

RESEARCH ON A NEW SPECTROPHOTOMETRIC METHOD FOR DETERMINATING TRACE AMOUNTS OF FLUORIDE

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Abstract - A new spectrophotometric method for determining trace amounts of fluoride has been introduced in this article. The principle of the method is based on the reaction of fluoride with a complex of aluminum ion and xylenol orange reagent (Al-XO). The concentration of fluoride in water is determined by measuring the red color of the Al-XO complex at 555 nm or measuring the yellow color of the XO reagent at 430 nm. The factors affecting the method for the determination of fluoride were examined. At the optimum condition, the limit of quantitation of this method is 0.08-2.1 mg/L. Based on an analysis of fluoride in the actual samples, the error of the method is less than 6%. A new point of this article is that this is the first time the type of calibration curve graph $A = f(\log C)$ in the spectrophotometric method (where: A – absorption; log - logarithm; C – concentration of fluoride) has been used in the world.

Key words - Spectrophotometric; aluminum; xylenol orange; fluoride

1. Introduction

Fluoride in drinking water has both beneficial and harmful to human health. The low concentration of fluoride in drinking water has been considered beneficial to prevent dental caries [1]. Long-term consumption of water containing the high concentration of fluoride leads to dental fluorosis [2, 3]. In the world, fluoride pollution phenomena occur relatively common, especially in countries such as Vietnam, India, China, Thailand, Bangladesh, etc. According to the World Health Organization (WHO), if the concentration of fluoride in drinking water is from 0.5 to 1.5 mg/L, the human teeth and bone will grow well. If the concentration of fluoride in drinking water is from 1.5 to 4.0 mg/L, the teeth will be black, brittle, and easily broken. If the concentration of fluoride ion is greater than 4.0 mg/L, the teeth will be black color, brittle bone disease, and fluorosis. However, if fluoride in drinking water is less than 0.5 mg/L, it will cause tooth decay [4].

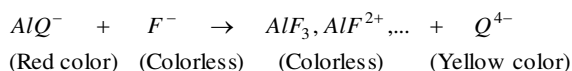
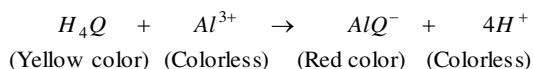
There are three groups of fluoride analysis methods: potential method, ion chromatography method and spectrophotometric method. The most common methods for fluoride assay are potentiometry using a fluoride selective electrode [5], ion chromatography method [6], and zirconium-alizarin method. Several other methods have been reported for the determination of fluoride in water, such as using resorcin blue complexes [1], using a complex of aluminum and xylenol orange (Al-XO) as a colored reagent [7], using capillary electrophoresis, using solvent extraction coupled to fluorometry [8, 9]. Because of some advantages of spectrophotometric methods, such as accuracy, simplicity and reproducibility, we have been interested to design a new spectrophotometric method for the determination of trace amounts of fluoride in water.

Based on the research by Javad Zolgharnein [7], we noticed that his method using a complex of aluminum and xylenol orange as a colored reagent for the determination of trace amounts of fluoride is quite good, because the

relative standard deviation of the method was 1.6%. The principle of his method is based on the reaction of fluoride with a complex of aluminum ion and xylenol orange reagent (Al-XO). The concentration of fluoride in water is determined by measuring the red color of the Al-XO complex at 555 nm. However, limit of quantitation of his method is only 0.08-1.4 mg/L. In addition, he has never conducted research at a wavelength of 430nm.

To expand the range of quantitative fluoride, we developed the study of Javad Zolgharnein. The concentration of fluoride in water is determined by measuring the red color of the Al-XO complex or measuring the yellow color of the XO reagent. A new point of this article is that this is the first time the type of calibration curve graph $A = f(\log C)$ in the spectrophotometric method has been used.

Principles for the determination of fluoride in water by using the Al-XO complex are based on the color change of the Al-XO complex in the presence of fluoride. The reaction occurs as follows:



Where: H_4Q is xylenol orange; AlQ^- is an Al-XO complex.

