*Asian Journal of Chemistry* Vol. 21, No. 9 (2009), 7117-7124

# Spectrophotometric Determination of Fluoride Using Ferric-thiocyanate Absorbing System

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A new analytical methodology has been proposed here for spectrophotometric determination of fluoride. In this study, the absorbance quenching capability of fluoride towards ferric-thiocyanate absorbing system was exploited for the quantitation of fluoride through measuring the absorbing system's permittance. The overall stability constant values of thiocyanate and fluoride complexes of Fe(III) elucidate that the fluoride complex of Fe(III) is much more stable than the thiocyanate complex. When the fluoride (analyte) solution is added into the red coloured ferric-thiocyanate absorbing system, fluoride displaces the thiocyanate ions from the coordination sheath of Fe(III) and hence the absorbing system experiences the quench in absorbance. For the quantitative determination of fluoride, the efficacy and validity of the method was confirmed by adding fixed volume aliquots of fluoride solution with increasing concentration into fixed and measured volumes of ferric-thiocyanate reagent. The % T measured at 480 nm of these different solutions showed that ferric-thiocyanate absorbing system of the constant path-length and concentration exhibit exponential increase in the clearance with arithmetic increase in concentration of fluoride. The calibration curve is constructed by plotting the absorbing system's permittance against the fluoride concentration. The absorbing system's best volumes of superior composition were tested for quantitation of fluoride up to 1 ppm.

**Key Words: Ferric-thiocyanate absorbing system, Clearance, Permittance, Fluoride absorbance quenching analyte.**

## INTRODUCTION

In the complex, metal-ligand bond formation process generally involves the transfer of electrons from the electron rich ligand molecules (nucleophile) to the electron deficient metal ion (electrophile). When the ligand molecules are weak nucleophile and the metal ion is weak electrophile, consequently the attraction between metal ion and the ligand is weak, that results in the formation of a labile complex. The labile complexes give rapid response to the nucleophilic substitution

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reactions whereas inert complexes undergo slow substitution reactions[1]. The labiality and inertness of the complex may be expressed by means of the stability constant[1] (log $K_f$), which is mostly associated with the complexing ability of the metal ion involved and characteristic of the ligand. The complex formation reaction involves the replacement of weakly bonded ligand molecules from the coordination sheath of metal ion by new stronger nucleophilic groups of ligand molecules[2]. When other ligand molecules (relatively stronger nucleophile) are added to a solution of labile complex, the ligand molecules from the labile complex are displaced by the molecules of the added ligand resulting in the formation of an inert complex. The process of conversion of labile complex to inert complex may take place with decolourization when the labile complex is coloured and inert complex formed is colourless.

## EXPERIMENTAL

The % T was measured with Shimadzu Pharmaspec UV-1700 double beam UV-visible spectrophotometer using quartz cuvettes having 1 cm internal diameter.

**Preparation of standard stock solutions:** (1) 2.0 L 0.01 M $Fe(NO_3)_3$ solution was prepared by dissolving the exactly weighed quantity of A.R. grade $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water. To prevent the hydrolysis of salt 20 mL of conc. $HNO_3$ was added. (2) 3.0 L 0.01 M KSCN solution was prepared by dissolving the accurately weighed quantity of A.R. grade KSCN in distilled water. Solutions (1) and (2) were used for preparation of ferric-thiocyanate absorbing system/reagent. (3) 1.0 L 1000 ppm of fluoride solution was prepared by dissolving the accurately weighed quantity of A.R. grade NaF in distilled water. Then 50 ppm fluoride solution was further prepared by diluting with distilled water 50.0 mL of this stock solution to 1.0 L.

**Preparation of ferric-thiocyanate absorbing system/reagent:** Following three different compositions of ferric-thiocyanate absorbing system were prepared:

(A) 1:1 Fe(III)-SCN system was prepared by adding 40.0 mL 0.01 M KSCN solution into 40.0 mL 0.01 M $Fe(NO_3)_3$ solution. (B) 1:2 Fe(III)-SCN system was prepared by adding 80.0 mL 0.01 M KSCN solution into 40.0 mL 0.01 M $Fe(NO_3)_3$ solution. (C) 1:3 Fe(III)-SCN system was prepared by adding 120.0 mL 0.01 M KSCN solution into 40.0 mL 0.01 M $Fe(NO_3)_3$ solution.

The Fe(III)-SCN absorbing system with volume 4.0 mL of 1:1 reagent, 6.0 mL of 1:2 reagent and 8.0 mL of 1:3 reagent contain equal concentration of iron(III).

