



A REVIEW ON ANALYTICAL METHODS FOR FLUORIDE DETERMINATION IN WATER

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ABSTRACT

Fluoride contamination in drinking water due to natural and anthropogenic activities has been recognized as one of the major problems worldwide imposing a serious threat to human health. The review of different analytical techniques and methodologies used in the analysis of fluoride in water is presented in this paper. Chromatographic, spectroscopic and electrochemical innovations appearing in the recent literature has been explored in this review. Among those, spectrophotometric techniques are widely used. This paper gives overall information about different techniques for fluoride determination in water

Keywords: Colorimetric Technique, Spectrophotometric Technique, Chromatography technique, Ion Selective Electrode, Water.

Introduction

Fluoride is a natural constituent of some ground water as it is present in many minerals such as topaz, fluorite, apatite, fluorapatite, cryolite, phosphorite and mica¹. Large population in India is still dependent on ground water for their daily requirements. So ground water is one of the important sources of fluoride for people in our country Fluoride is a natural element found at varying concentrations in all drinking water². Fluoride has been shown to cause significant effects in people health. Low concentration of fluoride in drinking water have been considered beneficial to prevent dental carries³, but excessive exposure to fluoride can give rise to a number of adverse effects such as causing fluorosis. Approximately 62 million people including 6 million children suffer from fluorosis. There is a narrow margin between the desired and harmful doses of fluoride. In India permissible limit of fluoride in drinking water is 1.0 – 1.5 mg/l (BIS). When concentration of fluoride becomes more than 1.5 mg/l in water, it shows adverse effect on human health in terms of fluorosis⁴. Many states of India are

suffering from dreadful fate of fluorosis some of them are Andhra Pradesh⁵, Haryana⁶, Rajasthan⁷, Punjab⁸ and Uttar Pradesh⁹. Recently some highly fluoridated areas in Chhattisgarh have also been located and dental and skeletal fluorosis was reported there. Many parts of Rajnandgaon¹⁰, Raigarh¹¹ and Surajpur¹² district of Chhattisgarh are badly affected by fluorosis. Therefore to avoid the dreadful health effects of fluoride, regular monitoring of fluoride concentration in water and removal of higher concentration of fluoride from water is essential. Therefore, an accurate, simple, rapid and cost effective analytical method is of high importance.

One of the constraints in fluorosis mitigation work is the testing of fluoride in the water. Fluoride concentration in water is determined by various methods which include potentiometry, with fluoride ion selective electrodes (ISE) spectrometry, chromatography and electrochemical methods¹³. This paper mainly focuses on the Fluoride detection in water.

Review and discussion about analytical methods for fluoride determination in water sample.

Several authors have investigated and reported successfully various techniques to determine fluoride ion in water such techniques are Ion selective electrode, Colorimetric, spectrophotometric, chromatographic technique. This review article is aimed at providing precise information on efforts made by various researchers in the field of fluoride detection in water.

Electro analytical methods

Electro analytical methods have a long history of development. Ion-selective potentiometry is one of the electro-analytical methods. There are some advantages of the use of Ion selective potentiometry (ISP) which is accurate, fast, and economic. The development of potentiometric ion-selective electrodes is a very interesting field because it has a wide range of applications in determining ions in water and other mediums. The basic idea of ion selective electrodes is the measuring of electrode potentials (voltages) and from that determining the concentration of analyte in the solution. Measuring voltages require two electrical contact points. One is a reference electrode whose potential is constant; the other is a sensing electrode, whose potential varies with concentration of analyte.

$$E_{\text{sensing}} - E_{\text{reference}} = E_{\text{measure}}$$

The use of ion-selective electrodes enables the determination of ion species in a trace. Ion-selective electrodes are suitable for analysis in industry, for control processes, for physiological measurements and environmental monitoring¹⁴.

