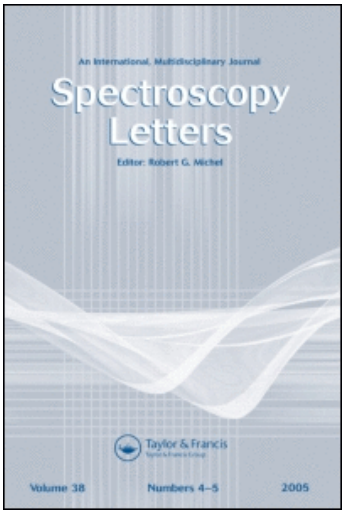

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A Sensitive Chemiluminescence Flow Injection Procedure for Assay of Fluoride in Waters and Humane Urine by Use of Immobilized Reagents

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A Sensitive Chemiluminescence Flow Injection Procedure for Assay of Fluoride in Waters and Humane Urine by Use of Immobilized Reagents[#]

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ABSTRACT

A new simple, rapid, selective and sensitive analytical procedure based on chemiluminescence (CL) detection is described for the determination of free fluoride at sub-nanogram levels by use of controlled-reagent-release technology in a flow injection system. The analytical reagents involved in the CL reaction, including luminol and periodate, were both immobilized on anion-exchange resins in a flow injection system. Through water injection, luminol and periodate were eluted from the anion exchange column to generate the chemiluminescence, which was enhanced in the presence of fluoride. The increased CL intensity was linear with fluoride concentration in the range from 0.1 to 10 ng·mL^{-1}. The limit of detection was 20 pg·mL^{-1} (3σ) and the relative standard deviation (RSD) was 1.02% (n = 5) for a 1.0 ng·mL^{-1} fluoride. At a flow

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rate of 2.0 mL·min^{-1}, including sampling and washing, a typical analytical procedure could be performed in 0.5 min with a RSD of less than 3.0%. The proposed method was successfully applied to determine the free fluoride in water and human urine, and the results were in good agreement with those obtained by ion chromatography.

Key Words: Fluoride; Flow injection; Chemiluminescence; Water; Urine.

INTRODUCTION

The importance of fluoride is due to its significance for human health. The majority of positive effects ascribed to fluoride supplementation are probably pharmacological, including the prevention of dental caries in children and osteoporosis in elderly women.[1] On the other hand, fluoride is regarded as a hazardous substance. An excessive amount of fluoride induces mottling of teeth, fluorosis and osteosclerosis. Some study shows that exposure of children to high levels of fluoride may carry the risk of impaired development of intelligence.[2]

Fluoride exists in plants and natural water, and its concentration is usually less than 0.1 μg·mL^{-1} in river and drinking waters. Different procedures and methods for the isolation and determination of fluoride in water and human urine have been proposed.[3–6] The determination is mainly carried out by potentiometry[7–14] or spectrophotometry.[15–18] Spectrophotometry and ion-selective electrodes have low sensitivity. For instance, the spectrophotometic detection limits for fluoride are rarely better than 20 ng·mL^{-1}, while it is frequently recommended that the fluoride ion-selective electrode should not be used for fluoride concentrations less than 0.1 μg·mL^{-1}. The most common techniques are ion chromatography (IC)[19–21] and capillary electrophoresis (CE).[22,23] The main limitation of the IC is used for the determination of fluoride in simple materials, for example high purity water, and the CE method suffers from a rather poor sampling efficiency. To the best of our knowledge, no chemiluminescence procedure for the determination of fluoride in water and human urine samples has been published previously. In this paper, it was found that the CL intensity from the oxidation between luminol and periodate could be enhanced in the presence of fluoride. Both CL reagents were immobilized on an anion-exchange resin. This allowed for the achievement of a homogeneous mixing of CL reagents, which resulted in a more stable background and more reproducible results than those using a reagent solution. The increased CL intensity was linear with fluoride concentration in the range