**Analytical methodology:** The analytical methodology of quantitation of fluoride was tested for its validity and linearity using the above three compositions of ferric-thiocyanate absorbing system and it was initially implemented through application of 1:3 Fe(III)-SCN absorbing system. The different standard or test solutions (TS)[3] of fluoride (from 1.0 to 20.0 ppm) were prepared by adding the different aliquots of 50 ppm fluoride solution sequentially into the 25 mL graduated flasks each containing 8.0 mL of 1:3 Fe(III)-SCN absorbing reagent. The reaction mixtures were mixed thoroughly and further diluted to 25 mL using distilled water. The reagent blank[3] (RB) solution was also prepared by diluting with distilled water 8.0 mL 1:3 Fe(III)-

SCN absorbing system to 25 mL in the graduate flask. The true blank (TB)[3] or reference solution was prepared by mixing 10.0 mL of 50 ppm fluoride solution with 6.0 mL of 0.01 M $Fe(NO_3)_3$ solution and further diluted with distilled water to 25 mL in the graduated flask. The % T of each true sample and also reagent blank was measured once at 480 nm against true blank as a reference. The % T of the reagent blank was used for obtaining clearance of each test solution. An analogous method of quantitation of fluoride was pursued using 4.0 mL and 6.0 mL volumes of 1:1 and 1:2 Fe(III)-SCN absorbing reagent, respectively.

After verification of validity (graph of clearance against conc. of fluoride) and linearity (graph of permittance against conc. of fluoride) for each composition of system, the parallel method was then after practiced for quantitation of fluoride from 1 to 20 ppm by employing 4.0, 5.0, 6.0 and 7.0 mL volumes of each 1:1, 1:2 and 1:3 Fe(III)-SCN absorbing reagent. The calibration curves of absorbing system's permittance *versus* concentration of fluoride were subsequently plotted for evaluation of system's best volume and suitable volume and resolving their maximum fluoride quantifying capacity.

## RESULTS AND DISCUSSION

The absorbance quenching capability of fluorides towards ferric-thiocyanate absorbing system is the basis of the proposed analytical method, was exploited for quantitation of fluoride through measuring absorbing system's permittance. As the absorbance of the absorbing system is not only governed by the concentration of Fe(III) but also the concentration of thiocyanate[1], so three compositions of the system were first tested to study the validity and linearity of the method. The graph of the system's clearance *versus* concentration of fluoride (Fig. 1) illustrates exponential increase in clearance with the arithmetic increase of concentration of fluoride indicate that the methodology is excellent for quantitation of fluoride. The graph of the system's permittance *versus* concentration of fluoride (Fig. 2) also executes the need of the linearity in these three compositions of the absorbing system.

The absorbance/colour of the absorbing species remains true in presence of dilute HCl, $H_2SO_4$ and $HNO_3$ therefore the system can be beneficial for determining analyte from acidic solution containing slight concentration of these acids. The log $K_f$ values of thiocyanate and fluoride complexes of Fe(III) respectively are 3.36 and 12.06, which clarify that relative thiocyanate, fluoride complex of Fe(III) is much more inert. On adding analyte solution of fluoride to the ferric-thiocyanate absorbing system, the quench in the system's absorbance takes place. The fact behind the quench in the system's absorbance is associated with the conversion of the labile red coloured thiocyanate complex of Fe(III) into the inert colourless fluoride complex of Fe(III) through the ligand substitution process.

For a metal ion with specific concentration, the course of complex formation reaction is reliant on the stronger or weaker nucleophilic nature of the ligand species and their concentration. At a fixed concentration of Fe(III), the concentration of thiocyanate determines the type of complex present in the absorbing system, thus

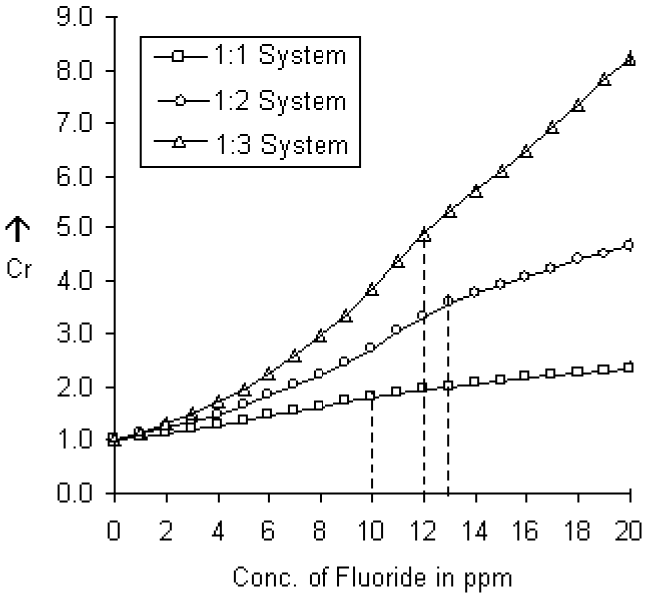

Fig. 1. Verification of proposed analytical methodology for quantitation of fluoride, the absorbing system with composition of 1:1, 1:2 and 1:3 Fe(III)-SCN, sustains the exponential increase in clearance (Cr), respectively up to 10,13 and 12 ppm of fluoride

