

Preconcentration with Anion-Exchange Resin in a Flow Injection System to Determine Low Levels of Chloride Ions in Interior Waters

B.F.Reis* and M.F. Giné

Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Caixa Postal 96 - 13400, Piracicaba, SP, Brasil.

M.M.Santos Filha

Departamento de Química, Universidade Federal de Sergipe.

N.Baccan

Instituto de Química, Universidade Estadual de Campinas.

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Baixas concentrações de cloreto em águas naturais foram determinadas, empregando pré-concentração com resina de troca iônica (AG1-X8). A coluna de resina foi incorporada em um sistema de análise química por injeção em fluxo, e a determinação foi feita por espectrofotometria empregando o método baseado na reação com tiocianato de mercúrio e nitrato férrico. Uma velocidade de 25 determinações por hora foi conseguida para a amostras com concentrações de cloreto na faixa de 0,05 a 0,5 mg/l. Precisão caracterizada por um desvio padrão relativo (r.s.d.) de 0,4% e recuperação melhor do que 98% foram encontradas.

Low levels of chloride ions in interior waters were determined employing preconcentration with an anionic resin (AG1-X8), in a flow injection system. The spectrophotometric detection was performed by using the mercury thiocyanide/iron nitrate method. The proposed procedure allows a throughput of 25 determinations per hour for sample chloride concentrations ranging from 0.05 to 0.5 mg/l. Precision was characterized by a relative standard deviation of 0.4 % and recovery was better than 98%.

Key words: *pre-concentration; flow injection; anionic resin; chloride determination.*

Introduction

Chloride concentrations in interior waters cover a wide range, depending on their source. However, waters from rain-forest regions present chloride concentrations lower than 1 mg/l. These concentrations are below the detection limit inherent to the method based on the reaction with mercury thiocyanide/iron nitrate¹⁻³ that is a widespread spectrophotometric method for chloride in water samples. To overcome this drawback, a preconcentration step using an anion exchange resin is suggested. The flow injection technique is also proposed, considering its facilities to handle samples, avoiding contaminations and permitting a high throughput in a reproducible way⁴. The main objective of this work was to improve detection limits of the spectrophotometric method by coupling a resin column in the flow injection network in order to preconcentrate chloride ions.

Experimental

Apparatus

A Micronal B342 II spectrophotometer with a flow cell of 14mm optical path, and 200 l volume was used with a Radiometer REC 61 strip chart recorder. A Ismatec mp13 GJ4 peristaltic pump furnished with Tygon tubing was used. All the flow system connectins and reaction coils were made of (0.8mm i.d.) polyethylene tubing.

An automatic sliding bar injector with three commutation sections similar to that already described⁵ was used. It was controlled by a laboratory-made microcomputer, based on the Intel 8085 microprocessor⁶, which energizes the injector solenoids at programmed times according to a software written in Assembly language.

The resin column was made by attaching 3 perspex blocks in a sandwich form with screw and by drilling a 15x5 mm hole into the central block for the resin. The resin was held in-

side the column by plugging the two ends with discs of porous polyethylene, with O'ring seals to avoid leakage. Polyethylene tube (3cm x 0.8 mm i.d.) was connected at both ends.

Reagents

All reagents were analytical grade. Freshly distilled and deionized water was used throughout. The reagent was prepared by dissolving 0,626g of $\text{Hg}(\text{SCN})_2$ in 150 ml of ethanol, adding 30g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 14 ml of concentrated nitric acid and completing the volume to 1000 ml. The final acid solution was 0.2 M in nitric acid.

The chloride stock solution (1000 mg/l) was prepared by dissolving 1.6485g of NaCl in 1000l of water.

As eluent 0.1, 0.2, 0.5, 1.0, 1.5 and 2.0M nitric acid solutions were used.

Solutions for investigating interference effects containing 0.5 mg/l of chloride plus nitrate, carbonate, sulphate and phosphate in concentrations of 0.5, 1.0, 3.0, 5.0 and 10 mg/l were prepared from the corresponding stock solutions. The 1000 mg/l stock solutions of potential interfering ions were prepared using sodium nitrate, disodium carbonate, disodium phosphate and diamonium sulphate, respectively.

The anion exchange resin AG1-X8 (200-400 mesh, chloride form) was supplied by Bio-Rad Lab. The resin was converted to the nitrate form, following the procedure described elsewhere⁷.