from 0.1 to 10 ng·mL^{-1}. The limit of detection was 20 pg·mL^{-1} (3σ) and the relative standard deviation was 1.02% (n = 5) for a 1.0 ng·mL^{-1} fluoride sample. At a flow rate of 2.0 mL·min^{-1}, including sampling and washing, the detection could be performed in 0.5 min with a relative standard deviation of less than 3.0%. The proposed method had been successfully applied to the determining of free fluoride in water and human urine samples, and the results were in good agreement with results obtained by IC.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade. Deionized water (from Easypure UF, Barnstead Co., US) was used throughout. Luminol (Fluka, biochemika) was obtained from Xi'an Medicine Purchasing and Supply Station, China. Potassium periodate and sodium fluoride was purchased from Xi'an Chemical Reagent Plant. Anion exchange resin (Amberlyst A-27, Rohm and Haas Co.) and cation exchange resin (Dowex APA-1, Dow Chemical Co.) were purchased from a local distributor.

Preparation of Resin with Immobilized Reagents

Amberlyst A-27 resin 2.0 g was shaken with 50 mL of 0.025 mol·L^{-1} luminol or 0.04 mol·L^{-1} potassium periodate for 12 h, and then the resin was filtered, washed with deionized water and dry-stored. The most convenient method to determine the amounts of luminol and potassium periodate immobilized was to measure the losses of these reagents from the immobilization solutions. The concentration was detected at 360 nm for luminol and at 225 nm for potassium periodate by UV-vis. In the proposed method, the amounts of luminol and potassium periodate immobilized were 1.99 ± 0.02 (n = 3) mmol·g^{-1} and 1.01 ± 0.01 (n = 3) mmol·g^{-1} resin, respectively.

Apparatus

The flow injection (FI) system used in this work is shown in Figure 1. A peristaltic pump (Shanghai meter electromotor plant, model ND-15, 15 rpm) was used to generate the flow. PTFE tubing (1mm i.d.) was used in the flow system. The anion exchange resins contain immobilized luminol

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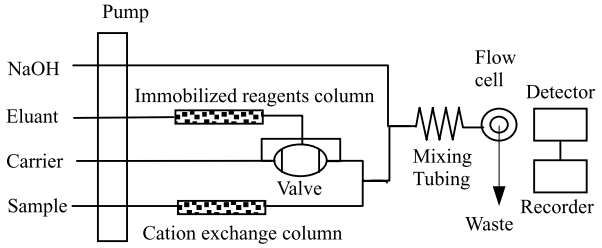

Figure 1. Schematic diagram of the flow-injection system for fluoride determination.

(0.05 g) and potassium periodate (0.10 g) were mixed together and packed into a glass column (3 mm i.d. and total volume of about 0.5 mL), and another loaded with cation exchange resins is placed in the sample pipeline. And both of the columns were plugged with glass wool at both ends to prevent the resins from leaking. A six-way valve injected 100 μL of eluant (see below for details). Before reaching the flow cell, the streams of luminol, periodate, sodium hydroxide and analyte were combined in a mixing tube (50 mm in length). The CL emission cell is a spiral glass tube (1 mm i.d., 15 cm length) producing a large surface area exposed to the adjacent photomultiplier tube (PMT) (Hamamatsu, model IP28). Extreme precautions were taken to ensure that the sample compartment and PMT were light-tight. The CL signal produced in the flow was detected without wavelength discrimination, and the PMT output was amplified and quantified by a luminosity meter (Xi'an Remax Electronic Science-Tech. Co. Ltd. model GD-1) connected to a recorder (Shanghai Dahua Instrument and Meter Plant, model XWT-206). All chromatographic experiments were performed using a DX-600 ion chromatograph (Dionex corp., Sunnyvale, CA, U.S.A.).