A commercially available fluoride electrode was evaluated by Harwood et al.¹⁵ for use in routine analysis. The electrode has been shown to yield good results, without the necessity for careful control of temperature, etc. According to his studies it is extremely useful in surveillance studies and in routine analyses generally. Tests on samples showed that aluminium interfered. With CDTA present, reliable fluoride analyses were possible in the presence of up to 5 mg/l aluminium.

M. B. Rajkovic et al.¹⁶ were analysed fluoride ions concentration in bottled mineral waters and water from Belgrade plumbing in two Belgrade districts (Palilula and Novi Beograd) and in tea, by using the fluoride selective electrode.

The performance of the fluoride ion selective electrode (F-ISE) potentiometric method was evaluated by Ji-Hyang Noh and Paul Coetzee¹⁷ for fluoride determination in natural and drinking water. The following aspects were evaluated: minimising electrode drift, electrode care and optimisation, the use of different TISAB (total ion strength adjustment buffer) solutions, calibration procedures for trace F, interference correction procedures, matrix effects, and the determination of the analytical parameters. The methodologies and procedures proposed in their work were applied in an SABS proficiency testing programme (Water Check Programme-2004) which included low-level F determination in natural water and synthetic samples with varying amounts of possible interfering elements. The accuracy of the results was excellent confirming the versatility of F-ISE for low-level F determinations in routine laboratories provided that the correct analytical procedures are followed.

K. Nicholson and E. J. Duff¹⁸ reported departure from linear response which often occurs at dilute fluoride concentrations of the calibration curve reduces the sensitivity of the electrode. The linear portion of the standard curve may be extended to lower fluoride levels by dilution of the buffer itself. Results revealed that TISAB III M. tri-Ammonium citrate (TAC) is the superior of the eleven buffer systems examined in terms of masking ability.

The influence of the composition of buffer solutions on fluoride analyses by the fluoride ion selective electrode was studied by [Pentti Kauranen](#)¹⁹. Residual fluoride content of reagents

was observed to restrict the use of some buffers and reagents in low-level work. The optimum pH for low-level fluoride determinations was found to be around 5, which can be maintained by a sodium acetate-acetic acid buffer. Of the complexing agents studied, citrate was observed to be the most efficient masking agent for aluminium, but this ability depended strongly on ligand concentration. Citrate was also effective in masking iron (III) and magnesium ions. Tris (hydroxymethyl) aminomethane showed a similar ability to complex aluminium at a pH around 8. However, at this pH the hydroxide ion interferes in fluoride analysis below 0.1 ppm.

Marc A.G.Tvan den Hoop et al.²⁰ determined fluoride concentrations in Dutch rain water sample by three different analytical techniques, i.e., (i) capillary electrophoresis (CE), (ii) ion chromatography (IC) and (iii) ion-selective electrode potentiometry (ISE). Performance characteristics in terms of precision, limit of detection and run time have been obtained for the three applied methods using standard solutions in the range of 0.5 to 10.0 $\mu\text{mol l}^{-1}$. Limits of detection were found to be similar for IC and ISE (0.2 and 0.3 $\mu\text{mol l}^{-1}$, respectively) and somewhat higher for CE (0.6 $\mu\text{mol l}^{-1}$). Statistical analysis of the fluoride concentrations in rain water samples as obtained by CE, IC and ISE indicated that there was no evidence for systematic differences between CE and ISE, whereas the fluoride concentrations obtained by IC were significantly higher. The observed differences are most likely due to the presence of aluminium ion.

[David E. Erdmann²¹](#) has described an automated fluoride ion selective for fluoride determination in water. The results obtained on 38 natural water samples are in excellent agreement with those determined by a similar manual method (average difference = 0.026 mg/l). This method is capable of analysing thirty samples per hour over a concentration range of 0 -2 mg/l and utilizes Auto Analyzer modules.

