



Study of complexation of aluminium with cinnamoyl derivative in the presence of fluoride ions using an optical probe: automated determination of fluoride

Alina Diuzheva¹ · Jana Šandrejová¹ · József Balogh^{2,3}

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Abstract

In this work, the complexation of aluminium (III) with 3-[4-(dimethylamino)cinnamoyl]-4-hydroxy-6-methyl-3,4-2H-pyran-2-one (ligand) in the presence of fluoride using an optical probe for absorbance measurement was studied. It was adjusted that the complex was formed in the molar ratio (Al–Lig)₃ to F 1:1. The reaction was applied to determine of fluoride. The optimum conditions were achieved at pH 8 with concentrations of Al³⁺ and ligand 6.75 and 0.195 mg L⁻¹, respectively. Under optimized conditions, the calibration curve showed good linearity ($r = -0.9976$) in the range 0.23–1.9 mg L⁻¹ of fluoride. The limit of detection of fluoride was found to be 0.02 mg L⁻¹. The proposed method was applied for determination of fluoride concentration in mineral water samples and fully automated by sequential injection system.

Keywords Fluoride · 3-[4-(dimethylamino)cinnamoyl]-4-hydroxy-6-methyl-3,4-2H-pyran-2-one · Probes · Sequential injection analysis

Introduction

Fluoride is an important trace element, which enters into the organism with consumption of drinking water. The significance of fluoride control is that, in the small amount, fluoride helps to maintenance of bone health, but in the excessive intake, it promotes different diseases, e.g., fluorosis, slowed metabolism and growth, deformed bones of the skeleton (Barberio et al. 2017; Everett 2011).

The 3-[4-(dimethylamino)cinnamoyl]-4-hydroxy-6-methyl-3,4-2H-pyran-2-one (ligand) is a cinnamoyl derivative, which is a good complexing agent, forming color complexes with metal ions, for instance, with aluminium (Elečková et al. 2015; Tykhanov et al. 2010). In its turn,

aluminium with fluoride ion forms strong complexes, with increasing an instability constant in the following sequence $[AlF]^{2+} < [AlF_2]^+ < [AlF_3]$ ($7.10 < 11.98 < 15.83$). This ability allowed to develop indirect methods for the determination of fluoride, based on the bleaching of color aluminium complex with xylenol orange (Zolgharnein et al. 2009), complex of zirconium with eriochrome cyanine R (Megregian 1954) and sodium 2-(p-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (Bellack and Schouboe 1958), complex of thorium with bromcresol orange (Khalifa and Hafez 1998), complex of ferrum with 2,4-diaminophenol (Themelis and Tzanavaras 2001) and as well as extraction methods based on ferrum thiocyanate complex (Farajzadeh 2004; Sahin et al. 2016) using spectrophotometric detection. Alternative methods for indirect determination of fluoride are ion chromatography (Jones 1992; Miyake et al. 2007; Lou et al. 2017), inductively coupled plasma mass spectrometry (ICP-MS) (Bayón et al. 1999; Guo et al. 2017), and a high-resolution continuum source atomic absorption spectrometry, based on evaluation of molecular absorption of aluminium (Ozbek and Akman 2012), barium (Ozbek and Akman 2014), gallium (Gleisner et al. 2010), and calcium monofluoride (Morés et al. 2011). Those methods provide low limits of detection, but require bulky and expensive equipments.

✉ Alina Diuzheva
adyuzheva@gmail.com

¹ Department of Analytical Chemistry, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovakia

² Department of Chemistry, University of Nyíregyháza, Sostói ut 31/B, Nyíregyháza 4400, Hungary

³ Department of Analytical Chemistry, Uzhgorod National University, Universytet'ska 14, Uzhgorod 88000, Ukraine

There are known only few works, where were reported the methods for automated determination of fluoride using flow injection system followed by electrochemical (Cardwell et al. 1987), spectrophotometric (Pérez-Ruiz et al. 1996), and ICP atomic emission spectroscopy detections (Manzoori and Miyazaki 1990).

Sequential injection analysis (SIA) was applied for simultaneous chloride and fluoride determination in waters with potentiometric detection (Alpízar et al. 1996), using two ion-selective electrodes in two serial flow-through cells. SIA methods are not commonly used for determination of fluoride; therefore, sensitive and automated methods for fluoride determination are still required.

