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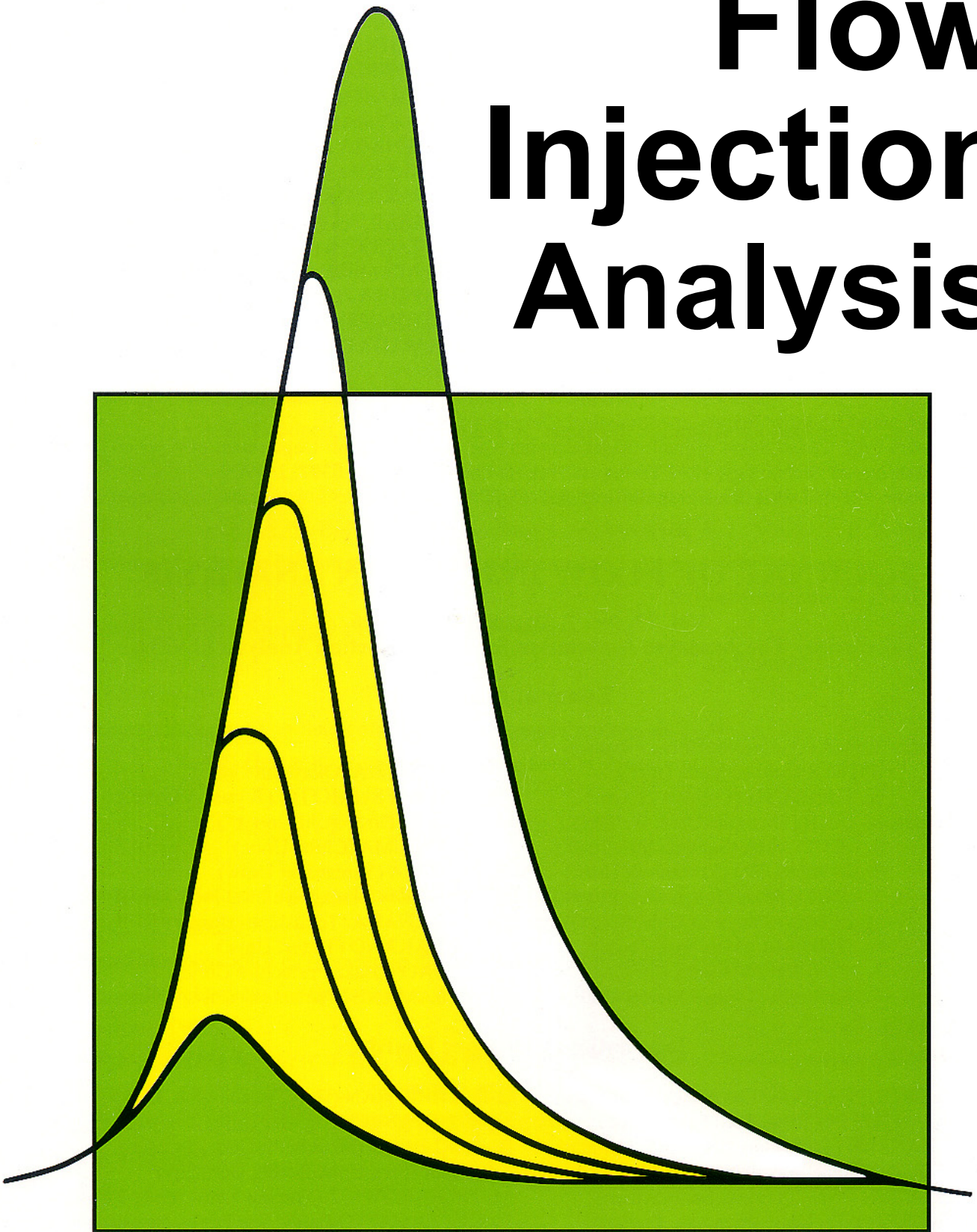
Flow Injection System for Chloride Determination with Multidetection Based on Potentiometric and Spectrophotometric Measurements

