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Indirect determination of fluoride in aqueous samples by inductively coupled plasma atomic emission spectrometry following precipitation of CeF_3

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ABSTRACT

An indirect fluoride determination method has been developed based on the ICP-AES determination of excess cerium(III) ion after precipitation. From four cations—Y(III), Sr(II), Ce(III), La(III)–cerium(III) proved to be the best precipitate forming cation in the 0–20 mg L^{-1} fluoride concentration range with the limit of detection of 1.4 mg L^{-1}. The precision (RSD) of the proposed method is 0.71% at 8 mg L^{-1} fluoride. The role of sulphate ions in the formation of the fluoride precipitate was studied as well. The applicability of the technique for the study of solid hazardous wastes as well as for groundwater monitoring of a fluoride contaminated area is demonstrated.

1. Introduction

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is an excellent technique for determination of metal, semi-metal, and even for non-metal elements. However, this method has not been widely used for the determination of fluoride.

The direct atomic spectroscopic determination of fluoride ions encounters several difficulties. Excitation of the fluorine atom requires high energy, which is difficult to provide by an argon plasma. An additional obstacle is that the wavelengths of the resonant lines are under 100 nm requiring a sophisticated optical system. Only a few papers are published about fluorine determination in gaseous samples at the non-resonant line (F I 685.602 nm) by ICP-AES using direct injection *via* a gas sampling loop or a gas chromatographic apparatus [1–3]. The fluorine emission line of 685.602 nm can be detected not only with ICP-AES but also with gas chromatography microwave induced plasma atomic emission spectrometry (MIP-AES) [4,5].

A direct fluoride determination method in aqueous samples by ICP-AES technique was reported by Okamoto et al. using an electrothermal vaporisation sample introduction system [6]. A better limit of detection was achieved by improving this method using ICP-MS analysis [7].

Direct fluorine determination was also carried out using an atomic absorption spectrometer for detecting aluminum(III)–monofluoride complex at 227.45 nm using a Pt hollow cathode lamp [8–10]. Among the indirect methods available, the one using aluminum-monofluoride complex formation has the most favourable limit of detection. With this method, fluoride is detected as AlF^{2+} after separation from Al^{3+} on an ion-exchange column by inductively coupled plasma mass spectrometry (ICP-MS) [11]. Two other methods were published involving volatile silicon tetrafluoride formation. In these cases silicone was determined by an optical emission spectrometer [12,13].

Besides the atomic spectroscopy methods, fluoride determination has been performed using techniques such as potentiometry with fluoride ion selective electrodes (ISE) [14–16], ion-exchange chromatography with conductivity detection [17,18], spectrophotometry [19–22] and most recently capillary electrophoresis [23] but there are interferences of several cations and anions, therefore the sample preparation is time-consuming. Most interferences in fluoride determination come from the presence of high levels of iron or aluminum in the sample. These interference effects can be eliminated by distillation of fluoride as HF.

Our indirect method is based on the fact that fluoride ions form a stable precipitate with cerium(III) ions:

$$Ce^{3+} + 3F^{-} = CeF_3 \quad \lg K_s = 16.3 \quad [24]$$

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After the separation of the cerium(III) fluoride precipitate, the cerium concentration of the solution can be measured by ICP-AES. The determination of the excess cerium concentration by ICP-AES provides a high precision method for fluoride determination in various samples.

2. Results and discussion

2.1. Selection of the precipitate forming metal ion

Four cations (Y(III), Sr(II), Ce(III), La(III)) were tested as precipitate forming reagents in the fluoride concentration range of 0–20 mg L^{-1}. These cations were selected on the basis of the solubilities of their fluoride precipitate and the crystallization property of the fluoride compounds. The concentration of each metal ion was the same (70 mg L^{-1}). The influence of the type of counter ion (chloride, nitrate and sulphate) on the precipitation was investigated as well.

A linear curve with an appropriate slope can be fitted to the calibration points only in the case of lanthanum(III) sulphate and cerium(III) sulphate (Fig. 1). The solubility of the cerium(III) fluoride (16.3) in less than that of the lanthanum(III) fluoride (15.3) [24] and our experimental results presented in Fig. 1 suggest the application of the cerium(III) ion as a precipitation reagent for further studies. The regression is better and the fitted curve has a higher slope in the case of cerium ($y = -2.7214x + 67.44, R^2 = 0.9988$) than in the case of lanthanum ($y = -2.5614x + 69.91$, $R^2 = 0.9973$) providing higher sensitivity.

