



ELSEVIER

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: [www.elsevier.com/locate/talanta](http://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<sup>-1</sup>, with the detection limit, coefficient of variation and sampling rate estimated as 0.02 mg L<sup>-1</sup>, 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<sup>-1</sup>) 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<sup>-1</sup> and in unpolluted seawater in the range of 1.2–1.5 mg L<sup>-1</sup> [1]. According to the WHO guidelines, the permissible limit for fluoride in drinking water is 1.5 mg L<sup>-1</sup>. 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<sup>-1</sup> for temperatures of 26.3–32.6 °C and 0.9–1.7 mg L<sup>-1</sup> 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. Multicommutated 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](mailto:nmmcoelho@ufu.br) (N.M.M. Coelho).

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<sup>®</sup> 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  $\mu$ L 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 multicommutated 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

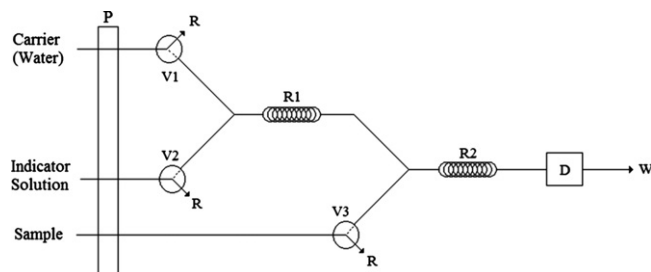


Fig. 1. Flow diagram of the multicommutated system for fluoride determination. P—peristaltic pump; V1, V2 and V3—three-way solenoid valves; R—recirculation of solution; R1 and R2—reaction coils and D—detection, W—waste.

Download English Version:

<https://daneshyari.com/en/article/7683568>

Download Persian Version:

<https://daneshyari.com/article/7683568>

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