Procedure

The carrier water and the solutions (NaOH, sample and eluant) were propelled at a constant flow rate on each flow line. The pump was started to wash the whole flow system until a stable baseline was recorded. Then 100 μL of eluant solution was injected into the carrier stream, trace amounts of luminol and periodate were eluted, which was then mixed with the sample stream, the mixed solution was delivered to the CL cell, and the peak height of the CL signal was detected with the PMT and the

luminometer. The concentration of sample was quantified by increased CL intensity, $\Delta I = I_s - I_o$, where I_s and I_o were CL signals in the presence and in the absence of fluoride, respectively.

RESULTS AND DISCUSSION

The CL Intensity - Time Profile

Before the FI method was carried out, the batch method for the CL profiles was used. Without any special eluant, the mixture of luminol and periodate rinsed by water gave an evident CL signal. As Figure 2 shows, the CL intensity reached a maximum 10 s after injection, and then died within 25 s. When the sample was added into the above mixing solution, an increased CL signal was recorded. The peak heights of the CL emission were proportional to fluoride concentration.

Designation for the FI-CL System

The assay could be carried out by a continuous flow mode in two different manifolds. Through injection of 100 μL of eluant (5.0×10^{-5} mol·L^{-1} of Na_3PO_4), the reagents on the anion-exchange resin column were eluted and in the presence of fluoride, the CL intensity increased, and

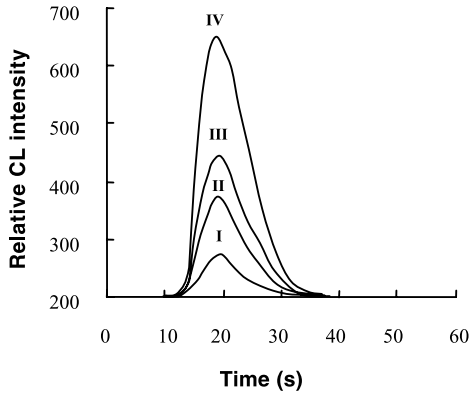

Figure 2. CL time profile in the batch system: I: CL intensity in the absence of fluoride; II: CL intensity in the presence of fluoride (0.5 ng·mL^{-1}); III: CL intensity in the presence of fluoride (1.0 ng·mL^{-1}); IV: CL intensity in the presence of fluoride (5.0 ng·mL^{-1}).

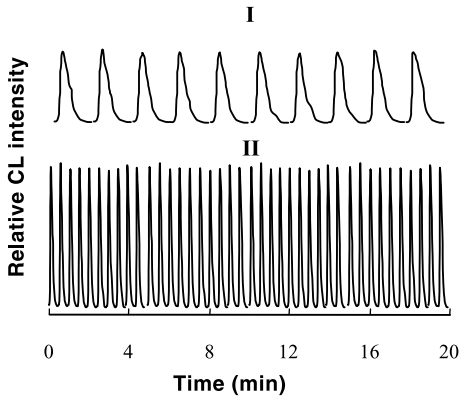

Figure 3. CL signals in two manifolds; I: The column set behind the injector; II: The column set in front of the injector.

the increase of CL intensity was recorded. It was found that when the column with immobilized reagents was put in front of or behind the valve, two significantly different results were observed. Probably, the reason is that the length of the pipeline had an effect on the intensity of chemiluminescence. As illustrated by results in Figure 3, the whole analysis process, including sampling and washing, could be accomplished in 0.5 min if the column was put in front of the valve, as shown in Figure 1, whereas the process took more than 2.0 min if the column was put behind the valve manifold. Figure 1 gave the better precision; therefore, the manifold depicted in Figure 1 was chosen for subsequent work.