2.2. Influence of sulphate ion

Based on Fig. 1, it was found that the presence of sulphate ion is essential for the indirect fluoride determination. Cerium(III) nitrate can also be used with the addition of sulphate ions in the form of potassium sulphate.

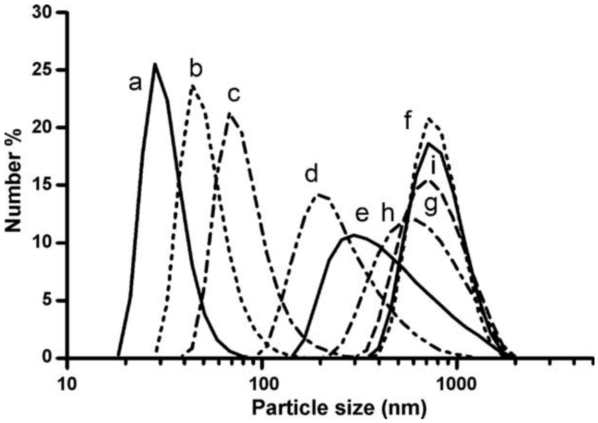

Fig. 2. Particle size distribution by number with different sulphate ion concentrations (a: 0 mg L^{-1}, b: 15 mg L^{-1}, c: 20 mg L^{-1}, d: 30 mg L^{-1}, e: 40 mg L^{-1}, f: 50 mg L^{-1}, g: 70 mg L^{-1}, h: 100 mg L^{-1} and i: 200 mg L^{-1}) ([Ce^{3+}]$_0$ = 70 mg $^{-1}$; [F$^-$] = 8 mg L^{-1}).

XRD analyses revealed that the precipitate contained only CeF$_3$. Sulphate ions were present on the surface only, as indicated by SEM-EDX measurements.

Particle size distribution analysis was used to confirm the precipitation (Fig. 2). In this experiment cerium(III) nitrate was used. Obviously, the size of the CeF$_3$ particles depends on the sulphate concentration. If the sulphate concentration is higher than 50 mg L^{-1}, the particle size will be larger than 0.45 μm, and can be separated by the applied membrane filter.

The minimum sulphate concentration required for a linear relationship between the excess metal and the fluoride concentrations is 40 mg L^{-1} at a cerium ion concentration of 70 mg L^{-1} (Fig. 3). Certainly, no sulphate addition is necessary if cerium(III) sulphate is used as precipitation reagent.

