

Selective spectrophotometric determination of fluoride in water samples using an Alizarin red S complex as a colored reagent

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Abstract

A simple, selective and sensitive spectrophotometric determination of fluoride in water samples has been developed using Alizarin red S-ZrOCl₂ yellow colored complex. The method is based on the reaction of fluoride with the coloured complex. This method produces colourless complex resulting in the release of free ligands. The relationship of the reaction of fluoride with the complex is sixth-order polynomial function. The reaction reaches equilibrium at fluoride concentration of 0.054 mM. Beer-Lambert law is obeyed in the range 0.0 - 0.024 mM of fluoride (0.0 - 1.0 mg·L⁻¹). The molar absorptivity at 502 nm is 6.45 × 10³ L·mol⁻¹·cm⁻¹. The method was applied to determine the fluoride level under optimum conditions (pH 4.0, 25 °C). The recovery of fluoride in the range of 98.0-99.0% (SD: 1.12%) was successfully performed. The detection limit and quantitation limit were found to be 0.07 mg·L⁻¹ and 0.2 mg·L⁻¹ respectively. The proposed method was applied to determine trace amount of fluoride content in various water samples.

Keywords : Fluoride; drinking water, Spectrophotometric Method, Alizarin red S complex

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1. Introduction

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Fluoride (F⁻) occurs in almost all waters from trace to high concentration ¹. It has been shown to cause significant effects in humans through drinking water. WHO has set a limit value of 1.5 mg ℓ⁻¹ for fluoride in drinking water². There is a narrow margin between the desired and harmful doses of fluoride in drinking water ³. There is a narrow margin between the desired and harmful doses of fluoride ⁴. Low concentration of fluoride in drinking water has been considered beneficial as it prevents dental caries ⁵. WHO has set a limit value of 1.5 mg L⁻¹ for fluoride in drinking water ⁶. This necessitates the developing of an accurate, simple, rapid and cost effective analytical method for detection of fluoride in water. Spectrophotometric methods, which are widely used in the determination of fluoride, are based on the reaction of fluoride with coloured metal chelate complexes, producing either a mixed-ligand ternary complex or replacement of the ligand by fluoride to give a colourless metal-fluoride complex and the free ligand with a colour different from that of the metal-ligand complex ⁷. Fluorine, unlike sulphur, nitrogen, and even chlorine, is not an essential element for plants. Because the natural occurrence of F in the air is usually close to the detection limit, and plants take up little from the soil, the background concentration in plants is generally quite low (often as low as 1 and usually less than 10µg F/g dry weight in most species) ⁸. Triphenylmethane (TPM) dyes of most value today are those with auxochromic and bathochromic groups like amino and hydroxyl in para position to the methane carbon ⁹. TPM dyes with groups capable of holding metals in stable combination, such as eriochrome cyanine R and azurol S, have been used successfully as spectrophotometric reagents for fluoride determination¹⁰. TPM dyes absorb strongly in the visible region to produce intense, brilliant shades of red, violet, blue, and green.

Alizarin Red S (1,2-dihydroxy-9,10-anthra-quinone sulfonic acid sodium salt) is a water-soluble, widely used anthraquinone dye. It is synthesized by sulfonation of alizarin which is a natural dye obtained from madder (*Rubiatinctorum*, L. *Rubiaceae*). In clinical practices, it is also used to stain synovial fluid to assess detect basic calcium phosphate

crystals. Spectrophotometric procedures have received considerable attention for quantitative determination of many organic compounds of pharmaceutical interest employing many dyes including alizarin red S. The present study is aimed developing spectrophotometric method for determination of fluoride in different water samples using Alizarin red S-ZrOCl₂ yellow colored complex with fluoride ions.

2. Experimental

2.1. Apparatus

Hitachi U-1500 UV/V is single beam spectrophotometer with 1.0 cm quartz cells. It was used for the absorbance measurements. Orion's Portable 210 a pH Meter with Orion Triode electrode was employed for the pH measurements.