Selection of Eluant

One hundred microliters of different eluants was injected through the resin column to release different amounts of luminol and periodate, thus producing the CL emission. The results are shown in Table 1. It was found that sodium sulfate gives a maximum CL emission while sodium carbonate showed some inhibitory effects on the CL reaction. Nevertheless, it was observed that a continuous flow of eluant through the column results in a rather short lifetime of the column down to only a few hours. It was shown that the immobilized luminol and periodate anions on the anion exchange resin undergo dissociation with water, releasing amounts of luminol and periodate from the column, and the increase of CL signal in the presence of fluoride could be easily observed. As a compromise between higher CL

Table 1. Character of eluants for fluoride determination.[a]

Type of CL intensity	Relative CL intensity				
	H_2O	NaCl	Na_2CO_3	Na_2SO_4	Na_3PO_4
I	241 ± 3.1	332 ± 7.0	140 ± 2.7	423 ± 9.3	387 ± 4.3
II	282 ± 5.6	443 ± 6.6	255 ± 4.1	616 ± 10.5	537 ± 7.5
III	41	111	15	193	150

I: CL intensity in the absence of fluoride.
II: CL intensity in the presence of 1.0 ng·mL^{-1} fluoride.
III: The increase of CL intensity.
[a]The concentration of each solution was 1.0×10^{-4} mol·L^{-1}.

intensity and longer lifetime of the column, discussed in the application section, water was used as eluant in subsequent work.

Effect of pH on CL and Column Lifetime

The effect of the pH of the eluant, water, on the performance of the system was evaluated. It was found that along with the increase of pH of the eluant, the CL intensity increased while the lifetime of the column decreased considerably (Figure 4), which may be due to the elution by hydroxide anions. A pH of 6.5 was then chosen as a compromise between column lifetime and sufficient CL intensity. Pure deionized water, pH 6.5, was used as eluant directly throughout. In this case, the column, with immobilized CL reagents, could be used for more than 80 h in a continuous-injection system.

Effect of Molar Ratio of Immobilized Luminol and Periodate

To examine the influence of the mixing ratio, resins (0.15 g) with different mixing ratios were packed into a column with the same internal diameter and volume. By the injection of water at a fixed volume of 100 μL, different amounts of luminol and periodate were eluted from the resins and gave CL signals with different intensities. As Figure 5 shows, the CL intensity dropped drastically from the beginning to the next day, and then it went down slowly. The most stable CL signal was found with a molar ratio of 1:2 (luminol to periodate), and an appropriate CL intensity is in favor of measuring an enhancement effect on fluoride in the CL reaction.

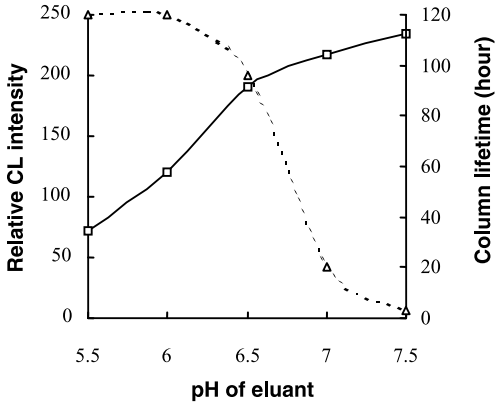

Figure 4. —□— Effect of eluant pH on CL intensity. —△— Effect of eluant pH on column lifetime.

Effect of NaOH Concentration

The CL reaction of luminol with periodate was favorable in an alkaline medium. The effect of NaOH concentration on CL was tested from 0.01 $mol \cdot L^{-1}$ to 0.2 $mol \cdot L^{-1}$. As Figure 6 illustrated, the maximum intensity was found with 0.1 $mol \cdot L^{-1}$ NaOH, while a NaOH concentration of less than 0.05 $mol \cdot L^{-1}$ leads to an apparent decrease in ΔI. When the concentration of NaOH is higher than 0.2 $mol \cdot L^{-1}$, there is a scattering

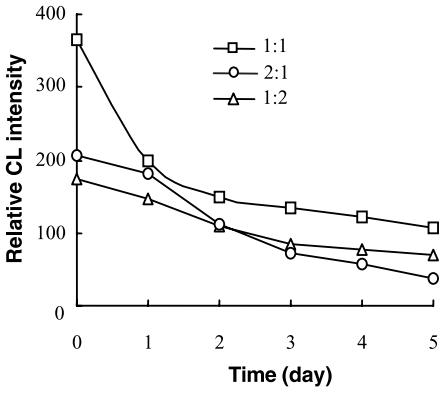

Figure 5. Effect of molar ratio of luminol and periodate on CL intensity and column lifetime.

effect in the flow cell due to the discrepancy between the refractive indices of various components. Thus, 0.1 mol·L^{-1} NaOH was selected as an optimal condition.

