Talanta 105 (2013) 69–74

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Proposed flow system for spectrophotometric determination of fluoride in natural waters

Thiago L. Marques, Nívia M.M. Coelho*

Institute of Chemistry, University of Uberlândia Av. João Naves de Ávila 2121, CEP 38400-902, Uberlândia, MG, Brazil

ARTICLE INFO

Article history:
Received 26 September 2012
Received in revised form
26 November 2012
Accepted 26 November 2012
Available online 2 December 2012

Keywords:
Fluoride
In-flow system
SPADNS method

ABSTRACT

An environmentally-friendly flow system was developed for the determination of fluoride in natural waters, based on its reaction with zirconium ions and 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonate (SPADNS). The flow system was designed with solenoid valves in order to increase the versatility and improve the analytical performance, since each device handles the solution independently leading to a more efficient use of reagents. The minimization of reagent consumption and waste generation favors the development of a noteworthy system. Under optimized conditions, a linear response was observed within the range of 0.1–2.2 mg L^{-1}, with the detection limit, coefficient of variation and sampling rate estimated as 0.02 mg L^{-1}, 4.1% and 60 determinations per hour, respectively. In order to analyze samples containing high fluoride content a wider linear range (0.3–6.6 mg L^{-1}) can be obtained by using a low sample flow rate and low sample volume. In comparison with other methods, the proposed system offers advantages such as wider analytical range (1.7–2.2 times), higher sample throughput (1.5–4.0 times) and lower quantification limit (by a factor of 5–68). Along with the consumption of reagents being 20–55 times lower, the generation of wastes is 1.2–3.0 times lower, which contributes to the development of a 'greener' system. This method is fast, amenable to automation, environmentally-friendly and of low-cost. In addition, it could be successfully applied to the determination of fluoride in water samples, the results obtained being in agreement with those of the ISE method.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Fluoride is widely distributed in natural waters at low concentrations and is generally present in unpolluted freshwater bodies in concentrations of 0.01–0.30 mg L^{-1} and in unpolluted seawater in the range of 1.2–1.5 mg L^{-1} [1]. According to the WHO guidelines, the permissible limit for fluoride in drinking water is 1.5 mg L^{-1}. However, it should be noted that this limit may vary according to the maximum temperature of the air. Control limits have been found to range between 0.6 and 0.8 mg L^{-1} for temperatures of 26.3–32.6 °C and 0.9–1.7 mg L^{-1} for temperatures of 10–12 °C [2]. Excess fluoride in drinking water causes various diseases such as fluorosis (teeth and bone) and is associated with renal, gastrointestinal and immunological toxicity. Fluorosis is an endemic disease in at least 25 countries. However, the total number of people affected is not known, although a conservative estimate would be tens of millions [3]. Therefore, continuous monitoring of the fluoride levels in water samples is important to ensure good water quality.

Several analytical methods have been developed and described for fluoride determination in water including potentiometry [4], atomic spectrophotometry [5], solid-phase spectrophotometry [6], colorimetric [7], chromatography [8], ion chromatography [9], and fluorometry [10]. Of these methods, potentiometry and ion chromatography are widely used because of their simplicity and convenience, but their sensitivity and selectivity are limited. Ion chromatography can be performed only if weak solvents are used to separate the fluoride peaks from interference peaks. However, various chemical reactions are adopted in colorimetric and fluorometric methods and they have the advantages of selectivity and higher sensitivity [11]. The batch procedures have several drawbacks, such as high reagent consumption, resulting in large amounts of waste, and they are time consuming and laborious processes [12,13].

The potential to develop greener analytical procedures is inherent to flow analysis, and changes in system design as well as the exploitation of new flow approaches have led to ingenious alternatives to minimize reagent consumption and waste generation without hindering analytical performance. Multicommuted flow analysis employs a set of discrete commutators (e.g., solenoid valves) to design flow manifolds that can be configured by software, thus increasing the system versatility and resulting in more effective reagent use. Based on the papers related to

---

* Corresponding author. Tel./fax: +55 34 3239 4174.
E-mail address: nmmcoelho@ufu.br (N.M.M. Coelho).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.11.071

multicommuter flow analysis it can be observed that low reagent consumption and generation of waste are inherent features of this process [14]. Methods based on flow injection analysis using different detection techniques have also been reported [11,12,15].