2.2. Reagents and solutions

Alizarin red S and Zirconyl chloride octahydrate, provided by Sigma Aldrich, were used without any further purification. All the chemicals were of analytical reagent grade except where stated otherwise. Solutions were prepared using double distilled water. Standard fluoride stock solution was prepared by dissolving 0.1382 g of sodium fluoride provided by Merck in 250 ml water. The stock solution was further diluted as needed. SPADNS (0.958 g) was dissolved in 100 mL of distilled water and diluted to 500 mL. This solution is stable indefinitely if protected from direct sunlight. Zirconyl chloride octahydrate (0.133 g) was dissolved in 25 mL of distilled water and concentrated hydrochloric acid (IR grade) was added to it. The mixture was then diluted with water to increase the volume 500 mL.

2.3. Preparing of the Metal Complexes Solutions

Job's method of continuous variation was adopted for determination of the composition of the coloured complex [16]. Zirconium to ligand ratio was also studied by making comparison between the spectra of complexes of different metal to ligand ratios such as 1:1, 1:2, 1:3, 2:1, 3:1, 2:3, and 3:2. The blank was prepared by the same procedure using the solvent instead of the Zirconium ion solution. Zirconium to ligand ratio was found to be 1:2 (data not included).

The complex solutions for the spectrophotometric measurements were prepared by mixing zirconium, alizarin red S (1:2) ratio of 5×10^{-3} M of zirconium and 5×10^{-3} M of alizarin red S in ethanol solution, which was then diluted to (2×10^{-4} M) that is suitable for the spectrophotometric measurements. The stability of the complex in ethanol solution was examined for two weeks, the complex was found to be stable .

2.4. Reaction of fluoride with the prepared complexes solutions

Various amounts of fluoride were added in the range of 0.2-2.0 $\text{mg} \cdot \text{L}^{-1}$ to zirconium 1:2 complex solution of Alizarin red S in ethanol (2×10^{-4} M, 24.5 ml). The absorbance was measured at the wavelength of the maximum difference between the absorption spectra of the complex and the ligand which was 620 nm.

2.5. Determination of fluoride in water samples

The study area is located in southeastern part of Anantapur District of Andhra Pradesh and lies between longitudes $77^{\circ} 30'$ – $78^{\circ} 15'$ East and latitudes $14^{\circ} 0'$ – $14^{\circ} 30'$ North, and falls in the Survey of India topo sheets 57 F/14, F/15, J/3, J/4 as shown in Figure1. The study area mainly contains peninsular gneisses of Archean age consisting of pink granites, schists and composite gneisses of Dharwar age, intruded by a few younger pegmatite dykes and numerous dolerite dykes and the possible diamondiferous volcanic pipes. The geological map of the study area is shown in the Figure2. Geomorphic features of the study area include denudational hills, dissected pedimonts, pediplain and flood plain. The climate is semi arid with mean monthly temperatures of January and May reaching 15°C and 39°C respectively. The normal rainfall of the Anantapur District is 553 mm that recorded the lowest rainfall compared to other parts of Rayalaseema in Andhra Pradesh. The samples were collected from bore wells which were extensively used for drinking and other domestic purposes. The samples were collected in pre-cleaned and sterilized polyethylene bottles of two litres capacity. The depth of the bore wells varied between 250 and 700 feet. Figure 1 shows Location of Kadiri, Mudigubba and Nallamada Mandals of Anantapur District,

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Andhra Pradesh, India .The District is underlain by granite gneisses and schists of the Archaean age. The NE part of the district is covered by consolidated sedimentary formation of Cuddapah Super Group. Geologies have estimated Precambrian and that its age fallen between the Paleozoic Age. River alluvium occurs essentially along major river courses and to some extent along minor streams. The Archaean crystalline rocks include granites, gneisses and Dharwarian schists. The ground water in these formations occurs in the weathered and fractured zones under water table and semi-confined conditions. These rock types do not possess primary porosity. Due to fractures and weathering, they have developed secondary porosity often giving rise to potential aquifers at depth. The degree of weathering in the Archaean formation is less than 20 m. This weathered zone has been tapped extensively by dugwells and bore wells, which invariably tap the fractures occurring below the weathered zone. Ground water occurring in these formations is generally digging and using bore wells. The depth of open wells ranges from 6.0 to 25.0 m below ground level and depth to water level varies from 1.5 to 23 m bgl. The yield of dug wells varies from 10-200 cm/day for a pumping period of 3 to 6 hrs/day. The sample was collected in June 2014 from a ground water well in Anantapur District, Andhra Pradesh, India. Fluoride was analysed spectrophotometrically using SPADNS as fluoride reagent and ELICO UV - VISIBLE SL244 Double beam spectrophotometre .

