CHAPTER - III

SPECTROPHOTOMETRIC DETERMINATION OF
FLUORIDE IN WATER

SUMMARY

A new spectrophotometric method is proposed for the determination of micro-amounts of fluoride in water. Method is based on measuring the decrement in the colour of thorium-chromotrope 2B complex on addition of fluoride. Fluoride reacts with thorium-chromotrope 2B complex and forms stable thorium fluoride and simultaneously displaces the red coloured chromotrope 2B dye. The Beer's law is obeyed in the range of 0.25 to 2.0 ppm of fluoride. Effect of interference and other analytical parameters have been studied. Proposed method is successfully applied for the determination of fluoride in polluted river water and effluent of a fertilizer factory.

SPECTROPHOTOMETRIC DETERMINATION OF FLUORIDE IN WATER

Fluoride is one of the important air and water pollutant. It is ubiquitous, detectable traces occur in almost all substances. Fluorine is potentially toxic trace element present in human and animal nutrition (1,2). Industrial plants processing fluoride containing minerals, manufacturing phosphatic fertilizers and aluminium are the most important sources of fluoride. Fluorides are used in steel making, opacifying of glass and enamels, electroplating, insecticide, petroleum, plastic, dye and pharmaceutical industries. Brick and ceramic works also contribute to considerable pollution from fluoride (3-6). Its wide distribution in nature and frequent exposure to men, animals and vegetation has stimulated extensive research on its toxicology and estimation in environment.

Several reports are available on the toxicology of fluoride (7-11). The toxic effects of the organic fluorine compounds are unlike those of inorganic fluorides. The organic compounds like fluorocarboxylates are the most important and their metabolic activity have been studied extensively. An extraordinary feature of their activity is that those members of the series \( f(CH_2)_n COOH \) for which \( n \) is odd are extremely toxic, whereas those for which \( n \) is even have little or no toxicity at all. The first member, monofluoracetic acid is widely used in...
the form of its sodium salt to kill rodents and other pests (12). Pesticidal activity of polyfluorinated esters have also been reported (13). Fluoride compounds in the atmosphere are generally considered to be toxic to plants and animals (14,15). It is highly reactive and complexes with many organic and inorganic biological components and alters the metabolism of tissues (16). The acute toxic effects of fluoride include vomiting, abdominal pain, diarrhoea, convulsion, generalized and muscular weakness, collapse, dyspnea, paresthesia, difficulty in articulation, thirst, weakness of pulse, disturbed colour vision, loss of consciousness and motar unrest. Inhalation of fluoride dust and fumes causes irritation of nasal passages and can cause pulmonary edema which is the cause of death (17,18). Eyes and skin burns are the possible hazards caused by fluoride in contact with skin and eyes (11). A chronic skin disease acne rosacea is also reported to be related to fluoride(19). Nephritis, hemorrhagic gastroenteritis and more or less definite pathologic damage to other organs are found to be caused by acute poisoning of fluoride. It reduces the calcium content of blood and thus interferes with the clotting of blood. It also acts as an inhibitor of certain intercellular enzymes concerned in anaerobic glycolysis of many type of cells, plant as well as mammal (5,20).

The chronic toxic effects are fluorosis, identified by skeletal abnormalities, or damage ranging from rammatism to permanent crippling, anaroxia, muscular
weakness and impairment of dental development (21). However, the symptoms of preskeletal fluorosis, which are usually ignored and incorrectly attributed to other causes are headache, polyuria, polydipsia, epigastric distress, severe osteoarthritis bone pain, painful nodules on the extremities and disturbed kidney function (22). It has been studied that the incidence of fluorosis is particularly high in parts of south India where calcium intake is low (23,24).