Nevertheless, the Zr–SPADNS spectrophotometric method remains an attractive simple, low-cost, reliable and rapid alternative, which is also amenable to automation and to field use [15]. In this study, a flow system with solenoid valves was designed for the colorimetric determination of fluoride in water, based on the SPADNS method, using smaller volumes of reagents and generating low volumes of waste, in order to develop an ecologically-attractive methodology. Although the SPADNS method developed by Arancibia et al. [15] presents high tolerance for sulfate interference (characteristic of the sample studied), the procedure requires data processing as well as a relatively high consumption of reagents (SPADNS, $ZrOCl_2$ and HCl) since there is continuous injection of the indicator solution into the system. The methodology proposed herein is simple and rapid, with good reproducibility, sensitivity and accuracy, besides being an environmentally-friendly flow system. This method could be successfully applied to natural water samples with no pretreatments being required.

2. Experimental

2.1. Apparatus

The flow injection analysis (FIA) system was designed with three three-way solenoid valves (N Research, West Caldwell, NJ, USA), polyethylene tubes (Ismatec, Germany, 0.80 mm), two Perspex joints and two reaction coils (Ismatec, Germany, 0.80 mm). A Minipuls TM 3 (Gilson, Villiers Le Bel, France) peristaltic pump equipped with eight channels and Tygon® was used to pump the solutions through the system. The active devices were controlled through the parallel port of a Pentium IV microcomputer using a power drive based on a ULN2803 integrated circuit. The control software was developed in Visual Basic 6.0 (Microsoft, Seattle, WA, USA) which was used to control the on/off switching time of the solenoid valves and also the time that they remained open or closed. The HyperTerminal software and RS232C port were used for data acquisition.

Spectrophotometric measurements were performed on a Femto 600S spectrophotometer (São Paulo, SP, Brazil) equipped with a Hellma 178.010-OS flow cell with an inner volume of 80 μL and 10 mm light path. In the batch analysis carried out to validate the proposed method a combined fluoride electrode HI4110 (Hanna Instruments, Rhode Island, United States) was used. A Gehaka PG1800 pH meter (São Paulo, Brazil) was used to adjust the pH of the samples and working solutions.

2.2. Reagents and solutions

All reagents and standards were of analytical grade and all dilutions were carried out with deionized water obtained from a Milli-Q water purification system (Gehaka, São Paulo, Brazil). All laboratory glassware was washed with neutral detergent and then kept overnight in 10% (v/v) nitric acid solution and washed with deionized water prior to use. The stock solution of 1000 mg L^{-1} sodium fluoride (Merck, Darmstadt, Germany) was prepared after weighing 221 mg of the solid in 100 mL of deionized water. Working standards were obtained by proper dilution of the stock solution and the pH was adjusted with 0.01–0.1 mol L^{-1} HCl (Scharlau, Barcelona, Spain, 37 wt%) and NaOH (Vetec, Rio de Janeiro, Brazil) solutions.

The indicator solution was prepared by diluting 192 mg of SPADNS (Vetec, Rio de Janeiro, Brazil) in 100 mL deionized water. To obtain the zirconyl chloride solution, 26.6 mg of zirconyl chloride octahydrate (Vetec, Rio de Janeiro, Brazil) was dissolved in approximately 25 mL of deionized water, 20 mL of HCl was added and the solution was then made up to 100 mL by adding deionized water. The SPADNS and zirconyl chloride solutions were mixed in equal volumes to produce an indicator complex, which is stable for more than 2 years if stored away from light [16].

The total ionic strength adjustment buffer (TISAB) solution was prepared by dissolving, in approximately 50 mL of deionized water, 5.8 g sodium chloride (Vetec, Rio de Janeiro, Brazil) and 1.2 g sodium citrate (Vetec, Rio de Janeiro, Brazil) and adding 5.7 mL of concentrated acetic acid (Scharlau, Barcelona, Spain, 100 wt%). The pH of this solution was then adjusted using a pH meter and adding a solution of 5.0 mol L^{-1} NaOH (4.0 g in 10 mL) to give a pH of 5.0–5.5, the ideal range for a working electrode sensitive to fluoride.

2.3. Flow diagram and procedure

A multicommuted flow system was designed and optimized for fluoride determination (Fig. 1). A given volume of indicator solution was injected into a carrier stream (deionized water), passing through reaction coil R1, for the dispersion and dilution of the indicator solution in the carrier. A given volume of standard or sample was then pumped into the FIA system, converging with the aliquot of indicator dispersed in the carrier and passing through reaction coil R2 for the reaction between fluoride and the Zr–SPADNS complex. The sample zone was set to detection at 570 nm and the analytical signal was based on the peak height. Measurements were taken in triplicate. The analytical response was estimated as the difference between the analytical and blank signals. The optimization of several parameters was carried out in order to improve the sensitivity, precision, sample throughput and repeatability with minimum reagent consumption and waste generation. These studies were carried out using a 1.0 mol L^{-1} fluoride standard solution.

