



# A flow injection procedure using Layered Double Hydroxide for on line pre-concentration of fluoride

Diego P. Rocha<sup>a</sup>, Gabriel C. Terra<sup>a</sup>, Thaís S. Nery<sup>a</sup>, Jairo Tronto<sup>b</sup>, Frederico G. Pinto<sup>b</sup>,  
Sidnei G. Silva<sup>a</sup>, Nívia M.M. Coelho<sup>a,\*</sup>

<sup>a</sup> Federal University of Uberlândia, Institute of Chemistry, Avenue João Naves de Ávila, 2121, Santa Mônica, Uberlândia, MG CEP 38400-902, Brazil

<sup>b</sup> Federal University of Viçosa, Campus de Rio Paranaíba, Institute of Exact and Technological Sciences, Rodovia MG-230 - Km 8, Rio Paranaíba, MG CEP 38810-000, Brazil

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## ABSTRACT

This work showed a flow system designed with solenoid valves for preconcentration of fluoride using SPADNS method in water samples. The analyte was preconcentrated in a mini-column coated with Layered Double Hydroxides (LDH) used as adsorbent. Then, the fluoride ions were eluted with 0.5 mol L<sup>-1</sup> sodium hydroxide and determined by spectrophotometry. The variables that affect the system such adsorbent mass, type of eluent, solutions flow rate, reagent concentration and pH effect were critically evaluated. Under optimized conditions, the detection limit, coefficient of variation, linear range and preconcentration factor were estimated at 15 µg L<sup>-1</sup> (99.7% confidence level), 0.8% (500 µg L<sup>-1</sup>, n = 10), 50–500 µg L<sup>-1</sup> and 10, respectively. The accuracy of the method was evaluated by analysis of ALPHA APS 1076 (Simulated Rain Water) certified material, the values were not significantly different at a 95% level of confidence. The method was applied for fluoride determination in water samples and the levels found were below the maximum values established by Brazilian environmental and health legislations.

## 1. Introduction

Fluorine occurs naturally in many regions of the world. Human beings are frequent expose to fluorine through food, water and other products [1]. Studies regarding fluoride content in water, for human consumption, have proved a strait relation between dental and skeletal fluorosis and increased of dental caries incidence [2]. One of the greatest consumptions sources of this element is the ingestion of water, in which the ion can be presented naturally in these samples, or inserted in wastewater treatment. The maximum limit recommend of fluoride in water for human consumption varies from 1.4 to 4.0 mg L<sup>-1</sup>, according to Environmental Protection Agency of the United States [2,3].

Considering the importance of fluoride monitoring in different areas, it is possible to find a vast literature of analytical methods for determination of fluoride [4–7]. Several analytical techniques has been used for determination of fluoride are: potentiometric [8–10], graphite furnace atomic absorption spectrometry [11,12], solid phase spectrophotometry [13], colorimetric [14–20], fluorimetry [21,22], inductively coupled plasma atomic emission spectrometry and microwave induced plasma optical emission spectrometry [23,24], high pressure liquid chromatography [25], ionic chromatography [26,27], gas

chromatography [28,29] and capillary electrophoresis [30,31].

Due to its simplicity, methods based on potentiometry and ion chromatography are widely used for determination of fluoride [22]. However, despite potentiometry offers advantages such as: low cost, good sensibility and low limit of quantification, it shows automation difficulties, due the necessity of the use of a specific detection cells that contains fluoride sensitive electrode and reference electrode in the same cell [32]. Regarding the ionic chromatography, it can be used to determine fluoride only when is used weak eluents which do not cause the removal of fluoride sign. However, in addition to the potentiometric and chromatographic methods, various colorimetric and fluorimetric methods are described in the literature for determination of fluoride. These compared to the two previously described have the advantage of ease adaptation to the analysis of flow systems [22]. The analyzes described above are usually carried out in batch, and these have the general disadvantages: the high reagent consumption, generation of large volumes of waste, besides being slow and laborious procedures [10,33].

Some methods for fluoride analyses utilizing different detection techniques and based on flow injection analysis are described in the literature [10,14,16,21,22,32,34–37]. These methods have been

\* Corresponding author.