Vegetation is also affected by fluoride pollution. It is amongst the most phytotoxic of common air pollutants. Fluoride enters the leaves through stomata in their surfaces from the atmosphere. The symptoms of acute fluoride injury to monocotyledon plants appear at the leaf tips, which become brown and necrotic and in dicotyledon plants the necrosis is initially confined to the margins of the leaf (25). Chronic injury of fluoride appears as an interveinal chlorosis. Large seed fruits, grapes, pines, maize, and gladioli are most sensitive to fluoride, showing up as over-ripening with separation of the fleshy parts of the fruit. Fluoride also causes wide spread damage to livestock. The effects from eating contaminated forage are abnormal calcification of bone and tooth structures, milk production is also decreased, animal lose weight, acquire a stiff posture and hair coat becomes rough (9,26). Fluoride also plays a major role in deteriorating the aquatic ecosystem (27).
In the absence of industrial exposure the chief source of fluoride is drinking water. The deleterious effects on bones and teeth are observed in community consuming high concentration of fluoride but 0.8 to 1.5 ppm of fluoride is artificially added to potable water supplies to reduce the incidence of dental caries (5, 28) without producing adverse effect on bones and physical health (11, 29). Fluoride is mainly accumulated in bones and teeth and is excreted by kidney. Thus urinary fluoride levels are widely regarded as one of the best indicators of fluoride intake (30). Fluoride reduces the rate of dissolution of bone. Recently, fluoride has been used in the treatment of osteoporosis in an attempt to rebuild bone lost due to this disease and has a profound effect on osteoblasts and bone formation (31).

**Fluoride level in Drinking Water** (32)

<table>
<thead>
<tr>
<th>Parts per million of Fluoride</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 0.5</td>
<td>High incidence of dental caries, no mottling</td>
</tr>
<tr>
<td>1</td>
<td>Low incidence of dental caries, little or no mottling</td>
</tr>
<tr>
<td>Greater than 2.5</td>
<td>Disfiguring mottling</td>
</tr>
<tr>
<td>10 to 20</td>
<td>Severe mottling or fluorosis</td>
</tr>
</tbody>
</table>
The threshold limit value as recommended by American Conference of Governmental Industrial Hygienists (ACGIH) is 3 ppm (7). Due to its critical level and importance in drinking water the accurate determination of fluoride has great importance with the growth of fluoridation of public water supply.

Several methods for the determination of fluoride have been reviewed in the literature (33-35). Fluoride does not form coloured compounds thus only few direct methods are reported which are based on the formation of ternary complexes of fluoride with cerium, lanthanum or zirconium and alizarin complexan (36-39), eriochrome cyanine R (40), quinalizarin (41), sulfonated alizarin blue (42,43). Ternary complexes with zirconium and xylenol orange or methyl thymol blue (44), chromotropic bisazo (45) and thorium-chromeazurols-cetyltrimethyl ammonium (46), etc. are also reported.

Generally all the other methods are indirect and are based on the liberation of dye or chelating anions from its metal complex with the formation of more stable metal fluoride complex. The colour of the liberated anion differs sufficiently with its metal chelate and permits the determination of fluoride concentration. The reaction can be generalized as: \( F^- + MeR \rightarrow MeF + R^- \) where MeR is metal complex of chelating dye, MeF is a metal fluoride complex and R\(^-\) is a liberated dye anion. Various chelating dye form coloured complex with metals such as
zirconium, thorium, lanthanum, aluminium, etc. are used
for spectrophotometric determination of fluoride, the
widely used systems are alizarin with zirconium (47),
or thorium (48), quinalizarin with zirconium (49),
eriochrome cyanine R with zirconium or aluminium (50,51),
SPADNS with zirconium or lanthanum (52,53), chloroanilic
acid with thorium (54), hemotoxyline with aluminium (55).
Some other reagents are chlorosulphophenol S (56),
salicilflavone (57), 4-(2 pyridyl azo) resorcinol (58),
Arsenazo III (59,60) and chrome azurol S (61) with zirconium,
salicylamide-iron (62), racetophenone oxime-uranium (63)
and titanyl oxalate (64), pyrocatechol violet-aluminium
(65), carboxyarsenazo-thorium (66), rufigallic acid-
zirconium (67), sulphoalizarin-scandium (68), 2-hydroxy-
1-(2-hydroxy-4 sulfo-1-naphthylazo) 3 naphtholic acid-
aluminium (69), chromotrope-2R-thorium (70), rutin-
zirconium (71) and metal oximates (72). Solid reagents
have also been proposed for the determination of fluoride
(73-75). Other available methods for determination of
fluoride are titrimetric (77), fluorimetric (78,79),
potentiometric (80,81), ion selective electrode (82,83),
ion chromatography (84,85), activation analysis (86),
molecular absorption spectrometry (87,88) and flow
injection analysis (89,90). The colorimetric determina-
tion of fluorides has been incorporated in automated
procedure for the analysis of fluorides.
In the present investigation a new rapid and sensitive method for the determination of fluoride in water is developed. The method is based on the bleaching action of fluoride on the purple coloured thorium-chromotrope 2B dye complex (λ max 550 nm) and measurement of the decrease in colour intensity at 570 nm i.e., the wavelength of maximum difference. The pure dye chromotrope 2B has maximum absorption at 510 nm and it forms a purple coloured complex with thorium. On addition of fluoride to the dye-metal complex, fluoride forms more stable compound with thorium and displaces the red coloured dye which is measured spectrophotometrically. The method is successfully applied for the determination of fluoride in polluted river water and effluent water. Reaction can be given as under:

\[
\text{Chromotrope 2B} + \text{Th}^{4+} \rightarrow \text{Thorium - chromotrope 2B complex}
\]

\[
\text{Thorium - chromotrope 2B complex} + 6F^- \rightarrow \text{Chromotrope 2B} + \text{ThF}_6^{2-} + nH_2O
\]
EXPERIMENTAL

Apparatus

All spectral studies were made with ECIL spectrophotometer and a Carl Zeiss spekol using 1 cm matched glass cells.

Reagents:

Standard solution of fluoride - 0.211 g of A.R. grade sodium fluoride was dissolved in 100 ml of glass distilled water. Working standards were prepared by appropriate dilution of the stock containing 1 mg of fluoride per ml.

Chromotrope 2B (p-nitrobenzene azo chromotropic acid) solution - A 0.002 M solution of chromotrope 2B dye was prepared in glass distilled water.

Thorium nitrate solution - 0.001 M solution of thorium nitrate was prepared in glass distilled water.

Mixed reagent - Equal volume of 0.002 M chromotrope 2B solution and 0.001 M thorium nitrate were combined to give red-violet complex. Mixed reagent was prepared daily.

Reference solution - 1 ml of mixed reagent and 0.2 ml of 0.02 M hydrochloric acid were taken in 10 ml volumetric flask and volume was made upto the mark with glass distilled water.

Diverse ions solution - Solutions of diverse ions were prepared by the reported method (91).
All reagents used were of analytical reagent grade.

Procedure

An aliquot of water sample containing 2.5 to 20 μg of fluoride was taken in 10 ml volumetric flask. To this 1 ml of mixed reagent was added and the pH maintained at 2.5 to 3.0 by adding 0.02 M hydrochloric acid. Then its volume was made up to the mark with glass distilled water. After 1 min absorbance was measured at 570 nm against the distilled water as reference. Absorbance of blank or reference solution was also measured at 570 nm against the distilled water.

RESULTS AND DISCUSSION

Spectral characteristics

The absorption spectra of chromotrope 2B show that the dye has a maximum absorption at 510 nm. The dye metal complex has maximum absorption at 550 nm. The differential absorbance of the chromotrope 2B-thorium complex with various concentrations of fluoride against a reference solution shows maximum difference at 570 nm which was used for spectrophotometric determinations (Fig. 1).

Effect of varying reaction conditions

The optimum pH for maximum colour development was found to be in the range 2.5 to 3.0. At lower pH the dye
FIG. 1. ABSORPTION SPECTRA

A. CHROMOTROPE 2B DYE AGAINST WATER

B. CHROMOTROPE 2B DYE + THORIUM AGAINST WATER
was liberated even without the addition of fluoride and at higher pH the dye was not liberated at all.

The reaction was rapid at room temperature. No change was observed up to 15°C - 40°C. The liberated dye was found to be stable for ~12 hours. The effect of time on reaction of fluoride with thorium-dye complex was evaluated and it was observed that only one min. was required to complete the reaction and later constant results were obtained.