Effect of Flow Rate and the Length of Mixing Tubing

The CL signal was also dependent on the flow rate of carrier and eluant. The signal-to-noise ratio decreased at a higher flow rate because the higher flow rate would influence the rate of contact of sample molecules with the ion-exchange resin. The lower flow rate caused a broadening of the peak and slowing of the sampling rates. Nevertheless, the high flow rate could lead to an unstable baseline and shortening of the column lifetime. A rate of 2.0 mL·min^{-1} was then chosen as a suitable condition with good precision and lower reagent consumption. The length of the mixing tubing was also adjusted to yield maximum light emission in the cell. It was found that 5.0 cm of mixing tubing afforded the best results with regard to sensitivity and reproducibility.

Performance of the Flow System for Fluoride Measurements

Under the above optimum conditions, the linearity of fluoride was tested by determining a series of standard solutions with the flow system.

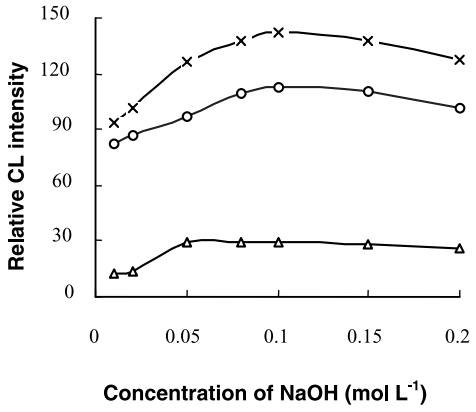

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Figure 6. Effect of concentration of NaOH on CL intensity. —○— CL intensity in the absence of fluoride (I_o); – × – CL intensity in the presence of fluoride (I_s); —△— The increase of CL intensity (ΔI).

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The enhancive CL intensity was found to be proportional with the fluoride concentration. The linear range is from 0.1 to 10.0 ng·mL^{-1} and the regression equation is $\Delta I = 13.95C_{fluoride} + 25.81$, $R^2 = 0.9996$. The relative standard deviation (RSD) of five determinations was 1.02% with fluoride concentration of 1.0 ng·mL^{-1}, and the limit of detection was 20 pg·mL^{-1}. At a flow rate of 2.0 mL·min^{-1}, the determination of analyte could be performed in 0.5 min, including sampling and washing, giving a throughput of about 120 times per hour with a RSD of less than 3.0%.

Interference Studies

The effect of foreign ions was tested by analyzing a standard solution of fluoride, to which increasing amounts of interfering ions were added. Without the cation exchange column, the tolerable concentration ratios with respect to 1.0 ng·mL^{-1} fluoride for interference at 5.0% level were over 1500 for Cl^-, NO_3^-, $A\bar{c}$, I^-, SO_4^{2-}, PO_4^{3-}, $Cr_2O_7^{2-}$, borate, oxalate, and urea, 1200 for NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, and Cr^{3+}, 800 for methanol, and ethanol, 20 for Cu^{2+}, and Fe^{3+}, 5 for uric acid. While, in the presence of the cation exchanger column (4.5 mEq·g^{-1} resin), none of metal ions especially Cu^{2+} and Fe^{3+} at a concentration of 100 ng·mL^{-1} showed any effect on CL signal compared to the 1.0 ng·mL^{-1} fluoride, which confirmed the efficacy of the ion exchanger in removing the metal ions interferences commonly existing in water. Compounds abundant in human urine such as urea, uric acid, salt and glucose have almost no effect on the determination of fluoride at sub-nanogram level.

