested by the American Society for Testing and Materials was used as the reference procedure. Thus the chloride content in the samples was determined by potentiometric titration performed with a Crison Model μTit 802 automatic titrator, and using a 0.100 M silver nitrate standard solution (Titrisol Merck ref. 9990) as titrant. An $Ag_2S/AgCl$ crystalline membrane ion - selective electrode [10] and a Metrohm ref. 6.0726.100 double-junction AgCl/Ag electrode were used, respectively, as indicator and reference electrodes.

RESULTS AND DISCUSSION

Flow Path in the Manifold

For achieving two concentration working ranges, the way the solutions enter and leave the valve (Fig. 2) was set in such a manner that, when the loop is filled with water, only the color reagent circulates within the system (Fig. 2A).

By rotating the valve (Fig. 2B), the flowing reagent and sample solutions, separated from each other by an amount of deionized water contained in the loop, only come in contact inside the reactor after partial dispersion, thereby simulating the chasing-zones technique [11]. The volume of the loop determines the amount of water inserted between samples and reagent and consequently, the extent of the dilution, thus making it possible to determine the anion at higher concentrations.

When the valve returns to the initial position (Fig. 2C), the sample plug and the reagent come into direct contact within the reactor thus enabling monitoring lower levels of chlorides.

In this way, for each injection cycle, the sample is subjected to two different degrees of dilution allowing to establish two different calibration curves.

It is worth noting that similar flow rates were used in every channel of the manifold in order to ensure a constant flow in the reactor each time the valve is rotated.
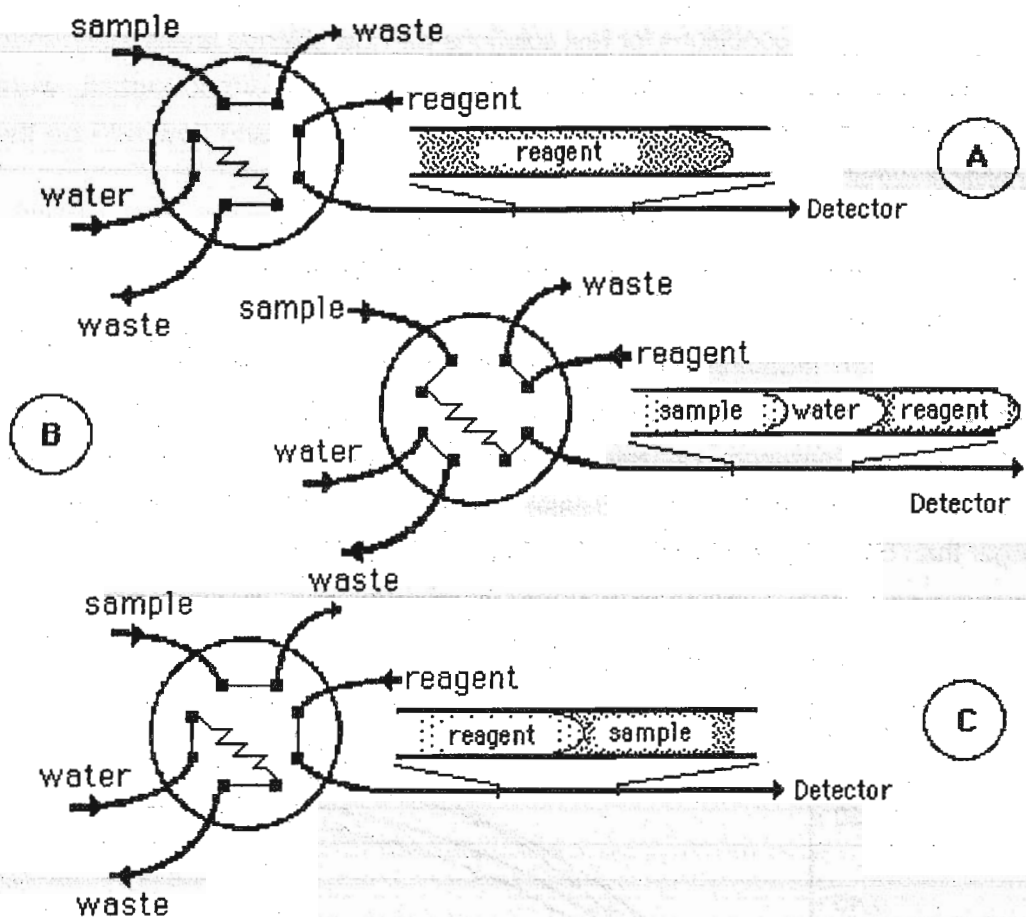
FIG. 2 - 8-port injection valve mode of functioning in the FIA manifold. A and C - loading the valve loop with deionized water; B - injecting the content of the valve loop in the reactor.