Recently, the optical probe was applied for analysis as measuring cell in SIA for headspace single drop microextraction (Zaruba et al. 2017) and sugaring-out liquid–liquid extraction procedures (Pochivalov et al. 2017). The advantage of this detection approach is that the absorbance is monitored online during the whole reaction process and allows to record when the equilibrium of the system is reached.

The aim of this study was to develop an automated sequential injection procedure for indirect determination of

fluoride, based on bleaching the complex of aluminium (III) with 3-[4-(dimethylamino)cinnamoyl]-4-hydroxy-6-methyl-3,4-2H-pyran-2-one (ligand; Lig) by fluoride ion using an optical probe for absorbance measurement.

Theoretical

A red-colored complex of aluminium with a ligand (Elečková et al. 2015) can be decomposed in the presence of fluoride ions which results in the formation of a stronger aluminium fluoride complex. The formation of this complex was observed at pH 8. The selection of pH 8 could be explained by tautomeric equilibrium of the ligand. The ketone form (I) is in equilibrium with the enol form (II) which, when the proton is cleaved, is capable to complexation (Fig. 1).

The UV–Vis spectra (Fig. 2) showed that the maximum of the UV–Vis absorbance for the ligand was at 390 nm, upon the addition of Al^{3+} the spectrum was bathochromically shifted (460 nm) and a new band at 520 nm appeared, while the color of the ligand solution changed from yellow to red. It proved the formation of aluminium–ligand complex.

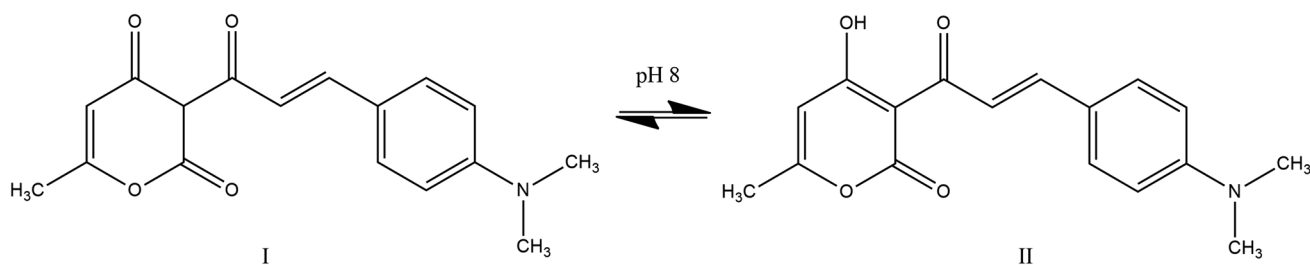
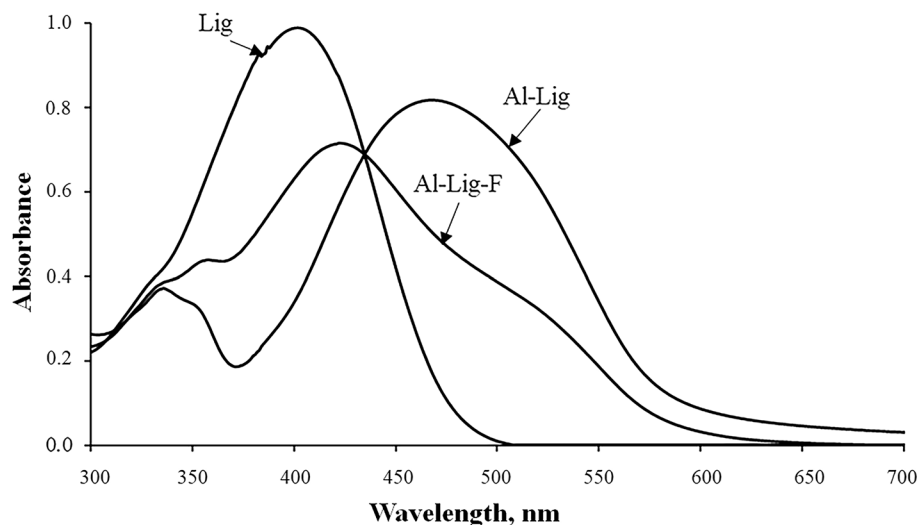


Fig. 1 Ketone–enol equilibrium of the ligand

Fig. 2 UV spectra of 0.23 mg L^{-1} of ligand (Lig), aluminium–ligand (Al–Lig) with concentration 6.74 and 0.23 mg L^{-1} , respectively; aluminium–ligand–fluoride (Al–Lig–F) with the concentration 6.74, 0.23, and 1.9 mg L^{-1} , respectively, at pH 8, $l = 1 \text{ cm}$



After the addition of fluoride ions, the aluminium–ligand solution was bleached to orange–yellow color, upon the hypochromically shift of the spectrum to 420 nm. The mechanism is shown in Fig. 3.

