

Indirect Colorimetric Estimation of Fluoride Ion in Water and Pharmaceutical Preparation Samples

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ABSTRACT

An indirect method for the estimation of fluoride ion has been developed. The method is based on the bleaching action of fluoride ion on the color of Ti (IV) with 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthanic acid (HHSNNA) complex with proportional decrease of absorbance. Therefore, the decrease in color intensity is proportional to the concentration of fluoride ion. Molar absorptivity is $0.1166 \times 10^4 \text{ l. mol}^{-1} \cdot \text{cm}^{-1}$ at wavelength 685 nm. Beer's law is obeyed over the concentration range of 0.2-4 $\mu\text{g/ml}$. The proposed method is applied successfully to determine fluoride ion in different real water samples and pharmaceutical preparations (Tablets). The proposed method is compared favorably with Eriochrome cyanine R – Zirconium method.

Keywords: fluoride ion, pharmaceutical preparations, water samples.

HHSNNA-

/ (4-0.2)

685

$\text{l}^{-1} \cdot \text{cm}^{-1}$

0.1166×10^4

INTRODUCTION

Availability of adequate fluoride confers significant resistance to dental caries. It is now believed that the topical action of fluoride on enamel and plaque is more important than the systemic effect (British National Formulary, 2016). Fluoride is very much essential for healthy growth of teeth and bones if it present between 0.6 and 1.5 ppm in drinking water, but if the level is higher than 1.5 ppm, it causes dental and skeletal fluorosis, decalcification, and nervous disorder, but with less than 0.6 ppm, bones and teeth will be fragile (Martindale, 2009; Dutta *et al.*, 2010). According to WHO guideline, maximum concentration level of fluoride in drinking water is 1.5 mg/l. Also the optimal fluoride range is considered to be between 0.7-1.2 mg/l. The range is based on average ambient air temperature of 50 to 90 F° (WHO, 2004). The lethal dose for adults is 0.2-0.35 gm F⁻ per kg body weight. Fluoride is widely used in various branches of industry (Tokalioglu *et al.*, 2004). Fluorides are released into the environment naturally through the weathering of minerals, industrial products, and phosphate fertilizer (Okibe *et al.*, 2010). The methods for the determination of fluoride fall into three principle groups: classical titrimetric (United States

Pharmacopeia, 2018) and spectrophotometric (Barghouthi and Amereih, 2012; Farajzadeh, 2004; Lida *et al.*, 2013). The potentiometric methods (Tokalioglu *et al.*, 2004) are most widely used for the determination of fluoride, but they are not so good in low level fluoride samples (Dutta *et al.*, 2010). Therefore, the use of spectrophotometry is still investigated. Spectrophotometric methods can be classified into two categories; Direct methods based on mixed ligand complex formation (Okibe *et al.*, 2010) and indirect methods based on substitution of colored complexes with F⁻ (Javad *et al.*, 2009; Suresha *et al.*, 2006). In this work, the reaction between Titanium (IV) and HHSNNA is used for the determination of fluoride in real water samples and pharmaceutical preparations.

EXPERIMENTAL

Apparatus

A Genway 6405 UV / visible spectrophotometer with 1.0 cm quartz cells and Genway 3310 pH meter were used.

Reagents

All chemicals used are of analytical or pharmaceutical grades. All glassware was soaked in nitric acid for 24 hrs, rinsed with distilled water before use.

Titanium Stock Solution (100)ppm

This solution is prepared by fusing 0.167 g of TiO₂ with 1.5 g of K₂S₂O₇. The melt after powdering was extracted by cold dilute (0.1 N) H₂SO₄ and diluted to 1 liter by dilute H₂SO₄. (Vogel, 1974)

Titanium Working Solution (10)ppm

This solution is prepared by diluting 10 ml of stock solution to 100ml with dilute H₂SO₄ in a volumetric flask.

HHSNNA Reagent Solution

This solution is prepared by dissolving 0.035gm of the compound in 25ml ethanol and complete to 100 ml with distilled water in a volumetric flask.