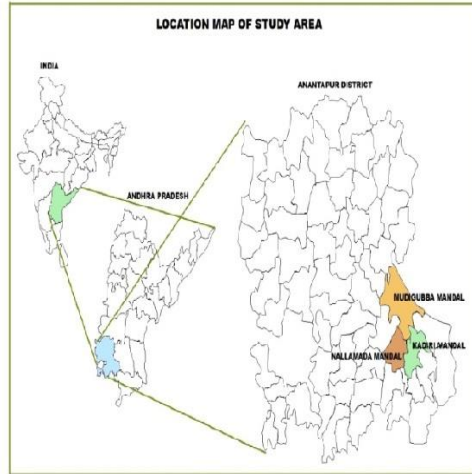


Figure - 1 Location map of Kadiri, Mudigubba and Nallamada Mandals of Anantapur District, Andhra Pradesh.

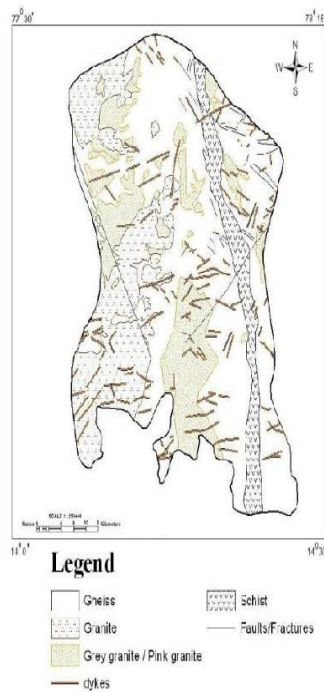


Figure - 2. Geological map of Kadiri and Nallamada Mandalas of Anantapur District, Andhra Pradesh, India

3. Results and Discussion

3.1. Alizarin red S and its Zirconium Complexes

Alizarin red S is soluble in ethanol ($20 \text{ mg}\cdot\text{mL}^{-1}$), methanol, acetic acid, acetone and slightly soluble in ether. Alizarin red S exhibits the molar absorptivity at $4.91 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ respectively (Figure 3.). The obtained results from applying of Job's method of continuous variation indicated that zirconium to Alizarin red S complex ratio is 1:2. The ratio was also determined spectrophotometrically by comparing the spectra of Zr (IV) Alizarin red S yellow complexes of different ratios with each other's. A possible structure for the complex is given in Figure 4.

The complex exhibits brown colour in ethanol solution and has one band in the visible region at 510 nm where the molar absorptivity is $6.45 \pm 0.22] \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Thus, there is hypsochromic shift (decrease in the wavelength) of about 115 nm after complexation with Zr(IV). This is results in the ligand changing the colour from red to yellow of the complex of yellow. Alizarin red S displays two bands in the visible region at **496 and 591** nm while its zirconium complex exhibits some band at 483 nm in water solutions. Therefore, using of water instead of ethanol as a solvent results in a hypsochromic shift in the absorption spectra of the Alizarin red S ligand and its zirconium complex of about **26 and 19** nm, respectively. Thus, the solvent has a negative solvatochromism effect on the spectra of both the ligand and its zirconium complex where increasing of the polarity of the solvent, as we move from ethanol to water, leads to a hypsochromic shift (a decrease in the wavelength). The difference in the absorption spectra between the complex and the ligand is bigger in ethanol than in water solution. This is due to the polarity of water and its ability to form hydrogen bonds in comparison with ethanol. This leads to destabilization of the excited state . This will be less polar than the ground state . Therefore the effect of fluoride on the absorption spectra of the complex was examined in ethanol solution