Thus, when fluoride is present in the aqueous solution, the red color of the Al-XO complex decreases, while the yellow color of the XO reagent increases. When measuring the color change of the aqueous solution, the fluoride concentration in water will be determined.

2. Experimental

The reagents used in the experiment consisted of NaF, $Al_2(SO_4)_3 \cdot 18H_2O$, xylenol orange, HNO_3 , KNO_3 , CH_3COOH , $CH_3COONa \cdot 3H_2O$, ascorbic acid, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, $CaCl_2$, $NaCl$, Na_2SO_4 , $MgCl_2 \cdot 5H_2O$. All reagents were analysis-graded and purchased from E. Merck Company.

pH meter (model 420A+ Plus); Ultraviolet-visible spectrophotometer (model Libra S22); pipettes (1 mL, 2 mL, 5 mL, 10 mL; 25 mL); micropipettes (0.1 mL, 1 mL, 5 mL); volumetric flask (50 mL, 100 mL, 500 mL, 1000 mL); plastic bottles polyethylene 1000 mL using to contain fluoride solution.

3. Results and discussion

3.1. Determination of optimal pH and wavelength

The solution of XO at $pH \leq 6$ is the yellow color, $pH > 6$ is red-purple color and the solution of Al-XO is the

red color. In addition, the absorption spectra of the red solution and purple-red solution overlap each other. Therefore, in this section, we only determined the absorption spectra of the XO and Al-XO in the range of $\text{pH} \leq 6$. Experimental results were presented in Figure 1.

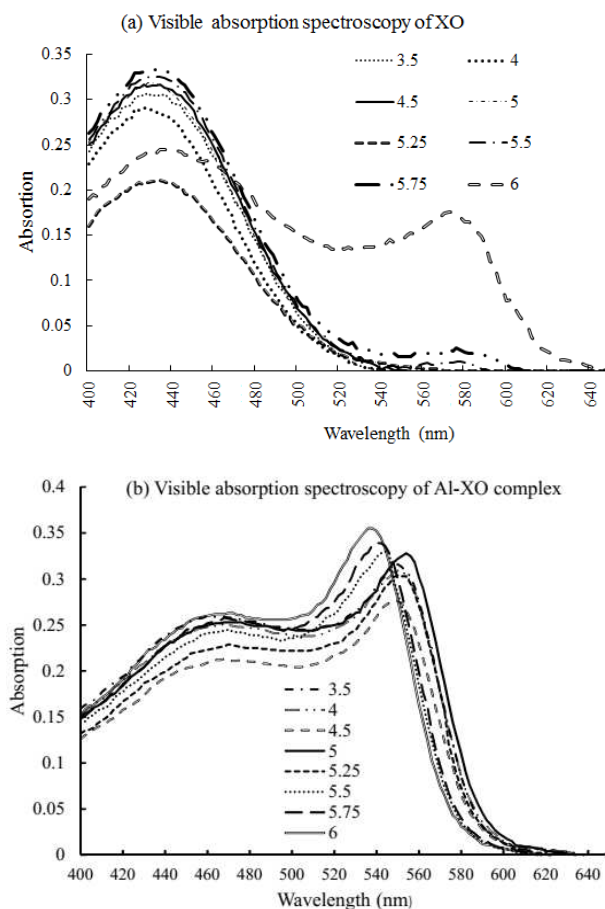


Figure 1. Absorption spectroscopies of the XO (2.10^{-5} M) and Al-XO (2.10^{-5} M) in the range of $\text{pH} = 3.50$ - 6.00

The data in Figure 1(a) shows that absorption spectroscopies of XO in the range of $\text{pH} = 3.50$ to 5.25 have a peak at 430 nm. Absorption spectroscopies of XO in the range of $\text{pH} \geq 5.5$ have two peaks at 430 nm and 574 nm. The cause of this problem is probably due to the contributions of H_3Q^+ , H_2Q^{2+} , HQ^{3+} , Q^{4+} (They are the ions of XO reagent at different pH) [7].

