Fluorine, a Dreaded Element: A Review on Occurrence of Fluorine in Environment and its Standard Methods of Analysis

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Abstract

The purpose of this review is to describe various geological and chemical factors that are controlling the fluoride concentration in soil, rocks, water, air, plants, animals and food stuffs. Further to discuss well established method that is used as the standard methods of analysis. Rock, Soil, Water, air, plants, animals, foodstuffs all contain fluoride in widely varied concentration. Industries are the main source of polluting atmosphere with fluorine. In an earth crust because of precipitate of CaF$_2$, calcium rich sedimentary rocks have high concentration of fluorine. A list of 150 fluorine bearing minerals was given by Strunz of which 63 are silicates, 34 are halides and 24 are phosphates. Even in similar rocks, the fluorine contents of mineral increases as the alkali or silica content of host rock increases. Fluorine content in soil entirely depends upon their composition and fluorine content of rock from which they have been derived. The fluoride content in ground water varies greatly depending upon the type of rock from which it originates. Pressure, temperature and chemical composition of reservoir also controls the concentration of fluorine. Three factors are controlling the fluoride distribution in ground water. (a) Size and distribution of fluorite and other fluoride bearing minerals (b) Availability of ground water in contact with those minerals (c) The duration of contact of ground water with fluoride bearing minerals and rocks. Weathering of alkaline silicic igneous rock contributes a major portion of fluoride in natural water. Fluorine content of hot springs increases with
increasing temperature. Fluoride is widely used in various branches of industry and some fluoride compounds are formed as by products in certain process. Excessive amounts of fluoride in the form of different compounds can enter the human body by means of polluted air, water and food chain. Fluoride prevents tooth decay at 1-mg/lit concentration but causes mottled teeth (dental fluorosis), bone damages (Skeletal fluorosis) at about 5mg /lit. For adults the lethal dose is 0.2-0.35 gm F per kg body weight. Fluoride in foodstuffs depends on the nutrient uptake from the soil. Tea plant leaves are containing maximum concentration of fluoride. Concentration of fluoride in black and green tea leaves was determined by Zerabruck et al. Measurement of fluorine in various matrices involves three steps (a) Dissolution of fluoride (b) Separation of fluoride (c) Measurement of fluoride. Concentration of fluoride can be measured by (1) Ion selective electrode method (2) Photometric method (3) Ion Chromatography method (4) Ion selective Electrode flow injection analysis method. The above discussion reveals that fluorine is an essential element in human diet based upon its important role in bone and teeth mineralisation, stimulatory and inhibitory effects on many soft tissues enzymes and dental caries resistance. The increased fluoride intake with water and food as well as on occupational exposure on fluoride dust could be reason for skeletal and dental fluorosis in humans.

**Keywords**: - Ion selective electrode (ISE), Spectrophotometer, Ion Chromatography (IC), Total ionic Strength Adjustment Buffer (TISAB), Flow injection analysis (FIA), Fluorosis.

**Introduction**
Fluorine is having electronic configuration 1S^2, 2S^2 2p^5 and is just one electron short of electronic configuration of inert gases. It tries to have inert gas structure and is because of this reason it is highly reactive. Its electronegativity is highest among all elements of periodic table. On account of its chemical reactivity, fluorine is one of the most dispersed elements in the environment and occurs as fluoride ion in different types of samples.

**Materials And Methods Of Analysis**
Following methods are used for analysis of fluoride in soil, water, food, beverages and gas samples [Ray and Ruikar 1979; Ramteke and Moghe 1986; Raghuramulu et al; 1983; Clasceri et al; 1998; Das 2007].

1. Ion selective electrode method
2. Photometric method
3. Ion Chromatography method
4. Ion selective electrode flow injection method.
Every method involves three steps.
(A) **Dissolution of fluoride:** - Fusion technique were used for silicate rocks, coal and plant materials which have high silica ash content. Fusion is done in platinum or Nickel crucibles. Fusion temperature is kept between 450-600°C. Potassium-hydroxide [Hall 1968] Sodium hydroxide [Fabbri and Donati 1981] Sodium carbonate [NadKarni 1980] Mixture of Sodium carbonate and potassium Nitrate [Haynes 1978]. Calcium oxide followed by Sodium hydroxide [Horwitz 1980] Zinc oxide [Dolan et al; 1978] are used as fusion material. Magnesium acetate is used as a fusion material for blood samples [Alary et al; 1983]. Fused mixture is dissolved either in water [Haynes 1978; Ingram 1970] or acid. (Nadkarni 1980) Citric acid at pH 3.3 releases the fluoride in milk (Beddows and Kirk 1981). Successive reaction with 0.05mol/dm³ Nitric acid then 0.05 mol/dm³ potassium hydroxide was used for extraction of fluorine from plant material [Malde et al; 1997; Harwitz 1980]