E-mail address: [niviammcoelho@gmail.com](mailto:niviammcoelho@gmail.com) (N.M.M. Coelho).

developed to overcome the disadvantages of batch methods, and fit the principles of Green Chemistry. Thus, by changing the design of the systems, as well as the exploration of new flow approaches, new methods developed have led to minimizing reagent consumption and waste generation. An example is the analysis of a multicommuted flow, which employs a discrete set of commutators (for example, solenoid valves), making the most versatile, economic and ecological systems [38].

Due to the narrow limits of the safety of fluoride and its harmfulness to human health it is necessary to develop more sensitive methods to determine these small concentration differences safely. However, these instrumental methods mentioned above do not always have high sensitivity and selectivity to detect directly ions at very low concentration levels, there is a need to combine analytical procedures with an efficient instrument in the search for greater sensitivity.

In this content, stands out the phase solid extraction (SPE) for pre-concentration on-line. In addition to increasing sensitivity, it offers simplicity, low risk sample contamination by generally prevent the introduction of reactants, and high enrichment factors. These are attractive features for the development of analytical procedures. Therefore, SPE employs sorbents filled in cartridges, syringes or disks; the retention mechanism is dependent on the existing affinity between the analyte and the filling, causing the immobilization of the surface of the sorbent [39].

In this present work one Magnesium Aluminum Layered Double Hydroxide intercalated with nitrate ( $\text{MgAl-NO}_3\text{-LDH}$ ) was utilized as sorbent in SPE for on-line pre-concentration of fluoride. Layered Double Hydroxides (LDHs) are materials formed by stacking layers of mixed hydroxides of divalent and trivalent cations containing hydrated anions intercalated between the layers. In LDHs, the mobility presented by interlamellar anions is responsible for one of the most important properties of these materials, the anion exchange capacity. The anion exchange capacity of LDHs depends on the ratio of the metal cations, the anion capacity involved in stabilizing of the lamellar structure, and the molecular mass of the cations and anions present. According Miyata [40], the ion-exchange equilibrium constant for LDHs of monovalent anions are in the sequence  $\text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$ . Several methods for fluoride removal using different types of LDHs are reported in the literature [41–48], however these methods are time-consuming, highly dependent on the analyst and none explores the pre-concentrating power of LDH.

Thus, the use of adsorptive process in phase solid extraction is even more attractive when is applied in flow injection analyses directly coupled to a detection system. The flow injection analysis system coupled phase solid extraction and UV–Vis detection (FIA-SPE-UV–Vis) is quite advantageous to minimize contamination problems inherent to the analyst and the bench procedures and increase the sensitivity of the method. It is not reported in literature works using LDHs for pre-concentration of fluoride on-line in the water using the colorimetric method SPADNS. The present study evaluated the ability of this sorbent to pre-concentrate fluoride on-line in water with spectrophotometry detection by SPADNS method employing analysis systems in a multicommuted flow.

## 2. Experimental

### 2.1. Apparatus

X-ray diffraction (XRD) was performed on a Shimadzu XRD-6000 diffractometer using graphite crystal as monochromator to select  $\text{Cu-K}\alpha_1$  at a radiation of  $\lambda = 1.5406 \text{ \AA}$ , with a step size of  $0.02 \text{ s}^{-1}$ .

For Attenuated Total Reflectance with Fourier Infrared Spectroscopy (ATR-FTIR), a Jasco FTIR 4100 spectrophotometer was used. Spectra of 60 scans were collected, in a wavelength range of  $4000\text{--}400 \text{ cm}^{-1}$ .

