CHAPTER II

A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF FLUORIDE IN WATER

SUMMARY

A new sensitive method is proposed for the determination of fluoride in traces. The method involves the decomposition of the coloured thorium-chromotrope 2R complex by fluoride which then forms more stable fluoride-thorium complex subsequently releasing the red coloured dye. The colour of the dye released is measured at 570 nm. Beer's law is obeyed in the concentration range of 0.2 - 2 ppm of fluoride. Various analytical parameters for full colour development have been evaluated. The method has been successfully applied for the determination of fluoride in effluent water of a fertilizer factory and tap water.

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A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF FLUORIDE IN WATER

Fluoride is one of the several trace elements in coal, receiving much attention owing to its possible harmful ecological effects. It is also essential to both plant and animal life at low concentrations, but is toxic at higher concentrations. The potential toxicity of fluoride has been classified as 'high' for terrestrial life and 'low' for aquatic life (1). Although fluorine was discovered by Moissan in 1886, the biochemical aspects of compounds containing C-F bond received greater attention only since the late 1940s when Rudolph Peters elucidated the mechanism of the toxic action of fluoroacetate and established the concept of lethal synthesis (2). It is liberated into the atmosphere from industrial plants which produce aluminium, phosphate fertilizers, glass ceramics and steel. Lesser uses of fluorides are found in the disinfection of hides and skins and also in dyeing industries (3,4). Hydrogen fluoride is used as a corrosion inhibitor in certain rocket systems and is also an ingredient of certain tooth pastes (5,6).

Fluoride is intimately involved in the hard tissue physiology and pathology. However, it is known to exert subtle influence on other systems of the body and thereby play an overall paramount role in human health and disease.
manifestable not only through its deficiencies but also its excess. Interestingly, the margin between its curative and the harmful doses is quite narrow (7). In plants fluoride toxicity led to decreased chlorophyll and carotenoid levels (8). Fluoride and its compounds enhance carcinogen induced cell transformation in embryonic cells and is also mutagenic in nature (9-11). Fluoride toxicity produces focal myocardial necrosis, damages the heart and produces blood pressure changes (11). A sublethal concentration of fluoride (5.2 mg F/kg) when administered to rats showed a decrease in body weight and an increase in white blood cells (12). Acute fluoride intoxication in man causes diarrhea, weakness of the pulse and motor unrest. Chronic toxic effects are characterized by loss of weight and impairment of dental development and of growth in the young. The most striking symptom is that of osteosclerosis, often called fluorosis which is usually observed as skeletal abnormality or damage, ranging from stiffness and rheumatism to a permanent crippling skeletal rigidity (4,13).

Acnerosis, a chronic skin disease is also reported to be related to fluoride (14). Fluoride in small quantities in drinking water supplies, is beneficial for dental health by preventing caries. When fluorides are present in concentrations greater than 1.5 - 2 ppm, their beneficial effect is lost and cause mottling of teeth in children. More than 3 ppm cause irregular out growth of osseous tissues on the long bones and the ossification of intercoastal
ligaments (15). Chronic intoxication of fluoride on the enamel develops endemic hypoplasia and is known as mottled enamel. The mottled teeth are characterized by minute flecks and yellow or brown spot areas, scattered irregularly over the tooth surface (16). Alteration in the regularity of collagen fibrils is a part of complex disturbances of the fluorotic bone (17). Supplementation of drinking water with 100 ppm of fluoride results in an increase in the serum triglycerides (18). The threshold limit value as recommended by ACGIH is 3 ppm (4,19). For a 60-70 kg human a daily intake of 1.5 - 1.7 mg in food, 1.2 mg in water and 1 mg in air, i.e. a total of ~ 4 mg fluoride is assumed as the tolerance level (20).

With the increasing spread of fluoridation of drinking waters the importance of reliable methods for its determination has become essential. For that purpose several instrumental methods are cited in the literature for its trace determinations (21-29).