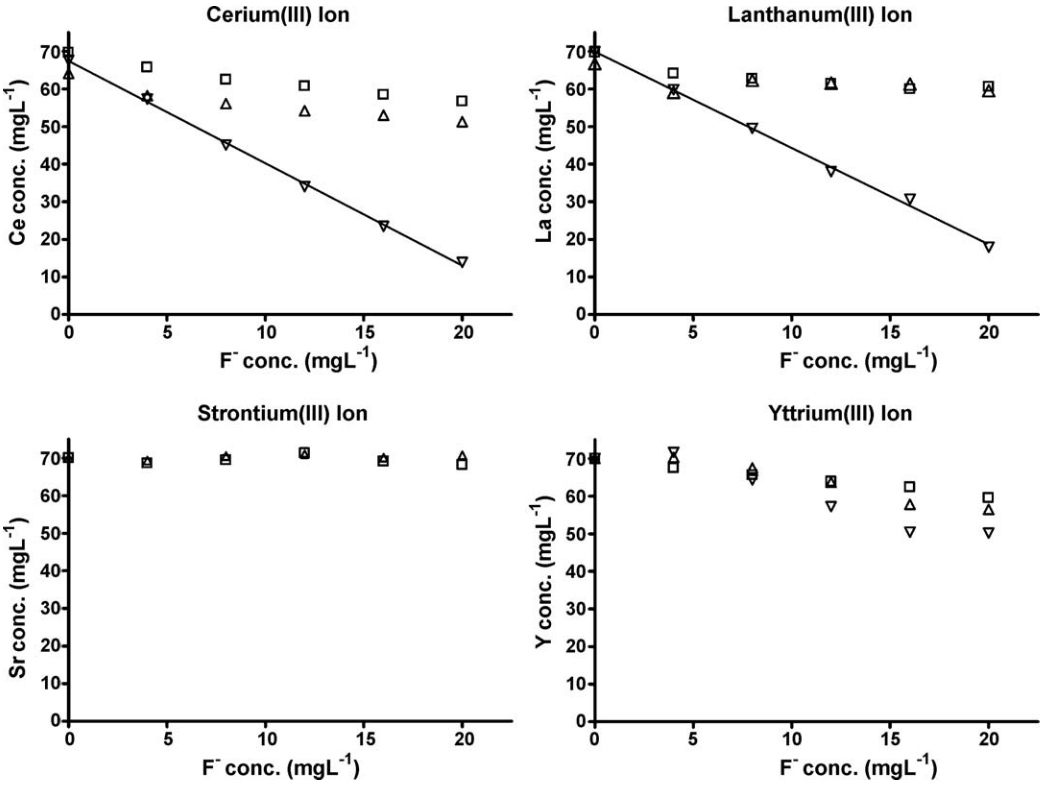

Fig. 1. Excess metal–fluoride concentration relationships for fluoride determination in the 0–20 mg L^{-1} range (□, chloride; △, nitrate; ▽, sulphate).

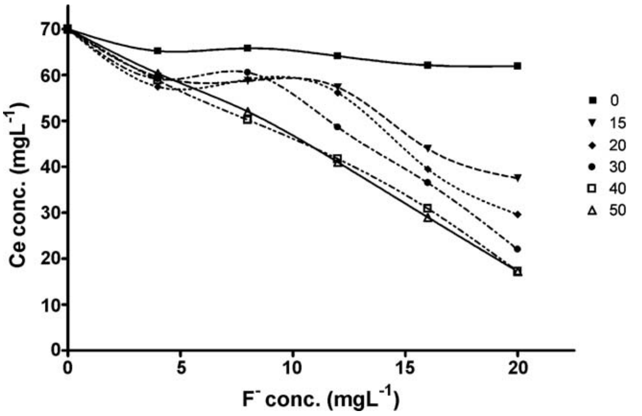

Fig. 3. Effect of sulphate concentration (0, 15, 20, 30, 40 and 50 mg L^{-1}) on the cerium concentration in the liquid phase at different fluoride concentrations.

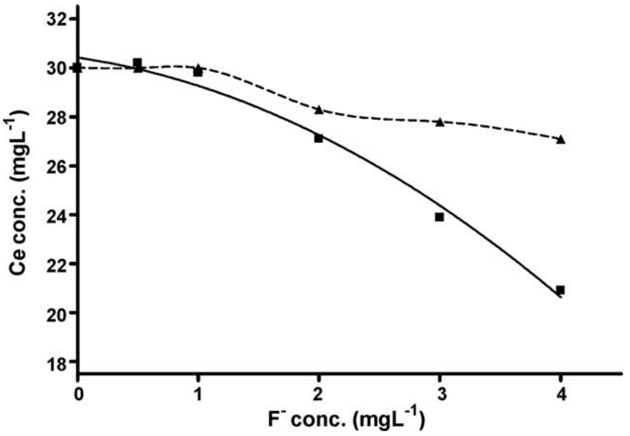

Fig. 4. Cerium concentration in the solution as a function of fluoride concentration (0–4 mg L^{-1}). Calculated (▲) and measured (■) curves.

2.3. Investigation of fluoride concentration ranges

Three fluoride concentration ranges (0–4, 0–20 and 20–90 mg L^{-1}) were studied with cerium(III) ion concentrations of 30, 70 and 300 mg L^{-1}. The calculated (from the solubility constant of CeF_3: lg K_s = 16.3 [24]) and experimental data showed quadratic relationships between cerium(III) and fluoride concentrations. The main analytical characteristics of the determination with different initial cerium concentrations (initial cerium(III) concentration means the cerium(III) concentration of the blank sample after addition of the reagent solution) are presented in Table 1. The calibration curve using 30 mg L^{-1} initial cerium concentration is shown in Fig. 4: the precipitate formation starts at significantly lower fluoride concentration than the calculated values. Obviously the presence of the sulphate ions affect the precipitation (complex formation with cerium fluoro species), consequently the fluoride determination is possible with appropriate sensitivity in the range of 2–4 mg L^{-1} fluoride concentration. At 70 and 300 mg L^{-1} initial cerium(III) concentration the measured Ce concentrations in the solutions are also lower than the calculated ones, because the precipitate can bind the metal ions on its surface (according to the Paneth-Fajans rule).

