

METHODS FOR DETERMINING FLUORINE CONCENTRATION: A REVIEW

Ashish Jaiswal*, Arpita Ghosh*, Radha Sawant*,

Dr. Anupama Sawant², Mr. Ravindra Joshi^{3*}

BE Student, Chemical Engineering Department, Thadomal Shahani Engineering College, Mumbai

2 Sr. Scale Professor, Chemistry Department, Thadomal Shahani Engineering College, Mumbai

3 Assistant Professor, Chemical Engineering Department, Thadomal Shahani Engineering College, Mumbai

Abstract - Fluorides which are naturally found in soil, water, and foods play a role in the mineralization of our bones and prevent dental decay. Traces of fluorides are present in many water sources; higher concentrations are often associated with underground sources or due to industrial effluents. When present in lower quantities in drinking water it has beneficial effects on dental health, but excessive amounts can lead to several health effects on reproductive organs, nerves, muscle and, other problems like dental/skeletal fluorosis. Based on scientific results, groundwater sources such as bore-wells and hand-pumps in several states of India is contaminated with fluorides beyond the permissible limit of 1 – 1.5 ppm. 17 out of 32 Indian states are reported to have endemic fluorosis. Various methods are widely used for the determination of fluoride. Therefore, there must be a provision for supplying fluoride-free water and the fluoride contents of commercial toothpaste must be monitored.

This paper moreover reviews the methods used for the determination of fluoride content. It also suggests potential ways to reduce the hazardous ingestion of fluorides through regularly used toothpaste and water. Also, experimental determination of fluoride content was carried out in different samples to support the paper using spectrophotometric methods. Various other research papers in the concerning field, articles and, journals, self-examination by the experiments, performance and, knowledge gained through the Engineering Chemistry course have also been significant contributors to this paper.

Key Words: Complexometric Titration, Fluoride, Ion Selective, Spectrophotometric method, Colorimetric method

1. INTRODUCTION

Fluorine (F) exists as a pale-yellow diatomic gas. It is also one of the members of the halogen family. The element is found in soil, refrigerants, toothpaste, and groundwater.

It is an element that we encounter daily. Fluorine is water-soluble and gets accumulated in the bones when absorbed by an organism. It has an important role in the prevention of dental caries, and its deficiency might initiate some dental issues. Fluoride in drinking water has beneficial effects on teeth at low concentrations. It increases the rate of the

remineralization process and slows down the breaking of enamel and thus prevents tooth decay.

Water fluoridation is usually accomplished by adding (H_2SiF_6) fluorosilicic acid, (NaF) sodium fluoride, or (Na_2SiF_6) sodium fluorosilicate to drinking water.

A higher concentration of fluorine causes serious health hazards. It has also been previously claimed that fluoridated water causes a variety of health problems such as low IQ scores in children, bone cancer, arthritis and, kidney disease.

The Majority of the people in the world cannot even afford the expenses of the dentist for checkups and children are most commonly affected by problems such as tooth decay. These can be prevented by adding fluorine as specified in toothpaste.

Fluorosis is a major public health problem caused by the intake of excessive amounts of fluorides over a long period resulting in permanent and irreversible damages like dental, skeletal and, non-skeletal fluorosis. Excessive fluoride intake can destroy the bone formation and resorption process, which may lead to bone turnover disorders and result in skeletal fluorosis.

The extensive studies conducted claim to have no effective cure for these diseases. Therefore, it is desirable to drink water below 1.5 ppm concentration.

In the Indian Sub-continent, a large amount of the population suffers or is prone to fluorosis, due to excess fluoride in drinking water particularly in villages. Approximately, the excessive fluoride in groundwater is noticed in 177 districts covering 21 states, affecting 62 million people, including 6 million children.