Operational Stability of the Column

One hundred microliters of water was flow-injected through the system in the presence of 1.0 ng·mL^{-1} fluoride solution and the ΔI ($I_o - I_s$) was recorded to test the operational stability of the column. The experiment lasted for 10 days and the flow system was regularly used for more than 8 h per day. Figure 7 shows the stability of the column, and the ΔI was calculated in 10 spot check determinations with RSDs of less than 3.0%. The column showed remarkable stability and could be easily reused for more than 80 h.

Possible Mechanism

The chemiluminescence behavior of luminol and periodate in the presence of fluoride was tested by a static CL method, and the results were

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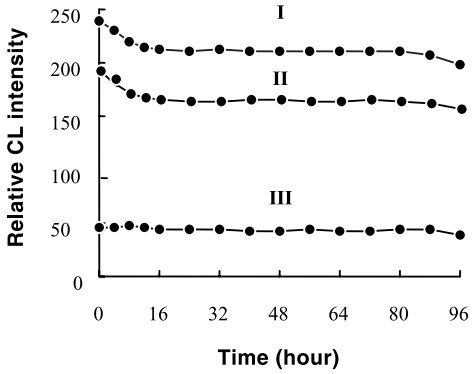

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Figure 7. Stability of the flow system. I: CL intensity in presence of 1.0 ng·mL^{-1} fluoride (I_s); II: CL intensity in absence of fluoride (I_o); III: The increase of CL intensity ($\Delta I = I_s - I_o$).

listed in Table 2. It was found that fluoride could enhance the luminol with dissolved oxygen[24] or periodate[25] CL reaction in alkali medium, which are well known CL systems. As a strongly electron donor, fluoride may catalyze the decomposition of the six-membered ring of peroxide intermediate[26] which had been confirmed by White et al. in 1964.[27] Through oxidation luminol forms a six-membered ring of peroxide intermediate, by the decomposition of which the excited state of the 3-aminophthalate are produced, yielding emission of light ($\lambda_{max} = 425$ nm). Therefore, in the proposed system, the CL intensity could be enhanced in the presence of fluoride.

Table 2. The chemiluminescence character of luminol - fluoride- periodate.

Species[a]	Relative CL intensity[b] (n = 5)
luminol + fluoride (all degassed)	2
luminol + fluoride (undegassed)	24
luminol + periodate (undegassed)	43
fluoride + periodate + luminol (undegassed)	99

[a]The concentration for luminol and periodate were 5×10^{-6} mol·L^{-1} with the same injection volume of 1.0 mL. That of fluoride was 5 ng·mL^{-1}.
[b]HV = $-$650V.

Table 3. Determination of fluoride in different water samples.

Samples	Results by the proposed method[a]					Results by IC
	Added ($ng \cdot mL^{-1}$)	Found ($ng \cdot mL^{-1}$)	Recovery (%)	RSD (%)	Concentration ($ng \cdot mL^{-1}$)	Concentration ($ng \cdot mL^{-1}$)
Underground water 1	0	0.26 ± 0.01	106.3	1.94	52.5 ± 1.1	53 ± 2
	3.0	3.45 ± 0.11		3.14		
Underground water 2	0	2.33 ± 0.05	88.0	1.99	233.3 ± 4.6	249 ± 6
	3.0	4.97 ± 0.17		3.51		
Spring water 1	0	4.79 ± 0.16	101.2	3.34	957.1 ± 32.0	945 ± 35
	3.0	7.82 ± 0.22		2.82		
Spring water 2	0	3.84 ± 0.12	96.8	3.21	767.7 ± 24.6	755 ± 28
	3.0	6.74 ± 0.21		3.18		
Distilled water 1	0	2.29 ± 0.03	93.0	1.51	22.9 ± 0.4	22 ± 1
	3.0	5.08 ± 0.08		1.61		
Distilled water 2	0	3.23 ± 0.13	97.4	3.87	32.3 ± 1.3	33 ± 1
	3.0	6.16 ± 0.12		1.97		
Tap water 1	0	3.07 ± 0.06	95.9	1.92	61.5 ± 1.2	64 ± 1
	3.0	5.95 ± 0.14		2.39		
Tap water 2	0	1.39 ± 0.02	96.4	1.17	69.6 ± 0.8	71 ± 2
	3.0	4.29 ± 0.17		3.90		
Lebashi drinking water	0	3.00 ± 0.11	98.3	3.51	3.0 ± 0.1	undetected
	3.0	5.95 ± 0.04		0.65		
Wahaha drinking water	0	0.64 ± 0.01	96.4	1.38	0.6 ± 0.0	undetected
	3.0	3.54 ± 0.05		1.40		