Flow Diagrams

In order to match the solid phase extraction with the flow injection technique to preconcentrate chloride ions, the flow system depicted in Fig. 1 is proposed. It provides facilities to investigate effects of changing the sample flow rates and column loading time on the amount of analyte ions adsorbed on the resin.

The effect caused by either the flow-rate or concentration of the eluent solution on the analyte distribution in the eluted

band was investigated by employing the zone-sampling configuration shown in Fig.2. This approach⁸ provides facilities to investigate the cited variables without affecting the chemical reaction conditions.

Procedure to investigate the experimental variables.

Looking at Fig. 1, the sample (S) is pumped through the resin column (C) where the analyte ions are retained and the column effluent is directed towards the waste (W). Displacing the injector to the other rest position, the resin column is inserted into the analytical path, the eluent solution (E) being pumped through it to perform the elution. The analyte ions released from the resin column are carried by the eluent solution and merge with the reagent (R) at the confluent point (x). A well-defined concentration zone of the light-absorbing complex is produced while being transported through the reaction coil (RC) towards the spectrophotometric flow-cell (D) and the transient signal is monitored. Commutating the injector back, another loading step is initialized.

The zone sampling process was implemented with the flow diagram shown in Fig.2. The injector is positioned to perform elution of the analyte previously adsorbed by the resin. Eluent solution (E) is pumped through the resin column and the released analyte ions are carried out through the sampling loop (L). At a defined time delay, the injector is switched back for resampling a portion of the eluted band by the loop L and inserting it into the analytical path. Afterwards, this analyte zone is carried by Cs, receiving the reagent R, and transported through RC towards detection. Thus, programming the micro-computer to change the resampling time interval, different fractions of the eluted band can be selected and analysed. This procedure constitutes a tool to study effects of the eluent solution flow-rate and concentration on the elution efficiency.

Interferences tests

The solutions containing the potential interfering ions ni-

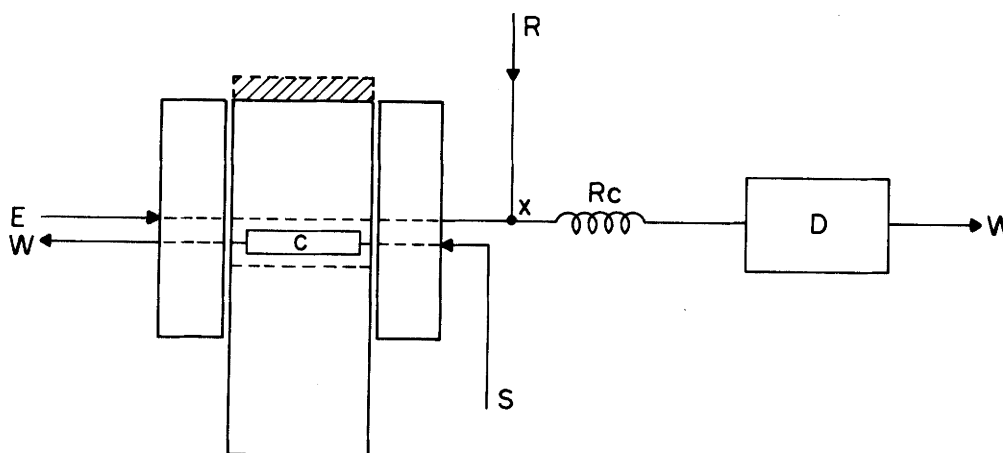


Figure 1. Flow diagram of the system used to investigate sample flow rate and column loading time. The three rectangular pieces correspond to an overview of the sliding bar injector. S represents the sample, R the reagent pumped at 0.8ml/min, C the resin column (15 x 5mm), E the eluent, Rc the reaction coil of 100 cm, X the confluent point, D the detector at 480 nm and W the waste. Dashed lines indicate inner holes and the hatched area indicates the injector in the elution position. Arrows indicate direction of pumping. The two solenoids used to switch the sliding bar of the injector were omitted to simplify the diagram.

