Fluorimetric determination of fluoride in a flow assembly integrated on-line to an open/closed FIA system to remove interference by solid phase extraction

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Abstract

A simple flow injection fluorimetric method for fluoride determination is proposed. The method is based on the enhanced fluorescence of quercitin–Zr(IV) complex when fluoride ion is present in the sample. An open/closed FIA manifold with a mini-column of Dowex 50W X8 resin was used to remove the most important interference (aluminum). The two FIA assemblies were integrated on-line to automate the pretreatment of the water sample and fluoride determination. The calibration graph was linear over the range $0.1–3.0$ μg ml^{-1} of fluoride with a correlation coefficient of 0.999 and LOD 0.06 μg ml^{-1}. The relative standard deviation was 2.5% and the sample throughput was 52 h^{-1} without pretreatment and 10 h^{-1} with pretreatment of the sample. The method was applied to the determination of fluoride in water samples.
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1. Introduction

In spite of the known profitable effects of fluoride for human beings, at higher concentrations harmful effects are produced on bone and dental tissues.

The World Health Organization (WHO) suggests 1.5 μg ml^{-1} F^-, as the upper limit for drinking waters.

Therefore, fluoride determinations in bottled, tap and well water by simple and fast methods, results of a great interest for laboratory routine techniques.

The most of fluoride determinations have been performed using different techniques as potentiometry with fluoride ion selective electrodes (ISE) [1,2], ion-exchange chromatography with conductivity detection [3,4], spectrophotometric [5] and most recently capillary electrophoresis [6].

The use of ISE has been preferred technique for this determination, as well as the SPADNS colorimetric method, but both analytical methods undergo some errors, which are caused by the

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presence of interferent ions. A fluoride distillation as HF from the sample should be performed, it becomes complicated the analytical techniques [7]. Concentration ranges where ISE and SPANDS methods can be used are 0.1–10 and 0–1.40 mg l^{-1}.

Ion chromatography method can be performed only if weak solvents are used to separate fluoride peaks from interference peaks.

An important approach for the use of the quercitin–Zr complex as a fluorescent compound is that the presence of fluoride causes an enhancement of the fluorescent signal. So, a simple flow injection analysis (FIA) method with fluorimetric detection for fluoride determination is proposed. The proposed method was applied to water samples and aluminum was the most severe interference. Thus, an open/closed FIA system was developed to remove the aluminum interference. This manifold was integrated with the FIA system with fluorimetric detection, in order to obtain an automated method with an on-line pretreatment of the sample and following fluoride determination.

2. Experimental

2.1. Instrumentation

An Aminco Bowman Serie 2 luminescence spectrophotometer equipped with a Hellma 176752-QS flow cell with an inner volume of 25 μl and 1.5 mm light path. All the reaction coils were made of PTFE tubing (i.d. 0.5 mm). Two Gilson Minipuls-3 peristaltic pumps, two Rheodyne 5041 injection valves and a Rheodyne 5011 six position rotary valve are used.

2.2. Reagents and solutions

Analytical grade reagents were always used as well as distilled, deionized water. Quercitin working solution 3.0×10^{-4} M was prepared by dissolving 0.0100 g of quercitin (Fluka AG). In 50% v/v of ethanol (Merck). This solution was prepared daily. Zirconium stock solution 2.7×10^{-2} M was prepared by dissolving 5.0019 g of

$Zr(SO_4)_2 \cdot H_2O$ (B.D.H. Laboratory Reagents) in 33.9 ml of concentrated H_2SO_4 to prevent the polymerisation of Zr and then making up the volume to 500 ml with water [8,9]. Zirconium working solution (3.0×10^{-4} M) was daily prepared from stock solution.

Fluoride stock solution 9.1542 g of NaF (Merck) were weighed and dissolved in 1000 ml of water. This solution was stored in polyethylene container. Standard solutions were prepared by appropriate dilution of the stock solution.

