



## 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

### ARTICLE INFO

#### Keywords:

Flow analysis  
Multicommutation  
SPADNS  
Fluoride  
Layered double hydroxides

### 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: [niviamcoelho@gmail.com](mailto:niviamcoelho@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 multicommutated 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 (MgAl-NO<sub>3</sub>-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 OH<sup>-</sup> > F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup>. 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 multicommutated 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 Cu-Kα<sub>1</sub> 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 4000–400 cm<sup>-1</sup>.

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

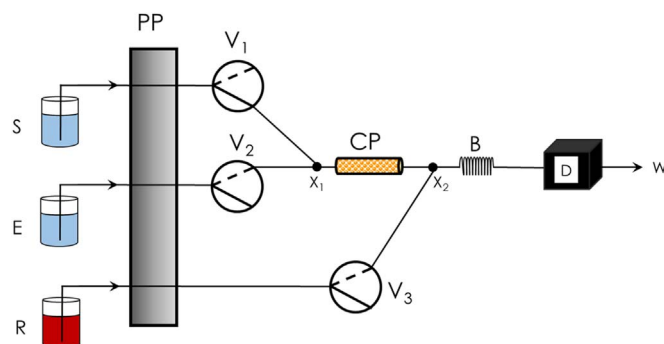


Fig. 1. Flow diagram of the system for fluoride determination. V<sub>1</sub> – V<sub>3</sub> three-way solenoid valves; PP: peristaltic pump; S: sample 3.0 mL min<sup>-1</sup>; E: eluent 1.0 mL min<sup>-1</sup>; R: reagent solution 1.0 mL min<sup>-1</sup>; X<sub>1</sub> and X<sub>2</sub>: confluence point; B: long reaction coil 50 cm; CP: mini-column of pre-concentration 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 MgAl-NO<sub>3</sub>-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 pre-concentration mini-column was obtained from 5-cm long polymeric tubes (2.0 mm i.d.), filled with

Download English Version:

<https://daneshyari.com/en/article/5140381>

Download Persian Version:

<https://daneshyari.com/article/5140381>

[Daneshyari.com](https://daneshyari.com)