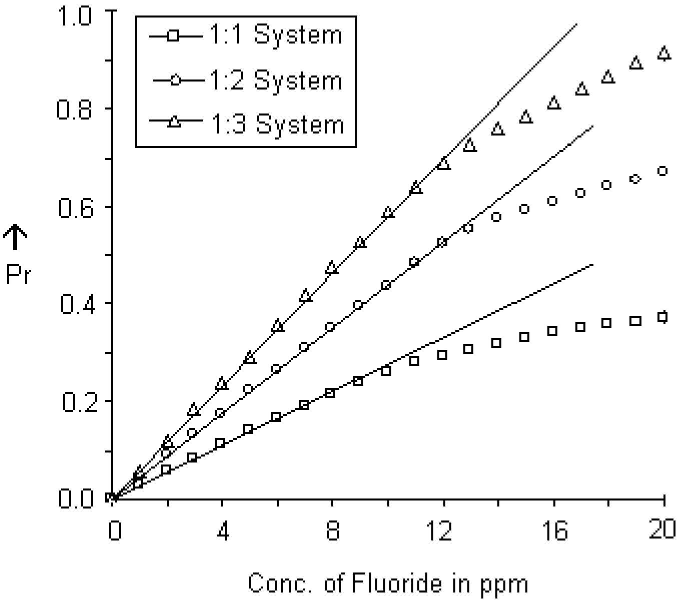

Fig. 2. Calibration curves of system's permittance (Pr) *versus* concentration of fluoride using the 1:1, 1:2 and 1:3 Fe(III)-SCN absorbing reagent at 480 nm

eqn. 1-3 represents the absorbance quenching mechanism, respectively of 1:1, 1:2 and 1:3 Fe(III)-SCN absorbing reagent. In all three compositions the quenching action results in the formation of inert, colourless hexafluoroferrate(III), $[FeF_6]^{3-}$ complex[4].

$$[Fe(SCN)]^{2+} + 6F^{-} \rightarrow [FeF_6]^{3-} + SCN^{-} \quad (1)$$

$$[Fe(SCN)_2]^{+} + 6F^{-} \rightarrow [FeF_6]^{3-} + 2SCN^{-} \quad (2)$$

$$[Fe(SCN)_3] + 6F^{-} \rightarrow [FeF_6]^{3-} + 3SCN^{-} \quad (3)$$

These chemical equations also interpret that the quench in system's absorbance is entirely related to the concentration of Fe(III), but the higher concentration of the thiocyanate sustains the absorbing systems at minimum transparency, offering the benefits of maximum linearity in the calibration curve. The slope of the calibration curve (Figs. 2-5) is also governed by the concentration of thiocyanate in the absorbing system.

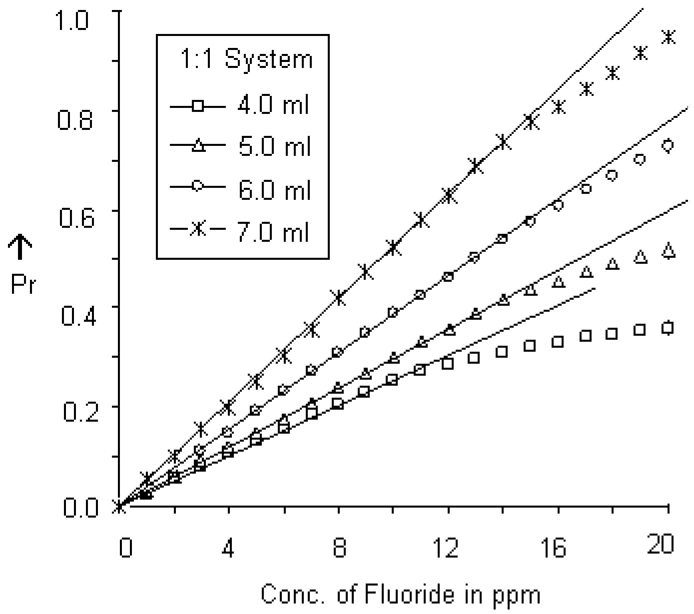

Fig. 3. Calibration curves obtained in the exploitation of different volumes of 1:1 Fe(III)-SCN absorbing reagent in quantitation of fluoride