The data in Figure 1(b) shows that absorption spectroscopies of Al-XO in the range of $\text{pH} = 3.50$ to 5.25 have a peak at 555 nm. If the pH is greater than 5.25 , the maximum point of the spectroscopy will tend to shift to the left of the graph. When the pH is greater than 5.25 , the absorption spectroscopy of the Al-XO complex overlaps with the absorption spectroscopy of the XO reagent.

The range of $\text{pH} = 3.50$ to 5.25 and wavelength of 540 - 560 nm, the optical density of Al-XO is the largest and the optical density of XO reagent is 0. In the range of $\text{pH} = 3.50$ to 5.25 , $\text{pH} = 5.00$ is optimal because the optical density of Al-XO complex at 555 nm is the largest. For ease of observation, we were drawing the absorption spectroscopy of the XO and Al-XO at $\text{pH} = 5.00$ on the same graph as Figure 2.

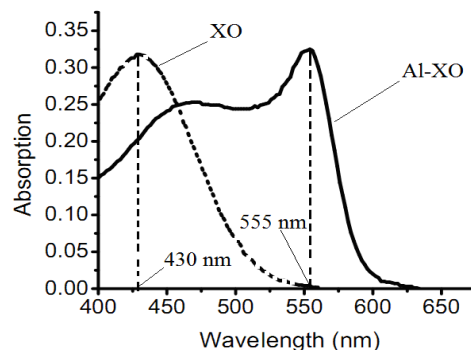


Figure 2. Absorption spectroscopy of Al-XO (2.10^{-5} M) and XO (2.10^{-5} M) at $\text{pH} = 5.00$

The data in Figure 2 shows that: when pH is 5.00 and wavelength is 555 nm, the optical density of the Al-XO is the largest; the optical density of XO is zero. Thus, the optimal wavelength and optimal pH for measuring the optical density of the Al-XO in the presence of XO are 555 nm and $\text{pH} = 5.00$, respectively.

3.2. Determination of optimal reactive environment

The experiment was conducted as Table 1.

Table 1. Environmental survey for the determination of fluoride

Reagent	Flask of 50 mL								
	Reference sample	1	2	3	4	5	6	7	8
Al ³⁺ 10 ⁻³ M (mL)	0	1.0							
XO 10 ⁻³ M (mL)	0	1.0							
F ⁻ 50 mg/L (mL)	0	0.05	0.1	0.3	0.8	1.2	1.6	2.0	3.0
Norm solution	Norms to 50mL, shake vigorously for 1 minute, wait for 30 minutes								

Where: Norm solution is 1 in 3 solutions as follows:

- The acetate buffer solution, $\text{pH} = 5.00$;
- The solution of HNO_3 , $\text{pH} = 5.00$;
- The solution of KNO_3 0.1M , HNO_3 , $\text{pH} = 5$.

The experimental results were shown in Figure 3. The data in Figure 3a shows that the concentration of fluoride is from 0.0 to 0.8 mg/L, the correlation coefficient R^2 is 0.9919 . The advantage of acetate buffer solution is easy to adjust pH. However, the reaction of fluoride with Al-XO occurs slowly because Al-XO is quite stable in acetate buffer solution. When measuring solutions of the standard color range if there is a slight difference in time (measured before, measured later), the analysis results will be wrong. In addition, if the concentration of fluoride is from 0.8 to 3.0 mg/L, it will be not suitable for graph type $A = f(\log C)$. Because optical absorption is an unstable increase and decrease. The main reason of this problem is that the acetate buffer does not increase the ionic force of the solution.

The data in Figure 3b shows that the concentration of fluoride is from 0.0 to 0.8 mg/L, the correlation coefficient R^2 is 0.8902 . Therefore, if the use of HNO_3 adjusts pH, it will be not suitable for the determination of fluoride.