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Abstract

The present paper describes the feasibility of a flow injection system with multidetection based on potentiometric and spectrophotometric measurements for chloride determination. Chloride determination by potentiometry was accomplished by using two electrodes of Ag/AgCl where the first one act as the indicator in the first zone sample and the second one act as reference electrode, resulting a an positive signal. After zone sample reaches the second electrode the first electrode will be the reference electrode, generating a negative signal. For the spectrophotometric determination, it was used the conventional reaction between $Hg(SCN)_2$ and chloride with further displacement of SCN^- and formation of complex with Fe (III) detected at 480 nm. The linear work range was limited by the spectrophotometric detector and resulted in 10 to 500 mg L^{-1}. The method was applied to determine chloride in samples of parenteral solutions and the results obtained, with both detectors, were in agreement at 95 % confidence level (paired t-test). The precision evaluated as repeatability (n=20) for samples analyzed showed relative standard deviations (RSD) smaller than 3.5% for multidetection employed. The FIA with multidetection results is better reliable, since it consists of doing two determinations of the same analyte with different detectors. It is similar to what is done with two independent determination of the analyte.

Keywords FIA, chloride, multidetection, parenteral solutions.

1. Introduction

The chloride ions are normally found in the potable water, wastewaters and spring water, besides being present in some pharmaceutical formulations. To be potable [1,2] the water should contain until 250 mg L^{-1} and the wastewaters, mainly from industrial processes and sanitary sewers, usually extrapolate those limits. The mineral water and natural spring water [3] can present until 100 mg L^{-1}. In the pharmaceutical area, the chloride is present in the isotonic parenteral solutions which contain NaCl 9 g L^{-1}. These solutions have as main purpose the rehydration of patients, but they are also used as vehicle for pharmaceutical formulations and as rinse and/or storage solutions of soft contact lenses, because they are isotonic substances, like tears, being of neutral pH [4]. Parenteral solutions are medicines that can be sold without medical prescription. Whether the preparation is incorrect it can be harmful to the patient, causing such problems as hipernatremia and diarrhea.

The chloride in water and in parenteral solutions can be determined through the analytical classic methods like argentometric methods (method of Mohr) and also instrumental methods as FIA system with potentiometric and spectrophotometric detection [1, 5-8].

In sum, the FIA system consists of introducing a sample in a carrier stream, which can receive reagents in its route, and the signal can be obtained through different type of detectors [8,9]. Moreover, as is well known, FIA system also provides low sample/reagent consumption, high sample throughput, high precision of measurements as well as less possibility of sample contamination if compared to batch methods.

For the potentiometric detection, in FIA system, there are several forms of electrode joining. It could consist of an adaptation of electrodes of conventional configuration through flow cells or, else, an adaptation of tubular electrode [10-15] is often used. Regarding the method most used for the spectrophotometric detection, it could be cited the reaction between mercury (II) thiocyanate leading to the displacement of thiocyanate and the formation of complex with Fe (III) [16].

The use of multidetection has the main intention of propitiating larger reliability to the result, since it consists of doing the determination of the same analyte twice. In this context, the work of Zagatto *et al.* [17] can be mentioned, in which the authors performed the chloride determination with spectrophotometric and turbidimetric detection. For turbidimetric detection, it was used the same detection system except by changing in the reactional course.

The aim of the present work is the development of an FIA system with multidetection, potentiometric and spectrophotometric, for the determination of chloride in samples of parenteral solutions. The detectors used have difference of principles and, therefore, the interference mechanisms that affect both are different, thus the results, when concordant, are more reliable.

2.Experimental

2.1.Apparatus

The equipments used in this work were: an UV-Visible spectrophotometer (FEMTO), 482 model, with flow cell; pH-meter (MICRONAL), B374 model; polyethylene tubes (0.8 mm i.d.) for fluids transport, loops and coils construction; a home-made proportional-commutator for FIA system; Milli-Q (MILLIPORE) system, Academic model. The electrodes (lab-made) were built, with silver threads as described below.

For data acquisition, an interface (ADVANTECH) PCL 711S model was used. A computational program was developed in an EXCEL$^®$ spreadsheet, using statement in macros of Visual Basic$^®$.

2.2.Reagents and solutions

All reagents, used in this work, were of analytical grade, and all solutions were always prepared with deionized (Milli-Q) water. The chloride stock solution was prepared with potassium chloride and the standards, for analytical curve, were prepared through appropriate dilutions of the stock solutions.