The absorbing system having composition such as 1:4, 1:5, 1:6 Fe(III)-SCN yields the absorbing species of negative charged complex ions like $[Fe(SCN)_4]^{-}$, $[Fe(SCN)_5]^{2-}$, $[Fe(SCN)_6]^{3-}$, *etc.* confirm deep red colour and negligible transmittance, consequently do not offer the change in the permittance for the lower concentration (below 5.0 ppm) of fluoride. The greater concentration of thiocyanate in the absorbing system create hindrance for fluoride to combine with Fe(III), which is deep inside the negatively charged complex ion, in addition decreases the sensitivity of the absorbing system.

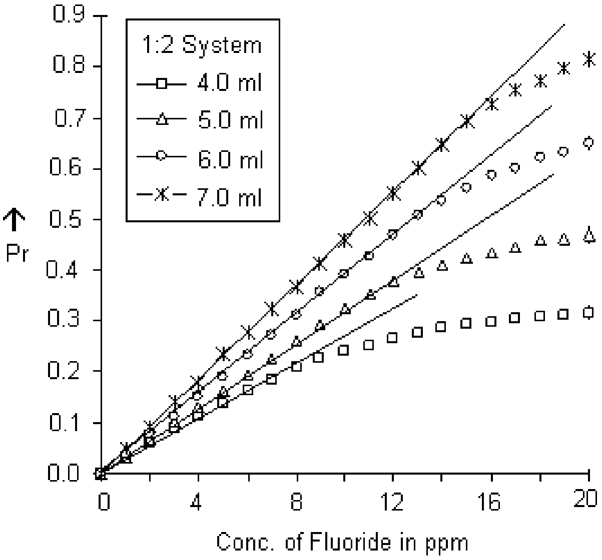

Fig. 4. Calibration curves obtained in the exploitation of different volumes of 1:2 Fe(III)-SCN absorbing reagent in quantitation of fluoride

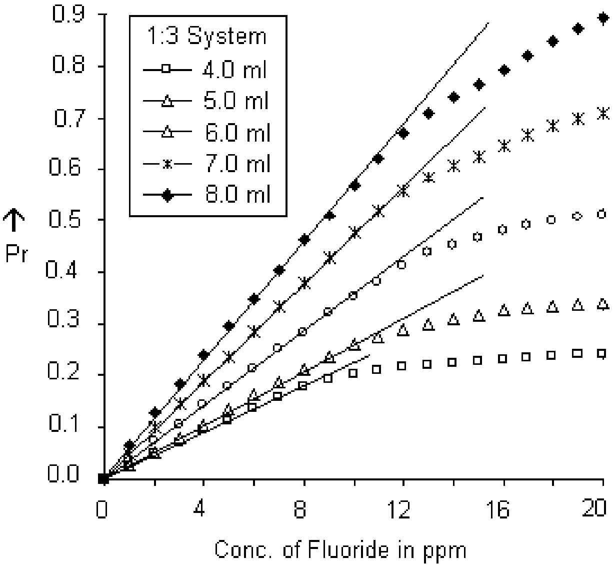

Fig. 5. Calibration curves obtained in the exploitation of different volumes of 1:3 Fe(III)-SCN absorbing reagent in quantitation of fluoride

The absorbing system with 2:1 composition [2 volume of 0.01 M $Fe(NO_3)_3$ plus 1 volume of 0.01 M KSCN] was in additionally tested with its 4.0 mL volume for quantitation of fluoride. This system do not offer the response to fluoride concentration below 5.0 ppm. Consequently the composition of absorbing system with

Fe(III) to thiocyanate ratio in the order as 1:1, 1:2 and 1:3 are only considered here as superior compositions for quantitation of fluoride.

For minimum possibility of relative error[2] the instrument output of % T should be confined in the region between 20 and 60 and to investigate the maximum fluoride quantifying capacity of the system's volume, then 4.0, 5.0, 6.0 and 7.0 mL volumes of absorbing reagent in superior compositions were tried again for quantitation of fluoride. Additionally 8.0 mL volume in case of 1:3 composition of the system was also tested in order to see the effect with equal concentration of Fe(III). The calibration curves of absorbing system's permittance *versus* concentration of fluoride (Figs. 3-5) provide the information about the system's best volume and suitable volume which accomplish the need of required instrument output (Table-1).