In general, fluoride is released into groundwater from fluorine-bearing minerals such as fluorite, amphibole, fluormica, and some micas which are worn due to exposure to weather conditions. Intake of small concentrations is beneficial for human health. The Bureau of Indian Standards (BIS) prescribes a limit between 1.0 and 1.5 mg/L. For example, In the Markapur Region of India, the concentration of fluoride ions varied from 0.5 ~ 6 mg/L with a mean of 2 mg/L, which indicates that the concentration of fluoride is non-uniform in the study area. The table shows variation in

fluoride ion concentration in samples from a different region of Markapur.

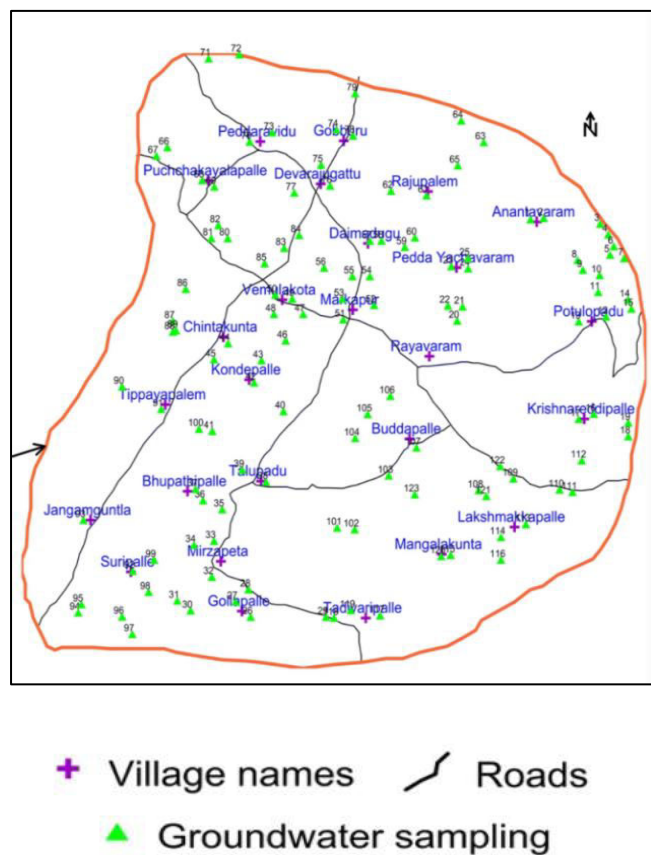


Fig1: Groundwater Concentration in various different regions of Markapur District

Fluoride Content (mg/L)	Percentage in Ground water sample
0.4 ~ 1.0	13%
1.1 ~ 1.5	49%
1.6 ~ 2.9	23%
3.2 ~ 5.8	21%

It was clear from the survey that the fluoride content in groundwater samples varied in different regions.

This paper mainly tries to focus on various techniques and innovative trends in determining the fluoride ion concentration in water and toothpaste samples which pose a threat to human health.

2. METHODS FOR DETERMINING FLUORIDE ION CONCENTRATION

2.1. Titrimetric Method

Determination of fluoride ion by complexometric titration:

In this method the fluoride ions are precipitated from the solution in the presence of chloride and ethanol as a reagent with standard lead nitrate solution of 0.05M concentration, which is readily available in bulk quantities in many laboratories.

A solution is prepared by dissolving 5 to 45 mg of pure sodium fluoride (NaF) in 8 ml of 0.2M sodium chloride and 13ml of 95% ethanol. The solution is then heated up to its boiling point and 25ml of 0.05M lead nitrate solution is added from a burette initially dropwise and rapidly when precipitate gets established. The solution is stirred continuously. The mixture is maintained at its boiling point for coagulating the precipitate. The next step is to cool the mixture to room temperature, the filtrate is then washed with four 15 ml portion of 20% (v/v) ethanol in aqueous 0.2M sodium chloride solution and, then it is titrated against 0.05M EDTA (complex) using xylenol orange as an indicator to reduce pH to 6 (approximately).