2.3.Electrode of Ag/AgCl construction and conditioning

For the construction of the electrodes, silver threads originating from broken glass electrode, with 10 mm length and 1 mm diameter, were used. For electric contact, the silver threads were welded in copper thread, being afterwards isolated with silicon glue. Then, an adaptation in polyethylene tubes was provided (Fig. 1).
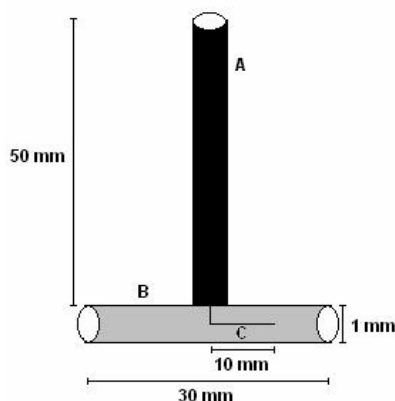

Fig. 1: Electrode built with isolated copper thread. (A), polyethylene tube (B) and silver thread (C).

To condition the electrodes, firstly the silver threads were leached with nitric acid 1.0 mol L^{-1} during 30 minutes and after that, for the formation of silver chloride in the electrode, 40 ml of ferric chloride saturated solution was used (see Reaction 1) [18].

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Reaction 1

$$3\,Ag^0 + FeCl_3 \rightarrow Fe^{+2} + 3\,AgCl$$
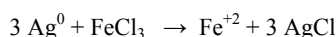
2.4.Studies of the FIA system configuration and characterization

The schematic diagram of flow manifold is showed in Fig. 2. The dimensions of the reactors, loops, etc., for both system, spectrophotometric and potentiometric, were based on previous published works [19-21].

The propulsion of the fluids was driven by gravity. Thus, reagents and carrier containers were maintained at 50 cm above the bench, the waste container was kept in the lab's floor (93 cm in relation to the bench), and thus, this height difference originated a system of constant pressure, with total flow of 2.67 mL min^{-1}. The non-peristaltic pump used produced a system with no flow pulsation and less expensive.

The sample was inserted in the carrier stream by the commutator, and transported towards the detectors. In the confluence X (Fig. 2) it receives the reagent solution of potassium nitrate 0.1 mol L^{-1} aiming at the adjustment of the ionic strength. When only carrier solution flows through the system both electrodes have the same potential, consequently the potential difference is zero. When the sample or standard is introduced in the flow system and reaches the first electrode, which is connected to the negative pole of the potentiometer, the monitored potential difference is increased (positively) since in the second electrode is still in contact with carrier solution. On the other hand, when the zone sample reaches the second electrode the negative signal is increased and in this situation the first electrode potential become zero. It is important to mention that the correct dimensions of the flow system (mainly B2) are fundamental to avoid overlapping of zone sample in the two electrodes.

The distance between the two electrodes, after optimization, was 300 cm, which avoids the overlapping of signals produced by the electrodes.

As soon as the zone sample leaves the second electrode, it goes to confluence Z (Fig. 2) where receives a solution constituted of 0.2 mol L^{-1} of nitric acid, 0.06% (w/v) of mercury thiocyanate and 3% (w/v) of ferric nitrate, then in reactor B3 (100 cm) the chromogenic reaction occurs (Reaction 2), which is detected in the spectrophotometer at 480 nm.