Mass coupled thermal analyses (TGA-DSC-MS) were recorded on a

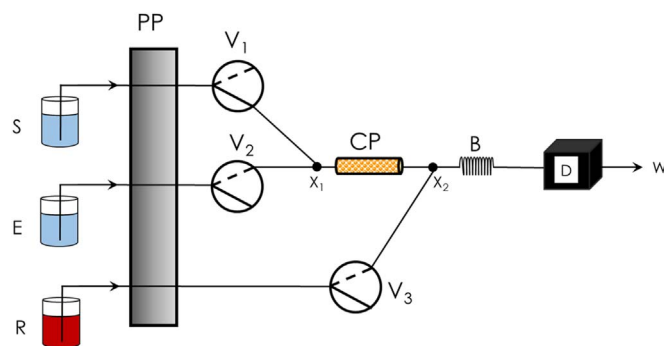


Fig. 1. Flow diagram of the system for fluoride determination.  $V_1$ – $V_3$  three-way solenoid valves; PP: peristaltic pump; S: sample  $3.0 \text{ mL min}^{-1}$ ; E: eluent  $1.0 \text{ mL min}^{-1}$ ; R: reagent solution  $1.0 \text{ mL min}^{-1}$ ;  $X_1$  and  $X_2$ : confluence point; B: long reaction coil 50 cm; CP: mini-column of preconcentration packed with HDL; W: waste. Arrows indicate the direction of the flow rate. Continuous line in solenoid valves indicates the flow direction in switch OFF position. Discontinuous line in solenoid valves indicates the flow in ON position.

Netzsch thermoanalyser model TGA-DSC 490 PC Luxx coupled to an Aëolos 403 C mass spectrometer, using a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  and under a  $50 \text{ mL min}^{-1}$  flow of synthetic air from the ambient temperature up to  $1000 \text{ }^\circ\text{C}$ .

The manifold for fluoride pre-concentration (Fig. 1) was constructed with three computer-controlled three-way solenoid valves (NRResearch, West Caldwell, NJ, USA), 0.8-mm i.d. polyethylene tubes and an acrylic confluence point. The active devices were controlled through a parallel port of a Pentium IV microcomputer equipped with an electronic interface (Arduino). The electric potential and current required to switch on the devices (12 V and 100 mA, respectively) were supplied by a lab-made electronic interface based on an ULN2803 integrated circuit. Fluid propelling was carried out by a peristaltic pump (Gilson, Villiers Le Bel, France) equipped with a Tygon® tube. Spectrophotometric measurements were carried out with spectrophotometer (Femto 600 S, São Paulo, Brazil) at 570 nm, equipped with a glass flow cell with 1-cm optical path and 80  $\mu\text{L}$  internal volume (Hellma, Plainview, NY, USA).

### 2.2. Reagents and solutions

All solutions were prepared with analytical grade chemicals and deionized water (Gehaka, São Paulo, Brazil). Particularly, deionized-decarbonated water was used during the synthesis and washing of  $\text{MgAl-NO}_3\text{-LDH}$ . Aluminum nitrate monohydrate, magnesium nitrate hexahydrate, sodium hydroxide, and sodium nitrate were purchased from Sigma-Aldrich®. Fluoride working reference solutions ( $1000 \text{ mg L}^{-1}$ ) were prepared by dissolving appropriate amounts of sodium fluoride (Merck, Darmstadt, German) in deionized water and stored in a polyethylene bottle. Calibration solutions were prepared by successive dilutions of a working solution. Reagent solution was prepared adding an equal volume of  $3.37 \text{ mmol L}^{-1}$  1,8-dihydroxy-2- (4-sulfophenylazo) -naphthalene-3,6-disulphonic acid (Vetec, Rio de Janeiro, Brazil) solutions and  $0.82 \text{ mmol L}^{-1}$  zirconium chloride (Vetec) in presence of  $1.8 \text{ mol L}^{-1}$  HCl [37]. The samples of bottled water purchased in local markets (Uberlândia, Minas Gerais, Brazil) and a tap water sample was collected in the laboratory. A standard reference material of Simulated RainWater (Level 2, ALPHA APS-1076, Stevensville, MI, USA) was used to test the accuracy of the fluoride determination.

Immobilization of adsorbent material was carried out as previously described [49], by dissolving 250 mg of cellulose acetate in 0.5 mL dimethylformamide plus 1.5 mL acetone and HDL material (1.0 g) was added to the mixture. After 10 min, the mixture was washed with deionized water and air dried. Finally, the resultant adsorbent material was cut into small particles. The preconcentration mini-column was obtained from 5-cm long polymeric tubes (2.0 mm i.d.), filled with

about 150 mg of the immobilized HDL, and with polyurethane pieces at both ends.