TABLE-1
MAXIMUM FLUORIDE QUANTIFYING CAPACITY OF ABSORBING SYSTEM'S 'BEST VOLUMES' AND 'SUITABLE VOLUME' OF DIFFERENT COMPOSITIONS

| Composition of absorbing reagent | Volume of reagent (mL) | Maximum fluoride quantifying capacity (ppm) | The range of % T in which the quantifying capacity was stretch out | The number of %T reading observed in between '20 to 60 %' | Remark for the system's volume |
|---|---|---|---|---|---|
| 1:1 System (Fig. 3) | 4.0 | 11.0 | 37.88 to 70.74 | 08 | – |
| | 5.0 | 14.0 | 20.80 to 54.35 | 15 | BV |
| | 6.0 | 15.0 | 09.33 to 37.61 | 12 | SV |
| | 7.0 | 14.0 | 03.33 to 21.39 | 05 | – |
| 1:2 System (Fig. 4) | 4.0 | 9.0 | 44.70 to 71.97 | 05 | – |
| | 5.0 | 12.0 | 29.10 to 69.30 | 10 | – |
| | 6.0 | 13.0 | 16.11 to 51.99 | 13 | SV |
| | 7.0 | 15.0 | 08.80 to 43.22 | 13 | SV |
| 1:3 System (Fig. 5) | 4.0 | 9.0 | 55.55 to 83.72 | 02 | – |
| | 5.0 | 11.0 | 42.41 to 77.32 | 06 | – |
| | 6.0 | 13.0 | 26.11 to 73.25 | 10 | – |
| | 7.0 | 12.0 | 14.95 to 54.01 | 11 | – |
| | 8.0 | 12.0 | 8.33 to 42.71 | 12 | SV |

## Conclusion

The wide difference in the formation constant of fluoride and thiocyanate complex of Fe(III) makes the ferric-thiocyanate reagent a good and sensitive absorbing system quantitation of fluoride up to 1 ppm through implementation of system's superior composition. After addition of fluoride analyte the quench in the system's absorbance takes place instantaneously and found to be irreversible (measurements after 10-15 min do not alter the values of permittance). The extent of formation of Fe(III)-fluoride complex in the absorbing system well related to decrease in system's absorbance which was alternatively measured as system's permittance for quantitation of fluoride. The method works well with all three superior compositions (Fig. 2), with the fixed concentration of Fe(III), since it measures the combining capacity of fluoride with Fe(III) in the absorbing system.

On the basis of analyte quantifying capacity of system's volume through producing more number of % T reading in the range 20 to 60 %, the system's best volume and suitable volume are scrutinized from Figs. 3-5. The absorbing system's best volume is considered here as the concentration of the absorbing reagent (in that volume) at which the system confirms the maximum analyte quantifying capacity through producing the instrument output of % T exactly in between 20 to 60 %. While the 'suitable volume' is the concentration of the absorbing reagent at which the system validates the greater analyte quantifying capacity through generating more number of % T reading in between 20 to 60 %. The absorbing system's best volume and suitable volume (Table-1) are constructive for quantitation of analyte through the minimum possibility of relative error[2].

It was observed that 5.0 mL, volume of 1:1 absorbing reagent found to be best volume for quantitation of fluoride up to 14.0 ppm, since the observed % T readings for this volume were in between 20.80 to 54.35 %, which were authenticate for minimum relative error. The absorbing system at higher concentration of thiocyanate (here as 1:3 Fe(III)-SCN system) contains the less concentration of Fe(III) in these volumes, as a result this system deviates to the lower concentration of fluoride (Fig. 5, Table-1).

**Interferences:** The quench in absorbing system's absorbance is related to combining capability of the analyte with the Fe(III) is the foundation of the proposed analytical methodology. Likewise with fluoride, the other anions like phosphate, oxalate, citrate also show strong complexing tendency towards Fe(III) are the serious interference. The metal ions like Hg(II), Cu(I) and Ag, that also form inert complex with thiocyanate, also plays role in quenching the absorbance of the system. Molybdenum if present produces red colour with thiocyanate acidic medium.

## ACKNOWLEDGEMENTS

The authors thank Dr. V.N. Pawar and the managing committee of N.D.M.V.P. Samaj, Nashik for providing the necessary infrastructure and funds. Thanks are also due to Dr. Ashok P. Pingle, Dr. M.N. Jachak, Dr. D.D. Dhavale and Dr. Arun Kumar for their encouragement and valuable suggestions during experimentation and preparation of manuscript.

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(*Received*: 29 December 2008; *Accepted*: 10 August 2009) AJC-7739