Reaction 2

$$Hg\,(SCN)_2 + 2\,Cl^- \rightarrow HgCl_2 + 2\,SCN^-$$

$$3\,SCN^- + Fe\,(NO_3)_3 \rightarrow Fe\,(SCN)_3 + 3\,NO_3^-$$
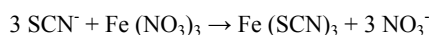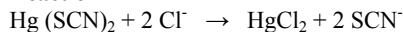
For FIA characterization, the analytical parameters[21], such as detection limit, quantification limit, sensitivity and linear response concentration range were studied. To obtain the figures of merit (Table 1), chloride standard solutions with concentrations of: 0.05 – 0.10 – 0.50 – 1.00 – 5.00 – 10.00 – 25.00 – 50.00 – 75.00 – 100.00 – 250.00 – 500.00 – 750.00 – 1.000.00 – 1.500.00 – 2.000.00 – 4.000.00 – 6.000.00 – 8.000.00 mg L^1 were prepared through appropriate dilutions of stock solutions. For spectrophotometry, the studied range of standards concentrations was of 10.00 to 500.00 mg L^{-1} and for potentiometry the studied range was 0.05 to 8.000.00 mg L^{-1}.
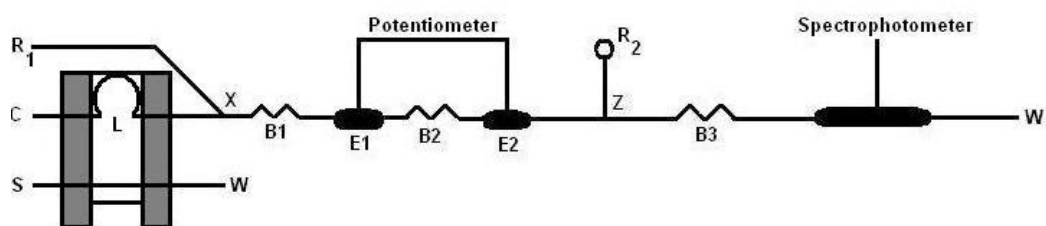
Fig. 2: Schematic diagram of FIA system used for potentiometric and spectrophotometric determination of chloride: C - Carrier stream (water); L – Loop sample (volume = 131 μL); S - Sample; R1 – Potassium nitrate 0.1 mol L^{-1}, R2 – Nitric acid 0.2 mol L^{-1}; mercury thiocyanate 0.06% w/v and ferric nitrate 3% w/v; B1 - Reactor (20 cm); B2 - Reactor (300 cm); B3 - Reactor (100 cm), E1 and E2 are silver chloride electrode; X and Z are confluences, W - waste. Total flow rate of the system: 2.67 mL min^{-1}.

3. Results and discussions

In order to optimize the reactor B2 (Fig. 2), placed between the electrodes, the loop sample was fixed at 125 microliters (25 cm) and reactors of the 65, 100, 150, 300, 350 cm were tested. The signals were checked with standard solution of the 250 mg L^{-1}. As observed, signal increased up to 300 cm and after that occur a signal decrease due to great dispersion of the zone sample owing to long way coursed (Fig. 3). So, the reactor of 300 cm was adopted in all the other measures. It is important to mention that there are three ways to compute the signals: the positive signal, the negative signal and the difference between positive signal and negative signal, thus we adopted the difference between signals, because it proportioned the more sensitive results.
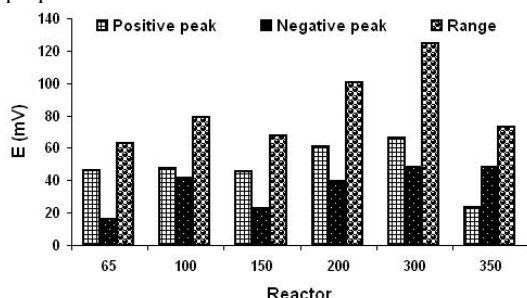

Fig. 3: Effect of reactor length (cm) on potentiometric signal. Range is difference between positive and negative peak.

All the other experimental conditions, such as reagent concentration and FIA dimensions, are based on previous works [12-15]. It was not made systematic study to improve sensitivity and the other analytical parameter, because satisfactory results with proposed manifold were obtained.

3.1. Analytical features of the FIA system

Standard solutions of potassium chloride were prepared with concentration of 0.05 mg L^{-1} to 8000 mg L^{-1}. The analytical curves obtained with potentiometer and spectrophotometer are shown in Figures 4 and 5, respectively. The records of the signals of the standard solutions are presented in Figures 6 and 7.