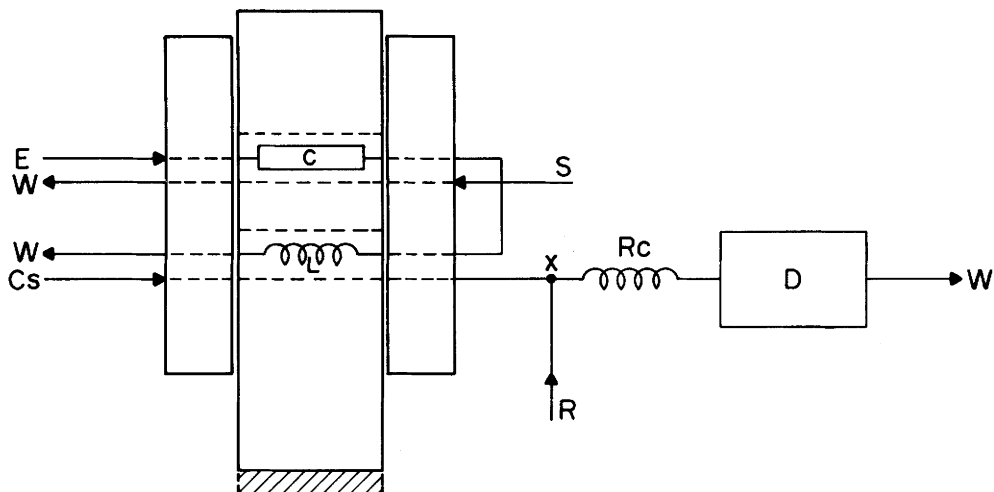


Figure 2. Flow diagram of the system used to implement the zone sampling process. *L* represent the loop of 100cm used for sampling the eluted band, *Cs* corresponds to the eluted band carrier stream. Other symbols as in Fig.1.

trate, carbonate, phosphate and sulphate were analysed employing the flow diagram depicted in Fig.1, with a sample flow rate of 4.2 ml/min., column loading time of 120s and 0.2M nitric acid with a flow rate of 2.0 ml/min for elution.

Results and Discussion

The amount of chloride ion adsorbed by the resin as a function of the column loading time and the sample flow-rate through the column are presented in Figs. 3 and 4, respectively. The spectrophotometer response corresponding to the column loading time is almost linear up to 0.8A. Nevertheless, the response curve for the sample flow-rate did not show a linear behavior in the same interval. Even when the mean speed of the ions through the resin column is increased with the sample flow-rate, the interactions between chloride ions and exchanger sites decrease, affecting the resin adsorbing efficiency. These results show that, to enhance the detection limit, it is more profitable to increase the column loading time rather than the sample flow-rate.

The effect of the time delay during the zone sampling process is shown in Fig. 5. The recorder tracing for the higher peaks was obtained by using a resampling time of 16.7s. The more concentrated portion of the eluted band emerges from the resin column after pumping 0.55 ml. Looking at the set of peaks, from right to left, the long tailed curve denotes the difficulty of removing completely the chloride ions from the resin. Similar results to those of Fig. 5 were obtained with different eluent solutions when flow rates of 2.0 and 3.9 ml/min were employed. As elution efficiency is not dependent on these parameters, the concentration of the eluent solution was chosen

identical to that of the reagent (0.2 M) and the flow rate of 2ml/min was chosen in order to avoid leakage.

The baseline drift observed in Fig.5 was ascribed to the formation of deposits inside the reaction coil and flow cell. In or-

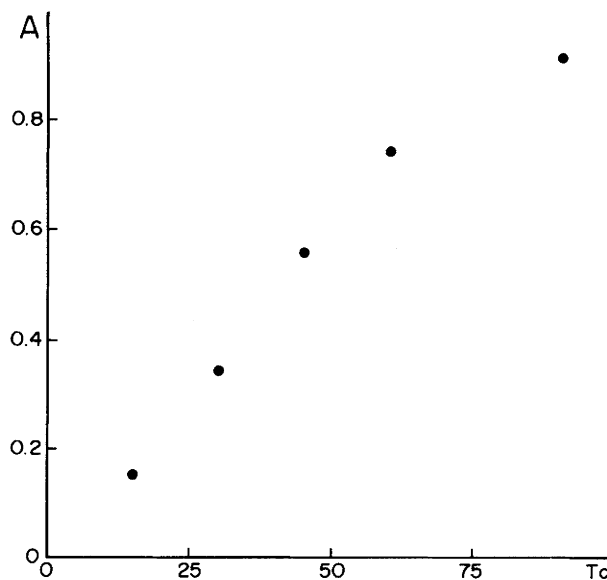


Figure 3. Effect of loading time. *A* is absorbance and *Tc* the loading time in s. A standard solution 0.5mg/l of chloride at flow rate 4.2ml/min was used. An eluent solution of 0.5M nitric acid was used at of 2.0ml/min and eluting time of 40 s.