As the concentration of the excess cerium is not calculable, a calibration curve has to be made before performing the analysis. In order to obtain the best performance, an initial cerium(III) concentration of 70 mg L^{-1} is recommended for general use, however the other two cerium(III) concentrations are also employable. Under the proposed conditions a detection limit of 1.4 mg F$^-$ L^{-1} can be achieved. The LoD was calculated by the formula LoD = $X_{\text{mean}} - 3\sigma$ where X is the concentration of the blank sample (initial cerium concentration) and σ is the standard deviation of 10 replicates. The developed method is an indirect type indicating the use of subtraction in the formula.

2.4. Interferences

Interferences can be divided into two groups: interferences of precipitation and spectral interferences. The first group contains the effects of external parameters (e.g.: temperature), the pH of the solution and the presence of anions in the sample. The presence of other metals, possessing spectral lines close to that of cerium, can cause the spectral interferences.

2.4.1. Effect of temperature

The effect of temperature is negligible. Experiments carried out at 13.5, 25 and 35 °C with fluoride concentrations of 8 and 16 mg L^{-1} resulted in a maximum deviation of 2.7% from the fluoride concentration measured at 25 °C. (Experimental results are presented in Table 2.)

2.4.2. Effect of pH

The influence of pH on the precipitation has been investigated separately. The pH of the fluoride solution was adjusted in the range between 1 and 11 pH units using HCl and NaOH. Fig. 5 shows that fluoride recovery is optimal within the 3–9 pH range. No cerium(III) fluoride is precipitated below pH 3, while cerium(III) hydroxide precipitate is formed above pH 9.

2.4.3. Effect of coexisting ions

The effect of different cations and anions on the precipitation reaction and on the determination of cerium concentration was separately studied by the addition of the following ions to solutions containing 10 mg L^{-1} F$^-$: Na(I), K(I), Li(I), Sr(II), Mg(II), Cu(II), Pb(II), Fe(II), Mn(II), Ni(II), BO_3^{3-}, HCO_3^-, Cl^- and NO_3^- ions.

The studied metal ions showed no significant interference (Table 3). However, Fe(III) and Al(III) cause problems if their concentrations are at mg L^{-1} level because they form complexes with the fluoride in the case of the common methods as well. The

Table 1
Analytical characteristics of fluoride determination with different initial cerium(III) concentrations.

Analytical characteristics	Initial cerium(III) concentration		
	30 mg L^{-1}	70 mg L^{-1}	300 mg L^{-1}
Precision (% RSD)	2.0% (3 mg L^{-1} F$^-$)	0.71% (8 mg L^{-1} F$^-$)	1.7% (40 mg L^{-1} F$^-$)
Dynamic range	1–4 mg L^{-1} F$^-$	2–20 mg L^{-1} F$^-$	5–90 mg L^{-1} F$^-$
Equation fitted	$y = -0.4318x^2 - 0.7153x + 30.40$	$y = 0.0162x^2 - 2.963x + 70.16$	$y = 0.0148x^2 - 4.181x + 298.4$
Regression coefficient (R^2) (n = 6 points)	0.9890	0.9999	0.9994
Calculated equation		$y = -0.0266x^2 - 1.636x + 70.97$	$y = -2.413x + 301.56$

Table 2
Effects of temperature at 8 and 16 mg L^{-1} fluoride concentration.

Temperature (°C)	Recovery (%)	
	8 mg L^{-1} fluoride concentration	16 mg L^{-1} fluoride concentration
13.5	98.2	98.1
35	102.7	101.4

Table 3
Effects of different ions at 10 mg L^{-1} fluoride concentration.