Thus, this system makes it possible to determine indirectly the concentration of fluoride. The procedure was automated by a sequential injection system, completed with an optical probe for online absorbance measurements. For this system, some preliminary studies were carried out, such as an investigation of adequate conditions for the Al–ligand complex formation (pH, concentration of aluminium and ligand). The conditions were established as follows: pH 8, 6.75 mg L^{-1} of Al^{3+} and 0.195 mg L^{-1} of ligand (see the section below). The measurements by flow system were carried out at 550 nm, to reduce the mean of error and decrease the mean of control test.

Experimental

Materials

Chemicals

All reagents were of analytical reagent grade. Salts: aluminium nitrate nine hydrate, sodium fluoride were obtained from Chemapol (Czech Republic), acetic acid was supplied by MikroChem (Slovak Republic), and ammonium hydroxide was obtained from CentralChem (Slovak Republic).

A 0.01 M stock solution of fluoride and aluminium (III) was prepared by dissolving appropriate amount in distilled water. 0.001 M solution of 3-[4-(dimethylamino)-4-hydroxy-6-methyl-2H-pyran-2-one (ligand)

was prepared by dissolving accurate amount in acetonitrile (Merck, Germany). The pH of the medium was adjusted with an acetic acid/ammonium hydroxide buffer, pH 8.

For a reference method, 500 mL of a buffer solution with pH 5 was prepared by mixing 52.0 g of sodium acetate, 29.2 g of sodium chloride [CentralChem (Slovak Republic)], 3.0 g of trisodium citrate, 8.0 mL of concentrated acetic acid, and 0.3 g of disodium ethylenediaminetetraacetate dehydrate. All reagents were supplied by Chemapol (Czech Republic).

Mineral water samples were purchased from local supermarkets (Košice, Slovakia and Nyíregyháza, Hungary), and a thermal water sample was taken from thermal springs in Hungary and were kept in a refrigerator at $4 \text{ }^\circ\text{C}$. Before analysis, additional pretreatment of water samples is not required, besides ultrasonication for 3 min.

Apparatus

The sequential injection analysis was carried out using FIA labs 3500 system (FIALabs Instrument Systems Inc., USA). The system was equipped with a 5 mL glass syringe pump and a central eight-port Cheminert selection valve (Valco Instrument Co., USA). For absorbance measurement, a double pass optical probe with 10 mm path length, combined with a USB 4000 fiber optic spectrometer (Ocean Optics Inc., USA), was applied. As a resource of light, an LS-1 tungsten halogen light source (Ocean Optics, USA) was used. Data acquisition was performed using Ocean View spectroscopy and FIALab software. Stirring was used a magnetic stirrer (IKA-Werke GmbH & Co. KG, D-79,219 Staufen Germany) and a $12 \times 2 \text{ mm}$ stirring bar. A Sonorex Digitec ultrasonic compact bath DT 31 (Bandelin Electronic,