Optimization of the manifold

The relation between the analytical signal and the concentration is not linear, similar to that observed with the conventional method. In fact, although the free thiocyanate anion varies in proportion to the chloride concentration, the iron (III) cation tends to form complexes with the anion in greater coordination numbers, which not absorb at the monitoring wavelength [11].

The optimization of the manifold was performed in two stages, each one corresponding to each interface, in order to obtain a compromise which would allow the widest possible working concentration range.

The best conditions for test solutions with low chloride levels, performed in the interface where the sample and reagent come in direct contact, were assessed by studying the influence of reactor length (L) and flow rate on the analytical signal.

The calibration curves for a set-up with different reactor lengths show that sensitivity increases up to a length of 200 cm and remains relatively constant for greater lengths.

When studying the influence of the flow rate (Fig. 3) we noted an increase in the sensitivity of the determination up to a flow rate of 2.45 mL/min, considering the maximum concentration range achievable in this interface. For higher flow rates, it was observed a decrease of absorbance values at concentrations larger than 50 mg/L, possibly due to insufficient reaction time.
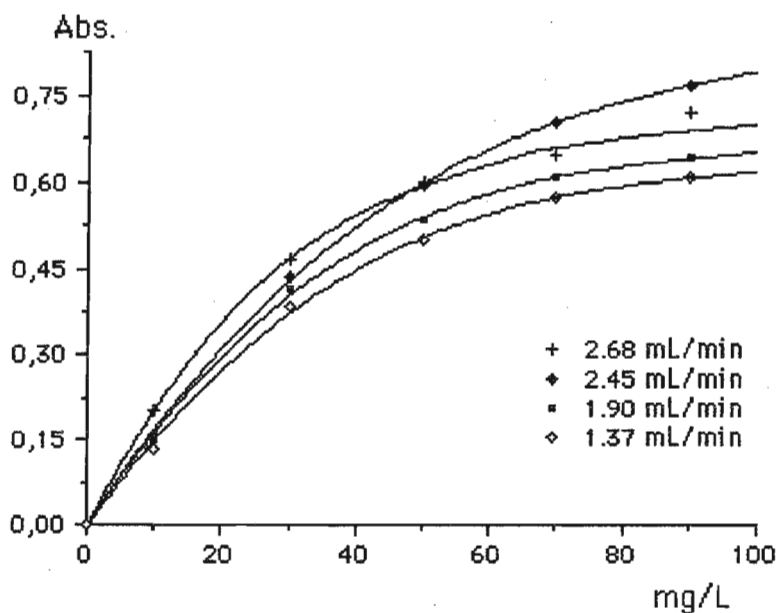

FIG. 3 - Influence of the flow rate in the calibration for determination of chlorides at low levels. The concentrations used in this experiment were, respectively: 10 mg/L, 30 mg/L, 50 mg/L, 70 mg/L and 90 mg/L.

The manifold optimization for the interface dedicated to higher chloride concentration determinations was performed by changing the length of the loop of the valve and the flow rate, and setting the remaining parameters at the values

optimized earlier.