1 ml of 0.05M lead nitrate \equiv 2.10mg of sodium fluoride.

In the absence of F⁻ ions lead chloride will not precipitate.

2.2. Colorimetric Method

Colorimetric analysis for detection of the presence of fluoride ions is a method of determining the concentration of the element in a solution with the help of a color reagent or dye. The equipment that is necessary for this process is a colorimeter, some cuvettes and, a suitable color reagent.

For the determination of fluoride content in various samples using colorimetric analysis, various types of coloring reagent might be used. Few examples are

2.2.1. Solid Analytical Reagent:

The solid reagent in principle is produced by the interaction of two bulky oppositely charged colored ions, capable of forming an insoluble compound in an aqueous medium. In many cases such ion-associated compounds possess sufficiently low aqueous solubilities and as such can serve as useful analytical reagents. Their analytical applications lie in the specific reaction of one of the components with the species of interest in solution thereby releasing the counter ion for spectrophotometric determination.

2.2.2. Hemicyanine dye:

The novel reagent is a hemicyanine dye (HC) for colorimetric determination, which forms a stable complex with Zr-EDTA. The hemicyanine-chelating Zr-EDTA complex (HC-Zr-EDTA) is prepared to react with fluoride ions to release HC. This results in a visibly remarkable color transition of the sensing solutions from red ($\lambda_{max} = 513\text{nm}$) to yellow ($\lambda_{max} = 427\text{nm}$) at a noted pH of 4.40. When this technique is applied to the colorimetric determination of fluoride ions in any sample, a linear range from 3.0×10^{-6} to $5.0 \times 10^{-5}\text{mol/L}$ with detection limit of $2.8 \times 10^{-6}\text{mol/L}$ and a correlation coefficient of 0.9993 is seen to be achieved under the optimized conditions.

2.2.3. Ferric Chloride:

The Colorimetric method for the determination of fluoride with this reagent (Ferric Chloride) is based on the observation that the intensity of the color produced in the sample with thiocyanate by a given amount of iron in the presence of fluoride is less than that produced in the absence of fluoride. By colorimetric determination of the excess of iron reacting with ammonium thiocyanate, the quantity taken up by the fluoride from a given amount of iron may be calculated or determined by difference and its equivalent in fluoride read from a curve which can be constructed by plotting known amounts of fluoride against the iron they take up from the amount of ferric chloride used in the determination process.

2.3. Ion Selective Method

An ion-selective electrode is a fluoride-sensitive electrode of the solid-state membrane type.

The physical and chemical properties of the membrane determine the degree of ion selectivity. The crystalline membrane composed of lanthanum fluoride doped with minute amounts of a divalent cation, such as europium, is selectively permeable to fluoride ions.

The measuring fluoride electrode contains a filling solution of fluoride and chloride ions each at fixed concentration levels. These levels maintain constant potentials between the Ag-AgCl internal reference electrode and the filling solution and also between the filling solution and the inside surface of the crystal. Any change in potential at the surface of the crystal is primarily due to variations of fluoride ions in the process. The fixed activity of the fluoride ions is represented by the filling solution contained within the measuring electrode.