Acetate Buffer Solution (pH 4.5)

This solution is prepared by dissolving 6.3 g of anhydrous sodium acetate in a suitable amount of water; add 9.0ml of acetic acid (100) and water to make 100 ml. (Japanese Pharmacopoeia, 2016)

Fluoride Stock Solution (100ppm)

This solution is prepared by dissolving 0.221g of sodium fluoride (previously ignited at 400 C⁰) in 1 liter distilled water. All fluoride solutions were stored in polyethylene containers (Marczenko, 2000; Suresha *et al.*, 2006).

Fluoride Standard Solution (10ppm)

This solution is prepared by diluting 10 ml of stock solution to 100ml with distilled water in a volumetric flask.

Recommended Procedure

A 7ml of 10 µg/ml titanium solution is transferred into a 25 ml calibrated flask followed by addition of 3 ml of pH 4.5 buffer solution and aliquots of sample solution containing 5-100 µg of fluoride, then followed by 5 ml of HHSNNA solution. Dilute to volume with distilled water, mixed well and allow to stand for 5 minutes at room temperature. Measure the absorbance at 685 nm against a reagent blank containing no titanium and fluoride.

Sampling

Drinking water samples are taken from different provinces in Mosul -Iraq and Zim-Zim (abundant, copious) water samples from Saudi Arabia. After the water samples were transported to the laboratory, fluoride analyses were performed immediately.

Determination of Fluoride in Water Samples

10.0 ml sample was taken and, fluoride concentrations of all samples were determined in duplicate using recommended procedure and Eriochrome cyanine R – Zirconium (Marczenko, 2000).

Determination of Fluoride Tablets (Sinaflor and Zymafluor)

Two different types of sodium fluoride tablets, provided from local markets were selected for analysis, to minimize a possible variation in the composition of the tablet, the mixed content of 10 tablets were weighed and grounded, then the powder equivalent to 1 mg of fluoride is weighed into 100ml volumetric flask containing about 75 ml of distilled water. It was shaken thoroughly for about 20-25 minutes, filtered through a whatman filter paper No. 40 to remove the insoluble matter and diluted to the mark with distilled water. Treat 10 ml of this solution as mentioned under recommended procedure and Eriochrome cyanine R – Zirconium (Marczenko, 2000).

RESULTS AND DISCUSSIONS

Fluoride ion forms stable complexes with titanium (IV). Therefore, it is required to develop sensitive determination methods of fluoride ion. The reaction of titanium with HHSNNA has been investigated and the results indicated that the mole ratio of titanium to HHSNNA is 1:2 complex. This reaction has been used for the determination of titanium spectrophotometrically in aqueous solution of pH 4.5 at 685nm (Ahmad, 2002). This method was adopted for determination of fluoride through measurement of the quantitative decrease in the absorbance of the Ti-HHSNNA complex (bleaching the color of the complex), at 685 nm Fig. (1).