Various spectrophotometric methods are also proposed and reviewed nicely (30,31). Fluoride does not form coloured complexes, therefore only a few direct methods are reported which are based on the formation of ternary complexes of fluoride with cerium or lanthanum and alizarine complexan (32-37), eriochrome cyanine - R (38,39), quin-alizarin complexan (40), alizarin red-S (41) and alizarin black (42).
However, the common indirect spectrophotometric methods for the determination of fluoride are based on the ability of the fluoride ion to abstract metal ions from strongly absorbing complexes thus liberating the free dye stuff and to form stable fluoride complexes. The chemistry of this method (3) can be represented in general as

\[
F^- + MeR \rightarrow MeF + R^-
\]

where \(MeR\) is a coloured complex of metal and \(MeF\) is a colourless fluoride complex of this metal. Fluoride forms complexes with many cations like thorium, zirconium iron, titanium, aluminium and others. The most popular reagents for fluoride analysis are SPANS (sodium 2-(p-sulphophenylazo) 1,8-dihydroxynaphthelene 3,6 disulphonic acid) with zirconium or aluminium (43-45). Chromotrope 2R-thorium (46), pyrocatechol violet-aluminium (47), rutin-zirconium (48), rufigollic-zirconium (49), quinalizarin sulphonate-aluminium (50) and eriochrome cyanine R-zirconium (51,52). Some solid reagents are also proposed for the determination of fluoride (53-64).

Present work reports a sensitive and rapid method for the determination of fluoride in water. The method involves the formation of a blue-violet complex of chromotrope 2R with thorium which is stable in acidic medium. On addition of fluoride the dye-thorium complex decomposes and a very stable fluoride-thorium complex is formed releasing the dye. Thus the method involves the bleaching
of the coloured complex with fluoride and subsequent liberation of the free dye which is measured spectrophotometrically at 570 nm. Various analytical parameters have been evaluated and the method has been successfully applied for the determination of fluoride in effluent water and tap water.

**EXPERIMENTAL**

**APPARATUS** - A Carl Zeiss spekol with 1 cm matched silica cells was used for all spectral measurements.

**REAGENTS** -

Standard fluoride solution - 1 mg/ml solution was prepared by dissolving 0.221 g of sodium fluoride in 100 ml glass distilled water. Working standards were prepared by the appropriate dilution of the stock.

Thorium nitrate (0.001 M) - 0.0588 g in 100 ml glass distilled water.

Chromotrope-2R dye - 0.1% solution in glass distilled water.

Mixed reagent - Prepared by taking equal proportion of thorium nitrate and chromotrope 2R solution. It should be prepared daily.

Reference solution - To 1 ml of mixed reagent 0.5 ml of 0.005 M hydrochloric acid was added and volume was made upto 10 ml with glass distilled water.

All reagents used were of AnalaR grade.
PROCEDURE - Aliquots containing 2 - 20 µg of fluoride were taken in a 10 ml volumetric flask. pH of the solution was maintained between 2 and 2.5 by adding 0.005 M hydrochloric acid. To it 1 ml of mixed reagent was added and the volume was made up to the mark with glass distilled water. After 2 minutes the absorbance was measured at 570 nm against a reference solution.

RESULTS AND DISCUSSION

Spectral characteristics - The absorption spectra of the chromotrope-2R dye shows a maximum absorption at 515 nm. Fig. 1 shows that on addition of thorium to the dye, the absorption band of the blue-violet dye-thorium complex shows an absorption peak at 530 nm.

The differential absorbance of the chromotrope-2R thorium complex with various concentrations of fluoride against a reference solution shows maximum difference at 570 nm. Therefore, this wavelength was chosen for spectral measurements (Fig. 2).