The data in Figure 3c shows that the concentration of fluoride is from 0.0 to 0.8 mg/L, the correlation coefficient R^2 is the largest. The cause of this problem may be that

KNO_3 is a strong electrolyte, which increases the ionic force of the solution, making the reaction between fluoride and Al-XO happen faster.

Thus, the best environment for determining fluoride is the solution of KNO_3 0.1M and HNO_3 with $\text{pH} = 5$. Where: KNO_3 is a strong electrolyte which increases the ionic force of the solution; HNO_3 is to adjust pH to 5.

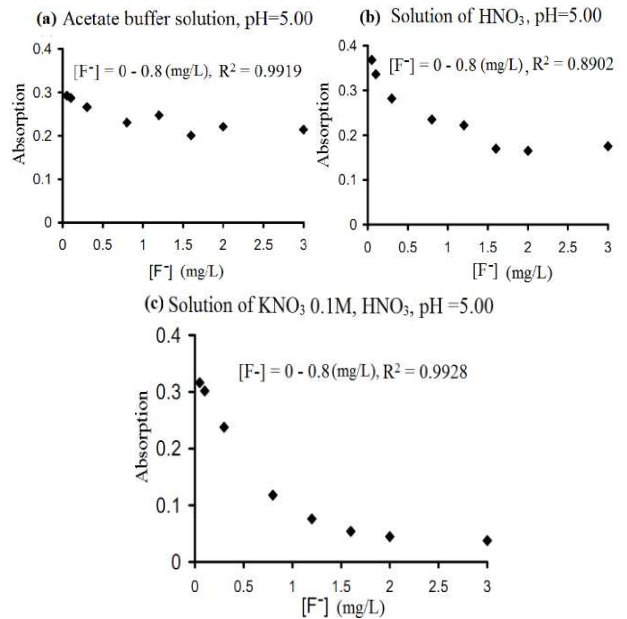


Figure 3. Determination of optimal reactive environment

3.3. Determination of optimal reaction time

3.3.1. Optimal reaction time of Al and XO

The experiment was conducted as follows:

- Solution 1: Taking exactly 5 ml of KNO_3 1M poured into the flask 50 ml. Then, using the HNO_3 solution with $\text{pH} = 5.00$ poured into the flask to the mark with 50 ml.
- Solution 2: Taking exactly 1 ml $\text{XO } 10^{-3} \text{ M}$ and 1.0 ml $\text{Al}^{3+} 10^{-3} \text{ M}$ poured into the flask 50 ml. Then, adding 5 ml KNO_3 1 M and using the HNO_3 solution with $\text{pH} = 5.00$ poured into the flask to the mark with 50 ml.

The optical density of the solution 2 was measured at 555 nm (reference sample was solution 1). The experimental result was shown in Figure 4. This figure shows that the optimal reaction time of the aluminum ion and reagents XO is 5 minutes. We used this condition to study the next factors.

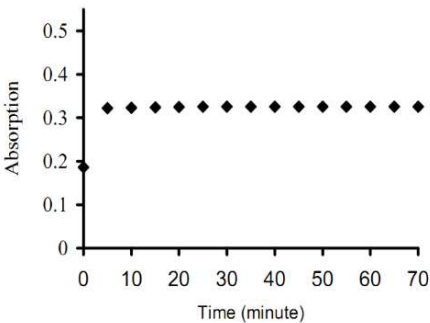


Figure 4. The relationship between reaction time and optical density of Al-XO complex

3.3.2. Optimal reaction time of Al-XO complex and fluoride

The experiment was conducted as Table 2. The experimental result was shown in Figure 5.