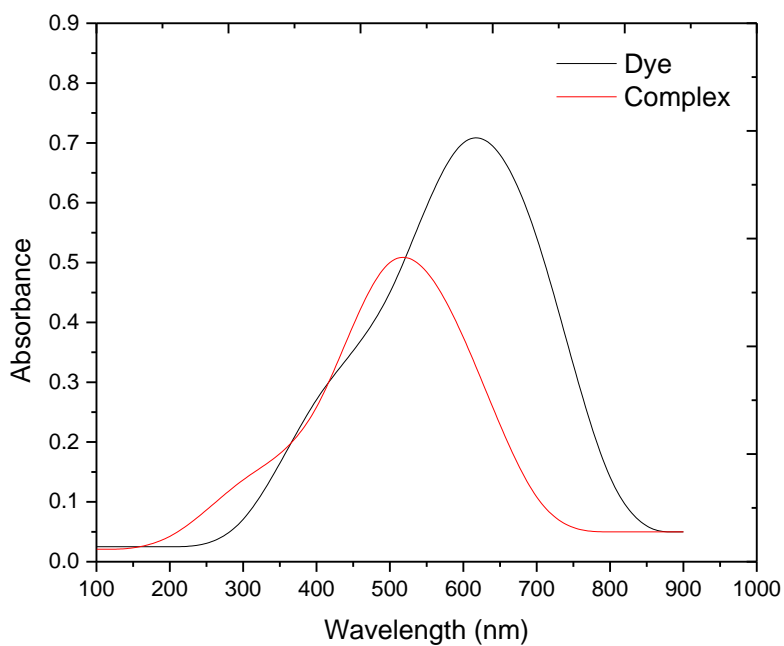


Figure - 3 Electronic spectra of Alizarin red S complex and its zirconium 1:2 complex in ethanol at 2×10^{-4} M.

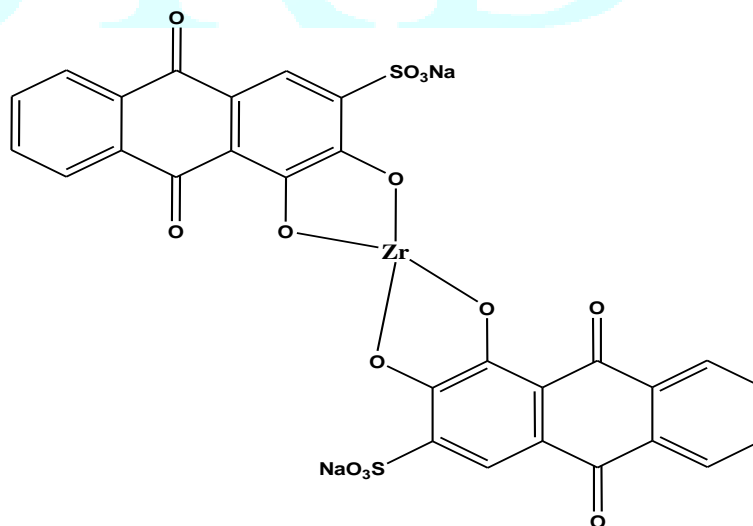


Figure - 4 Possible structure for zirconium Alizarin red S 1:2 complex.

3.2. Reaction of Fluoride with the Alizarin red S Complex

Fluoride reacts with the zirconium Alizarin red S blue 1:2 complex to produce a colourless zirconium fluoride complex by replacement of the Alizarin red S by fluoride and

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liberating of the free ligand. This is results in a change in the colour from brown to red. The colour of the free ligand according to the equation below. Zirconium reacts with fluoride to give compounds of the nature of $(ZrF_6)^{3-}$ or $[ZrF_y(OH)_{6-y}]^{3-}$ (see the Figure 5.).