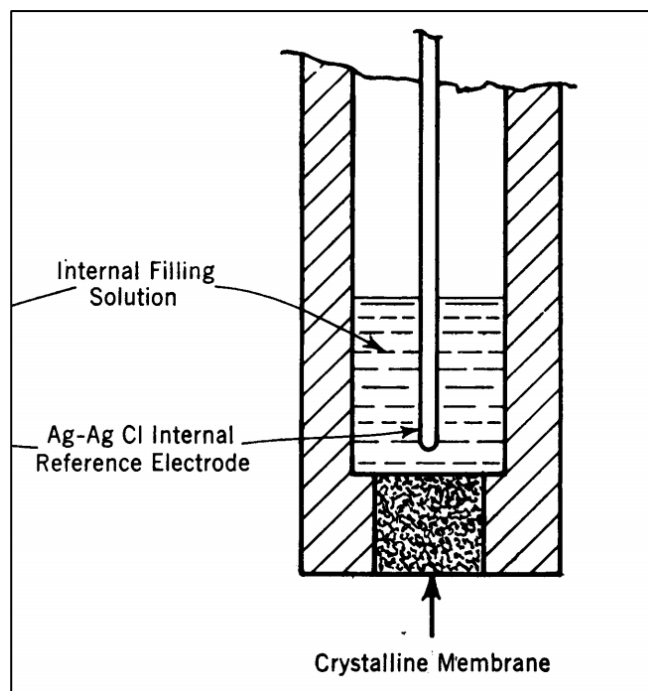


Fig 2. Schematic Diagram of Ion-Selective Electrode

A reference electrode is necessary to measure the potential across the measuring electrode. This electrode too contains an internal reference Ag-AgCl contacting the filling solution which then contacts the process solution via the liquid junction.

The Fluoride ion activity measurement follows the Nernst equation:

$$E = E^0 - 2.3nRTF \log(aF)$$

Here E changes by 59.16 mv for each tenfold change in fluoride ion activity. Potentials become increasingly negative as the solutions become more concentrated and more positive in increasingly dilute solutions. The electrode is useful below 0.19 mg/l, although the electrode response does not exactly follow the Nernst equation below 0.10 mg/l. Below this level, the potential approaches a constant value.

The electrode fundamentally responds to the fluoride activity, while it is the fluoride concentration that is of greater interest. These are related to the equation.

$$A = \gamma C$$

A = Activity

C = concentration

γ = activity coefficient.

The activity coefficient is not constant but varies with the total ionic strength of the sample. By knowing the composition of

the sample, the total ionic strength can be computed and the activity coefficient can be obtained.

2.3.1. Effect of Temperature:

Wide variations in temperatures only moderately affect the concentration of fluoride ions. At the iso-potential point i.e. when the fluoride activity of the process equals the activity of the filling solution of the electrode, both the electrodes are affected by the temperature to the same extent and therefore no temperature variations occur.

2.3.2. Effect of pH:

At pH value less than 4, hydrogen ions form a complex with free fluoride to form hydrogen fluoride (HF) which is generally not detected by the electrode.

At the high end of the pH scale, a notable interference is introduced by hydroxyl ions, this is due to the similarities between the ionic radii and charges on the fluoride and hydroxyl ions. When the Fluoride ion concentration is less than ten times the hydroxyl ion concentration, the electrode will respond to both ions. At this point the fluoride activity measured will equal approximately twice the actual fluoride activity. At pH of 7 or less aluminum and iron ions are known to be complex with fluoride ions. At pH greater than 7, hydroxyl ions are preferentially complex with the aluminum and iron ions.

2.4 Spectrophotometric Method:

Spectrophotometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through a sample solution

A spectrophotometer is an instrument that measures the amount of photons (the intensity of light) absorbed after it passes through a sample solution. With the spectrophotometer, the amount of a known chemical substance (concentrations) can also be determined by measuring the intensity of light detected.



Fig 3. Image of Spectrophotometer

2.4.1. EXPERIMENTAL ANALYSIS:

- Standard 0.01-0.08 mg/ml of NaF solution was prepared.
- 0.024g of methyl salicylate was dissolved in alcohol to prepare 100ml methyl salicylate – alcohol known solution.

2.4.2 FeCl₃ Preparation:

- About 1 gram of ferric chloride reagent was weighed accurately and transferred to a volumetric flask of 100 mL capacity. To the above reagent, 50 ml of ethanol was added and shaken well for reagent to get dissolved then the volume was made up using ethanol.