(B) **Separation of Fluoride:** - Three methods are used (1) Diffusion (2) Distillation (3) Pyrohydrolysis.

- **Diffusion:** - Sample is mixed with perchloric acid saturated with hexamethyl-disiloxane and distilled. Fluorides react with hexamethyldisiloxane in distillation apparatus forming volatile fluorosilanes which are transferred at room temperature in stream of nitrogen to an absorption vessel containing dilute alkali. The fluorosilane undergo rapid hydrolysis in alkali and estimation may be effected by any of the conventional methods. [Hall 1969; Sara and Wannienen 1975].

- **Distillation:** - Sample is mixed with Sulfuric acid and Perchloric acid and distilled. Hydrogen fluoride formed is collected in fluorine free water. Silver perchlorate is added to prevent the co-distillation of other halogens and sulphides (Horwitz 1980; Ma and Gwirts man 1957; Marczenko and Lenarczy 1976).

- **Pyrohydrolysis:** - In this process fluoride is displaced from refractory materials, organic compounds, organometallics and coal by heating the sample to 1120°C in a stream of super heated steam and the vapours are collected in water. It is then analysed by any of the conventional method [Berns and Vander Zwaan 1972; Vanleuven et al; 1979].

(C) **Measurement of fluorine:** - Four methods are used for chemical characterisation of fluorine.

- **Ion selective Electrode method:** - This method is most frequently used and is applicable to biological materials (urine, saliva, Tissues , Bone, Hair, Fingernail etc) and environmental samples (Air, Water, Food, Beverage, Tea, Milk, Peas, soil). Ion selective electrode for fluoride was developed by Frant and Ross [Frant and Ross 1968]. The electrode is available both as single electrode to be used in conjunction with calomel reference electrode or as a combination electrode with reference electrode incorporated in outer sheath of electrode body. Electrode follows Nernst equation $E = E^0 - \frac{RT}{F} \ln [F^-]$ where R is gas constant, T is the absolute temperature. Lower limit for analysis is around 1 x 10⁻⁶ mol/dm³ fluoride. Nicholson [Nicholson and Duff 1981; Nicholson 1983] discussed various errors and problems associated with the use of ion selective electrode in his reviews. Interference of polyvalent-
cations, Al\(^{3+}\), Fe\(^{3+}\), Mg\(^{2+}\) is removed by adding TISAB (Total ionic strength adjustment buffer). This reagent serves three functions, maintains pH (5-5.5), provides constant high ionic strength, release of fluoride from complexes and prevents the formation of bifluoride ion (HF\(^{2-}\)) which is not detected by ion sensitive electrode. The complexing agents used are citrate, CDTA (Trans 1, 2 – diaminocyclohexane –N, N, N, N,– tetra- acetic acid [Harwood 1967], Tiron (Pyrocatechol -3, 5- disodium disulfonate) [Tanikawa et al.; 1975; Wolfganj and Peter 1986], Mannitol and triethanolamine. In most analytical work the potential developed in analyte solution is compared with that obtained for series of standard solution similarly treated with TISAB solution. To save time, fluoride ion selective electrode is inserted directly into analyte solution without purification. Concentration of fluoride ion is determined by Ion selective electrode following the instruction for operation of the electrode by manufacturer. Regents required are

a) **Stock fluoride solution** :- Dissolve 221.0 mg anhydrous NaF in distilled water and dilute to 1000ml by same water 1.00 ml = 100 µg F\(^-\). Make other working standards with the stock fluoride solution.
b) **TISAB Buffer** : - Mix 500 ml distilled water, 57ml glacial acetic acid, 58gm NaCl, and 4.0gm, 1,2- Cyclohexylenediamine tetraacetic acid (CDTA). Cool and add 6NNaOH (about 125 ml) with stirring until pH is between 5.3- 5.5, make it 1000 ml by distilled water.