Colorimetric and Spectrophotometric determination:

Spectrophotometry and colorimetry are techniques, which can be used to identify the molecules depending on their absorption and emission properties. This is an easy technique to determine the concentration of a sample, which has a color. Though the molecule does not have a color, if we can make a colored compound from it by a chemical reaction, that compound can also be used in these techniques. Energy levels are associated with a molecule, and they are discrete. Therefore, discrete transitions between the energy states will only occur at certain discrete energies. In these techniques, the absorption and emission arising from

these changes in the energy states are measured. This is the basis of all spectroscopic techniques²².

J.F. Zhang, et al.²³ reported that colorimetric method depends upon bleaching action of fluoride on a particular organo-metallic dye complex. The fluoride reacts with the dye lake, dissociating a portion of it into a colourless complex anion and the dye. As an amount of fluoride increase colour produced becomes progressively lighter depending on the reagent used. On the other hand spectrophotometric method are widely used in the determination of fluoride, method 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.²⁴

Zaher Barghouthi, et al.²⁵ determined fluoride in water calorimetrically by using ferric chloride. It is based on the fact that intensity of colour produced with thiocyanate by given amount 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 amount of 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.

Macejunas, Anthony G. et al.²⁶ reported determination of fluoride, using zirconium with xylenol orange for positive colour development, was presented as the first practical catalytic method for assaying fluoride content in water, with extreme sensitivity as its major advantage over older methods such as zirconium-alizarin and SPADNS-zirconium.

Fluoride (5–70 µg) in a final volume of 100 ml was determined by S. A. Rahim et al.²⁷ The analysis was based on the colored reaction of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthyl azo)-3-naphthoic acid and the bleaching effect of fluoride on it. The method is simple and rapid, and the accuracy is satisfactory when applied to different types of water. The procedure compared favourably with the conventional colorimetric method.

Kimiya et al.²⁸ have developed a method for determination of fluoride ion with a zirconium salt of tetraphenylporphine trisulfonate (TPPSZr). Slightly water soluble TPPSZr, which may be a polymer bridged by zirconium ion, liberates tetraphenylporphine trisulfonate (TPPS) by the reaction with fluoride ion. Fluoride ion can be determined spectrophotometrically on the

basis of the amount of released TPPS corresponding to fluoride ion. Zirconium salt of water soluble porphine –TPPSZr- is found to be applicable for determination of fluoride ion in water.

The zirconium-SPADNS method for the determination of fluoride based on the effect of fluoride ion on the color system (Zr-SPADNS), has been adapted to the continuous flow spectrophotometry. The decrease in the absorbance of Zr-SPADNS reagent at 590 nm is linear with fluoride concentration in the range 0.00-3.5 ppm. The method has a detection limit of 0.02 ppm fluoride. At a sampling rate of 50 determinations per hour, the precision was about 1% relative standard deviation. The method is applied to the determination of fluoride in natural water samples. The effects of reaction conditions, flow parameters, and interferences on the FIA-spectrophotometric signals were reported by Amin T. Haj-Hussein et al.²⁹

[R. M. Patel](#) et al.³⁰ have developed a simple, fast and selective flow injection analysis (FIA) procedure for monitoring of fluoride in surface and ground water. The method is based on destruction of Zr(IV)-SPADNS[2-(p-sulphophenylazo)1,8-dihydroxynaphthalene-3,6-disulphonic acid trisodium salt] complex with fluoride ions in the presence of neutral surfactants *i.e.*, TX-100, TX-300. The detection limit is 9 ppb F⁻ at 4M HCl. The sample throughput is 80 samples/hr. Optimization of FIA variables and detailed studies of interferences of sulphate and phosphate with respect to acidity and sample volume injected were carried out. None of the tested ions interfere in the determination of F⁻.