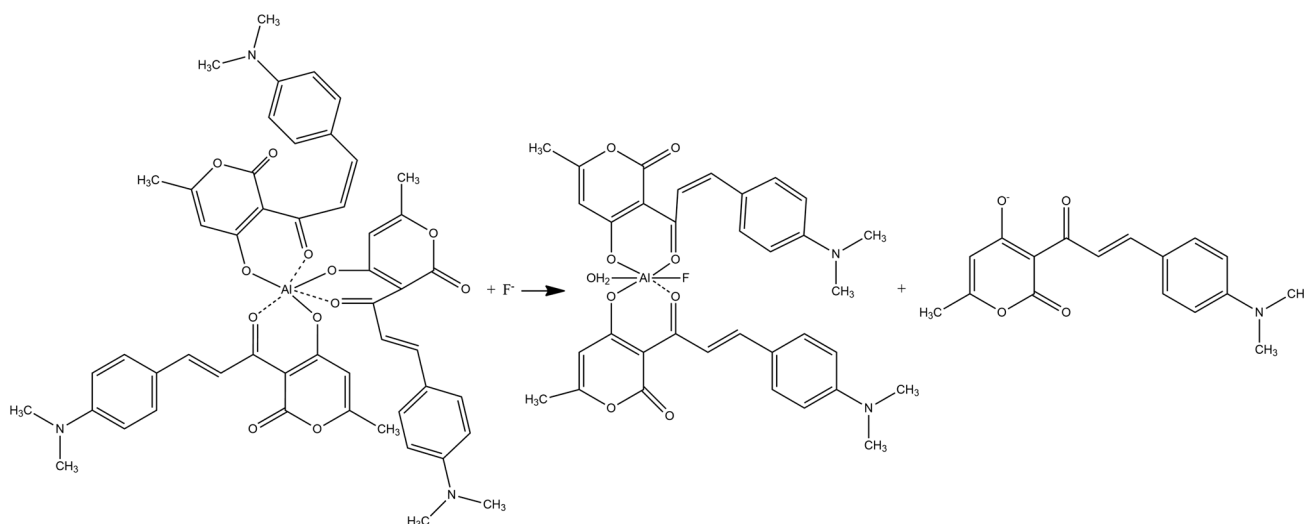


Fig. 3 Interaction of Al–Ligand complex with fluoride

Germany) was used for sonication of water samples. For pH control, an ORION 720A + pH meter with a glass electrode was employed. For reference method, calomel electrode and fluoride ion-selective electrode were combined with the same instrument.

The procedure of sequential injection analysis

The SIA is shown in Fig. 4. The procedure started with the aspiration of 1500 μL of water from the reservoir with the flow rate 500 $\mu\text{L s}^{-1}$ into the syringe pump. After, the reagents were aspirated into the holding coil with the flow rate 35 $\mu\text{L s}^{-1}$ in this order: Al^{3+} (100 μL) (port 1), sample (200 μL) or standard solution of fluoride (port 4), and buffer solution pH 8 (1000 μL) (port 3). Afterward, the whole volume, containing all reagents, was dispensed into the 4 mL vial at flow rate of 200 $\mu\text{L s}^{-1}$. Then, 600 μL of the ligand (port 5) was aspirated into the holding coil and dispensed to the vial with the same dispensing and aspiration speed 35 $\mu\text{L s}^{-1}$ and 200 $\mu\text{L s}^{-1}$, respectively. Then, the vial was filled with water up to 4000 μL (port 6). After a delay of 2 s, which was needed for immersing of the optic probe, the absorbance measurement was performed at 550 nm wavelength during 200 s. In the final step, the holding coil was cleaned three times using methanol (port 8). The determination of fluoride was accomplished in less than 400 s.

Results and discussion

Optimization of SIA manifold

To achieve optimal conditions for fluoride determination, the main variables of flow system affecting on the

destroying of the aluminium–ligand complex by fluoride ion were considered.

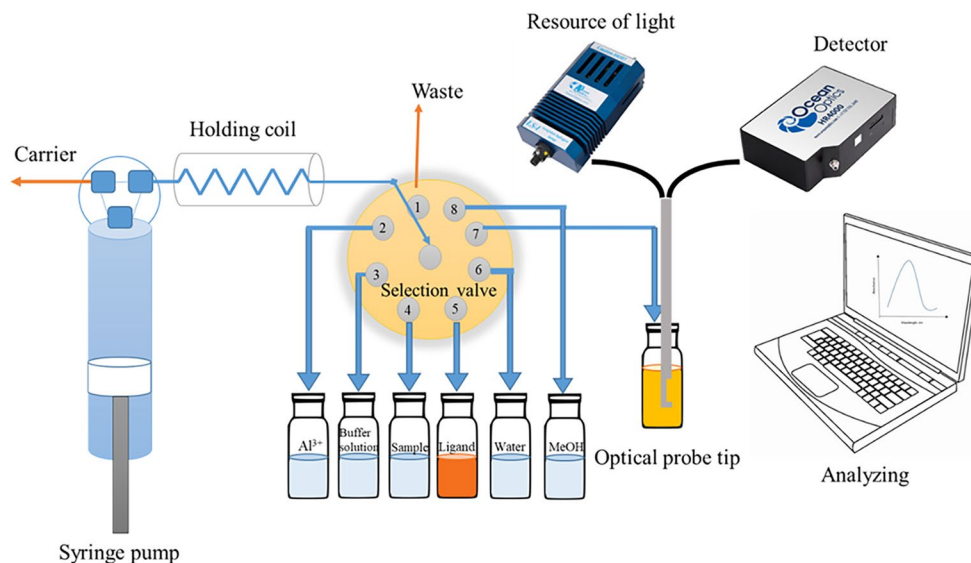
The first step of optimization included the providing of better mixing of the components by changing the flow rate of SIA, keeping the aspiration rate of 35 $\mu\text{L s}^{-1}$ constant. Into the 4 mL vial with different rates 50–250 $\mu\text{L s}^{-1}$, 100 μL of aluminium (III) solution, 200 μL of the standard solution of fluoride at the concentration level 1.9 mg L^{-1} , 1000 μL of buffer solution, and 600 μL of ligand were dispensed. Increasing the flow rate resulted in an improved absorbance and achieved its maximum at 200 $\mu\text{L s}^{-1}$ (Fig. 5a). Hence, the flow rate 200 $\mu\text{L s}^{-1}$ was selected for further analysis.