2.3. Procedure

A FIA manifold was designed and optimized for fluoride determination (Fig. 1a). A sample volume was injected in a bi-distilled water carrier stream. The quercitin–Zr complex was formed on line. Thus, HCl, quercitin and Zr solutions were pumped into the FIA system, the three streams merged into the reactor R1 where the quercitin–Zr complex was formed at a suitable acid medium. When this stream merged with the sample stream into the reactor R2, the fluorescence of the quercitin–Zr complex was enhanced owing to the fluoride present in the sample and signals were
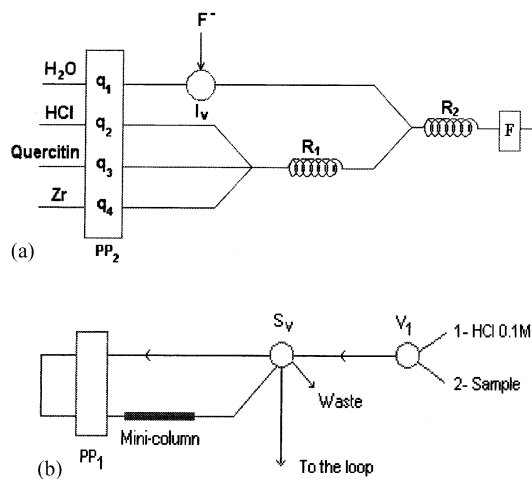

Fig. 1. (a) FIA manifold for fluoride fluorimetric determination. Iv, injection valve; R1 and R2, reactors; PP_2, peristaltic pump; $q_1–q_n$, flow rates; F, spectrofluorimeter; W, waste. (b) Open/closed FIA manifold for the sample pretreatment. PP_1, peristaltic pump; S_v, selection valve; V_1, six position rotary valve.

measured at 491 nm (excitation wavelength 422 nm).

An open/closed FIA system was designed and optimized to remove aluminum interference. This system was coupled to the sample loop of the FIA manifold above mentioned.

The open/closed FIA manifold is shown in Fig. 1b. A mini-column was packed with a Dowex 50W-X8 resin to remove the interference. The resin was regenerated by passing HCl 0.1 M stream through the mini-column during 2 min. Then the sample was pumped into the system and when the manifold was loaded the selecting valve (Sv) was switched to closed the manifold. The sample plug was trapped to recycle through the closed system during 4 min. The Al(III) was retained in the resin during this time. Then, the Sv valve was switched again to open the manifold and the sample stream free of aluminum interference was pumped to load the loop sample. The resin must be regenerated before the next water sample is treated.

3. Results and discussion

3.1. Optimization of FIA manifolds

The chemical and FIA variables were studied and optimized in order to obtain higher fluorescent signals and good reproducibility.

The concentration of the quercitin–Zr(IV) on-line obtained, is an important key for obtaining a higher fluoride analytical signal. As molar ratio of the above mentioned complex is 1:1 [10], the two streams for quercitin and Zr solutions were held with the same concentration and flow rate. The studied concentration range was $0.8–8.9 \times 10^{-4}$ M. The optimum value was 3×10^{-4} M for both solutions. Also, the HCl concentration was optimized in order to give an optimum medium for the quercitin–Zr complex formation. It was tested between 1.5 and 3.0 mol l^{-1} and the optimum value was 1.75 mol l^{-1}.

Quercitin solution was prepared in ethanol–water. So, different percentages (v/v) of ethanol were tested, for a quercitin concentration 3×10^{-4} M. The optimum value was 50% v/v.

Two different sorbents were tested, DETATA and Dowex 50W X8 [11,12] for the sample treatment. The best results were obtained with the Dowex resin.

A mini-column was packed with the selected resin, the size and inner diameter were optimized and results are shown in Table 1.

The amount of resin into the mini-column is an important key to remove the aluminum interference. So, with a mini-column of 76 mm of column length and 4 mm of inner diameter was possible to retain up 0.8 mg l^{-1} of aluminum.

An optimum medium to retain aluminum in the Dowex resin was obtained by passing a HCl 0.1 M stream through the mini-column [12].

The time which the sample was trapped into the closed FIA system was optimized, also the flow rate and the time that HCl solution was passing through the mini-column to regenerate the resin. All the variables tested for the two manifolds are shown in Table 1.

The efficiency of the open/closed continuous flow system to remove the aluminum interference

Table 1
Optimization of FIA variables

Variable	Studied range	Optimum value
Carrier flow rate (ml min^{-1})	0.52–1.23	0.82
Quercitin flow rate (ml min^{-1})	0.52–1.23	0.82
Zirconium flow rate (ml min^{-1})	0.52–1.23	0.82
HCl flow rate (ml min^{-1})	0.43–1.23	0.52
Reactor length (R1) (mm)	100–600	100
Reactor length (R2) (mm)	100–1000	600
Sample volume (μl)	100–200	150
Time to recycle the sample in the closed circuit (min)	2–6	4
Time to regenerate the resin (min)	1–4	2
Mini-column length (mm)	30–76	76
Inner diameter (mm)	2.5–4.0	4.0
Flow rate into the closed circuit (ml min^{-1})	1.79–2.72	2.45

was proved by using spiked samples. For that purpose, three fluoride standard solutions were prepared at different concentrations (0.48, 0.99 and 1.98 µg ml^{-1} F$^-$) and they were spiked with 0.8 mg l^{-1} of Al^{3+} The three samples were analyzed by the proposed method and the results (0.49, 1.00 and 2.00 µg ml^{-1} F$^-$) showed around 100% of recovery.