[a]The average of five determinations.

Table 4. Determination of fluoride in spiked urine.

	Sample	Fluoride supplement ($ng \cdot mL^{-1}$)	Mean[a] ($ng \cdot mL^{-1}$)	RSD (%)	Recovery (%)	Urine ($\mu g \cdot mL^{-1}$)	t-test ($t_{0.05,\,4} = 2.78$)
Volunteer 1	Sample 1	0	2.04 ± 0.03	1.41	93.3	2.04 ± 0.03	1.31
		1	3.26 ± 0.03	0.78			
	Sample 2	0	3.10 ± 0.04	1.38	102.2	3.10 ± 0.04	2.37
		2	4.99 ± 0.09	1.77			
	Sample 3	0	3.26 ± 0.05	1.55	101.2	3.26 ± 0.05	2.15
		3	6.19 ± 0.10	1.55			
Volunteer 2	Sample 1	0	2.07 ± 0.03	1.22	98.7	2.07 ± 0.03	0.47
		1	3.11 ± 0.05	1.61			
	Sample 2	0	2.96 ± 0.07	2.2	91.6	2.96 ± 0.07	1.06
		2	5.41 ± 0.11	2.1			
	Sample 3	0	3.03 ± 0.03	0.91	91.2	3.03 ± 0.03	2.87
		3	6.61 ± 0.08	1.26			
Volunteer 3	Sample 1	0	2.05 ± 0.04	1.86	92.4	2.05 ± 0.04	2.49
		1	3.30 ± 0.09	2.59			
	Sample 2	0	2.64 ± 0.10	3.61	89.1	2.64 ± 0.10	1.37
		2	5.21 ± 0.11	2.12			
	Sample 3	0	2.91 ± 0.07	2.40	95.2	2.91 ± 0.07	3.19
		3	6.21 ± 0.11	1.83			

[a]The average of five determinations.

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APPLICATIONS

Determination of Fluoride in Water Samples

Following the procedure detailed in the experimental section, the proposed method was applied with preliminary success to the determination of fluoride in various water samples, including underground water, spring water, distilled water, tap water and drinking water, and the results of trial determinations are summarized in Table 3. The recovery studies were performed on each of the analyzed samples by adding a known amount of fluoride to the sample before the recommended treatment. The regression equation is $Y_{IC} = 0.986X_{CL}+2.1168$, $R^2 = 0.9997$, which shows the relation of results between the proposed method and ion chromatography (IC).

Determination of Fluoride in Human Urine

The proposed method was also applied with preliminary success to the determination of fluoride in human urine. Urine samples were collected respectively from three healthy volunteers in different time, diluted with deionized water directly and sometimes supplemented with fluoride to test the recovery of the method. Thus, urinary fluoride could be determined relatively simply by FI-CL without any pre-treatment procedures. The results of determination were summarized in Table 4, and the data were verified by use of Student's ''t'' test. The results were also in the normal range of the concentrations of urinary fluoride in China.

CONCLUSIONS

The proposed method is the first flow injection chemiluminescence method for determination of free fluoride in water and human urine, and it is rapid, accurate, precise, easily handled and with low operational cost. Compared with other methods, the proposed method offers advantages in instrumental simplification, high sensitivity and reducing reagent consumption.

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