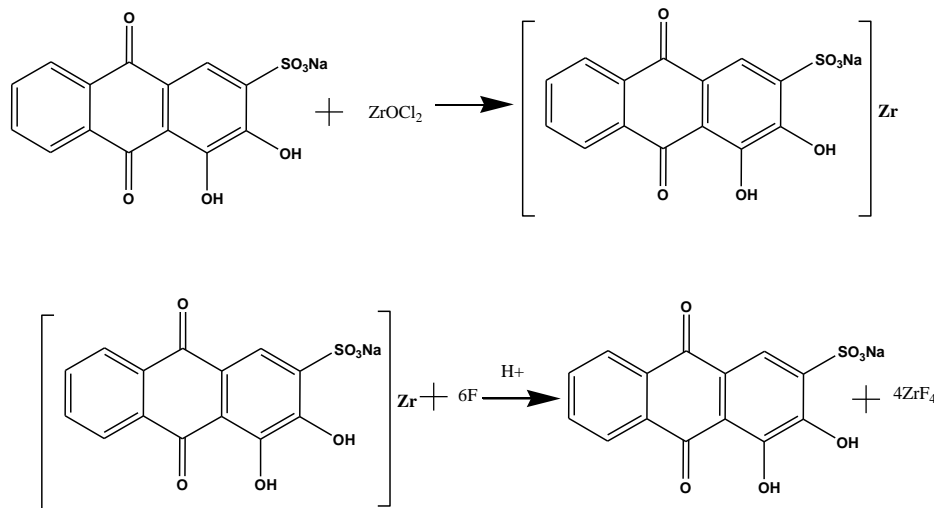


Figure - 5. Reactions involved in the method for estimation of fluoride

Fluoride interacts with complex under investigation to cause an increase in absorbance at 624 nm due to the releasing of the free ligand. The absorbance of the released free ligand is related linearly at 624 nm to the concentration of fluoride in the range 0.0 to 0.024 mM (0.0 to 1.0 mg·L⁻¹) (Figure 6). The squared correlation coefficient R², is 0.993, and the equation of the linear calibration curve is($y = 0.3567x + 0.2773$). The relationship of the reaction of fluoride with zirconium Alizarin red S 1:2 complex was best described by a sixth-order polynomial function (Figure 7), where the squared correlation coefficient R² is 0.9982. The reaction reaches equilibrium at fluoride concentration of 0.054 mM (≈2.27 mg·L⁻¹). The equilibrium constant (K_{eq}) was calculated from the equilibrium equation given below as 1.12×10³⁴. The large value for K_{eq} indicates that the equilibrium lies far to the right.

$$K_{eq} = [(ZrF_6)^{3-}] [Alizarin Red S]^2 / [Zr(Alizarin red S)_2] [F^-]^6$$

Where: [Alizarin red S] is measured using the molar absorptivity for Alizarin red S, which was found to be $[5.67 \pm 0.07] \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 624 nm, and the absorbance at the

equilibrium;

$[Zr (Alizarin Red S)_2]$ is

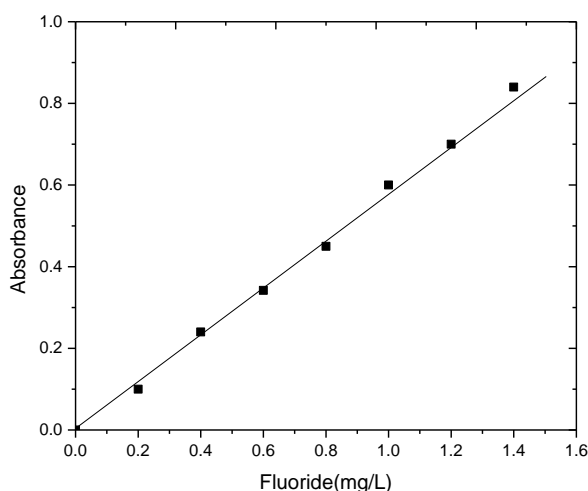
$[Zr(Alizarin red S)_2]_{initial} - \frac{1}{2}[Alizarin red]$

$[(ZrF_6)^{-3}]$ is $\frac{1}{2}[Alizarin red S]$ and

$[F^-]$ is $[F^-]_{initial} - [(ZrF_6)^{-3}]$

Figures 3 and 4 show that zirconium Alizarin red S complex is suitable for determination of fluoride in the range of 0.2 to 1.0 mg·L⁻¹. The sensitivity, detection limit, limit of quantification, percentage recovery of fluoride in real water sample, and the percentage recovery of 0.70, 1.2, and 2.0 mg·L⁻¹ fluoride of the zirconium Alizarin red S for the spectrophotometric determination of fluoride at 624 nm are given in (Table 2) and experimental parameters are given in (Table 1).