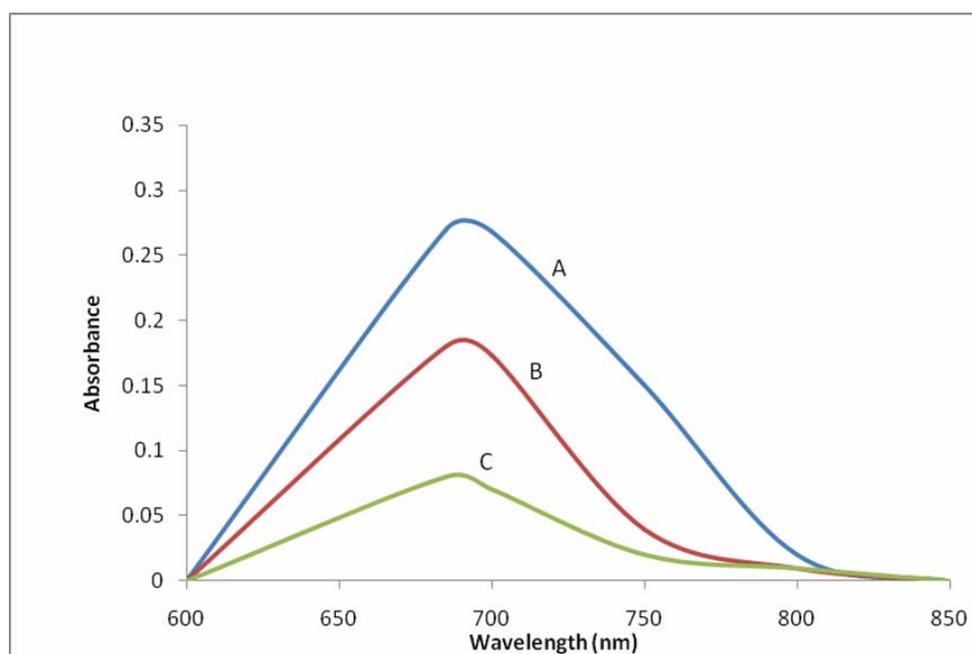


Fig. 1: Absorption spectra of A: Ti-HHSNNA complex (70 μ g Ti) against blank. B: Ti-HHSNNA complex (70 μ g Ti +25 μ g fluoride) against blank. C: Ti-HHSNNA complex (70 μ g Ti +75 μ g fluoride) against blank

Employing the conditions described in the recommended procedure, a linear calibration graph of fluoride was obtained Fig. (2), which shows that Beer's law is obeyed over the concentration range 0. 2-4 μ g/ml with R^2 of 0.9987, intercept of 0.0001 and slope of 0.0614. The conditional molar absorptivity of the product formed and sandell's sensitivity was found to be 0.1166×10^4 $\text{l.mol}^{-1}.\text{cm}^{-1}$ and $0.016 \mu\text{g}/\text{cm}^2$ respectively.

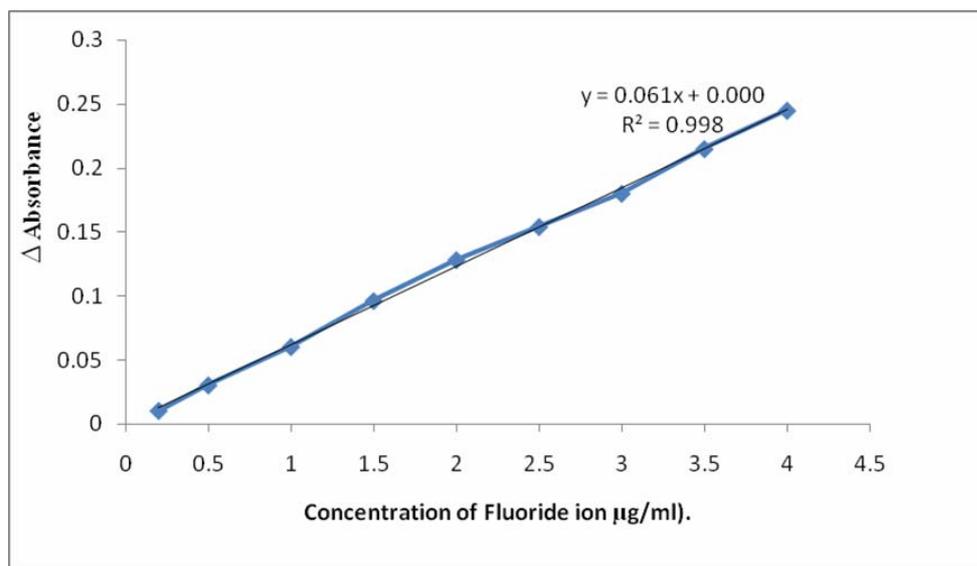


Fig. 2: Calibration graph of fluoride ion determination.