3.2. Analytical figures of merits

Calibration graph was linear over the range 0.1–3.0 µg ml^{-1} of fluoride ($y = 1.50$ [F$^-$ µg ml^{-1}] + 0.03); $r^2 = 0.999$, the LOD was 0.06 µg ml^{-1} F$^-$ ($S_b + 3s$ and $n_b = 10$). The relative standard deviation (RSD) calculated for nine samples containing 1.0 µg ml^{-1} F$^-$ injected by duplicate was 2.5%. The sample throughput was 52 h^{-1}. When the open/closed FIA manifold was used the same calibration curve was obtained, the RSD and sample throughput were 2.9% and 10 h^{-1}, respectively.

3.3. Interferences

The effect of foreign ions on the determination of 2.0 µg ml^{-1} F$^-$ was studied. The tolerance limit shown in Table 2 were obtained by considering that foreign ions do not cause interference if the signal is not different than 3% of the analyte

Table 2
Tolerance limits of interfering ions

Ion tested	Tolerance limit (mg l^{-1})
Cl$^-$	>900
Br$^-$	>500
SO$_4^-$	280
HPO$_4^-$	1
NO$_3^-$	>900
Na$^+$	>900
K$^+$	>900
Mg$^+$	200
NH^{4+}	>900
Ca^{++}	>900
Fe^{+++}	0.3
Al^{+++}	005

signal. Al^{3+} causes the greatest interference. Good tolerance to most of the species commonly found in waters was observed.

3.4. Determination of fluoride in real water samples

The proposed method was applied for fluoride determination in several water samples.

The first six water samples (Table 3) showed that Al^{3+} was not present in them. Therefore, the fluoride concentration determination was performed without sample treatment. On the other hand, these samples were spiked with Al^{3+} and the sample pretreatment was carried out on them before doing fluoride determinations. Also, a tap water and a drinking water samples were analyzed with and without sample treatment.

In order to asses the quality of the obtained results using the developed flow injection system, the samples above mentioned were run by SPANDS standard method [7] and the results were compared. The results obtained are shown in Table 3 and they indicate good agreement between the two methods.

4. Conclusion

The proposed FIA manifold for fluoride determination in water samples with fluorimetric detection is an alternative to other methodologies. It is a fast simple, selective and sensitive method and a high sampling frequency was attained.

An open/closed FIA manifold was incorporated in order to remove the aluminum interference so the treatment of the sample and the further F$^-$ determination are automated. The main advantage is the simplicity since the majority methods require fluoride distillation as HF from samples.

The applicability of the method to real samples has also been demonstrated by comparing with standard method and they present good agreement.

Table 3
Fluoride determination in real samples (μg ml^{-1}, $n = 4$)

Sample	Proposed method		Reference method	E%
	With pretreatment	Without pretreatment		
1	–	4.61 ± 0.07	4.68	1.50
2	–	1.02 ± 0.01	1.02	0.00
3	–	1.69 ± 0.02	1.75	3.40
4	–	2.82 ± 0.07	2.85	1.05
5	–	0.81 ± 0.07	0.81	0.00
6	–	0.24 ± 0.07	0.23	4.30
1 [a]	4.76 ± 0.05	–	4.68	1.70
2 [a]	1.05 ± 0.06	–	1.02	2.90
3 [a]	1.82 ± 0.04	–	1.75	4.00
4 [a]	2.83 ± 0.03	–	2.85	0.70
5 [a]	0.80 ± 0.04	–	0.81	1.23
6 [a]	0.22 ± 0.01	–	0.23	4.35
Tap water	0.79 ± 0.02	0.79 ± 0.04	0.80	1.25
Drinking water	1.50 ± 0.01	1.48 ± 0.005	1.50	1.33

1: Sample of well water from Copetonas (Bs. As. State, Argentine); 2 and 5: sample of Paso Piedras Dike. Bahia Blanca (Bs. As. State, Argentine); 3: sample of well water from Guamini (Bs. As. State. Argentine); 4: sample of tap water from Copetonas (Bs. As. State, Argentine); 6: sample of Rio Negro river (Rio Negro State, Argentine).

[a] Spiked samples with 0.75 mg l^{-1} Al^{3+}.

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