**Photometric Method** : - This method is mostly used to determine fluoride concentration in environmental samples (water, waste water, Food, Beverages and Tea). This method depends upon the bleaching action of fluoride on the intensity of colour of the complex / lake formed between dyestuff and metal. For example coloured complex formed between zirconium and SPANDS [Sodium 2- (p-Sulfophenylazo)-1,8-dihydroxynaphthalene -3,6-disulfonate (Clesceri et al; 1998), Zirconium and eriochrome cyanins –(R Sharma 1964) or Zirconium and 3- alizarin in sulfuric acid [Clesceri et al, 1998] are used for analysis of fluoride ion. This colourimetric method is based on the reaction between fluoride ion and Zirconium dyelake. Fluoride ion reacts with dyelake dissociating a portion of it into a colourless complex anion \([Zr F_6^{2-}]\) and dye. The rate of reaction between fluoride ion and Zirconium ion is influenced greatly by acidity of the reaction mixture and polyvalent metal ion present in the mixture. In another reaction intensity of the colour of the complex formed between cerium or Lanthanum with alizarine fluorine blue [3-(N,N-di-carboxymethylaminomethyl)-1,2-dihydroxyan-thraquinone] increases with the increasing concentration of fluoride ion [Belcher and west 1968]. Greenhalgh and Riley (Greenhalgh and Riley 1961) found increased stability and sensitivity of the Lanthanum/alizarine comlexone reagent in 16% acetone and applied the method to the determination of fluoride in natural waters including seas water. [ Chan and Riley 1966] urine (Hargreaves et al; 1970) and plant materials (Leonard et al., 1970). It is found that sulfonated alizarine fluorine blue 3- [ N, N-di( Carboxymethyl) aminomethyl]-1,2- dihydroxyan-thraquinone -5- sulfonic acid gives better results (Leonard and Murray 1974; Dean et al.,
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1978). Chlorine is removed by adding a drop of sodium arsenite. Polyvalent cations are removed by methods discussed above. Regents required for SPANDS method are (a) Standard Fluoride solution: Prepared by dissolving NaF in distilled water (already discussed). (b) Spands solution: - Dissolve 958mg SPANDS in distilled water and dilute to 500ml. (c) Zirconyl–Acid reagent: - Dissolve 133 mg of Zirconyl Chloride Octahydrate ZroCl₂₈H₂O in about 25 ml distilled water. Add 350 ml concentrated HCl and dilute to 500 ml with distilled water. (d) Acid-Zirconyl SPANDS reagent (Mix equal volumes of SPANDS solution with zirconyl-Acid solution. The combined reagent is stable for two years. e) Reference solution: - Add 10ml of SPANDS solution to 100 ml distilled water. Dilute 7 ml of concentrated HCl to 10 ml and add to the diluted SPANDS solution. The resulting solution used for setting instrument Zero. (f) Sodium Arsenite Solution: - Dissolve 50.0gm NaAsO₂ and dilute to 1- litre with distilled water. Regents required for Alizarine fluorine blue method are: - (a) Acetate Buffer Solution: - Dissolve 60gm anhydrous sodium acetate in about 600 ml distilled water. Add 100 ml conc. Acetic acid and dilute to 1- litre. (b) Alizarine–fluorine stock solution: Add 960 mg alizarine fluorine to 100 ml distilled water. Add 2ml glacial acetic acid, dilute to 250 ml and store it in amber coloured bottle in refrigerator. (c) Lanthanum Nitrate stock solution – Dissolve 1.08gm La(NO₃)₃ in about 100 ml distilled water. Dilute to 250ml and store in refrigerator. (d) Working Colour regent: - Mix in the following order: 300 ml of acetate buffer solution, 150 ml acetone, 50 ml tertiary butanol, 36ml alizarine fluorine blue stock solution, 40 ml Lanthanum Nitrate stock solution and 2 ml poloxyethylene Lauryl ether. Dilute to 1-litre with distilled water. The reagent is stable for 2-4 days. Absorbance of the colour formed is measured from spectrophotometer at recommended wave length. Plot a curve of the milligrams fluoride-absorbance relationship. Concentration of fluoride in unknown sample is calculated by comparing the absorbance from the graph.