Colour reaction - The colour reaction involves 2 steps. In the first step the dye, chromotrope-2R forms a weak complex with thorium in acidic medium and in the second step the dye-thorium complex decomposes on the addition of fluoride to form a very stable fluoride-thorium complex releasing the dye.
FIG. 1 ABSORPTION SPECTRA OF CHROMOTROPE-2R

A. DYE AGAINST WATER.

B. DYE + THORIUM AGAINST WATER.
1. **Chromotrope-2R (I)**

   \[
   \text{N} \quad \text{N} \quad \text{N} \quad \text{OH} \quad \text{OH} \quad \text{NaO}_3\text{S} \quad \text{SO}_3\text{Na} \quad + \text{Th}^{4+}
   \]

   Thorium-chromotrope-2R complex II

2. **II + 6 F^-**

   \[
   \text{N} \quad \text{OH} \quad \text{OH} \quad + \text{ThF}_6^{2-} \quad + \text{n H}_2\text{O}
   \]

   Chromotrope-2R
EFFECT OF VARYING REACTION CONDITIONS

The effect of acidity for the colour reaction was evaluated. Various concentrations of hydrochloric acid ranging from 0.001 M to 0.06 M were studied and results show that (Fig. 3) 0.005 M acid was found most appropriate for the reaction. Constant absorbance was obtained upto 0.007 M acid. On addition of higher concentrations of acid the thorium-chromotrope 2R complex decomposes even in the absence of fluoride. The pH of the final solution was maintained between 2 and 2.5.

The determination may be carried out at any convenient temperature within the range of 15° to 30°C because absorbance remains constant at this temperature range. Time taken for completion of the reaction was found to be 2 minutes. Maximum absorbance was obtained with 1:1 proportion of thorium nitrate and chromotrope-2R solution. The colour was found to be stable for ~12 hours.

Beer's law, molar absorptivity and Sandell's sensitivity - The colour reaction was found to obey Beer's law over a concentration range of 2 - 20 µg of fluoride per 10 ml (0.2 - 2 ppm) of solution (Fig. 4). The molar absorptivity and Sandell's sensitivity were found to be 1.85x10⁴ lit mol⁻¹ cm⁻¹ (± 100) and 0.001 µg cm⁻² respectively.

Reproducibility of the method - The standard deviation and relative standard deviation were found to be ± 0.014 and ± 3.04% respectively for a solution containing 10 µg
Fig 3 Effect of acidity on reaction of fluoride with thorium and dye.
Concentration of fluoride = 10µg/10ml

Fig 4 Calibration curve for the determination of fluoride.
of fluoride in 10 ml solution analysed over a period of seven days (Table - 1).

**Effect of foreign species** - The analytical applicability of the method was assessed by studying effect of various interfering copollutants. Various amounts of copollutants were added to a solution containing 15 µg of fluoride per 10 ml of solution. It was found that sodium, potassium, nitrate, nitrite, chloride, acetate, etc. do not interfere with the method. The tolerance limits of various other copollutants are given in Table II. Phosphate and sulphate interfere seriously in the method. Sulphate was removed by precipitating as benzidine sulphate (65) and other interferences were eliminated by distillation of fluoride prior to analysis (30).

**APPLICATION OF THE METHOD**

**Effluent water** - Waste water from a nearby fertilizer factory was analysed for its fluoride content. The samples contained high amounts of fluoride and sulphate. Sulphate was removed as benzidine sulphate (65) and phosphate was removed by distillation of the sample prior to analysis (30). Owing to the high fluoride concentration the sample was diluted to a known amount and analysis was carried out as recommended in the procedure. The results are shown in Table III A.

**Tap water** - Analysis of fluoride was carried out in tap water. The tap water did not contain any fluoride, hence,
TABLE - I

REPRODUCIBILITY OF THE METHOD

Concentration of fluoride = 10 μg/10 ml (1 ppm)

<table>
<thead>
<tr>
<th>No. of days</th>
<th>Absorbance 570 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.460</td>
</tr>
<tr>
<td>2</td>
<td>0.465</td>
</tr>
<tr>
<td>3</td>
<td>0.470</td>
</tr>
<tr>
<td>4</td>
<td>0.455</td>
</tr>
<tr>
<td>5</td>
<td>0.470</td>
</tr>
<tr>
<td>6</td>
<td>0.455</td>
</tr>
<tr>
<td>7</td>
<td>0.440</td>
</tr>
</tbody>
</table>