The accuracy and precision of the method are established by analyzing the pure fluoride solution at three different levels. The average recovery which is a measure of accuracy is 100 ± 0.95 revealing high accuracy of the method. The relative standard deviation (RSD), which is an indicator of precision is better than $\pm 2\%$. The results are compiled in (Table 1).

Table 1: Optical characteristics and statistical data for regression equation of the proposed method

| Parameters | Value |
|--|----------------------|
| λ max (nm) | 685 |
| Beer's law limit ($\mu\text{g} \cdot \text{ml}^{-1}$) | 0.2- 4 |
| Molar absorptivity ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) | 0.1166×10^4 |
| Determination coefficient (R^2) | 0.9987 |
| Regression equation ($Y = a \times + b$) | |
| Slope (a) | 0.0614 |
| Intercept (b) | 0.0001 |
| Recovery % | 100 ± 0.95 |
| Relative standard deviation (%) | $< \pm 2$ |

Application of real samples

To evaluate the efficiency of the proposed method, it was used in determining of fluoride content of three water samples and their fluoride content were analyzed by the proposed method. The results were also compared statistically by student t-test with those obtained by Eriochrome cyanine R – Zirconium method, at 95% confidence level. The calculated t- values did not exceed the theoretical values indicating that there was no significant differences between the precision of the proposed and literature method as cited in (Table 2).

Table 2 : Determination of fluoride ion in water samples

| Sample | Amount of fluoride $\mu\text{g/ml}$ *t-value | |
|----------------------------------|--|--------------------------------|
| | Proposed method | Eriochrome cyanine R-Zirconium |
| Tap water | 0.66 | 0.67 1.18 |
| Zim-Zim(abundant, copious) water | 0.99 | 0.981.2 |
| Bottled water (Life) | | 1.421.44 1.56 |

*Average of ten determinations.

T values (n=10, at 95% confidence level tabulated value 2.262).

For the determination of fluoride in pharmaceutical preparation (tablets) the results of the assay of the pharmaceutical preparations revealed that there is a close agreement between the results obtained by the proposed method, Eriochrome cyanine R-Zirconium method and the label claim (Table 3).

Table 3: Determination of fluoride ion in pharmaceutical preparation (tablets)

| Pharmaceutical formulations (Tablets) | Amount of fluoride $\mu\text{g/ml}$ * | |
|---|--|-------------|
| | Proposed-Eriochrome cyanine R-Zirconium-Method | |
| 1-Sinaflor tablets [Avicenna. Prod. Damascus-Syria] 0.45mg/tab | 0.448mg/tab | 0.449mg/tab |
| 2-Zymaflor tablets [Rottapharm. Paris-France] 0.5mg/tab | 0.504 mg/tab | 0.497mg/tab |

*Average of ten determinations.

Application of the Proposed Method to Content Uniformity

Content uniformity or the uniformity of dosage unit was defined as the degree of uniformity in the amount of active substance among dosage units (Ahmad, 2017). The proposed method proved to be suitable for the content uniformity test, where a great number of assays on individual tablets are required. Data presented in (Table 4) indicate that the proposed method can determine accurately and precisely quantities Fluoride (0.45mg) in its commercially available tablets. The mean percentage (with RSD%) of the labeled claim found in ten tablets was (1.8%) which falls within the content uniformity limits specified by the USP 33 (United State Pharmacopeia, 2010).

Table 4: Content uniformity testing of fluoride tablets by the proposed method

| Parameter | % of the label claim |
|-----------------------------------|----------------------|
| Mean(X) of ten individual tablets | 99.55 |
| % RSD | 1.8% |
| Max. allowed unit (USP.2010) | $\pm 15\%$ |

CONCLUSION

In this work, simple and precise indirect colorimetric method is developed and validated for the determination of fluoride ion in pharmaceutical preparations (tablet) and different water samples. The method does not need heating or solvent extraction step. The method relies on the use of simple and cheap chemicals and techniques and can be used for routine determination and quality control of fluoride ion.

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