- **Ion Chromatographic Method:** - Ion exchange chromatography utilizes ion exchange mechanism to separate analyts. This method is applicable to mining samples, Aluminum reduction, ceramic, glass etchings, electroplating, semiconductors, water and florochemical industries. Anion exchange resin was first of all used by Stevens & Bauman [Small et al., 1975] Ion exchange Chromatography uses a charged stationary phase of an insoluble matrix to which charged groups have been covalently bound. The charged groups are associated with mobile counter ions. These counterions can be reversibly exchanged with other ions of same charge without altering the matrix. This method was used for determination of fluoride in geological material (Willson and Gent 1983; Lash and Hill 1979) and other organic compounds (Wang and Tarter 1983) Process for determination of fluoride in air by ion Chromatography is given NIOSH 7906 [NIOSH 1994]. Sodium tetraborate was used as eluent. Follow the instruction given by manufacturer of Ion Chromatograph for separation of fluoride ion. After separation concentration
of fluorine can be determined by any conventional method. Regents required for separation of fluorine from rest of the matrix are (a) **Alkaline fixative solution**: Dissolve 25 gm Na$_2$CO$_3$ in de-ionized water add 20 ml glycerol. Dilute to 1-litre.  

(b) **Calibration stock solution**: Dissolve 0.2211gm NaF (dried at 105°C for 2 hrs ) in deionised water. Dilute to 1 litre.  

(c) **Sodium hydroxide, 20% (W/V)**: Dissolve 200gm NaOH in deionised water dilute to 1 litre.  

(d) **Acetate Stock Solution**: Dissolve 0.13 gm sodium acetate in deionised water. Dilute to 50ml.  

(e) **Mixed anion solution**: Add 0.10 ml of fluoride stock solution and 0.10 ml acetate stock solution to deionized water. Dilute to 50ml.  

(f) **Eluent 1.25 m M sodium tetraborate** :- Dissolve 1.9079 gm Na$_2$B$_4$O$_7$. 10H$_2$O in deionized water. Dilute to 4-litre. Lower limits of detection is 1 x 10$^{-6}$ mg/l. Set the ion chromatograph according to manufacturer instruction inject the sample aliquot and measure the concentration.

- **Ion Selective Electrode flow Injection Analysis**: - (Clesceri et al., 1998) this method is applicable to water, Industrial waste water as well as leachates. Flow injection analysis (FIA) is an automated method of introducing a precisely measured portion of liquid sample into continuously flowing carrier stream. The sample portion is injected into carrier stream by either an injection valve with a fixed volume sample loop or an injection valve in which fixed time period determines injected sample volume. As the sample portion leaves the injection valve it disperses into the carrier stream and forms an asymmetric Gaussian gradient in analyte concentration. This concentration gradient is detected continuously by either a colour reaction or another analyte specific detector through which the carrier and gradient flow. It is important that FIA flow rates, injected sample portion volume, temperature and time the sample is flowing through the system (residence time) be the same for calibration standards and unknown. In this method fluoride is determined potentiometrically by using a combination fluoride-selective electrode in a flow cell. Interference of cation is removed by adding TISAB. Setup manifold instrument as per instruction suggested by manufacturer. Concentration of F ion is determined from the curve observed by plotting electrode response to standard response processed through the manifold Vs. fluoride concentration. Standards greater than 1.0mg/litre will give positive peaks. Standards less than 1.0mg F/litre will give negative peaks and the 1.0mg F/litre standard having same concentration as the carrier will give no peak.