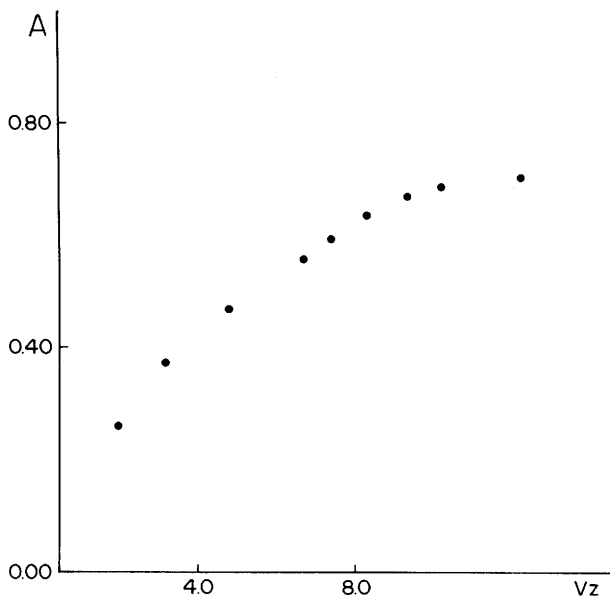


Figure 4. Effects of sample flow-rate. A is absorbance and Vz the sample flow rate, in ml/min. Column loading time was 120s and other parameters were the same as in Fig. 3.

Table 1. Effects of foreign anions. Concentrations in mg/l.

Run	Cl ⁻	NO ₃ ⁻	CO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	A ₁ *	A ₂	Recovery %
			[mg/l]					
1	0.5	0.5	0.5	0.5	0.5	0.415	0.476	99.8
2	0.5	1.0	1.0	1.0	1.0	0.490	0.490	100
3	0.5	3.0	3.0	3.0	3.0	0.480	0.475	101
4	0.5	5.0	5.0	5.0	5.0	0.490	0.465	105
5	0.5	10	10	10	10	0.497	0.437	114
6	0.5	10	-	-	-	0.490	0.480	102
7	0.5	-	10	-	-	0.495	0.485	102
8	0.5	-	-	10	-	0.493	0.475	104
9	0.5	-	-	-	10	0.495	0.430	115

*A₁ and A₂ are the absorbance without and with addition of the other anions, respectively.

der to prevent this drawback, the flow system shown in Fig.6 was implemented. In this case the reagent (R) is recycled during the resin loading time, improving baseline stability.

Anions such as nitrate, carbonate, sulphate and phosphate, which are generally present in waters, are also adsorbed by the resin, competing with the chloride ions. The effect of these anions as interferences with chloride adsorption were tested