Table 2. The experiment for determination of the optimal reaction time of Al-XO with fluoride

Reagent	Flask of 50 mL			
	Reference sample	1	2	3
$\text{XO } 10^{-3} \text{ M (mL)}$	0	1.0	1.0	1.0
$\text{Al}^{3+} 10^{-3} \text{ M (mL)}$	0	1.0	1.0	1.0
Reaction time	Shake vigorously and wait 5 minutes			
$\text{KNO}_3 1 \text{ M (mL)}$	5			
$\text{F}^- 50 \text{ mg/l (mL)}$	0	0.5	1.0	1.5
$\text{HNO}_3, \text{pH} = 5$	Norms to 50mL and shake vigorously			
Absorption	Measuring at 555 nm			

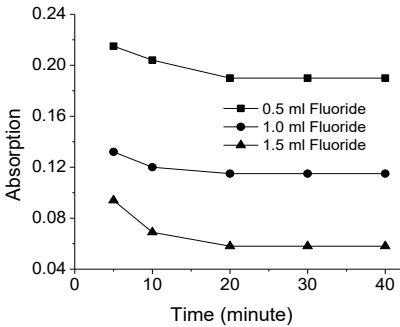


Figure 5. The optimal reaction time of Al-XO and fluoride

The data in Figure 5 shows that the optimal reaction time of Al-XO complex and fluoride is not dependent on the concentration of fluoride. The optimal reaction time is 20 minutes. We used this condition to study the next factors.

3.4. Studying the effects of hindering substances

The aim of the research in this article was to determine fluoride in groundwater and surface water. In groundwater and surface water generally contains ions, such as Fe^{3+} , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , PO_4^{3-} . Therefore, we only studied these ions. The experiment was conducted as in Table 3.

Table 3. Studying the effects of hindering substances

Reagent	Flask of 50 mL							
	Reference sample	1	2	3	4	5	6	7
Al ³⁺ 10 ⁻³ M (mL)	0	1						
XO 10 ⁻³ M (mL)	0	1						
Reaction time	Shake vigorously and wait for 5 minutes							
KNO ₃ 1M (mL)	5							
F ⁻ (mL)	0	1						
Hindering substances 200 mg/L (mL)	0	0	1	2	3	4	5	6
HNO ₃ pH=5	Norms to 50 mL							
Reaction time	Shake vigorously and wait for 20 minutes							
Absorption	Measuring at 555 nm							

(Where: Hindering substances are Fe^{3+} , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , PO_4^{3-}).

The results of the experiment were shown in Figure 6.

The data in Figure 6 shows that: Cl^- , SO_4^{2-} , PO_4^{3-} , Ca^{2+} and Mg^{2+} do not affect the method of determining fluoride

by Al-XO complex. The only serious interference was due to Fe^{3+} , which was removed by the addition of a portion of ascorbic acid [9].

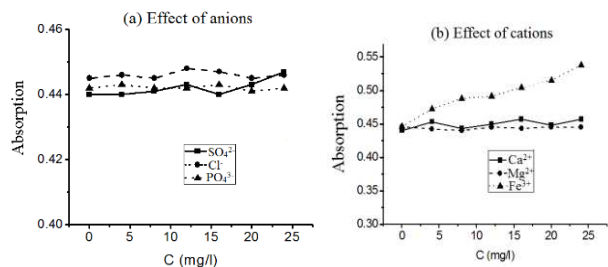


Figure 6. The effects of hindering substances

3.5. Research on calibration curves for the determination of fluoride in water

From the research results of Sections 3.1-3.4, we have found the optimal conditions for determination of fluoride in water. The optimum conditions for the determination of fluoride in water are presented in Table 4.