2.4. Reference methods

The potentiometric procedure (Ion Selective Electrode—ISE) was used as the reference for sample analysis and validation of the proposed method. The methodology is based on determination of the fluoride ion using a fluoride-selective electrode with samples being diluted using a TISAB solution to give a 1:1 volume ratio before measurement.

3. Results and discussion

3.1. General aspects

The commonly-employed SPADNS reference method for the determination of fluoride in waters is based on the effect of the fluoride ion on the absorbance of the complex formed by zirconium

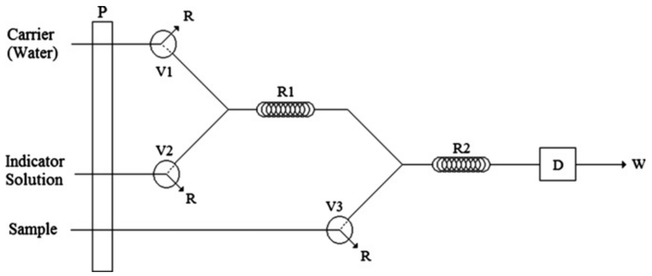

Fig. 1. Flow diagram of the multicommuted system for fluoride determination. P—peristaltic pump; V1, V2 and V3—three-way solenoid valves; R—recirculation of solution; R1 and R2—reaction coils and D—detection, W—waste.

ion and 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonate (SPADNS). The wavelength of 570 nm corresponds to the maximum absorption of the Zr–SPADNS and in the presence of fluoride the decrease in the absorbance of this wavelength is proportional to the concentration of fluoride ions in the sample. This decrease occurs because Zr forms a colorless species of general composition ZrF_n^{4-n} with fluoride [15].

3.2. System optimization

In the optimization of the proposed system, the effects of several FIA analytical parameters were investigated, including the flow rate (carrier, indicator and sample), volume (indicator and sample), reactor coil length (R1 and R2), sample pH and indicator concentration (SPADNS, $ZrOCl_2$ and HCl). The analytical signal was based on the peak height and was estimated as the difference between the analytical and blank signals. Optimization of these parameters led to improved sensitivity of the fluoride determination using a 1.0 mol L^{-1} fluoride standard solution in all studies.

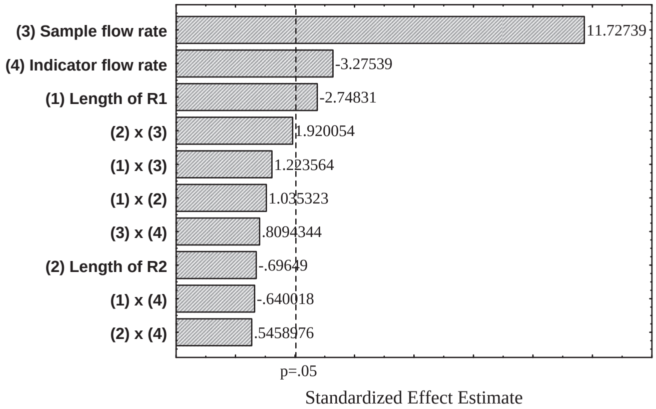

Fig. 2. Pareto chart obtained in the optimization study of the physical variables for the determination of fluoride.

Firstly, the following physical parameters: flow rate (indicator and sample) and length of the reaction coils (R1 and R2) were optimized using a 2^4 full factorial design to evaluate whether there is interaction between these variables in order to better determine the optimization conditions (univariate or multivariate). To this aim, 250 μL of standard (1.0 mg L^{-1} of fluoride) and 50 μL of indicator (960.0 mg L^{-1} of SPADNS, 133.0 mg L^{-1} of $ZrClO_2$ and 0.3 mol L^{-1} of HCl) were injected into the flow carrier (6.0 mL min^{-1}) and the parameters studied were optimized according to the following levels: flow rate of 1.5 and 3.0 mL min^{-1} for the indicator and sample and reaction coil lengths of 25 and 50 cm for R1 and R2. As shown in the Pareto chart in Fig. 2, the main factors such as sample flow rate, indicator flow rate and R1 length had a significant effect on the magnitude of the signal. It was verified that the best conditions for the FIA system in the range studied according to the Pareto chart were the higher level for the sample flow rate (3.0 mL min^{-1}) and lower levels for the indicator flow rate (1.5 mL min^{-1}) and the length of reaction coils R1 and R2 (25 cm). However, as no significant interaction was observed between the parameters evaluated, univariate optimization was carried out. The optimum values found were applied in subsequent optimization experiments.