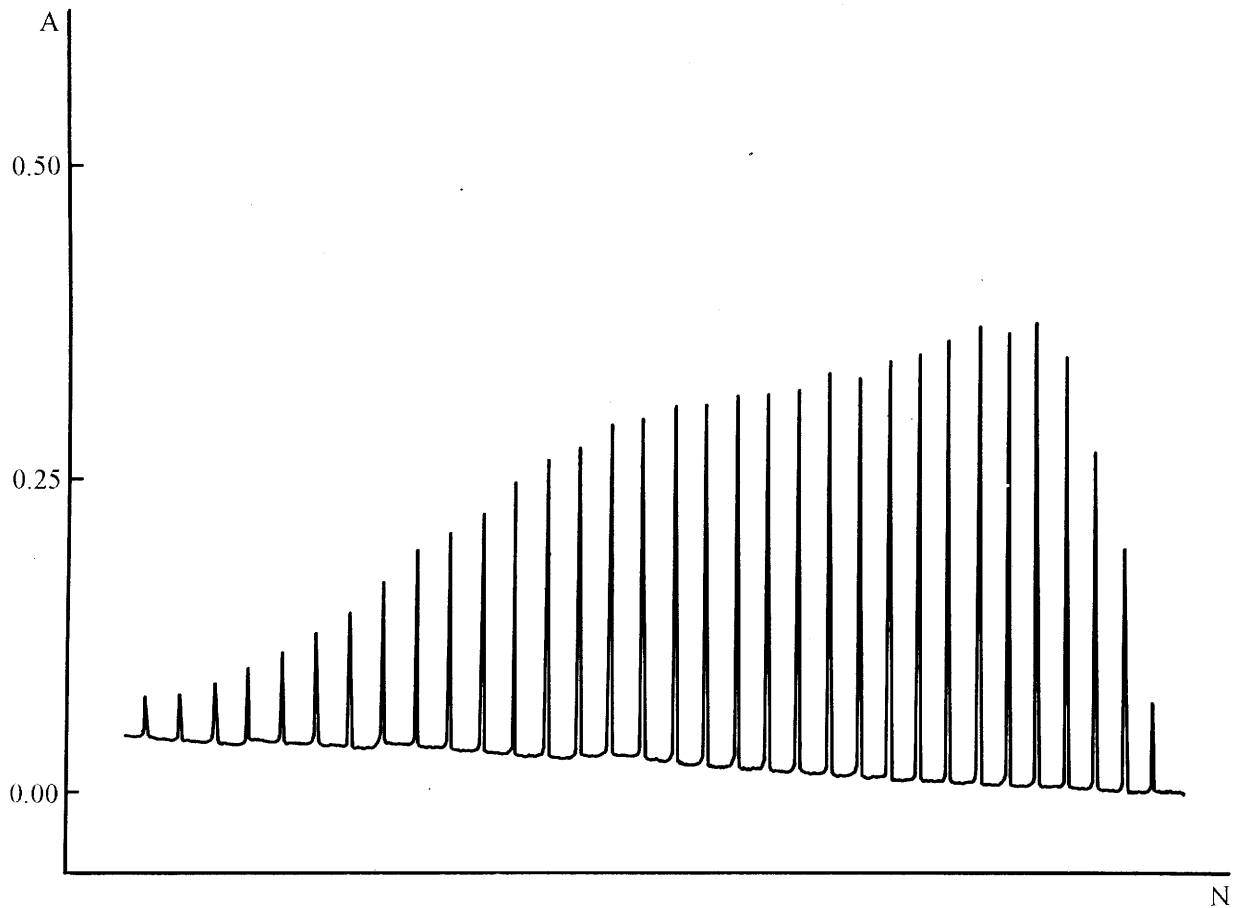


Figure 5. Recorder tracing obtained by sampling the eluted band. A is absorbance and N is the number of sampling steps. Elution time was increased from 11.7s in 1 s steps producing the peak distribution observed. Column loading time was 120s. The standard solution and flow rates were the same as those used to obtain Fig.3.

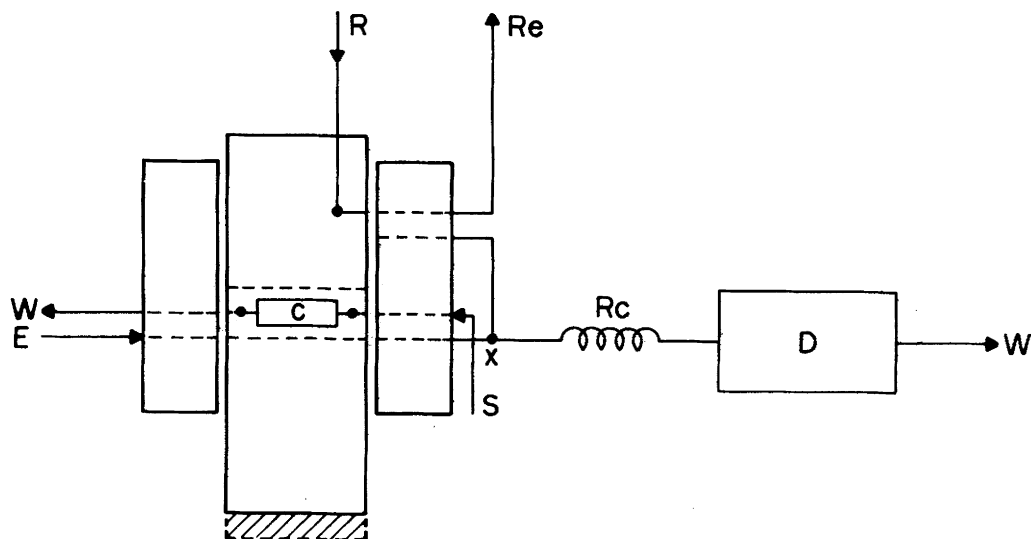


Figure 6. Flow diagram to save reagent during resin loading. Re is the reagent recovery and other symbols are the same as in fig.1.