Figure - 6 Calibration curve for determination of fluoride in the range (0.0 - 1.0) mg·L⁻¹ at 624 nm by Alizarin red S zirconium complex of 2.0×10⁻⁴ M.



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Figure - 7 Absorbance of zirconium Alizarin red S 1:2 complex of 2.0×10^{-4} M versus fluoride concentration in the range 0.0 -0.119 mM at 624 nm.

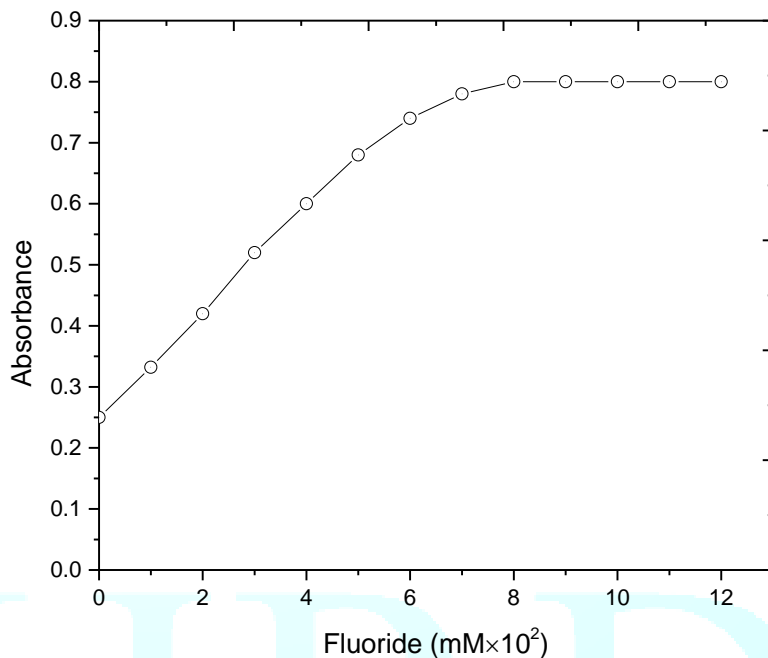


Table- 1 Parameters of the experimental procedure

Parameters	Values at 624 nm
Sensitivity [$\mu\text{g}\cdot\text{mL}^{-1}$]	0.357 ± 0.005
Detection limit [$\text{mg}\cdot\text{L}^{-1}$]	0.07
Quantification limit [$\text{mg}\cdot\text{L}^{-1}$]	0.2
Linear range/ g mL^{-1}	0.1- 0.4
pH	5.5 - 6.2
Recovery range	99.60-99.98

Table - 2 Determination of fluoride in water samples

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Source	Area	pH	Flouride (mg L ⁻¹)
Sample 1	Kadiri	7.30	0.19
Sample 2	Mudigubba	7.20	0.55
Sample 3	Nallamada	7.89	0.31

The sensitivity was taken as the average of the slope of the calibration curve for five replicates. The detection limit and the limit of quantification were calculated as (3.3 σ/S) and (10 σ/S) respectively, where σ is the standard deviation of response and S is the slope of the calibration curve. The recovery was measured as the average of 10 replicate. The recovery of high fluoride concentration such as 1.5, and 2.0 mg·L⁻¹ fluoride was calculated by measuring the absorbance for the diluted solutions. The interference studies were done by measuring the influence of the anions such as chloride, nitrate, and sulphate in such concentration commonly found in the natural water on the determination of 1.0 mg·L⁻¹ fluoride. Chloride and nitrate which were added in the range of 100 – 500 and 5 - 100 mg·L⁻¹ respectively do not interfere with the determination of fluoride. Sulphate interferes with the most visual and photometric methods for determination of fluoride by its competition with fluoride to form a complex with the metal and therefore it results in higher concentrations. In the present work, sulphate up to 100mg·L⁻¹ does not interfere with the determination of fluoride. However, at higher concentration, sulphate interferes with determination of fluoride by causing a positive error of about 25%. This error can be overcome by precipitating sulphate in the cold by the addition of aqueous barium chloride solution and aqueous agar-agar solution. Then the precipitate should be separated by filtration. The results are tabulated in (Table 5).