2.4.3. Calibration of Spectrophotometer:

- Select the range as per the wavelength required and set the required wavelength (525nm).
- Keeping the cuvette slot empty, set the function knob to transmission mode and set the transmission to zero using the set zero knob.
- Filling the cuvette with blank distilled water and placing it in the spectrophotometer, set the transmission to 100 using coarse and fine adjustment knob and switch the function knob to absorbance mode. The absorbance is 0.00.

2.4.4. For standard curve of known concentration of NaF:

- Take 1 ml each of NaF (say of 0.01mg/ml), freshly prepared FeCl₃-alcohol solution freshly prepared methyl salicylate-alcohol solution in a beaker.
- Transfer a small of mixture from beaker to cuvette.
- Ensure that the cuvette is clean and wiped with cotton.
- Place the cuvette in a spectrophotometer and observe the value of absorbance displayed.
- Similarly perform for other concentrations of NaF solution to obtain values and hence plot a graph of absorbance v/s concentration.
- We observe a linear graph.

2.4.5. Estimation of unknown concentration:

- Prepare solution of samples of unknown concentration of fluoride.
- Take one ml each of solution of unknown concentration, freshly prepared FeCl₃-alcohol solution, freshly prepared methyl salicylate-alcohol solution in a beaker.

- Transfer a small amount of mixture from beaker to cuvette.
- Ensure that the cuvette is clean.
- Place the cuvette in a spectrophotometer and observe the value of absorbance displayed.
- Plot these values on the standard curve of NaF obtained to determine the concentration in these solutions.

Fig 4: Calibration Curve.

Table 2: Experimental values obtained for Different Concentrations of NaF.

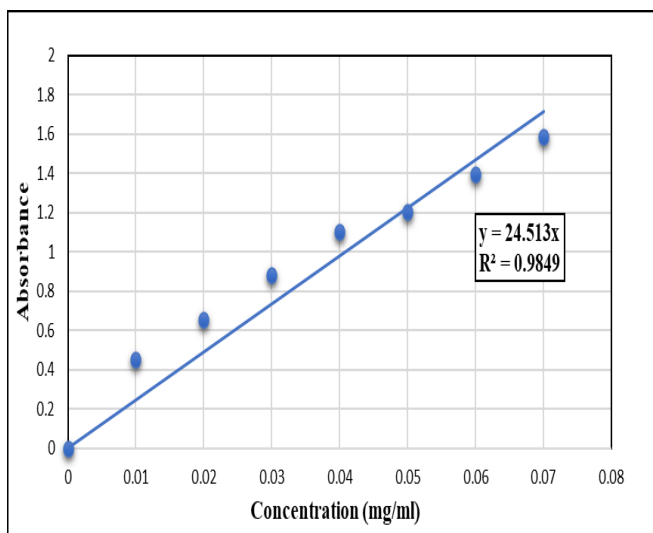
Concentration (mg/ml)	Absorbance
0	0
0.01	0.451
0.02	0.656
0.03	0.881
0.04	1.102
0.05	1.205
0.06	1.395
0.07	1.587
0.08	1.792

Table 3: Experimental Obtained for various Commercial Toothpaste brands and Groundwater

Brand	Absorbance	Concentration (mg/ml)
A(Kids)	1.781	0.07-0.08
B(Ayurvedic)	1.780	0.07-0.08
C	1.994	>0.08
D (Mouth Wash)	0.468	0.01-0.02
Ground Water	1.294	0.05-0.06

3. CONCLUSION

Excess Amounts of Fluoride Concentration in Toothpaste and Drinking Water Can pose a threat to human health. This review includes various laboratory techniques to determine the fluoride concentration including Complexometric Titration, Ion-Selective Electrode, Spectrophotometric and colorimetric methods. All these methods are very simple, cost-effective and, give accurate results. The spectrophotometric method was performed on various commercial toothpaste brands and the results found were tabulated in Table 3. The values of concentrations were found to be well within the specified range. Table 1 gives the fluoride concentration values in the various regions of the Markapur District. Thus this paper gives overall information on different methods for Fluoride Ion determination.



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