**Result and Discussion**

**Occurrence of fluorine in earth atmosphere**: Industries are the main source of polluting atmosphere with fluorine. Industrial plants like manufacture of hydrofluoric acid, Aluminum, Superphosphate, Enamal, Bricks and industries consuming high sulfur non cooking coal like thermal power plants are main source of fluoride pollution (Griffin et al., 1980). Burning of low grade coal in thermal power station produces fly ash with other type of ash (Bottom ash, economizer ash and aerators
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ash). Major constituent of these fly ash are CaO, MgO, Na₂O, K₂O, SiO₂, Fe₂O₃, Al₂O₃, MnO, TiO₂, P₂O₅ and several trace element like Cu, Pb, Zn, Ni, Co etc. Coal ash is rich in fluorine content probably due to CaF₂ formed during coal burning (Keller 1988). Fly ash contains particle of fine size having higher concentration of sulfate and fluoride radical. The normal fluorine content in unpolluted air is less than 0.11µg/m³ (Bowen. 1966). Fluorine in Earth Crust :- Fluorine on account of its higher reactivity occurs as highly mobile fluoride ion but its mobility is severely restricted across a calcium barrier due to calcium fluoride precipitation (Perelman 1977). It is because of this reason that under supgene environment, the average fluorine content of calcium rich sedimentary rocks like calcareous shale, limestone, dolomite, calcareous sandstone etc is high. Amphiboles and micas also contain fluoride is because of similarity in the ionic radii of OH and F ion. OH ions are substituted by F ions. A list of 150 fluorine bearing minerals was given by Strunz (Strunz 1970) of which 63 are silicates, 34 are halids and 24 are phosphates. Fluorine in common Igneous rocks :- Fluorine bearing igneous rocks are Granite, Gabbro, Pegmatite, Quartz or Kimberlite. Main mineral are Apatite, Hornblende, Muscovite or Sphene etc. Because of the similar ionic radii (F=1.33Å⁰) (OH=1.40Å⁰) complete replacement of OH ions with F ions is possible. Electronegativity also plays an important role in substitution. In fact substitution of OH by F ion in the structure of mineral entirely depends upon bond energy and coordination number of OH sites (Rimsaite 1967). It is also seen that even in similar rock the fluorine content of the mineral increases as the alkali or silica content of host rock increases. (Wedepohl 1974). In all acidic melts evolved either by differentiation or by any other process all minerals which contain alkali and OH bond are good geochemical host’s for fluorine. Range and average fluorine content of some rock forming minerals is given in table below. [Taborszky 1962; Shamkin and Shiryayeva 1968; Nemec 1968; Buddington and Leonhard 1953; Kostetskaya and Mordvinova 1968]

<table>
<thead>
<tr>
<th>Name of the mineral</th>
<th>Name of the rock</th>
<th>Average of fluoride range in weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>Gabbro</td>
<td>1.83</td>
</tr>
<tr>
<td>Apatite</td>
<td>Pegmatite</td>
<td>2.97</td>
</tr>
<tr>
<td>Biotite</td>
<td>Hornblende granite</td>
<td>1.67</td>
</tr>
<tr>
<td>Hornblende</td>
<td>Granite</td>
<td>1.50</td>
</tr>
<tr>
<td>Sphene</td>
<td>Granite</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Fluorine in Soil : Since Soil is formed by weathering of rocks. Fluorine contents of soil entirely depend upon their composition and fluorine content of the rocks from which they have been derived [Keller 1986]. The average fluorine content in soil ranges between 90-980 ppm. Decomposition of organic remains is the main source of fluorine in soil in warm and humid climate. From acid soil fluorine is readily leached while biogenic accumulation prevents it. Fluorine in sediments: - The Chief fluorine bearing mineral in sedimentary rocks are Fluorite (48.7%) fluorine, apatite (3.5% fluorine Mica (between 0.14 to 0.22% fluorine) Illite (between 0.11 to 0.26% fluorine) and montmorillonite (0.03% fluorine) [Koritnig 1963]. It is interesting to
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note that fluorine in sedimentary rocks is due to presence of fluorine bearing minerals like fluorite and apatite or due to presence of clays which absorbs fluoride by $F$ to $OH$ replacement or by admixture of skeleton debris in which hydroxyl bonds are replaced by fluorine in the hydroxyl apatite structure [Carpenter 1969]. It is the kind and distribution of fluorine bearing minerals ultimately determines the fluorine content of the sedimentary rocks. The average fluorine content of sedimentary rocks (Micas and Illite) is more than 1.5 times the average fluorine content of igneous rocks. The average fluorine content in different sedimentary rocks are given in table below. (Fleischer and Robinson 1963).