The figures of merit [22] obtained in the present work (Table 1) are similar to other works and adequate for proposed determination.
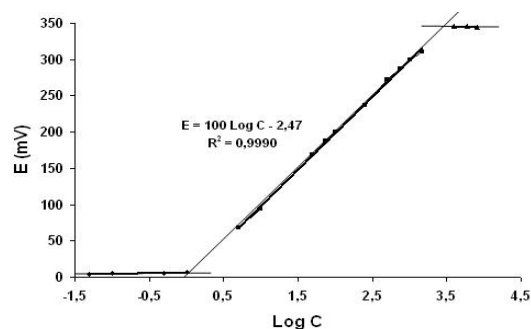

Fig. 4: Analytical curve of the potentiometric system, denoting the detection limit and the linear range. Standard solutions of 0.05 mg L^{-1} to 8000 mg L^{-1}.
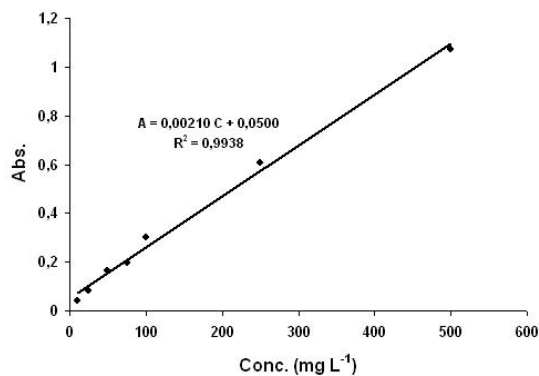

Fig. 5: Analytical curve of the spectrophotometric system. Standard solutions of 10 mg L^{-1} to 500 mg L^{-1}.
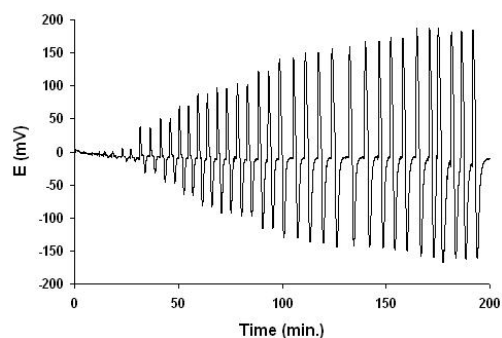

Fig. 6: Records of the signals, in duplicate, of the standard solutions of 0.05 mg L^{-1} to 8000 mg L^{-1} in the potentiometer system.
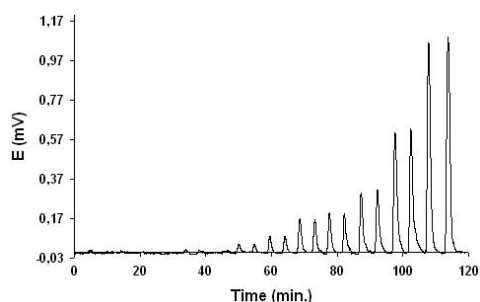
Fig. 7: Records of the signals, in duplicate, of the standard solutions of 10 mg L^{-1} to 500 mg L^{-1} in the spectrophotometer system.

Table 1. Comparison among the analytic parameters of the detectors

Analytical parameters	Potentiometer	Spectrophotometer
LOD	1.23	2.94
LOQ	———	9.81
Linear range	5 – 1500	10 – 500
Sensitivity	100 (mV Dec^{-1})	2.10 x 10^{-3}
r[*]	0.9995	0.9969

LOD = limit of detection and LOQ = limit of quantification in mg L^{-1}. [*]Linear correlation coefficient.

3.4.Application

Determinations of eight samples were accomplished (Table 2). The results obtained with both detectors were in agreement at a confidence level of 95 % (paired t-test). The relative standard deviation was always smaller than 3.5%. For samples defined as H, four measurements were performed.

Table 2. Determination of Chloride in parenteral solutions samples

Samples	Concentration (g L^{-1}) Potentiometer	Concentration (g L^{-1}) Spectrophotometer
A	5.85 ± 0.67[*]	5.23 ± 0.42
B	5.69 ± 0.69	5.26 ± 0.63
C	5.79 ± 0.05	5.24 ± 0.21
D	5.79 ± 0.48	5.08 ± 0.00
E	6.01 ± 0.04	5.31 ± 0.42
F	5.97 ± 0.01	5.42 ± 0.61
G	5.86 ± 0.27	5.10 ± 0.65
H	5.99 ± 0.01	5.31 ± 0.42

[*]Coefficient of variation, n = 2.

4.Conclusions

The multidetection FIA system proposed in this work, presented satisfactory results for chloride determination in parenteral solution samples. The new feature of this study was the use of two detectors with different principles that assure better accuracy in the determination, and better reliability.

6.References

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