### 2.3. Synthesis of Layered Double Hydroxide

The MgAl-NO<sub>3</sub>-LDH was prepared by coprecipitation method at constant pH as follows: a solution containing  $5.40 \times 10^{-2}$  mol of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and  $1.80 \times 10^{-2}$  mol of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 0.250 L of water was added dropwise to a solution containing  $7.30 \times 10^{-2}$  mol of NaNO<sub>3</sub> in 1.00 L of H<sub>2</sub>O under vigorous stirring and N<sub>2</sub> atmosphere. During synthesis, a 2.00 mol L<sup>-1</sup> NaOH solution was added dropwise to maintain the pH constant at 10.0. The resulting gel was stirred for 24 h at a temperature of 338 K under N<sub>2</sub> atmosphere. After synthesis, the solid in suspension was washed five times by centrifugation. Then, the material was dried at reduced pressure in the presence of silica gel.

### 2.4. Flow diagram and procedure

Fluoride determination was performed using flow system depicted in Fig. 1. In the first step, the sample solution was pumped through the mini-column by the switching ON of the V<sub>1</sub> valve (14 min). After this, in the second step, the valve V<sub>1</sub> was switched OFF and the valve V<sub>2</sub> was switched ON to perform the elution procedure with 0.5 mol L<sup>-1</sup> of NaOH solution, during 1 min. Elapsed 9 s of the second step, the reagent solution was inserted in the flow system by the switching ON of the V<sub>3</sub> valve. In the third step, the eluate containing the pre-concentrated analyte and the reagent aliquots undergo fast mixing at the confluence point (X2) being carried out through the long reaction coil (B). In this point (X2), the flow rate was 1 mL min<sup>-1</sup> and maintained constant. Triplicate measurements were based on peak height.

## 3. Results and discussion

### 3.1. Characterization of Layered Double Hydroxide

The diffractogram of MgAl-NO<sub>3</sub>-LDH is presented in Fig. 2. This diffractogram is characteristic of hydrotalcite-type compounds. This material presents the basal peaks (001), (003) and (009) in 2θ equal 10.8 and 19.9 θ, respectively. The basal spacing value calculated by Bragg's equation was 8.80 Å, this value coincides with the value reported in the literature for intercalation of NO<sub>3</sub><sup>-</sup> ions between the inorganic layers of LDHs [50]. It is also possible to note by the width in the mid-height of the basal peaks of the diffractogram that the synthesized material presents good structural organization and phase purity. The determination of the average apparent diameter (L<sub>110</sub>) and thickness (L<sub>003</sub>) for MgAl-NO<sub>3</sub>-LDH particles was performed by Scherrer method, using KCl as an internal standard [51,52]. The values of L<sub>110</sub> =

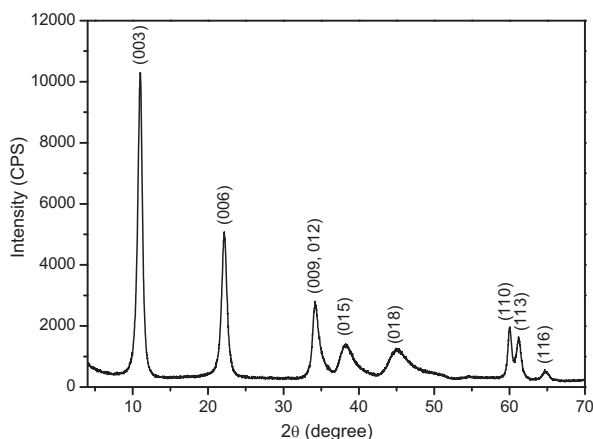


Fig. 2. Diffractogram of MgAl-NO<sub>3</sub>-LDH.

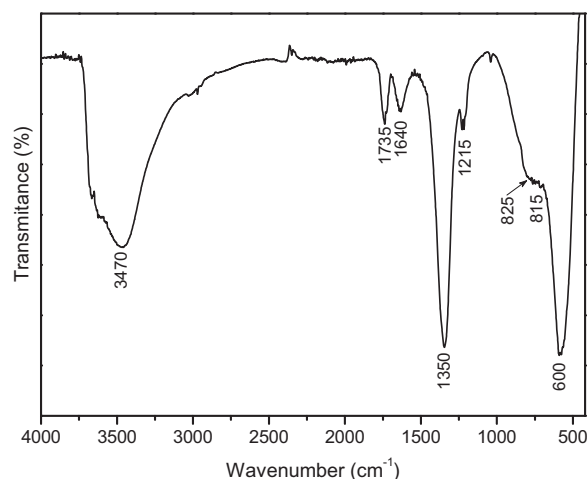


Fig. 3. FTIR-ATR of MgAl-NO<sub>3</sub>-LDH.