The effect of flow rate on the shape, width and intensity of the FIA peaks was investigated in the following ranges: 1.0–5.0 mL min^{-1} for the carrier; 0.5–5.0 mL min^{-1} for the sample and 0.6–3.0 mL min^{-1} for the indicator, keeping constant the indicator (50 μL) and sample (250 μL) volumes and using the volumetric fraction of the official method (1:5 indicator:sample). As can be seen in Fig. 3, there was an increase in the absorbance with an increase in the flow rate of the

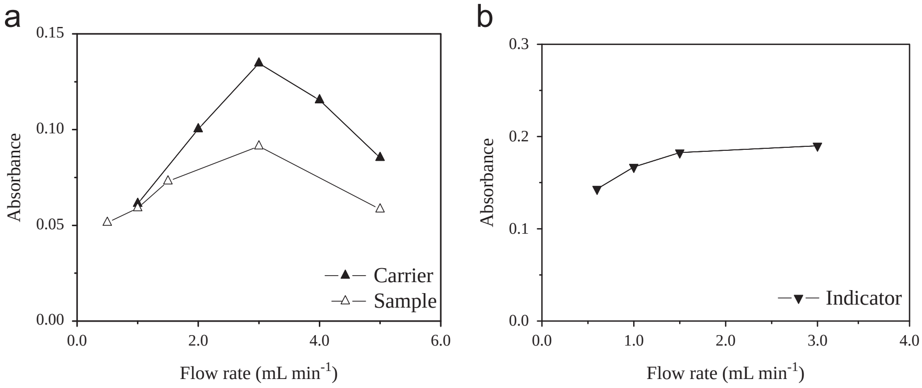

Fig. 3. Effect of the flow rate on the signal intensity, (a) carrier and sample flow rate and (b) indicator flow rate.

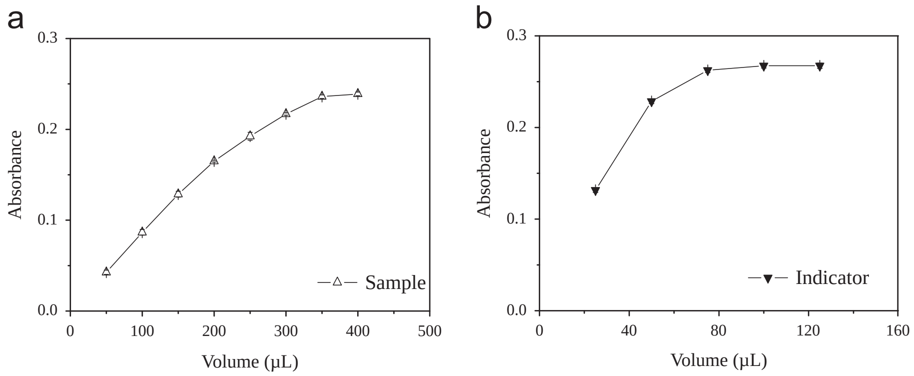

Fig. 4. Effect of the sample volume (a) and indicator (b) on the signal intensity.

carrier and of the sample up to 3.0 mL min^{-1} and a sharp decrease in the signal at higher flow rates. This effect occurs due to the degree of dilution of the indicator and sample at the different carrier flow rates. The small increase in the signal on increasing the flow rate from 1.5 to 3.0 ml min^{-1} is the opposite to the effect observed in the Pareto chart. This occurs because in the experimental design the carrier flow rate used was twice as fast as the optimized flow rate observed in the univariate testing. Thus, the dilution effect of the indicator was more evident in the full factorial design study than in this experiment. The optimal values found were 3.0 mL min^{-1} for the carrier and sample and 1.5 mL min^{-1} for the indicator, and these values were kept constant in subsequent experiments.

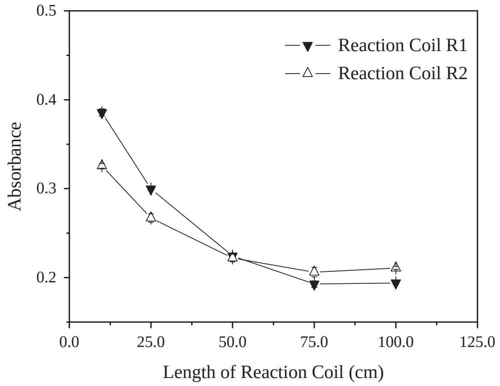

Fig. 5. Effect of the length of reaction coil (R1 and R2) on the signal intensity.