In the second step, the effect of reagents volume was investigated. For optimization of the ligand volume, the procedure was performed as described above, with changing of ligand volume from 200 to 600 μL of the standard solution of ligand. The highest difference in absorbance between Al–Lig complex and Al–Lig–F was achieved at 500 μL of the ligand (Fig. 5b). With further increasing of the volume after 600 μL , a residue was formed, which made measurement impossible.

The effect of the volume of aluminium (III) on the fluoride determination was studied by changing aluminium (III) volume from 50 to 150 μL of standard solution. Figure 5c shows that 100 μL was optimal and due to the equilibrium shift method, and the molar ratio of complex formation of (Al–Lig)₃:F[−] was found 1:1.

To establish the effect of the volume of the buffer solution, acetate buffer solution at pH 8 was taken in the volume range from 400 to 1500 μL . Figure 5d illustrates that the highest sensitivity was obtained at 1000 μL . Therefore, this volume was chosen as the optimal volume and selected for future analysis.

Fig. 4 Schematic of the SIA procedure



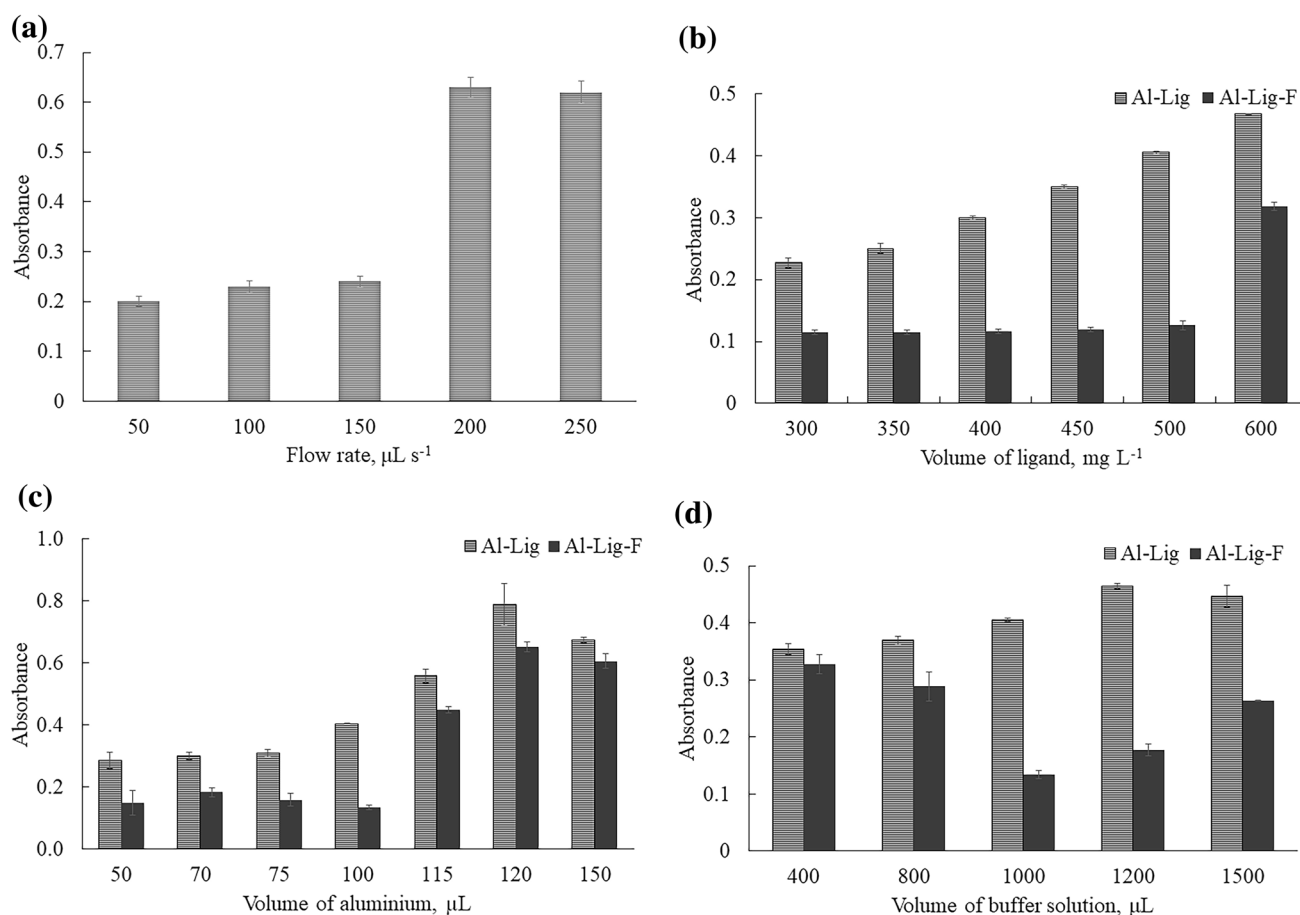


Fig. 5 Optimization of SIA procedure. **a** Effect of flow rate of Al-Lig [V (Al)=100 μL , V (Lig)=600 μL , V (buffer solution)=1000 μL at pH 8]. **b** Effect of volume of ligand (increasing concentration of ligand, V (Al)=100 μL , V (buffer solution)=1000 μL at pH 8). **c**

Effect of volume of aluminium (increasing concentration of aluminium, V (Lig)=500 μL , V (buffer solution)=1000 μL at pH 8). **d** Effect of buffer volume (increasing concentration of buffer solution, V (Al)=100 μL , V (Lig)=500 μL at pH 8)

Table 1 Optimal conditions to determine fluoride by SIA

Parameter	Value
Flow rate of dispense to the vial	200 $\mu\text{L s}^{-1}$