Ion	Concentration (mg L^{-1})	Recovery %
Na^+	200	100
K^+	200	98.1
Li^+	100	102
Sr^{2+}	100	102
Mg^{2+}	50	102
Cu^{2+}	100	98.1
Pb^{2+}	50	97.7
Fe^{2+}	100	100
Mn^{2+}	100	97.7
Ni^{2+}	100	99.2
$BO_3{}^{3-}$	200	95.3
$HCO_3{}^-$	200	101
Cl^-	200	102
$NO_3{}^-$	100	99.0

concentration of these ions should be determined by preliminary ICP-AES analysis of the sample. The mentioned ions can be removed by distillation or by ion-exchange (see Section 1). In case of some metal ions, e.g. lanthanides, there is no interference because if their concentration is considerable they will form precipitate in the sample before the addition of the reagents. Moreover, carbonate and phosphate ions do interfere. The interference of carbonate can be eliminated by adjusting the pH between 3 and 5. Phosphate ions over 0.5 mg L^{-1} concentration have to be removed from the solution prior to analysis. As the phosphate ion has three negative charges in alkaline solution, it can effectively bind on anion exchange resin, while the fluoride binds weakly therefore the separation is possible. The phosphate content of the sample can easily be checked by ICP-OES determination of phosphorus.

2.5. Determination of fluoride in real samples

The accuracy and precision of the present indirect ICP-AES method were tested using hazardous waste and groundwater samples. According to the relevant Hungarian Standard, fluoride concentration was determined in solid hazardous wastes after extraction with water. Fluoride concentrations were adjusted to be within the 2–20 mg L^{-1} range by dilution. Potentiometric control analyses were carried out using a fluoride selective electrode (ISE) and a standard addition method. A comparison of the results is listed in Table 4.

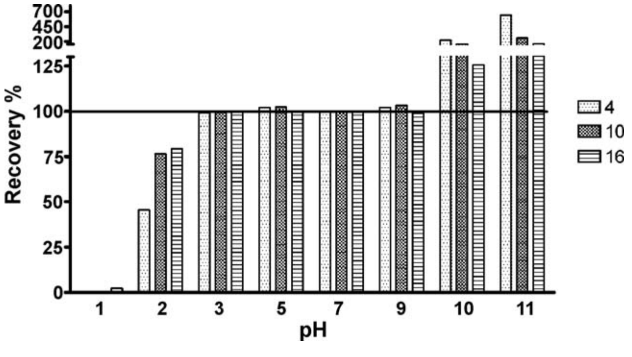

Fig. 5. Effect of pH at 4, 10 and 16 mg L^{-1} fluoride concentrations.

Table 4
Comparison of the ICP-AES and ISE results for solid hazardous waste samples.

Sample	Fluoride ion concentration (mg kg^{-1})[a]		Recovery %
	ISE	Ind. ICP-AES	
Cathode	6489 ± 691	6483 ± 421	99.9
Cyclone dust	2860 ± 90	2785 ± 22	97.4

[a] Mean ± standard deviation ($n = 3$).

Table 5
Analytical results of groundwater samples.

Sample	Fluoride ion concentration (mg L^{-1})[a]			Recovery %[b]
	IC	ISE	Ind. ICP-AES	
A2	64.1 ± 0.8	66.9 ± 1.0	68.9 ± 0.4	103
A4	202.1 ± 3.6	202.0 ± 10.0	200.7 ± 2.1	99.4
B-25	177.3 ± 1.3	175.4 ± 5.8	177.1 ± 0.2	101
ER 1	81.2 ± 1.3	79.6 ± 2.9	81.3 ± 0.9	102
ER 2	55.3 ± 0.4	57.7 ± 1.3	57.3 ± 1.2	99.4

[a] Mean ± standard deviation ($n = 3$).
[b] Calculated from the analytical results by ISE.

Table 6
Fluoride recovery after standard addition.

Sample	Fluoride concentration (mg L^{-1})			Recovery %
	Sample	Added	Determined	
A1	14.6	4	18.9	102
	14.6	8	23.0	102
A3	13.5	2	15.6	101
	13.5	4	17.4	99.2
	13.5	8	21.6	101

Groundwater samples from five observation wells were also analysed. In this case, potentiometric (ISE) and ion chromatographic (IC) techniques were chosen for control analysis (Table 4). The water samples were prepared with a fluoride concentration of 3–10 mg L^{-1} for the control analysis and a concentration of 5–20 mg L^{-1} for the ICP-AES determination. The calibration for the ion chromatographic and the ICP-AES determination were carried out measuring 5 solutions diluted from 1000 mg L^{-1} fluoride standard.

To prove the applicability of the method via standard addition, portions of 2–8 mg L^{-1} were added to the groundwater samples. The results of fluoride recovery are listed in Table 6.

Based on the data of Tables 5 and 6, the proposed method can be successfully applied to both types of samples. The precision (RSD) of the analysis is less than 2% for each groundwater samples.