12.5 nm and L<sub>003</sub> = 10.4 nm were obtained in the directions to the 110 and 003 reflecting planes.

The FTIR-ATR spectrum of MgAl-NO<sub>3</sub>-LDH is shown in Fig. 3. For this material, it is possible to note the presence of three bands located at 3470 cm<sup>-1</sup>, 1640 cm<sup>-1</sup> and 815 cm<sup>-1</sup>, which correspond to the various stretching modes of OH groups of intercalated and adsorbed H<sub>2</sub>O molecules and/or hydroxyl groups of the lamellar lattice. The high intensity thin band located at 1350 cm<sup>-1</sup> can be associated to the vibration mode (n<sub>3</sub>) of CO<sub>3</sub><sup>2-</sup> and/or the antisymmetric stretching of N-O vibration of free nitric ions. Despite of the use of decarbonated H<sub>2</sub>O during the synthesis and washing of LDH, as well as the use of N<sub>2</sub> gas flow during the synthesis, probably a small quantity of CO<sub>3</sub><sup>2-</sup> was adsorbed on the LDH surface during the handling of the sample in contact with CO<sub>2</sub> atmospheric. The bands of low intensity located at 825 and 600 cm<sup>-1</sup> are attributed to the vibration modes (n<sub>1</sub>) and (n<sub>4</sub>) of the NO<sub>3</sub><sup>-</sup>, respectively.

The TG-DSC-MS results for MgAl-NO<sub>3</sub>-LDH are shown in Fig. 4. The LDH show two stages of thermal decomposition. The first stage occurs from 30 °C up to close to 200 °C with a mass loss of 11.5%. This mass loss occurs, according to the result of the DSC curve, by an endothermic process. In this temperature range the mass spectrometry data indicates the loss of H<sub>2</sub>O (m/z = 18), this H<sub>2</sub>O refers to the adsorbed molecules on the surface of the crystallites and also intercalated between the inorganic layers of LDH. The second stage of thermal decomposition occurs between 200 °C and 600 °C. In this temperature range, the mass loss is 33.9%. In this step, the DSC curve shows the presence of an endothermic process. The analysis of the mass spectrometry curves in this region shows the loss of water (m/z = 18), referring to the dextroxylation process of the layers. In this temperature range, also it is possible to note loss of NO<sub>2</sub> (m/z = 46) from NO<sub>3</sub><sup>-</sup> intercalated.

### 3.2. General aspects

Fluoride can be determinate by the SPADNS method, in which, the complex formed between zirconium and the complexing agent 2-(parasulfophenylazo)–1,8-dihydroxy-3,6-naphthalene-disulfonate (SPADNS-Zr) leaving a red color complex. Under certain conditions, zirconium must be complexed by fluoride, resulting in a decrease of absorbance signal. However, this spectrophotometric method shows some disadvantages, such as poor sensitivity and high reagents consumption. Solid-phase preconcentration is an alternative for sensitivity enhancement and can be implemented in a flow-based system. A manifold with solenoid valves was selected due to the possibility of system control by microcomputer and reduced reagent consumption, inherent to flow injection analysis based on multicommunication. LDH was choice as adsorbent material due its high surface area and high