Volume of aluminium (III)	100 μL (6.75 mg L^{-1} , $2.5 \times 10^{-3} \text{ M}$)
Sample volume	200 μL
pH	8
Volume of buffer solution	1000 μL
Volume of ligand	500 μL (0.195 mg L^{-1} , $6.5 \times 10^{-7} \text{ M}$)

Therefore, the optimal conditions to determine fluoride, by bleaching of Al-Lig complex, are presented in Table 1.

Analytical figures of merit

Under optimized conditions, the calibration curve was plotted as mean of calculated absorbance (A_c) vs. concentration of fluoride (mg mL^{-1}):

$$A_c = \log \left(\frac{A_s}{A_b} \right),$$

where A_c —mean of calculated absorbance; A_s —mean of absorbance of the standard, A_b —mean of absorbance of the blank (Akhond et al., 2016).

Linearity was observed in the range of 0.23–1.9 mg L^{-1} (1.3×10^{-7} – $1.0 \times 10^{-4} \text{ M}$) for fluoride with a slope, intercept, and correlation coefficient value of -0.1134 , 0.4147 , and -0.9976 , respectively. The calculated LOD [estimated as $3 \cdot \text{SD}_b$, where SD_b —standard deviation of blank ($n=3$)] was found to be 0.02 mg L^{-1} . A precision of the method was evaluated by measuring intra- and inter-days relative to standard deviation (RSD) of spiked water sample per each concentration level 0.71 and 1.18 mg L^{-1} of fluoride over two consecutive days ($n=4$). The results are shown in Table 2. The effect of some interfering ions on the determination of fluoride was also tested. The interference studies were performed by measuring the influence of the cations

and anions on the system, where the error of measurements did not exceed $\pm 5\%$. 1000-fold excess of K^+ and Na^+ , Pb^{2+} , Cl^- , and I^- , 250-fold excess of Mg^{2+} , Co^{2+} , and Cd^{2+} , 100-fold excess of Ca^{2+} , Fe^{3+} , Cr^{3+} , Ga^{3+} , La^{3+} , and In^{3+} , and tenfold excess Cu^{2+} , Ni^{2+} , and Zn^{2+} are allowed to be present in the solution.