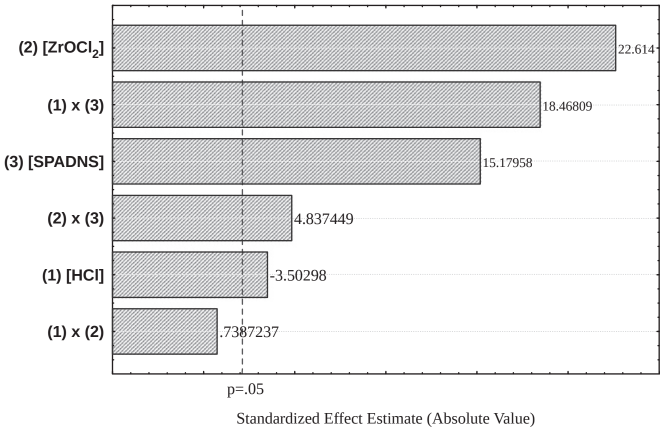

Fig. 6. Pareto chart obtained in the optimization of the chemical variables for the determination of fluoride.

The indicator and sample volumes were then optimized by changing the switching times of valves V2 and V3 at a previously optimized constant injection flow rate. The best responses found (Fig. 4) were using 75 μL of indicator and 350 μL of sample, maintaining the volumetric fraction of the official method (1:5). The optimum values found were applied in the subsequent experiments. The length of the reaction coils (R1 and R2) were then optimized by varying the length in the range of 10–100 cm. In Fig. 5 it can be observed that with an increase in the coil length there is a drop in the analytical signal, due to the increased dispersion of the indicator and the sample in the analytical path. The optimal values for the length of the reaction coils (R1 and R2) obtained and applied in subsequent tests was 10 cm.

In the optimization of the indicator concentration a 2^3 full factorial design was used to evaluate whether there is interaction between the variables in order to better determine the optimization conditions. To this end, all of the previously optimized values were employed and further parameters were optimized considering the following levels of concentration: 1.0 and 10.0 mmol L^{-1} for SPADNS; 0.1 and 1.0 mmol L^{-1} for ZrOCl_2 and 0.5 and 5.0 mol L^{-1} for HCl. As shown in the Pareto chart in Fig. 6, the main factors of the indicator used ([ZrOCl_2], [SPADNS] and [HCl]) and interaction between factors ([SPADNS] × [HCl] and [ZrOCl_2] × [SPADNS]) showed a significant effect on the magnitude of the signal. Thus, multivariate optimization of these parameters was carried out. According to the Pareto chart the best conditions in the FIA system in the ranges studied were the higher level for the ZrOCl_2 (1.0 mmol L^{-1}) and SPADNS (10.0 mmol L^{-1}) concentrations and lower level for the HCl (0.5 mol L^{-1}) concentration. According to the trend observed in the Pareto chart in the optimization of the variables, a response surface was constructed through the creation of a central composite design (CCD). The results are shown in Fig. 7 and the profiles presented by the surfaces show maximum points with critical concentrations of 7.0 mmol L^{-1} for SPADNS, 0.8 mmol L^{-1} for ZrOCl_2 and 3.3 mol L^{-1} for HCl. A summary of the ranges of the variables studied in the optimization step and the selected values is presented in Table 1.

Additional tests were performed to evaluate the effect of sample pH on the analytical signal in the optimized system in the pH range of 2.0–12.0. In Fig. 8a, a linear decrease in the signal can be observed with an increase in the sample pH. Thus, we selected a pH of around pH 7.0, at which the sample measurements can be performed without the need for pH adjustment and the interference at a fluoride concentration of 1.0 mg L^{-1} is less than 10%. This confidence interval is shown in Fig. 8b and applied to the pH range of 2.8–11.0. Therefore, there is no need to adjust the pH of drinking (tap) and mineral water samples.