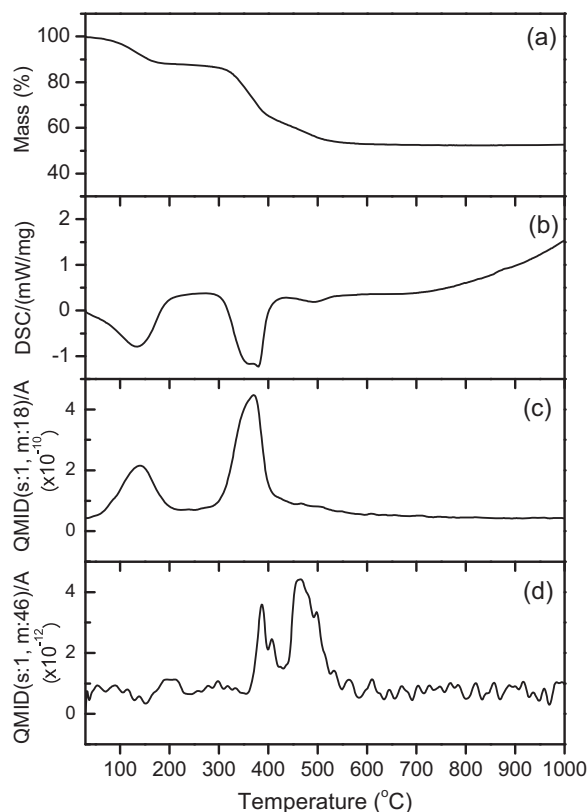


Fig. 4. (a) TG, (b) DSC, (c) MS ( $m/z = 18$ ), (d) MS ( $m/z = 46$ ); for MgAl-NO<sub>3</sub>-LDH.

anion exchange capacity. A mini-column coated with LDH was prepared after adsorbent immobilization, yielding solid particles of homogeneous size, minimizing back pressure drawback.

### 3.3. System optimization

The effect of chemical (reagent concentrations, pH, eluate concentration, and amount of the solid adsorbent) and physical variables in preconcentration system as flow-rate was evaluated by the univariate method. The effects of several FIA analytical parameters such as flow rate and reactor coil length were optimized previously [37]. In this work, the flow system was designed under the same conditions and analytical performance was maintained. The sensitivity, precision and reagent consumptions were taken into account in the optimization process. The ranges evaluated of each parameter and selected values are shown in Table 1.

Acidity has a critical effect on the analyte retention and elution. When LDH is used as adsorbent in acidic medium, the layered structure of the material can hydrolyze, destroying the adsorbent material. The effect of pH on the fluoride adsorption as shown in Fig. 5, was evaluated an initial range of solution pH that varied from 4 to 12, best results were obtained in pH value lower than 10. Besides this pH value, recovery efficiency decrease due to high hydroxide concentration, competing with fluoride ions in the adsorption. For further studies, sample

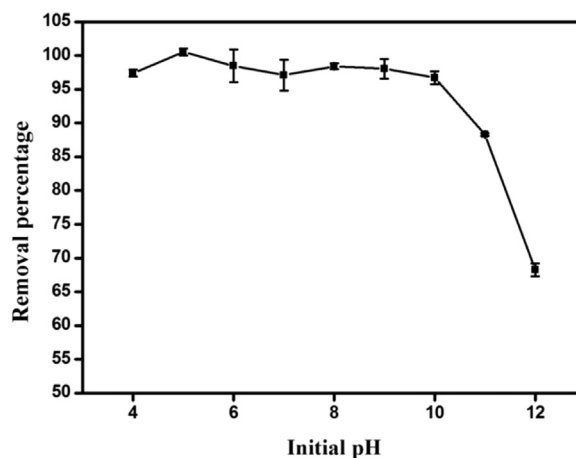


Fig. 5. pH effect on the fluoride removal.

pH adjustment was unnecessary, since that the pH of samples was in the pH range of 4–10. This condition was appropriate pH for complex SPADNS-Zr.

Several type of eluent was evaluated for fluoride desorption such as NaOH, KNO<sub>3</sub>, NaCl, and H<sub>2</sub>O. For the various eluents, the highest recovery was achieved with NaOH. Some works related that the ion exchange between OH<sup>-</sup> and F<sup>-</sup> is very favorable [40]. Therefore, the effect NaOH concentration as well as eluate flow-rate was evaluated in elution step, aiming optimizing fluoride recovery. The recovery increase with NaOH concentration up to 0.5 mol L<sup>-1</sup> (Fig. 6). This concentration was then selected for subsequent studies.

The sample flow in the preconcentration step may influence the interactions between the analyte and the sites of the adsorbent material. Larger flows provide more material passing through the preconcentration column. Thus, this effect was evaluated by varying a flow rate of 0.5–5.0 mL min<sup>-1</sup> and best results were observed when 3.0 mL min<sup>-1</sup> was used.

The effect of elution flow-rate was evaluated from 0.5–5.0 mL min<sup>-1</sup>. The eluent flow rate in the elution step may influence the eluate formation (eluent plus analyte), because if the kinetics of this process is slow, smaller flow rates are required. That is why best results were observed when 1.0 mL min<sup>-1</sup> was used.