Effect of molar ratios of chromotrope 2B and thorium was studied. Absorbance values were maximum for molar ratio of 1:1 of 0.002 M dye and 0.001 M thorium. At lower and higher molar ratios decrease in absorbance values were observed.

**Beer's law, molar absorptivity, Sandell's sensitivity and Reproducibility**

The Beer's law is obeyed in the range of 2.5 to 20 μg of fluoride per 10 ml (0.25 to 2 ppm) giving a standard curve which is straight line of negative slope (Fig. 2). Molar absorptivity and Sandell's sensitivity were $5.7 \times 10^3 \text{lit mol}^{-1} \text{cm}^{-1}$ ($\pm$ 100) and 0.0033 μg cm$^{-2}$ respectively.

Reproducibility was checked by determining 10 μg of fluoride per 10 ml, over a period of seven days. The results show that the method is reproducible. The standard deviation and relative standard deviation were found
FIG. 2. CALIBRATION CURVE FOR THE DETERMINATION OF FLUORIDE WITH CHROMOTROPE 2B AND THORIUM
to be $± 0.0105$ and $1.492 \%$ respectively for a solution containing $10$ \mu g of fluoride (Table I).

**Effect of diverse ions**

Effect of various diverse ions normally found in water along with fluoride was studied. Most of the common ions such as sodium, potassium, nitrate, nitrite, chloride, bromide, acetate, carbonate, sulphite, etc. do not interfere with this method. Cations such as calcium, magnesium and aluminium which also form complexes with fluoride interfere with this method. These were removed by cation-exchange resins. Sulphates if present can be removed after precipitation as benzidine sulphate (92). However, most of the interferences are removed by distillation of fluoride prior to its determination as recommended (93) (Table II).

**Application of the method**

The present method was applied for the determination of fluoride in drinking water and waste water. As the drinking water samples were found to be free of fluoride, known amounts of fluoride were added to the samples and analysed by proposed method, as well as SPADNS method.

To check the applicability of the method polluted water samples of Kharoon river which receives effluents from a superphosphate fertilizer plant were analysed. Method was also applied to determine fluoride in effluent water from fertilizer plant. Samples contained a number of anions and cations interferents along with large
TABLE - I
REPRODUCIBILITY OF THE METHOD

Concentration of fluoride = 10 \mu g/10 ml

<table>
<thead>
<tr>
<th>No. of Days</th>
<th>Absorbance $^{*}$ (570 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.570</td>
</tr>
<tr>
<td>2</td>
<td>0.565</td>
</tr>
<tr>
<td>3</td>
<td>0.580</td>
</tr>
<tr>
<td>4</td>
<td>0.575</td>
</tr>
<tr>
<td>5</td>
<td>0.570</td>
</tr>
<tr>
<td>6</td>
<td>0.565</td>
</tr>
<tr>
<td>7</td>
<td>0.570</td>
</tr>
</tbody>
</table>

Mean = 0.570,
Standard deviation = \pm 0.0105,
Relative standard deviation = 1.492%.

* Mean of three repetitive analysis.

TABLE - II
EFFECT OF DIVERSE IONS

Concentration of fluoride = 10 \mu g/100 ml

<table>
<thead>
<tr>
<th>Diverse ions</th>
<th>Tolerance limit $^{*}$ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$, K$^+$, Li$^+$, NH$_4^+$, NO$_2^-$, CH$_3$COO$^-$, CO$_3^-$</td>
<td>500</td>
</tr>
<tr>
<td>Hg$^{2+}$, Pb$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Cl$^-$, Br$^-$</td>
<td>400</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>200</td>
</tr>
<tr>
<td>Phenol, formaldehyde, aniline, Fe$^{3+}$</td>
<td>100</td>
</tr>
<tr>
<td>Ca$^{2+}$, Mg$^{2+}$</td>
<td>50</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>20</td>
</tr>
<tr>
<td>Al$^{3+}$, SO$_4^{2-}$</td>
<td>1</td>
</tr>
</tbody>
</table>

* Amount of diverse ions that causes an error of $\pm$ 2%.
amounts of phosphates and sulphates. Therefore the samples were distilled (93) prior to the analysis. Distillation of fluoride samples was carried out in concentrated sulphuric acid at 180°C. The traces of sulphate present in distilled sample was removed by its precipitation as benzidine sulphate (Table III). The method has been compared with some commonly used spectrophotometric methods reported for the analysis of fluoride (Table IV).