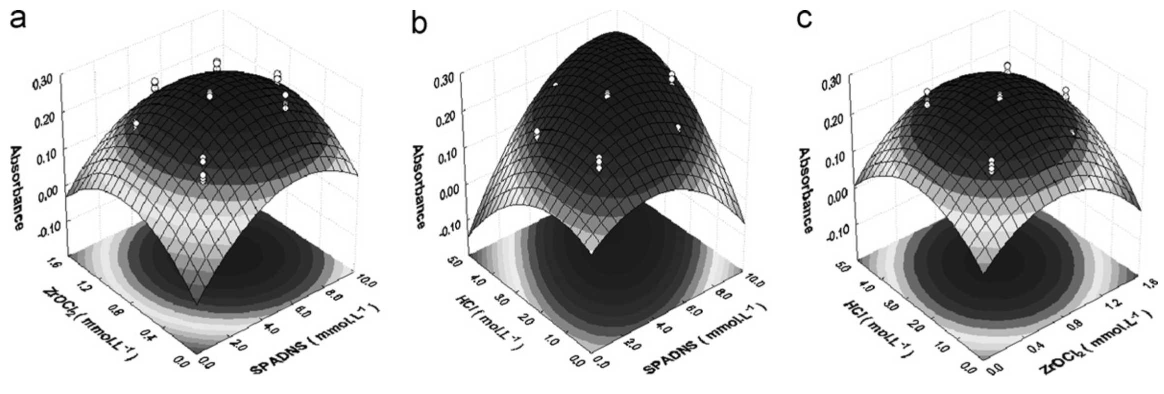

Fig. 7. Response surface for optimization of indicator reagent concentration for the determination of fluoride, (a) [ZrOCl_2] versus [SPADNS], (b) [HCl] versus [SPADNS] and (c) [HCl] versus [ZrOCl_2].

3.3. *Effect of interfering species*

In the proposed method negative interference is expected from some cations which may react with the fluoride complex formed and positive interference may result from anions which can form complexes with zirconium. The major interfering ions found in colorimetric methods are aluminum, iron, phosphate, sulfate and chloride [17] and for the batch method (SPADNS) they are Al(III), Fe(III) and PO_4^{3-} [18]. Thus, the concentration limit associated with a deviation of 10% at a fluoride concentration of 1.0 mg L^{-1} was determined according to an official method [18]. The values obtained were 0.2, 4.0 and 20.0 mg L^{-1} for Al(III), Fe(III) and PO_4^{3-}, respectively. These limits for the concentrations of Al(III) and Fe(III) are two times greater than those of the batch method and the PO_4^{3-} values are four times lower. The concentrations of these ions are lower than those set by Brazilian legislation for drinking water quality [19]. Thus, the proposed method can be applied without any pre-treatment to samples of potable water and bottled mineral water, with the exception of high-salinity water samples.

3.4. *Analytical figures of merits*

The calibration curves were linear in the ranges of 0.1–2.2 mg L^{-1} of fluoride ions, the equation of the calibration curve was $Y=-0.2122X+1.3106$ and the correlation coefficient was $r=0.9987$, where Y and X are peak heights for the absorbance and the fluoride ion concentration in mg L^{-1}, respectively. The limit of detection (LOD) was 0.02 mg L^{-1}. The relative standard deviation (RSD) of 12 measurements at 3 distinct points on the curve (high, medium and low) was 4.1%, and sample throughput was 60 samples/h. In relation to the SPADNS, $ZrOCl_2$ and HCl (37 wt%) consumption the values were estimated as 150.0 µg, 10.3 µg and 20.5 µL, respectively, with 3.5 mL of waste generated per determination. However, to analyze samples containing high fluoride content a wider linear range (0.3–6.6 mg L^{-1}) can be obtained using a sample flow rate of 1.0 mL min^{-1} and a sample volume of 116.7 µL, although this condition leads to a higher value for the LOD.

3.5. *Analytical applications and validation method*

The proposed method was applied to tap water, non-carbonated mineral water and carbonated mineral water. The samples did not undergo pre-treatment, except that the carbonated mineral water sample was submitted to an ultrasonic bath for 5 min before the analysis in order to release the gas from the sample. The results obtained in this study are shown in Table 2 together with the values obtained using the ISE method to validate the proposed method applying the *t*-test and *F*-test.

A significance test (paired *t*-test) revealed that the differences observed between the mean values for the two methods were not significant within 95% probability, and in all cases $t_{\text{calculated}}$ was less than $t_{\text{tabulated}}$, the highest values observed being 2.1 for $t_{\text{calculated}}$ and 2.4 for $t_{\text{tabulated}}$. The precision and accuracy of the method were confirmed by the *F*-test, where $F_{\text{calculated}}$ was lower than $F_{\text{tabulated}}$, the highest values observed being 4.8 for $F_{\text{calculated}}$ and 19.2 for $F_{\text{tabulated}}$.

All samples showed low concentrations of fluoride and the values were within those indicated by the WHO [2]. The proposed method can be applied to samples with high concentrations of fluoride, as reported by Garrido et al. [20], who determined high concentrations of fluoride (up to 4.76 mg L^{-1}) in water samples in Argentina.