The assessment of the deionized water volume controlled by the loop is important as it conditions the degree of sample dilution and overlapping extension with the color reagent. The influence of this parameter was studied by tracing successive calibration curves for several loops. In Fig. 4 the analytical signal for different standard solutions versus the volume of the loop is represented. It was observed that, for a volume of 120 μL, determinations for concentrations up to 1000 mg/L could be performed. For larger loop volumes the distance between the sample plug and the reagent did not permit mutual contact and, consequently, no analytical signal was obtained.
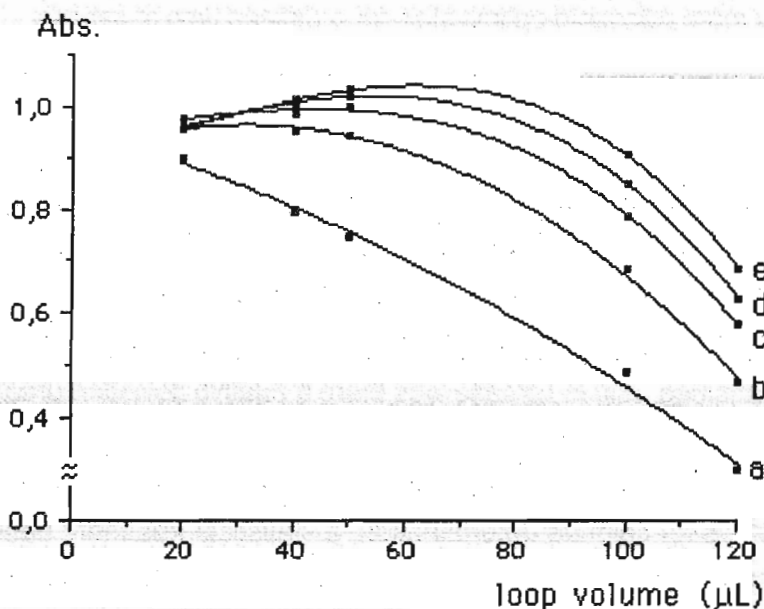

FIG. 4 - Influence of the loop volume on the analytical signals obtained by injection of chloride standard solutions of 200 mg/L (a), 400 mg/L (b), 600 mg/L (c), 800 mg/L (d) and 1000 mg/L (e).

Once the optimal loop volume had been established, the influence of the flow rate was re-evaluated to assess the possibility of a further extension of the analytical range. We have followed the procedure already described for the direct contact sample-reagent interface, but no improvement was accomplished regarding the 2.45 mL/min flow rate .

The optimization of this manifold enabled us to define the final set-up as having an injection valve loop of 120 μL, a flow rate of 2.45 mL/min in the three

channels and a 200 cm reactor length. This system enables us to establish two calibration curves. The first, between 0.1 (calculated detection limit as suggested by [12]) and 100 mg/L for the reaction occurring in the sample/reagent interface. The second, between 100 and 1000 mg/L resulting from the amount of colored product formed on the reagent/water/sample plug interface. A concentration of 1000 mg/L was selected as the upper limit of the manifold application, as the sensitivity for larger concentrations decreases rapidly.

The sampling rate with this set-up is of approximately 60 samples per hour.

It should be stressed that a simple decrease of the loop volume could enable determinations with better sensitivity but lower upper concentration limit, thus having a more adequate optimization for a defined type of sample.

Application to Water Analysis

In order to evaluate the quality of the results obtained by the FIA method, 18 samples of water, with chloride levels of between 10 and 560 mg/L, were analysed by this method and by the reference procedure. A correlation coefficient of 0.9998 for the regression curve FIA (mg/L) = -0.40 + 1.01 Titration (mg/L) was obtained, and in no case was there a relative deviation greater than 4 %.

To emphasize the agreement between the FIA and the argentometric titration methods for chloride determination, a statistical treatment based on the paired t-test was applied. The calculated t-value was 1.67, inferior to that tabulated for a 95% confidence level ($t_{0.025,17} = 2.11$), thus allowing us to conclude that there are no significant differences between the results provided by the two methods.

The FIA method in the two established chloride concentration ranges gave results which had within-run coefficients of variation below 1%, calculated on the basis of the values obtained for 10 consecutive injections of each of the samples tested.

CONCLUSIONS

This study showed that the use of an 8-port commercially available

injection valve may provide a simple and low cost manifold in order to automatize determinations in which a wide analyte concentration interval is expected. Furthermore, this technique avoids the need for more complex sample plug treatments as the use of flow splittings or rigorous time control devices.

In the proposed example of application, the developed FIA manifold permits the determination of chlorides within a large range of concentrations with the same single channel manifold, and provided results in good agreement with those obtained with the reference procedure.

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