Table 4. Procedure for the determination of fluoride

Reagent	Flask of 50 mL														
	1	2	3	4	5	6	7	8	9	10	11	...	21		
Al ³⁺ 10 ⁻³ M	0	1 mL													
XO 10 ⁻³ M	0	1 mL													
Reaction time	Shake vigorously and wait for 5 minutes														
KNO ₃ 1M	5 mL														
Ascorbic acid 1%	2 mL														
F-50mg/l (mL)	0	0	0.08	0.1	0.2	0.4	0.6	0.8	1.0	1.1	1.3	...	2.3		
HNO ₃ pH=5	Norms to 50 mL														
Reaction time	Shake vigorously and wait for 20 minutes														

When fluoride reacts with the Al-XO complex, the red color of the solution decreases, while the yellow color of the solution increases. If we measure the red reduction at 555nm wavelength or measure the increase in yellow color intensity at 430nm, the fluoride concentration in the water will be determined. Therefore in this research, fluoride concentration was measured at both 555 nm and 430 nm.

3.5.1. Measuring optical density at 555 nm

The result of the experiment was shown in Figure 7.

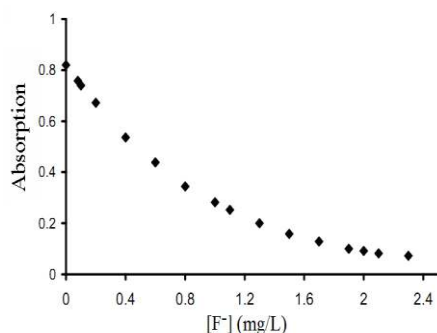
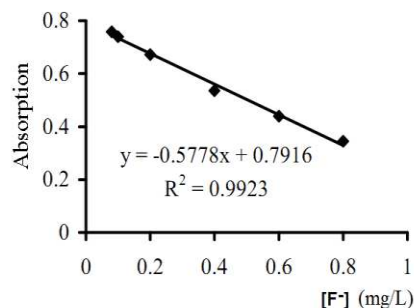


Figure 7. The correlation between the optical density and the concentration of fluoride at 555 nm

From Figure 7, we draw two calibration curve graphs as Figure 8. A new point of this article is that this is the first time the type of calibration curve graph $A = f(\log C)$ in the spectrophotometric method (where: “log” is logarithm; “C” is concentration) has been used.

(a) Calibration curve of fluoride at 555 nm (type 1)



(b) Calibration curve of fluoride at 555 nm (type 2)

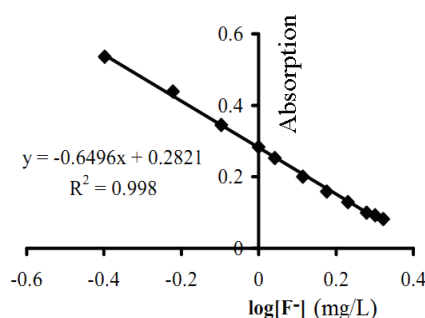


Figure 8. Two calibration curves of fluoride at 555 nm

Analyzing graph in Figure 8 (a) found that when the concentration of fluoride 0.08-0.8 mg/L, the relationship between an absorption and [F⁻] is highly linear.

To expand the quantitative limit of the method, we have developed a standard line graph form $A = f(\log [F^-])$. The result was shown in Figure 8 (b). Analyzing this graph, found that when the concentration of fluoride 0.4-2.1 mg/L, the relationship between an absorption and [F⁻] is highly linear.

Thus, if we combine the two graphs of Figure 8(a) and 8(b), the limit of quantification fluoride of proposed procedures measuring at 555 nm is 0.08 - 2.1 mg/L.

3.5.2. Measuring optical density at 430 nm

The result of the experiment was shown in Figure 9.

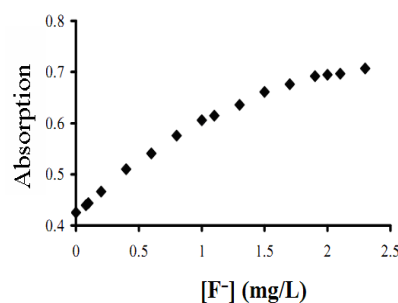


Figure 9. The correlation between the optical density and the concentration of fluoride at 430 nm

From Figure 9, we were drawing two calibration curve graphs as Figure 10.