3.6. *Comparison of the FIA system*

The proposed system was compared with other FIA systems designed for the determination of fluoride available in the literature

Table 1
Ranges studied and optimized conditions for fluoride determination.

Variable	Studied range	Optimum value
Carrier flow rate (mL min^{-1})	1.0–5.0	3.0
Sample flow rate (mL min^{-1})	0.5–5.0	3.0
Indicator flow rate (mL min^{-1})	0.6–3.0	1.5
Sample volume (µL)	50–400	350
Indicator volume (µL)	25–125	75
Reactor length R1 (cm)	10–100	10
Reactor length R2 (cm)	10–100	10
SPADNS concentration (mmol L^{-1})	0.8–9.2	7.0
$ZrOCl_2$ concentration (mmol L^{-1})	0.1–1.5	0.8
HCl concentration (mol L^{-1})	0.4–4.4	3.3

Table 2
Determination of fluoride in water samples and validation of proposed method.

Sample	**Proposed method (mg L^{-1})**	**ISE method (mg L^{-1})**
1[a]	0.13 (±0.03)	0.14 (±0.02)
2[a]	0.47 (±0.02)	0.49 (±0.02)
3[a]	0.10 (±0.02)	0.12 (±0.02)
4[b]	0.12 (±0.02)	0.14 (±0.02)
5[b]	0.43 (±0.03)	0.45 (±0.03)
6[c]	0.47 (±0.04)	0.47 (±0.04)

[a] Non-carbonated mineral water.
[b] Carbonated mineral water.
[c] Tap water.

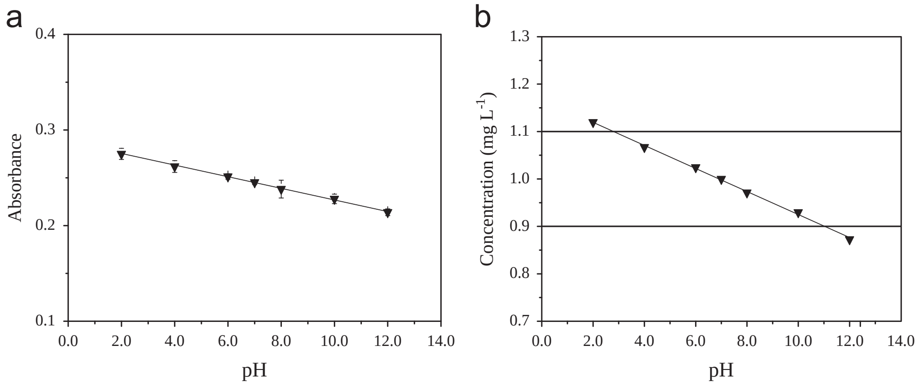

Fig. 8. Effect of sample pH on the signal intensity (a) and confidence interval (b) in the determination of fluoride.

Table 3
Analytical features of flow-based procedures for fluoride determination.

Method	Liner range (mg L^{-1})	LOD (mg L^{-1})	Indicator volume (mL)	Generated waste (mL)	Sample throughput (h^{-1})	Ref.
Fluorimetric	0.02–0.95	0.02	2.8	6.4	13	[11]
Potentiometric	1.90–190.0	1.37	4.2	10.4	78	[12]
Colorimetric	0.2–1.4	0.1	1.5	4.2	40	[15]
Colorimetric	0.1–2.2	0.02	0.075	3.5	60	Proposed method

Table 4
Analytical features using in the proposed method and in batch processing.

Analytical features	SPADNS in batch	Proposed method
Consumption of sample	50.0 mL	350.0 μL
Consumption of SPADNS	9.58 mg	150.0 μg
Consumption of $ZrOCl_2$	1.33 mg	10.3 μg
Consumption of HCl	3.5 mL	20.5 μL
Waste generated	60 mL	3.5 mL
Linear range	0–1.4 mg L^{-1}	0.1–2.2 mg L^{-1}

and the parameters evaluated are shown in Table 3. On comparing this method with that proposed by Nakaya et al. [11], despite presenting a lower coefficient of variation than the optimized method, it has as disadvantages a narrower linear range, higher consumption of sample and indicator (37 times higher), lower sample throughput and higher waste generation. On the other hand, the method proposed by Mesquita et al. [12] presents a wider linear range and higher sampling rate, but it has a higher limit of detection (LOD), higher consumption of sample and indicator (56 times higher) and higher volume of waste generated (3 times higher).