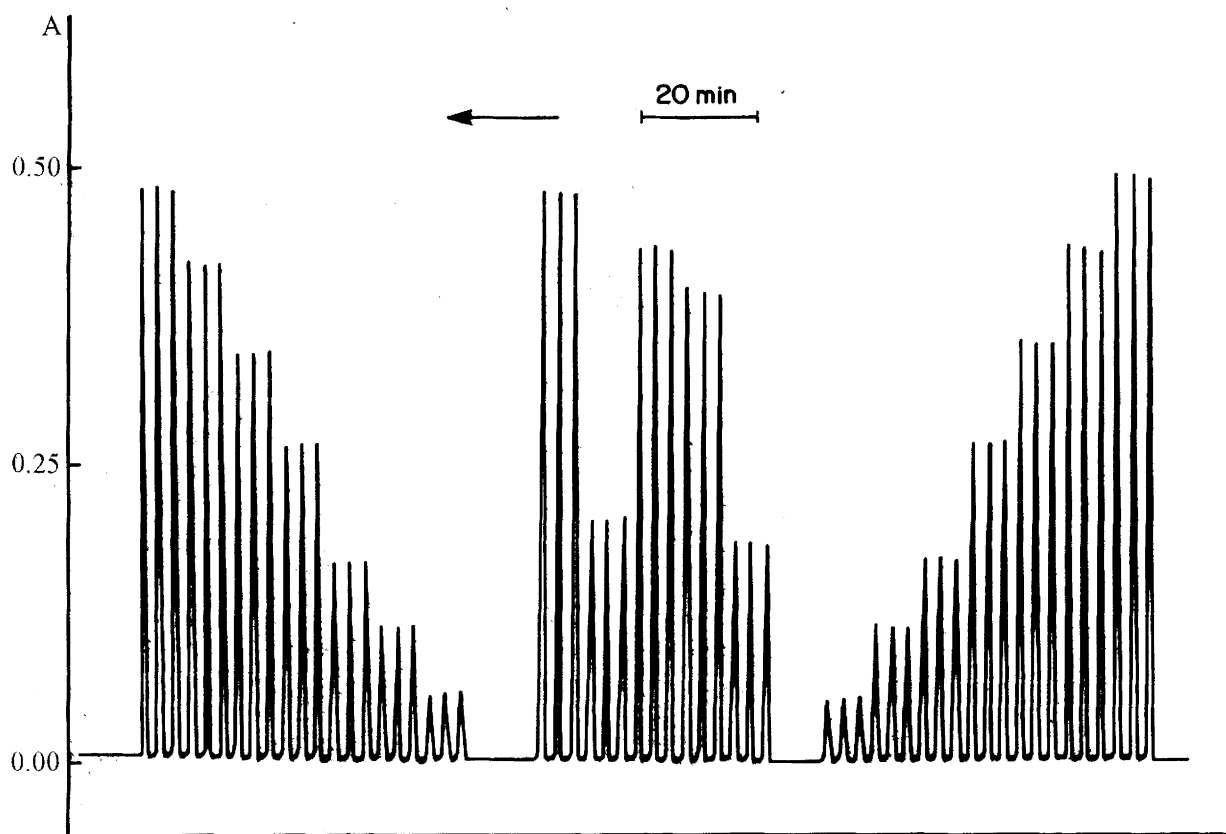


Figure 7. Recorder tracing of a routine analysis of natural waters. From left to right seven chloride standard solutions (0.50, 0.40, 0.30, 0.20, 0.10, 0.05, 0.00 mg/l) followed by five samples and the standards again, always in triplicate. Results obtained employing the flow diagram shown in Fig.6 with a sample flow rate of 4.2ml/min and column loading time 120s. Elution parameters were the same as in Fig.3.

and the results are shown in Table 1. Measurements concerning samples number 5 and 9 present a relative deviation higher than 10%. In the last run, only phosphate ions were added to the chloride standard solution, so that one can conclude that the interference is caused by phosphate ions. Considering that the resin column exchanger capacity is approximately 0.8 meq, higher than that of the working conditions, the phosphate interference can be related with to chemical reaction and not to the adsorption process. The proposed method is appropriate to analyse natural waters, where anion concentrations are usually below the studied range.

With the systems of Fig. 6, a set of water samples from the Rio Negro (Amazon basin) were analysed and the results are show in Figure 7. A throughput of 22 determinations per hour can be attained. The relative standard deviation was 0.4 %, calculated from 10 sequential measurements corresponding to a sample with 0.3 mg/l chloride. A detection limit of 4 ug/l was calculated following IUPAC recommendations⁹.

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