Mean = 0.461
Standard deviation = ±0.014
Relative standard deviation = ±3.04%

TABLE - II

EFFECT OF FOREIGN SPECIES

Concentration of fluoride = 15 μg/10 ml (1.5 ppm)

| Foreign species (Tolerance limit in μg/10 ml)* | **Al³⁺, **Cu²⁺, ***Fe²⁺, Mn²⁺ (100); Li⁺, Be⁺ (600); **Mg²⁺, NO₂⁻, Formaldehyde (1000); NH₄⁺ (1250); **Pb²⁺ (4000); **Ca²⁺ (5000); K⁺, Na⁺ (7000); Phenol (1500); Aniline, NO₃⁻ (2500); CH₃COO⁻ (10,000); SO₄²⁻ (1); PO₄³⁻ (20). |

* Tolerance limit may vary by ±2%
** Masked with 1 ml of 5% EDTA
*** Masked with 1 ml of 10% sodium potassium tartrate.
synthetic samples were prepared by adding known amounts of fluorides and was then analysed for the fluoride content. The recovery was found to be \( \sim 100\% \) (Table III B).

CONCLUSION

The proposed method is sensitive (Table IV) and rapid for the microgram determination of fluoride in water. Various copollutants are tolerated. The method can be successfully applied for the determination of fluoride in effluent water from a fertilizer factory and tap water. No prior distillation of fluoride sample is necessary for routine analysis.
### TABLE III A

DETERMINATION OF FLUORIDE IN EFFLUENTS OF A FERTILIZER FACTORY

<table>
<thead>
<tr>
<th>Sample Number</th>
<th><strong>Concentration of fluoride (µg)</strong></th>
<th>Present method</th>
<th>SPADNS method (44)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>25.4</td>
<td>25.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>50.2</td>
<td>49.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>70.5</td>
<td>70.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>100.5</td>
<td>111.0</td>
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</tr>
<tr>
<td>5</td>
<td>118.0</td>
<td>118.2</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>140.3</td>
<td>140.6</td>
<td></td>
</tr>
</tbody>
</table>

* Samples were collected from different points and diluted prior to analysis.
** Mean of three replicate analyses.

### TABLE III B

DETERMINATION OF FLUORIDE IN TAP WATER

Amount of sample taken = 1 ml

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Amount of Fluoride added µg</th>
<th>*Concentration of fluoride found (µg)</th>
<th>Present method</th>
<th>SPADNS method (44)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>1</td>
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<td>2</td>
<td>5.0</td>
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<td>4.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10.0</td>
<td>9.9</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>12.5</td>
<td>12.4</td>
<td>12.2</td>
<td></td>
</tr>
</tbody>
</table>

* Mean of three replicate analyses.
<table>
<thead>
<tr>
<th>Method/Reference</th>
<th>Range of Determination (ppm)</th>
<th>Time for full colour development</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Alizarin (64)</td>
<td>0.8 - 1.6</td>
<td>4 hrs</td>
<td>Long time required to achieve constant results.</td>
</tr>
<tr>
<td>Al-Eriochrome-cyanine (52)</td>
<td>1 - 6</td>
<td>10-15 min</td>
<td>Method is temperature dependent</td>
</tr>
<tr>
<td>4-(2-pyridylazo)resorcinol-hexadecylridinium chloride (58)</td>
<td>0.2 - 1</td>
<td>5 min</td>
<td>-</td>
</tr>
<tr>
<td>Zr-SPAINS (44)</td>
<td>0.0 - 1.4</td>
<td>5 min</td>
<td>Method is quick</td>
</tr>
<tr>
<td>Zr-Eriochrome cyanine-R (30)</td>
<td>0.04-0.3</td>
<td>5 min</td>
<td>Interference of many metals</td>
</tr>
<tr>
<td>Thorium-chromotrope 2R (Present method)</td>
<td>0.2 - 2</td>
<td>2 min</td>
<td>Method is simple, fast and sensitive</td>
</tr>
</tbody>
</table>
REFERENCES