Table -5 Tolerance limits of foreign ions .

Foreign ions	Tolerance limit (mg L ⁻¹)
NO ₃ ⁻ , Cl ⁻ , NO ₃ ⁻	1.0
Cl ⁻ , NO ₃ ⁻	100 – 500 and 5 - 100
SO ₄ ⁻²	100
Mn ²⁺ , Mo(VI), Cr ³⁺ , Fe ²⁺	1.0
Ti(IV), Bi(III), Zr(IV), Zn ²⁺ , Cu ²⁺	0.03
Tl (III), Ni ²⁺ , (Pt(IV)*, Ag+*)	0.01
Se(IV), Au ³⁺ , S ₂ O ₃ ²⁻ , Zr(IV), Th(IV)	0.02

The proposed spectrophotometric method can be applied without any calibrate preparations.

4. Conclusions

The relationship of the reaction of fluoride with zirconium-Alizarin red S complex is related linearly at 624 nm to the concentration of fluoride in the range 0.2 - 1.0mg·L⁻¹. However, at higher fluoride concentration, the relationship was best described by a sixth-order polynomial function. The reaction reaches equilibrium at fluoride concentration of 0.054 mM, and the equilibrium constant (K_{eq}) was found to be 1.12 × 10³⁴.

Zirconium-Alizarin red S complex was used successfully as new spectrophotometric reagent for determination of fluoride in water in the range of 0.2 to 1.0 mg·L⁻¹. Due to its simplicity and high sensitivity, the method can be recommended as new spectrophotometric reagent for determination of fluoride in drinking water at low concentration. However, determination of fluoride at higher concentration is possible by diluting of the water sample to fit the requirements of the proposed method.

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References

1. DAR MA, SANKAR K and DAR IA ., Fluorine contamination in groundwater: a major challenge. *Environ. Monit. Assess.* (173), 955–968 (2011)
2. RAFIQUE T, NASEEM S, BHANGER MI and USMANI TH ., Fluoride ion contamination in ground water of Mithi Sub-district, the Thar Desert, *Pakistan. Environ. Geol.* (56), 317–326 (2008)
3. CZARNOWSKI W, WRZESNIEWSKA K and KRECHNIAK J Fluoride in drinking water and human urine in Northern and Central Poland. *Sci. Total Environ* (191) ,177–184 (1996)
4. A.P.H.A, A.W.W.A and W.P.C.F ., *Standard methods of examination of water and waste water.* 14th ed (1975)
5. Bellack, E. and Schouboe, P.J., Rapid photometric determination of fluoride in water. *Anal. Chem.* ., (30), 2032-2034 (1958)
6. Larsen, M.J, Pearce, E.I.F and Jensen, S.J ., Defluoridation of water at high pH with use of brushite, calcium hydroxide and bone charcoal. *J. Dent. Res.* (72) , 1519-1525 (1993).
7. Mayadevi, S. Adsorbents for the removal of fluorides from water. *Indian Chem. Engr. Section A* (38) 155-157 (1996)
8. K. Harikrishna, B. S. Nagaralli, and J. Seetharamappa ., Extractive spectrophotometric determination of sildenafil citrate (viagra) in pure and pharmaceutical formulations, *Journal of Food and Drug Analysis*, 16 (1) , 11–17 (2008)

9. WITTERHOLT VG ., Triphenylmethane and related Dyes In: Kirk-Othmer. John Wiley & Sons, Wilmington. *Encyclopedia of Chemical Technology*. (2nd edn.) (20) , 672–737(1969)
10. THRUN WE., Rapid method for determination of fluoride in water. *Anal. Chem.* 22 (7) , 918–920 (1950)