CONCLUSION

The proposed method is sensitive, rapid and easy to carry out. It can be successfully applied for the determination of fluoride in drinking water, polluted water and effluent water.
### Table III

**Application of the Method**

(a) Analysis of fluoride in drinking water

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Fluoride added (µg)</th>
<th>Fluoride found* (µg)</th>
<th>Present method % Recovery</th>
<th>SPADNS method % Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3.0</td>
<td>3.0</td>
<td>100.0</td>
<td>2.95</td>
</tr>
<tr>
<td>2.</td>
<td>8.5</td>
<td>8.5</td>
<td>100.0</td>
<td>8.4</td>
</tr>
<tr>
<td>3.</td>
<td>12.0</td>
<td>11.9</td>
<td>99.1</td>
<td>12.0</td>
</tr>
<tr>
<td>4.</td>
<td>18.5</td>
<td>18.5</td>
<td>98.9</td>
<td>18.5</td>
</tr>
</tbody>
</table>

* Mean of three repetitive analyses.

(b) Analysis of fluoride in polluted water

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Fluoride found* (µg)</th>
<th>Present method</th>
<th>SPADNS method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>5.30</td>
<td>5.29</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>9.21</td>
<td>9.20</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>13.88</td>
<td>14.01</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>18.01</td>
<td>18.03</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>22.29</td>
<td>22.50</td>
<td></td>
</tr>
</tbody>
</table>

* Mean of three repetitive analyses.

(c) Analysis of fluoride in effluent water

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Fluoride found* (µg)</th>
<th>Present method</th>
<th>SPADNS method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3.40</td>
<td>3.46</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>6.85</td>
<td>6.85</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>8.21</td>
<td>8.19</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>10.40</td>
<td>10.50</td>
<td></td>
</tr>
</tbody>
</table>

* Mean of three repetitive analyses.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Reagents</th>
<th>$\lambda_{max}$, nm</th>
<th>$0.05 - 1.4$ mg l$^{-1}$ range</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zirconium-alizarine</td>
<td>520</td>
<td>0.0 - 1.4</td>
<td>Simple and repeat. Method is sensitive, rapid and stable.</td>
</tr>
<tr>
<td>2</td>
<td>Thorium-chromotrope</td>
<td>570</td>
<td>0.25 - 2</td>
<td>Method is sensitive, rapid and stable.</td>
</tr>
<tr>
<td>3</td>
<td>Chromotrope</td>
<td>540</td>
<td>0.2 - 2.4</td>
<td>Method is temperature dependent. Heavy metal, tartarate and ascorbate interfere.</td>
</tr>
<tr>
<td>4</td>
<td>Alizarine</td>
<td>580</td>
<td>0.05 - 7.4</td>
<td>Method is temperature dependent. Intensity of colour changes with time. Rapid and stable.</td>
</tr>
<tr>
<td>5</td>
<td>Zirconium-Alizarin</td>
<td>640</td>
<td>0.0 - 1.4</td>
<td>Simple and rapid.</td>
</tr>
<tr>
<td>6</td>
<td>Thoroium-Arsenazo III</td>
<td>665</td>
<td>0.1 - 1.4</td>
<td>Selective, interference less sensitive.</td>
</tr>
<tr>
<td>7</td>
<td>Zirconium-Chromotrope</td>
<td>570</td>
<td>0.1 - 1.4</td>
<td>Method is temperature dependent. Intensity of colour changes with time.</td>
</tr>
</tbody>
</table>

*Table IV: Comparison with Other Spectrophotometric Methods*
REFERENCES


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37. R. Belcher and T.S. West, Talanta, 8 (1961) 863.


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