Compared to the SPADNS method developed by Arancibia et al. [15], the method described herein provides a wider linear range, higher sample throughput and lower volume of sample, coefficient of variation and LOD. Although the method of Arancibia et al. offers a high tolerance for interference by sulfate (characteristic of the sample studied), data processing is required and there is a higher consumption of reagents (SPADNS, $ZrOCl_2$ and HCl) since there is continuous injection of the indicator solution into the system.

The relatively low volume of indicator used in this method compared to others is due to the use of a solenoid valve which allows the recirculation of the solution and also the controlled injection of the reagent system, while the other systems perform the direct injection of the indicator into the system. Thus, overall, the method developed in this study is simple and its advantages include a low LOD within a wide linear range, high sample throughput and low reagent consumption and waste generation, which makes this a rapid, environmentally-friendly and low cost method.

Compared to batch processing [1], the proposed method allows savings in terms of the reagents and less generation of waste. Moreover, the optimized conditions present a wider linear range than the batch method, as can be seen in Table 4. Other notable factors are the higher sample throughput of the proposed method and less intervention being required from the analyst, reducing the potential for errors.

4. Conclusions

In comparison with other systems, the FIA system proposed herein offers the advantages of higher sample throughput, wider analytical range, lower consumption of reagents and sample and lower generation of wastes, coefficient of variation and quantification limit. The use of solenoid valves in this optimized FIA system led to increased versatility and improved analytical performance, thus making this method fast, amenable to automation, environmentally-friendly and of low-cost. The procedure could be successfully applied for the determination of fluoride in water samples and the concentration values obtained are in agreement with those of the ISE standard method.

Acknowledgments

The authors are grateful for financial support from the Brazilian governmental agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and from the Minas Gerais State governmental agency Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG).

References

[1] Standard Methods for the Examination of Water and Wastewater, 21st ed., 2005, pp. 4–79.
[2] World Health Organization, Guidelines for Drinking-water Quality, 3rd ed., Geneva, 2006 p. 376.
[3] R.L. Kanwar, K.K. Rao, Sens. Actuators B 149 (2010) 245–251.
[4] A. Koblar, G. Tavčar, M. Ponikvar-Svet, Food Chem. 130 (2012) 286–290.
[5] H. Gleisner, J.W. Einax, S. Morés, B. Welz, E. Carasek, J. Pharm. Biom. Anal. 54 (2011) 1040–1046.
[6] O.A. Zaporozhets, L.Y. Tsyukalo, Anal. Chim. Acta 597 (2007) 171–177.
[7] X. Gao, H. Zheng, G. Shang, J. Xu, Talanta 73 (2007) 770–775.
[8] J. Musijowski, B. Szostek, M. Koc, M. Trojanowicz, J. Sep. Sci. 33 (2010) 2636–2644.
[9] H. Yiping, W. Caiyun, Anal. Chim. Acta 661 (2010) 161–166.
[10] W. Lu, H. Jiang, F. Hu, L. Jiang, Z. Shen, Tetrahedron 67 (2011) 7909–7912.
[11] M. Nakaya, M. Oshima, T. Takayanagi, S. Motomizu, H. Yamashita, Talanta 84 (2011) 1361–1365.
[12] R.B.R. Mesquita, I.C. Santos, M.F.F. Pedrosa, A.F. Duque, P.M.L. Castro, A.O.S.S. Rangel, Talanta 84 (2011) 1291–1297.
[13] H.D. Moya, P. Dantoni, F.R.P. Rocha, N. Coichev, Microchem. J. 88 (2008) 21–25.
[14] W.R. Melchert, B.F. Reis, F.R.P. Rocha, Anal. Chim. Acta 714 (2012) 8–19.
[15] J.A. Arancibia, A. Rullo, A.C. Olivieri, S. Nezio, M. Pistonesi, A. Lista, B.S.F. Band, Anal. Chim. Acta 512 (2004) 157–163.
[16] A.D. Eaton, A.E. Greenberg, L.S. Clesceri, E.W. Rice, M.A.H. Franson, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association/American Water Works Association/Water Environment Federation, New York, 2005.
[17] H. Parham, N. Rahbar, Talanta 80 (2009) 664–669.
[18] E. Bellack, P.J. Schouboe, Anal. Chem. 12 (1958) 2032–2034.
[19] Ministry of Environment, National Environmental Council—CONAMA. Resolution no. 357 of March 17, 2005. Available from: 〈http://www.casan.com.br/docs/CONAMA357_05.pdf〉, (accessed 16.08.12).
[20] M. Garrido, A.G. Lista, M. Palomeque, B.S.F. Band, Talanta 58 (2002) 849–853.