

Primary-Secondary Wavelengths Spectrophotometric Determination of Fluoride in Environment Water

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In the presence of lanthanum nitrite the reaction between fluoride and alizarine complexan at pH 4.1 was applied for the improvement of the determination of trace amounts of fluoride in environment water by primary-secondary wavelengths spectrophotometry (PSWS). Results showed that the recovery of fluoride was between 97.4 and 109% and the relative standard deviations less than 3.1% for the analysis of four water samples. In addition, the detection limit of fluoride was only 0.01 mg/L by PSWS which was one-fifth of that obtained by ordinary spectrophotometry.

INTRODUCTION

Fluoride (F) exists widely in nature, for example, surface water, mine-well water, wastewater, soil, rock, etc. At present, it is usually determined by selective electrode¹ or by spectrophotometry with alizarine complexan^{2,3}. The latter has higher sensitivity than the former but the former is simpler in operation than the latter. In this report, the reaction was studied for the improvement of determination of trace amounts of fluoride in environment water by primary-secondary wavelengths spectrophotometry (PSWS). PSWS has been applied for the determination of many micro-components^{4,5} because it may increase further the accuracy and precision of analysis of trace amounts and the calibration graph is stable. In this report, using the above reaction, such a new spectrophotometric method was applied to determine trace amounts of fluoride in environment water. Results showed that the detection limit of fluoride was only 0.01 mg/L and the recovery of fluoride was between 97.4 and 109%.

Principle

The following expression⁴ gave the main formula of primary-secondary spectrophotometric method:

$$\log \left(\frac{A_p + 1}{A_s + 1} \right) = \alpha X^\beta$$

where A_p and A_s are the absorbances of coloured solution at λ_p (named as primary wavelength often selected at peak absorption) and λ_s (named as secondary wavelength often selected at valley absorption) against reagent blank,

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respectively. Both α and β are constant and the main variable X gives indicates the color-developed substance concentration (mg/L or μg). Because of the buffer function of $(A_p + 1)/(A_s + 1)$ the above equation is considered to stabilize the effect of variable work environment on both α and β and to improve the precision and accuracy of trace analysis. In fact, this method named as primary-secondary wavelengths spectrophotometry (PSWS) is also one of the dual-wavelength methods but different from the others⁶⁻⁹.

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (made in Shanghai) in a 30 mm cell.

Standard fluoride solution, 100 mg/L: prepared by dissolving 0.2210 g of sodium fluoride (AR, Shanghai Chemicals) (after drying at 110°C for 2 h) in 1000 mL of non-ion water and storing in a plastic bottle.

Standard fluoride use solution, 2.00 mg/L: prepared by diluting the above solution.

Acetone (AR, Beijing Reagents).

Alizarine solution was prepared as follows: Weighed 0.1930 g of alizarine complexan (Shanghai Reagents) taken in a 500-mL volumetric flask. Added 5 mL of non-ion water and then dropped 1 mol/L sodium hydroxide to dissolve alizarine. Added 0.125 g of sodium acetate (AR, Shanghai Chemicals) and adjusted pH to 5 by 1 mol/L hydrochloric acid. Finally, this solution was diluted to 500 mL with non-ion water.

Lanthanum nitrate solution was prepared according to the following procedure. Dissolved 0.433 g of lanthanum nitrate (AR, Shanghai Chemicals) in 5 mL of 1 mol/L hydrochloric acid. Adjusted pH to 4.1 with 1 mol/L sodium hydroxide. Finally diluted to 1000 mL with non-ion water.

Buffer solution, pH 4.1 was prepared as follows: Dissolved 35 g of sodium acetate in 800 mL of non-ion water and added 75 mL of acetic acid (A.R., Shanghai Reagents) Diluted this solution to 1000 mL and adjusted pH 4.1 with acetic acid solution and sodium hydroxide solution.

Chromogenic agent solution was prepared as follows: Mixed 30 mL of alizarine solution, 10 mL of acetone, 30 mL of pH 4.1 buffer solution and 30 mL of lanthanum nitrate solution.

Recommended procedure: A known volume of a sample containing less than 16 μg of fluoride was taken in a 25 mL volumetric flask. Added 10 mL of chromogenic agent solution. Diluted to volume and mixed well. After 40 min, measured the absorbances at 650 nm, respectively, against reagent blank.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectrum of the above fluoride reacted solution is shown in Fig. 1. Because the absorption peak of this solution was located at 620 nm such a wavelength was selected as primary wavelength. The secondary wavelength was often selected at half-peak absorption point. *i.e.*, $\lambda_s = 650$ nm.

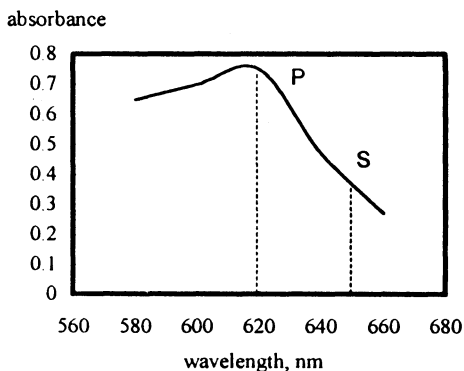


Fig. 1. Absorption of fluoride reacted solution in acidic solution: P, 620 nm; S, 650 nm

Effect of chromogenic agent concentration: Fig. 2 gives the effect curve of the addition of chromogenic agent solution. It was found that the factor y values remained constant and maximal when the addition was more than 8 mL. Therefore, 10 mL of chromogenic agent solution was added in this study.