3. Conclusions

An indirect fluoride determination method based on the precipitation by cerium(III) cation was elaborated using ICP-AES analysis. Among the candidate ions—Y(III), Sr(II), Ce(III), La(III)–cerium(III) proved to be the best one for analytical purposes. It was discovered that the presence of sulphate ion is necessary for the enhancement of precipitation. For common analyses in the 0–20 mg L^{-1} F^- range a cerium(III) concentration of 70 mg L^{-1} is recommended for best performance. The applicability of the method for the analysis of fluoride contaminated environmental samples was proved. The analysis of environmental samples is sometimes difficult or it is not possible by the common methods because there are many interferences.

It is apparent from the results that RSD % of the values measured by the proposed method is, in most cases, lower in comparison to the commonly used fluoride determination methods (potentiometry using ion selective electrode or ion-chromatography). A notable disadvantage of the method is that the limit of detection is poor as a result of the precipitate forming equilibrium and the particle size of the precipitate. This can be avoided by using method of standard addition. The detection limit of the proposed method is in the same range as with other atomic spectroscopic possibilities used for fluorine determination [6–10].

By the indirect ICP-AES method the concentration of the metal ion and fluoride ion in the same sample can be determined using the same instrument, which is a huge advantage for an automated determination based on this method. The analysis time is shorter in comparison to other methods, e.g. ion-exchange chromatography, however the sample preparation can be slightly longer. During the analysis the sample does not come into contact with expensive, sensitive parts of the instruments unlike to other methods such as the crystal or the membrane of the ion selective electrode or the chromatography column.

4. Experimental

4.1. Apparatus

A PerkinElmer Optima 2000 DV inductively coupled plasma atomic emission spectrometer was used for the determination of excess metal ions. The analytical wavelengths were as follows: Ce, 413.764 nm; La, 398.852 nm; Y, 371.029 nm; Sr, 407.771 nm.

A Zetasizer Nano ZS (Malvern Instruments) executed the particle size distribution analysis.

An Agilent 1100 type chromatograph with Alltech DS-Plus™ autosuppressor and Hitachi L-7470 conductivity detector was applied for the ion chromatographic control analysis. The parameters of separation are summarized in Table 7. The potentiometric reference analysis was carried out with a Radelkis OP-F-0711P type fluoride ion selective electrode, a Radelkis OP-0820P type silver/silver chloride reference electrode, and a Radelkis OP-208/1 type precision pH meter.

4.2. Chemicals

All reagents were of analytical grade. A fluoride standard solution (Teknolab, Kolbotn, Norway) and hydrochloric acid (37%) (Spektrum-3D, Debrecen, Hungary) were used for the experiments. All the solid chemicals were purchased from Reanal (Budapest, Hungary) except for cerium(III) nitrate (Merck, Darmstadt, Germany); cerium(III) sulphate, yttrium(III) sulphate, yttrium(III) chloride, and lanthanum(III) sulphate reagents were prepared by ion-exchange reactions.

4.3. Procedure for selection of precipitate forming cation

In a 25 mL volumetric flask, the fluoride ion standard solution and the metal stock solution were mixed in required proportion. After precipitation the flask was filled up to the mark with deionized water. An aliquot of 5 mL was withdrawn from the precipitated solution and filtered on a polyethersulfone (PES) membrane filter (diameter: 33 mm; pore size: 0.45 μm Millipore, Bedford, MA, USA). The metal concentration of the clear solution was analysed by ICP-AES.

Table 7
Conditions of chromatographic analyses.

Column	Transgenomic ICSep AN300B
Eluent	3.0 mM Na_2CO_3
Flow rate	1.0 mL/min
Temp.	35 °C
Detector	Suppressed conductivity
Range	100 μS/cm
Injection volume	20 μL

4.4. Analytical procedure for determination of fluoride in real samples

A known amount of the sample solution was transferred to a 25 mL volumetric flask. The pH of the solution was adjusted to be in the pH 3–5 range with 0.05 M HCl using methyl orange indicator. The required amounts of the cerium(III) and the sulphate stock solutions were added then the flask was filled up to the mark with deionized water. After 15 min (the optimal reaction time) an aliquot of 5 mL was withdrawn from the precipitated solution and filtered on a PES membrane. The cerium concentration of the clear solution was analysed by ICP-AES.

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