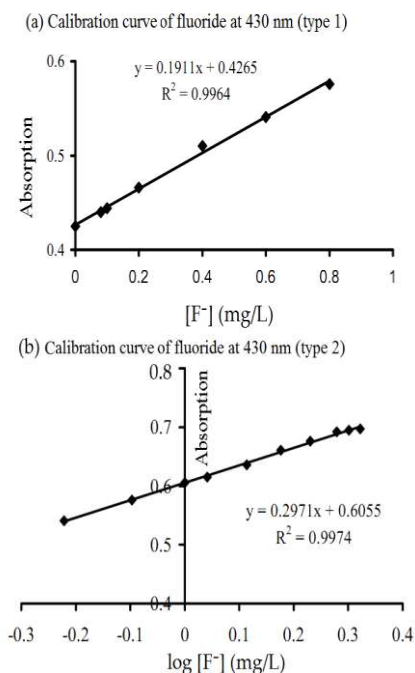


Figure 10. Two calibration curves of fluoride at 430 nm

Analyzing graph in Figure 10(a) found that when the concentration of fluoride 0.08-0.8 mg/L, the relationship between an absorption and $[F^-]$ is high linear. Analyzing graph in Figure 10(b), found that when the concentration of fluoride 0.6-2.1 mg/L, the relationship between an absorption and $[F^-]$ is high linear. Thus, if we combine the two graphs of Figure 10(a) and 10(b), the limit of quantification fluoride of proposed procedures measuring at 430 nm will be 0.08 - 2.1 mg/L.

3.6. Determining the accuracy of the method

To assess the accuracy of quantitative methods fluoride by using Al-XO complex, we conducted the experiment as Table 4. Then, we measured the optical density at 555 nm and 430 nm. The analytical results were shown in Table 5.

Table 5. Determining the accuracy of the method at 555 nm and 430 nm

Fluoride in standard samples (mg/L)	At 555 nm		At 430 nm	
	Fluoride was found (mg/L)	Recovery coefficient (%)	Fluoride was found (mg/L)	Recovery coefficient (%)
0.300	0.316 ± 0.002	105.3 ± 0.7	0.314 ± 0.002	104.6 ± 0.7
0.500	0.513 ± 0.002	102.7 ± 0.4	0.525 ± 0.002	105.0 ± 0.4
1.000	0.993 ± 0.003	99.3 ± 0.3	0.958 ± 0.002	95.8 ± 0.2
1.500	1.504 ± 0.004	100.3 ± 0.3	1.514 ± 0.003	100.9 ± 0.2
1.800	1.776 ± 0.004	98.7 ± 0.2	1.781 ± 0.004	99.0 ± 0.2

According to the principle of trace analytical methods, the error of the method can be accepted to 15%. Based on this principle and Table 5, we found that the method of determining the fluoride at the wavelength of 555 nm and 430 nm has a high recovery coefficient; the error of the analytical methods is less than 6%. This result shows that the method of quantifying fluoride by xylene orange reagent is very good.

4. Conclusions

This article has developed a new procedure for the determination of trace amounts of fluoride in water by Al-XO complex via the spectrophotometric method. We used two types of calibration graphs and measured at 2 wavelengths of 555nm or 430 nm, the results are as follows:

- When measuring at 555nm wavelength, the LOQ of the first line calibration graph is: 0.08-0.8 mg/L; The LOQ of the second-line calibration graph is: 0.4-2.1 mg/L. Combining 2 types of graphs, LOQ is in the range of 0.08-2.1 mg/L.

- When measuring at a wavelength of 430 nm, the LOQ of the first line calibration graph is: 0.08-0.8 mg/L; The LOQ of the second-line calibration graph is: 0.6-2.1 mg/L. Combining 2 types of graphs, LOQ is in the range of 0.08-2.1 mg / L.

The accuracy of fluoride analysis method at 555 nm or 430 nm is equivalent. When analyzing fluoride in the actual samples, the error of the method is less than 6%.

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