Javed et al.³¹ have introduced a new spectrophotometric reagent for the determination of trace amounts of fluoride. This method is based on the decolorization of a complex of Al(III) with xylenol orange (XO) as an ultra-sensitive colored reagent. Since the Al-XO complex plays an important role in this method, the protonation and complexation of XO with Al(III) at an ionic strength of 0.1 mol L⁻¹ at 25 degrees C has been studied by a spectrophotometric global analysis method. A spectrophotometric method for the assay of fluoride based on a decrease of the colour intensity of the Al-XO complex, in an aqueous solution has been designed. The effects of some important variables on the determination of fluoride based on the proposed method were investigated. The method was applied to the determination of fluoride under the optimum conditions (pH 5.2, ionic strength 0.1 mol L⁻¹, 25 degrees C). The determination of fluoride in the range of 0.08-1.4 microg mL⁻¹ (SD = 1.2%) was successfully performed. Interferences of Fe(III) were easily eliminated by using ascorbic acid. The proposed method was applied to the determination of trace amounts of fluoride content of some real water

samples

Parham et al.³² have developed a new, sensitive, fast and simple method using magnetic iron oxide nanoparticles (MIONs), as an adsorbent for extraction, preconcentration and determination of traces of fluoride ions. This determination method is based on the discoloration of Fe(III)-SCN complex with extracted fluoride ions which was subsequently monitored spectrophotometrically at $\lambda(\text{max})=458$ nm. Various parameters affecting the adsorption of fluoride by the MIONs have been investigated, such as pH of the solution, type, volume and concentration of desorbing reagent, amount of adsorbent and interference effects. A linear response for the determination of fluoride was achieved in the concentration range of 0.040-1.250 $\mu\text{g mL}^{-1}$. The limit of detection (LOD) and limit of quantification (LOQ) for fluoride based on 3 times and 10 times the standard deviation of the blank were 0.015 and 0.042 $\mu\text{g mL}^{-1}$ (n=20) for fluoride ion, respectively. The proposed procedure has been applied for determination of fluoride concentration in various water samples. The results obtained from this method were successfully compared with those provided by standard SPADNS method.

A modification of the spectrophotometric method for the determination of fluoride ions in iron-rich materials were proposed by Agata Jakóbi-Kolon et al.³³ In his method the iron matrix was successfully removed using Diphonixresin. The studied sample was a ferruginous mineral which contained about 38% of iron. The Euronorm certified reference material was used to validate the method. The concentration of fluoride ions was determined by a spectrophotometric method using a Zr:ER complex ($\lambda=540\text{nm}$). The result obtained for the ECRM was in good agreement with the certificate specification and thus proved the method to be applicable for the determination of fluoride ions in iron-rich materials. Due to the easy digestion step and simple requirements for equipment, this method can be used in most laboratories.

[Zaher Barghouthi](#) et al.³⁴ have developed a simple spectrophotometric method for determination of fluoride in drinking water by using complexes of chrysin. The method is based on the reaction of the coloured complexes with fluoride where its colour changes, due to the formation of the colourless fluoride complex and liberating of the free ligand, is dependent on the concentration of fluoride in water samples. The method allows a reliable determination of fluoride in the range 0.3–3.0 mg/l which is compatible to WHO limit value of 1.5 mg/l. The sensitivity, detection limit, quantitation limit, and correlation coefficient for the method were determined.

Thiago L. Marques et al.³⁵ developed an environmentally-friendly flow system for the determination of fluoride in natural waters, based on its reaction with zirconium ions and 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonate (SPADNS). Under optimized conditions, a linear response was observed within the range of 0.1–2.2 mg L⁻¹, with the detection limit, coefficient of variation and sampling rate estimated as 0.02 mg L⁻¹, 4.1% and 60 determinations per hour, respectively. In comparison with other methods, the proposed system offers advantages such as wider analytical range (1.7–2.2 times), higher sample throughput (1.5–4.0 times) and lower quantification limit (by a factor of 5–68). Along with the consumption of reagents being 20–55 times lower, the generation of wastes is 1.2–3.0 times lower, which contributes to the development of a ‘greener’ system. This method is fast, amenable to automation, environment-friendly and of low-cost. In addition, it could be successfully applied to the determination of fluoride in water samples, the results obtained were being in agreement with those of the ISE method.