The amount of LDH was evaluated in the range of 25–150 mg aiming to maximize the efficiency fluoride retention, and best results were observed when 150 mg was used.

The reaction between fluoride and the Zr-SPADNS complex was processed in acid medium. Indicator solution is prepared in hydrochloric acid medium, for kinetics of the reaction between the fluoride

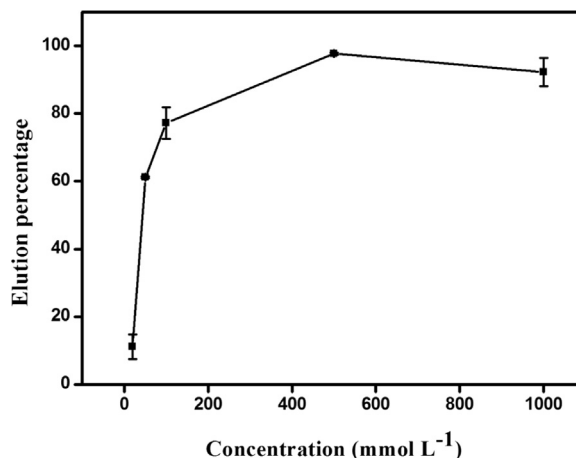


Fig. 6. Effect of sodium hydroxide concentration on fluoride desorption.

Table 1  
Flow procedure optimization to fluoride determination.

Variables	Studied range	Optimum value
NaOH concentration (mol L <sup>-1</sup> )	0.02–1.0	0.5
Mass of LDH (mg)	25–150	150
Preconcentration flow (mL min <sup>-1</sup> )	0.5–5.0	3
Elution flow (mL min <sup>-1</sup> )	0.5–5.0	1
HCl concentration (mol L <sup>-1</sup> )	1.2–2.1	1.8



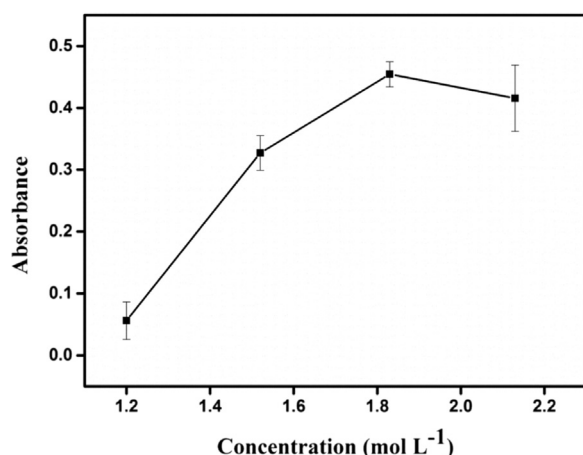


Fig. 7. Effect of hydrochloric acid concentration on the indicator complex reaction with fluoride.

and the indicator complex is influenced by pH variation, occurring rapidly under these conditions. As the eluent used in the present work is sodium hydroxide and the eluate (eluent plus analyte) has a high pH, it was necessary to perform the hydrochloric acid concentration study in the Zr-SPADNS complex so that the basicity of the eluate does not detract from the kinetics of reaction. Thus, this effect was evaluated by varying the concentration of 1.2–2.1 mol L<sup>-1</sup> (Fig. 7) and best results were observed when 1.8 mol L<sup>-1</sup> was used. Previous tests were performed to evaluate the effect of sample pH on the analytical signal [37]. Thus, in the studied pH range the sample measurements can be performed without the need for pH adjustment.

### 3.4. Figures of merit and applications

Under the selected conditions, a linear response for 50–500 µg L<sup>-1</sup> fluoride, after online preconcentration. The relation between absorbance (A) and fluoride concentration (C, µg L<sup>-1</sup>) can be describe by the equation  $A = 1.03 - 1.3 \times 10^{-3}C$ ,  $r = 0.990$ . The coefficient of variation was estimated as 0.8% (500 µg L<sup>-1</sup>,  $n = 15$ ) and 1.3% (50 µg L<sup>-1</sup>,  $n = 10$ ). The detection limit was estimated at 15 µg L<sup>-1</sup> (99.7% confidence level), which is 100 times lower than threshold value establish by Brazilian, European and America regulations [2,3,51]. Enrichment factor was estimated at 10 from the ratio of the slopes of the calibration curves obtained with and without preconcentration.