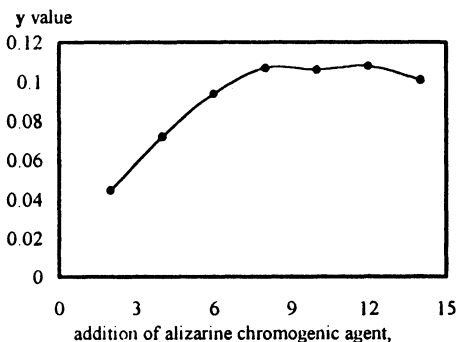


Fig. 2. Effect of the addition of chromogenic agent solution

Calibration graph: A series of standard fluoride solutions were prepared and the absorbance of each was measured and plotted. Curves $y-x$ and $\lg y-\lg x$ were drawn in Fig. 3. Curve 2 is highly linear. The calibration equation was developed from curve 2 as follows: $y = 0.0136x^{0.835}$.

Effect of foreign ions: Once the recommended procedure was carried out, none of the following ions were found to affect the direct determination of $50 \mu\text{g}$ of fluoride (< 20% error): 1 mg of Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Ca(II) , Mg(II) ; 0.1 mg PO_4^{3-} , Pb(II) , Mn(II) , Zn(II) , Cu(II) , Cr(III) ; 0.01 mg of Zn(II) , Hg(II) , Fe(II) , Ag(I) and 0.002 mg of Al(III) , Ni(II) , Co(II) . For analysis of wastewater, the co-existing metal ions must be removed before measurement.

Precision and detection limit: Six replicate determinations of standard V

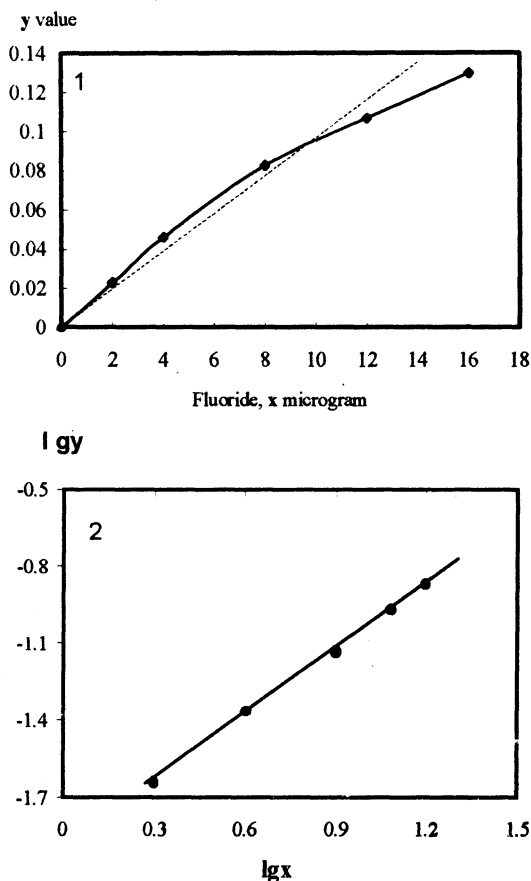


Fig. 3. Standard curve for determination of fluoride: 1. $y(x)$; 2. $\lg y (\lg x)$

solutions containing 2.00 and 15.0 μg of fluoride were carried out, the relative deviations (RSDs) being 1.6% and 0.7%, respectively. However, the RSDs obtained by the single wavelength spectrophotometry were 3.1 and 1.3%. The precision for PSWS was therefore better than that for ordinary spectrophotometry.

We used $L_{\min} = kS_b/S$ to calculate the detection limit of fluoride by PSWS, because the constant $k = 3$ and the sensitivity factor $S = 0.0136$ described in the above equation. The factor, S_b indicates the standard deviation of 20 replicate determinations of reagent blanks and it was determined and calculated to be 0.0005. Therefore, L_{\min} of fluoride was computed to be only 0.01 mg/L for analysis of 10.0 mL of water.

Samples analyzed: As a test of the method, trace of fluoride in natural water was determined. The results are listed in Table-1. Each of the averages obtained by PSWS (method 1) was found to be in accordance with the conventional method (method 2, reference 1). The recovery rate of fluoride was between 97.4 and 109% and the relative standards less than 3.1%.

TABLE-1
THE DETERMINATION OF FLUORIDE IN WATER

Unit: mg F/L

Sample	Method 2 (average of 3 determinations)	Method 1		
		Added	Found	Recovery, %
Underground water	0.5676	0	0.576 0.568 0.580 0.571 0.571 0.559	103
		0.500	1.08 1.09	
Drinking water	0.382	0	0.381 0.361 0.377 0.354 0.382 0.366	97.4
		0.200	0.559 0.571	
River water	2.18	0	2.19 2.18 2.06 2.21 2.14 2.09	101
		2.00	4.17 4.15	
Lake water	1.01	0	1.02 1.11 1.06 0.99 1.01 1.08	109
		1.00	2.14 2.20 2.06	

REFERENCES

1. M.S. Frant and J.W. Ross, *Anal. Chem.*, **40**, 1169 (1968).
2. R. Relcher and T.S. Wast, *Talanta*, **8**, 863 (1961).
3. The Fluorine Sub-committee of Analytical Methods Committee of the S.A.C., *Analyst*, **96**, 384 (1971).
4. H.W. Gao, *Asian J. Chem.*, **11**, 869 (1999).
5. ———, *Huanjing Kexue*, **2**, 80 (1993).
6. ———, *Asian J. Chem.*, **11**, 319 (1999).
7. ———, *Chem. J. Arm.*, **50**, 42 (1997).
8. H. Watanabe and H. Ohmori, *Talanta*, **26**, 959 (1979).
9. Y.L. Zhu, S.L. Li and J.X. Shao, *Fenxi Huaxue*, **19**, 162 (1991).

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