Kalanithi M, et al.³⁶ have analysed fluoride ion present in ground water of some areas in Theni district using aluminium methyl orange complex by spectrophotometric determination. In this method the absorbance of methyl orange complex was measured and related to the concentration of fluoride ion in water. Present analysis of fluoride ion was compared with the values given by District Water Board. The method provides a reliable determination of fluoride in the range of 0.25-2 mg/L present in ground water. .

Ravi Chavali et al.³⁷ have synthesized a new water soluble colourless chemical compound 7-O-tertbutyldiphenylsilyl-4-methylcoumarin (TBDPSC) that releases fluorescent molecules imparting blue fluorescence to the solution, upon interaction with fluoride ions in water. The blue fluorescence can be visualized using simple hand held ultraviolet (UV) lamps. Results revealed that TBDPSC shown excellent sensitivity and selectivity towards fluoride and fluoride concentrations as low as 0.2 mg/L can be accurately detected within a few seconds. Fluoride testing with TBDPSC is simple and rapid compared to the conventional methodologies without the requirement of trained personnel. Hence, this fluoride detection method can be easily field deployable and particularly useful for monitoring water quality in limited resource communities

Meena Chakraborty et al.³⁸ studied spectrophotometric method based on the bleaching effect of fluoride ions on the determination of fluoride in water samples in field conditions and results obtained were compared with the results of potentiometric ion selective electrode method. It was found that results of spectrophotometric method were very close to those of

potentiometric method. Therefore spectrophotometric method can be used for field determination of fluoride with an error limit of ± 0.1 mg/l. Study also confirms that higher concentration of chloride ion in water sample does not affect fluoride determination by this method. Spectrophotometric method is easy to operate and less expensive than potentiometric ion selective method, hence more suitable for field determination of fluoride in samples.

Saurabh Levin et al.³⁹ designs fluoride assay kit, the smartphone camera is used as colorimeter which is portable, battery powered and widely available in the market. This allows accurate testing to be performed inexpensively on the field. Test chamber and reagent capsule are designed to ensure accurate mixing of sample and reagent while it being simple enough to be used by a layman. Android app developed for this allows much greater accuracy in the measurement of color as compared to visual judgment. Results obtained are comparable with the laboratory based expensive Ion Selective Electrode method and does not need any technical expertise for interpretation of results. Around 200 samples, which consisted of laboratory prepared as well as field samples collected from different locations in Karnataka, India, were tested with Akvo Caddisfly. Results revealed that significant positive correlation between Ion Selective Electrode (ISE) method and Akvo Caddisfly (Phones A, B and C), with correlation coefficient ranging between 0.9952 and 1.000. Thus the smartphone method is economical and suited for groundwater fluoride analysis in the field.

Chromatography technique

Chromatography is a separation method based on the affinity difference between two phases, the stationary and mobile phases. A sample is injected into a column, either packed or coated with the stationary phase, and separated by the mobile phase based on the difference in interaction (distribution or adsorption) between compounds and the stationary phase. Compounds with a low affinity for the stationary phase move more quickly through the column and elute earlier. The compounds that elute from the end of the column are determined by a suitable detector. In ion chromatography, an ion exchanger is used as the stationary phase, and the eluant for determination of anions is typically a dilute solution of sodium hydrogen carbonate and sodium carbonate. Colorimetric, electrometric or titrimetric detectors can be used for determining individual anions.⁴⁰

The determination of anions by capillary electrophoresis (CE) in combination with indirect UV detection has been reported for eight of the most common anions (F^- , Cl^- , Br^- , SO_4^{2-} , NO_3^- , NO_2^- , $S_2O_3^{2-}$, PO_4^{3-}) in drinking water, serum, and urine. The ability of capillary ion electrophoresis to analyse primary and secondary anionic contaminants as well as other ions

of environmental concern in drinking water, groundwater, and wastewater has been demonstrated⁴¹. Analytical time is less than 5 minutes.