Analysis of real water sample

To evaluate the applicability of the proposed method, mineral water samples were analyzed. The results obtained are summarized in Table 3. The relative recovery was between 81 and 103%. These results show that the matrices of water have a significant effect on the results of the analysis, but experimentally were identified that the total concentration of cations and anions in mineral water samples (total mineralization) should not exceed 1500 mg L^{-1} . For instance, in the mineral water-2, the recovery of analysis was lower in comparison with the other samples. The error of measurements was caused by salt effect (total mineralization of water

was 1480 mg L^{-1}). It can be concluded that the proposed method provides good recoveries and has good precisions for the determination of fluoride in water samples.

To check the validity of the developed method, the results were compared with a potentiometric determination of fluoride according to ISO 10359-1:1992, using standard addition method. A good accordance with the results of the reference method (Table 3) was obtained.

As well, the developed method was compared with the other indirect methods reported in the literature for the determination of fluoride (Table 4) followed by spectrophotometric detection as well. The advantages of the present method are a good LOD, the absence of extraction procedure (Farajzadeh 2004; Sahin et al. 2016), and a full automation of the process. In addition, no sample pretreatment is required. The developed spectrophotometric method is cheaper in comparison with high-resolution continuum source atomic absorption spectrometry (Ozbek and Akman 2012, 2014; Gleisner et al. 2010; Morés et al. 2011) or ICP detection (Manzoori and Miyazaki 1990;

Table 2 Intra-day and inter-day precision and accuracy data for fluoride determination ($n=4$, $P=0.95$, $t=3.18$)

Added concentration, mg L^{-1}	Inter-day			Intra-day		
	Found concentration, mg L^{-1}	RSD, % ^a	R , % ^b	Found concentration, mg L^{-1}	RSD, %	R , %
0.71	0.69 ± 0.03	4.4	97	0.72 ± 0.05	6.9	101
1.80	1.79 ± 0.01	0.6	99	1.84 ± 0.14	7.6	102

^aRSD, %—relative standard deviation

^b R , %—recovery

Table 3 Results of real samples ($n=3$, $P=0.95$, $t=4.302$) and their comparison with a reference method

Water sample	Declared concentration, mg L^{-1}	Found concentration, mg L^{-1}	R , %	Found concentration according to a reference method, mg L^{-1}	R , %
Thermal water	2.75	2.82 ± 0.42	103	2.71 ± 0.23	99
Mineral water-1	2.60	2.52 ± 0.15	97	2.47 ± 0.13	95
Mineral water-2	1.40	1.13 ± 0.45	81	1.44 ± 0.11	103

Table 4 Comparison of the proposed methods with the other reported methods to determine fluoride indirectly followed by spectrophotometric detection

Method	Linear range, mg L^{-1}	LOD, mg L^{-1}	Ref.
Al–XO	0.08–1.4	0.07	Zolgharnein et al. (2009)
Zr–ECR	0–1.4	0.02	Megregian (1954)
Zr–SPADNS	0–1.4	0.02	Bellack and Schouboe (1958)
Th–BCO	0.02–3.0	0.02	Khalifa and Hafez (1998)
Fe–DAP	0–9.0	0.09	Themelis and Tzanavaras (2001)
Fe–SCN–MIBK (extraction)	0.5–7.0	0.10	Farajzadeh (2004)
Fe–SCN–OAA (extraction)	0.5–10	0.04	Sahin et al. (2016)
Al–Lig	0.01–1.9	0.01	Present work

XO xylene orange, ECR eriochrome cyanine R, SPADNS, sodium 2-(p-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate, BCO bromocresol orange, DAP 2,4-diaminophenol, MIBK methyl isobutyl ketone, OAA N-octyl acetamide

Guo et al. 2017), but concedes them in sensitivity (where the amount of fluoride was estimated in μg level).

Conclusions

In conclusion, bleaching of the color complex of aluminium (III) and cinnamoyl derivative followed by an optic probe detection was studied and applied for indirect determination of fluoride in water samples. This procedure is simple, sensitive, and fully automatic. The obtained results are in a good accordance with the potentiometric method, which was selected as reference.

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Compliance with ethical standards

Conflict of interest Authors have declared no conflict of interest.

Human and animal rights statement This article does not contain any studies with human or animal subjects.

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