The SPADNS method is susceptible to interference from alkalinity, aluminum, chloride, iron, phosphate and sulfate. The influence of potentially interfering species was verified by comparing the analytical signal of a solution containing only fluoride and a solution containing fluoride ions and potentially interfering species. The values obtained satisfactorily confirm the excellent potential for fluoride determination in water using proposed procedure, since the ions present in the matrix will not interfere with the fluoride determination [37]. However only at high concentrations, that is values that are not found in real samples according the Brazilian legislation for drinking water quality [53]. Interference comes from free chlorine which is easily removed by the addition of sodium arsenite to the solution (procedure adopted in this work) [54]. In addition, in acid medium (working condition) the interference from alkalinity as well as the presence of ferric chloride ions is largely eliminated.

The procedure's accuracy was checked by determining fluoride in a certified reference material of water (ALPHA APS-1076). No statistically significant difference was observed between determined ( $102 \pm 3$  µg L<sup>-1</sup>) and certified values (100 µg L<sup>-1</sup>) at a 95% confidence level. The method was applied to determine fluoride in water samples, and the results are shown in Table 2. All analyzed samples contained

Table 2

Fluoride concentrations present in drinking water.

Samples	Results (µg L <sup>-1</sup> )
Sample 1	461 ± 9
Sample 2	493 ± 8
Sample 3	169 ± 6
Sample 4	383 ± 5

Table 3

Comparison of the fluoride line preconcentration method and the official method.

Parameter	Batch SPADNS	This work
Sample consumption (mL)	50.0	42.0
SPADNS consumption (mg)	9.58	0.048
ZrOCl <sub>2</sub> consumption (mg)	1.33	0.007
HCl consumption (mL)	3.5	0.007
Waste volume (mL)	60	43.05
Linear range (mg L <sup>-1</sup> )	0–1.4	0.05 – 0.50

fluoride in concentration lower than the threshold limit specified by the Brazilian, European and American regulations (1.5 mg L<sup>-1</sup>) [2,3,53].

Compared with the batch method proposed by Bellack & Schoubroe in 1958 [54] and considered as one of the methods for determination of fluoride in water samples, the proposed method allows reagent saving and reduced waste production, as can be observed in Table 3. Other notable factor is the less intervention of the analyst, reducing the potential for errors generated by the manipulation of the sample.

Under optimized conditions the fluoride preconcentration system was compared according to the detection technique used with other preconcentration systems in the literature [18,21,34,55]. The evaluated parameters are shown in Table 4. As can be observed, the proposed method shows similar or better performance when compared with previously published studies in terms of linear range, detection limit and RSD. Although the method described by Haj-Hussein & Al-Momani presents a sampling rate of 50 determinations per hour and a detection limit (0.02 mg L<sup>-1</sup>) similar; however interferences on the FIA-spectrophotometric signals were widely reported.

## 4. Conclusions

The development of a flow system based on the controlled sample and indicator injection through the use of solenoid valves for fluoride preconcentration in line using LDHs as an adsorbent, allowed the determination of fluoride in drinking water supply and mineral water using the SPADNS method. The procedure can be applied successfully for fluoride determination in these samples. The method showed good accuracy with the analysis of the certified reference sample. The water samples analyzed are in compliance with the fluoride levels established by the legislation. There was no necessity for sample pre-treatment. The preconcentration system developed in this work is favorable to the environment, since small volumes are used and consequently there was a minimization of the amount of waste generated. This coupling of techniques resulted in good sensitivity, precision, accuracy and analytical speed. In addition, the use of this adsorbent had not been reported

Table 4

Comparison of on-line fluoride preconcentration methods.

Method	Linear range (mg L <sup>-1</sup> )	LOD (mg L <sup>-1</sup> )	RSD (%)	Ref.
Colorimetric	0.04–1.25	0.015	3.1	[18]
Fluorimetric	0.10–3.00	0.060	2.5	[21]
Colorimetric	0.10–4.00	0.055	3.0	[34]
Colorimetric	0.00–3.50	0.020	1.0	[55]
Colorimetric	0.05–0.50	0.015	0.8	This work

in a solid phase extraction study applied to the fluoride preconcentration. These characteristics make it an excellent procedure for preconcentration and on-line fluoride determination in water.

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