Hakim et al.⁴² have determined fluoride, chloride and nitrate anions in drinking water samples using techniques of ion selective electrode (ISE) and non-suppressed/suppressed ion chromatography (IC). Detection limit, percentage recovery and run time were evaluated for the two methods. Detection limits for ISE [0.02, 0.20 and 1.7 ppm (µg/mL) for fluoride, chloride and nitrate, respectively], were better than those for non-suppressed IC (2.0, 1.0 and 2.0 ppm for fluoride, chloride and nitrate, respectively). Suppressed IC was used to measure fluoride.

Marvin J. et al.⁴³ has determined selected anions (bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulphate) in water by ion chromatography. Ion chromatography is a rapid, sensitive, precise, and accurate method for the determination of major anions in rain water and surface waters. Chloride, nitrate, nitrite, orthophosphate, and sulfate, in several samples, were also determined independently by automated colorimetric procedures. An automated ion-selective electrode method was used to determine fluoride. Results are in agreement with results obtained by ion chromatography.

Maria Montes Bayon et al.⁴⁴ reported alternative method for the determination of trace levels of fluoride in drinking and sea-water samples. His method is based on the formation of the aluminium monofluoride complex in excess of Al^{3+} and separation of the two species formed (AlF^{2+} and Al^{3+} in a small (5 cm long, CG2) ion exchange guard column. The final determination is accomplished by both ICP-MS specific detection and post column derivatisation with fluorimetric detection. This method was applied to the determination of very low levels of fluoride in natural waters.

X. R. Xu et al.⁴⁵ have described method for the determination of fluoride by reversed-phase, high-performance liquid chromatography (RP-HPLC). This method is successfully applied to the determination of fluoride in river and tap water.

Hassan M. L et al.⁴⁶ have developed chromatographic method for drinking and raw water quality monitoring. Determinations of common anions by IC methods in Baghdad were carried out in his investigation; total time for anion analyses was about 14 min.

Ion chromatography (IC) hyphenated to a conductivity detector (CD) is a well-established and accepted technique for the quantitative analysis of inorganic anions in drinking water. Sébastien et al.⁴⁷ have developed method for the determination of trace and major inorganic anions in water. It allows in a single run the simultaneous analysis of fluoride, bromide, phosphate, nitrate, chloride, sulfate, chlorite, and bromate with limit of quantification suitable

for drinking water analysis. In comparison with the use of two methods for the determination of both major and trace inorganic anions, the proposed method is powerful and is time saving (and thus cost effective) which is suitable for laboratories doing high volume routine analysis. Nazaratul Ashifa Abdullah Salim et al.⁴⁸ have analysed fluoride and other ions on diverse natural waters using the suppressed ion chromatography method. The determination of inorganic anions and cations in many type of water continues to be the most widely used application of IC including natural water.

Conclusion

Global occurrence of Fluoride in water is considered to be a major risk factor, affecting human health. In this review, several analytical methods including Ion selective electrode method, Colorimetric and spectrophotometric method and chromatography methods are described in their great potentials in quality of water. Spectrophotometric determination of Fluoride provides simple, cost effective, good sensitivity and selectivity. By these methods Fluoride ions in water is detected and safe drinking water within its permissible limit is provided. Now days, Ion selective electrode method is getting more attraction due to its high accuracy, but it is very sensitive, expensive and need special training to operate. Chromatography method is laborious and time taking. Colorimetric and spectrophotometric are widely used methods especially in water testing laboratories and even Fluoride testing kit is also based on vision for instant results in villages. This paper gives overall information about different techniques for fluoride determination in water.

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