



ANALYTICAL DETERMINATION OF FLOURIDE IN GROUND WATER: A REVIEW

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ABSTRACT

This paper presents the review of different concepts of fluoride detection techniques and technologies in water. High Fluoride concentration is toxic to humans. It can create various health problems. There are various techniques to determine fluoride ion in water such as Titrimetric method, Ion selective Method, Colorimetric technique, Spectro photometric techniques. Among them spectro photometric techniques are widely used techniques. This paper gives comparative study of all these methods to detect fluoride in drinking water.

Keywords: *Colorimetric Technique, Drinking Water, Fluoride, Ion Selective Electrode, Spectro Photometric Technique.*

I INTRODUCTION

There are certain chemical substances, when if present in drinking water at concentration greater than definite limits, may be injurious to health. One such is fluoride ion.

FLUORIDE is the lightest member of halogen group and is one of the most reactive of all chemical elements. It is the most electronegative of all elements which mean that it has a strong tendency to acquire a negative charge and in solution form Fluoride ion. [1] Fluoride forms mineral complexes with a number of cations. Though fluoride enters the body through water, food drugs, cosmetics, etc. but drinking water is major source of daily intake. Fluoride occurs in almost all waters from trace to high concentration [2]. It has been shown to cause significant effects in humans through drinking water [3]. Low concentrations of fluoride in drinking water is an essential component for normal mineralization of bone, teeth and formation of dental Enamel, but excessive exposure to fluoride in drinking water can give rise to a number of adverse effects [4].

Concentration in range of 1.5-4.0 mg/l result in dental fluorosis and with prolonged exposure and higher fluoride conc (4-10 mg/l) progresses to skeletal fluorosis. In dental fluorosis there is dental mottling, which is characterized initially by opaque white patches on the teeth and in advanced stages leads to dental fluorosis (teeth display brown to black staining) followed by pitting of teeth surfaces. There is loss of luster and shine of dental enamel. In skeletal fluorosis there is increase in bone density leading for thickness of long bones and calcification of ligaments. The symptoms include mild rheumatic/arthritis pain in the joints and muscles to severe pain in the cervical spine region along with stiffness and rigidity of the joints. Symptoms are pain in neck, backbone, in joints and there is stiffness in neck and rigidity in hip region.



World health organization (WHO) has set a limit value of 1.5 mg/L for fluoride in drinking water [5]. So there is narrow margin between the desired and harmful doses of fluoride in drinking water [6]. Therefore an accurate, simple, rapid and cost effective analytical method is of high importance.

II. METHODS FOR DETERMINATION OF FLUORINE

- 1. Titrimetric Method:** In the titration procedure [7, 8] the thorium nitrate titrant is added to the test solution until a faint permanent pink colour is observed in the presence of the indicator, Alizarin Red S. The same volume of the titrant is then added to a comparison solution which becomes pinker than the test solution. The final titration is carried out with a standard fluoride solution that bleaches the comparison solution progressively to the matching point.
- 2. Ion Specific Electrode Method:** In this method [9] fluoride sensitive electrode is used in which potential developed across a lanthanum fluoride crystal is dependent on the ratio of fluoride activities on either side of the crystal. As the internal fluoride activity is constant-for all practical purposes, The potential developed depends only on the value of the fluoride activity in the external solution. In use, electrode forms a cell with an external reference electrode, normally the calomel electrode.
- 3. Colorimetric Methods:** This depends upon bleaching action of fluoride [10] on a particular organo-metallic dye complex. The fluoride reflect with the dye lake, dissociating a portion of it into a colourless complex anion and the dye. As a amount of fluoride increase colour produced becomes progressively lighter depending on the reagent used.

An imidazole based sensing probe to detect fluoride ion is discovered [11]. In their system, the colour of solution changes from yellow to red with addition of fluoride ions. For the fluoride ion detection, anaphthalimide-based highly selective ratiometric and colorimetric fluorescent probe is synthesized [12]. Upon reaction with the F^- ion in CH_3CN and aqueous buffer solution there is color change in probe from colorless to jade-green and ratiometric fluourescence signals is enhanced.

Colorimetric determination of fluoride in water was done by using ferric chloride [13] it is based on the fact that intensity of colour produced with thiocyanate by given amt of Iron in presence of fluoride is less than that produced in absence of fluoride, by an amount depending on quantity of fluoride present, if there is excess of Iron. By determining colorimetrically the excess of Iron reacting with Amm. thiocyanate, the quantity withdrawn by fluoride from given amount of Iron may be found by difference and its equivalent in fluoride read from curve which has been made by plotting definite amounts of fluoride against the Iron they withdraw from the amount of iron used in determination.

- 4. Spectrophotometric Determination:** These 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 colour different of the metal-ligand complex [14].
 - a) By Using Resorcin Blue Complexes [15] :** The complex solutions for the spectrophotometric measurements were prepared by mixing aluminium 1:2 resorcin blue ratio of 5×10^{-3} M of aluminium and 5×10^{-3} M of resorcin blue in ethanol solution, which was then diluted to (2×10^{-4} M) that is suitable for the spectrophotometric measurements. Various amounts of fluoride were added in the range $0-2 \text{ mg L}^{-1}$ to



25 ml volumetric flask containing aluminium 1:2 complex solution of resorcin blue in ethanol (2×10^{-4} M, 24.5 ml). The solution was completed to volume by water. The adsorbance was measured at the wavelength of the maximum difference between the absorption spectra of the complex and the ligand which was 624 nm.

- b) By using aluminium complexes of triphenylmethane dyes [16] :** Aluminium to ligand ratio was found to be 1:2 for both chrome azurol B and malachite green. Thus, the complex solutions for the spectrophotometric measurements were prepared as 1:2 ratios from aluminium and ligand of 1×10^{-4} M in ethanol solutions, and the solutions were then diluted to the concentration ($=5 \times 10^{-5}$ M) suitable for the spectrophotometric measurements. Various amounts of fluoride were added in the range 0-2 mg^{-1} to a 25 ml volumetric flask containing aluminium complex solution of chrome azurol B or malachite green in ethanol (5×10^{-5} M, 24.5 ml). The solution was made up to volume with water. The absorbance was measured at the wavelengths of maximum difference (425, 581 nm for chrome azurol B, 428, 622 nm for malachite green) in the electronic spectra between the ligand and the complex. The spectra for the reaction of different amounts of fluoride with the complex were compared.
- c) Zirconium-SPADNS Method :** It is based upon the effect of fluoride ion on the color system (Zr-SPADNS). A manifold consisting of two lines was used, there is decrease in absorbance of Zr-SPADNS reagent at 590 nm is linear with fluoride concentration in the range of 0.00-3.5 ppm. The method has a detection limit of 0.02 ppm fluoride [17].
- d) By using complexes of Flavonoid Chrysin [18] :** Chrysin ligand solutions and its aluminium complexes solutions were prepared using ethanol. Standard fluoride stock solution was prepared by dissolving 0.1382 g of sodium fluoride in 250 ml water. The stock solution was further diluted as needed. Various amounts of fluoride were added in the range 0-3 mg L^{-1} to 25 ml volumetric flask containing aluminium chrysin 1:3 complex in ethanol (5×10^{-4} M, 24.5 mL). Water was added to reach the required volume (25 ml). The absorbance was measured at the wavelengths of the maximum difference (393 nm) in the electronic spectra between the ligand and the complex. The spectra of the reaction of various amounts of fluoride with the complex were compared.

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