<table>
<thead>
<tr>
<th>Rocks</th>
<th>Range in ppm</th>
<th>Average range in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>Up to 1210</td>
<td>220</td>
</tr>
<tr>
<td>Dolomite</td>
<td>110-400</td>
<td>260</td>
</tr>
<tr>
<td>Sandstone and Greywake</td>
<td>10-1100</td>
<td>200</td>
</tr>
<tr>
<td>Shale</td>
<td>10-7600</td>
<td>940</td>
</tr>
<tr>
<td>Volcanic ashes and Bentonites</td>
<td>100-2900</td>
<td>750</td>
</tr>
<tr>
<td>Oceanic sediments</td>
<td>100-1600</td>
<td>730</td>
</tr>
</tbody>
</table>

In carbonate rocks fluorine is contributed by fluorapatite and clay minerals in different proportion. In limestones of chemical origin co-precipitation of CaF$_2$ and CaCO$_3$ is the major process which controls the fluorine distribution in the rocks. The fluorine contents of marine anhydrite is solely due to precipitation of CaF$_2$. [Schneider 1953]. Because of co-precipitation average fluorine content of Non marine sediments is always lower than sediments of marine origine. (Bloxam and Thomas 1969)

Fluoride in Natural Water: - Concentration of fluorine in natural water is controlled by weathering of rocks. Weathering is a complete process involving adsorption-desorption and dissolution precipitation reaction. During weathering the circulation of water in rocks and soils, fluorine can be leached out and dissolved in ground water. Fluorine in apatite is very stable while the fluorine from mica is leached out rapidly. Fluorite (CaF$_2$) if present is dissolved slowly by circulating water. The fluorine content of ground water varies greatly (0 to 35 ppm) depending upon the type of the rocks from which it originate (Bond 1945). In general abundance of fluorine in fresh water varies between 0.25 to 1.0 ppm (Hawkes and Webb 1962). Concentration of fluorine in natural water depends on the solubility of fluorapatite [Ca$_5$F(PO$_4$)$_3$] and fluorite [CaF$_2$]. It is very low and controlled by temperature, pressure and chemical composition of the host reservoir. (Appelo and Postma 1993; Handa 1977; Valyasko et al; 1968) In fact there exist two principal hydro-chemical domains in natural water. In one, the fluorine in water is totally contributed by soil, weathered zone and aquifer material. In the other domain, the fluorine in water is primarily partitioned off from the aquifer, rocks, and soil and subsequently fluorine and other mineral distribution (TDS) in water is enhanced by significant amount of evaporation specially in arid-desert type climates. Hydro-chemically therefore it is very apparent that fluorine distribution in natural water from domain one will be totally controlled by CaF$_2$ solubility product in particular type of water. Where evaporation is very strong factor (domain II) the mineralogy of natural water is totally controlled by sequential
precipitation reaction which do not necessarily fallow the dissolution reaction. The fluoride content of surface water also varies greatly from (Zero) to 6.4 ppm depending on the fluoride content of ground water feeding a given stream (Fleischer and Robinson 1963). Fluoride content in lakes varies from (Zero) to 0.34 ppm. In permafrost regions fluoride content of lakes is proportional to dissolved organic matter and it varies from 0.16 to 0.34 ppm. In arid regions it varies with the chemical class of lake, Na lakes being generally rich. The mean concentration of fluorine in ocean water is 0.03 to 1.32 ppm and is seen to increase with depth. [Riley 1965]  

**Fluorine in hot springs:**- The fluorine content of hot springs varies form 0.15 to 55.4 ppm (Matuura and Kokubun 1955; Sugawara 1967) and seen to increase with increasing temperature. In India hot springs (35°C to 100°C) are mostly distributed along the major lineaments and rifts and their fluorine content varies from 10 to 17 ppm (Ravishankar 1986; Chowdhury and Honda 1973)  

**Fluorine in ground water:**- There are three factors controlling the fluoride distribution in ground water (1) size and distribution of fluorite and other fluoride bearing minerals (2) Availability of ground water in contact with those minerals (3) The duration of contact of ground water with fluoride bearing minerals and rocks. Fluoride occurs in fluorite, apatite, mica, garnet and lattices of amphiboles. It is usually considered that fluoride content of these rocks were transferred to the subsequently formed sedimentary and metamorphic rocks. (Briz –Kishore 1988). Weathering of alkaline silicic igneous rocks (specially shale) contribute a major portion of fluoride in natural water (McNeely et al; 1979; Meenakshi et al.; 2006). Apart from Natural sources considerable amount of fluoride may be contributed due to phosphatic fertilizers, steel, alluminium and brick industry. It is also released in burning of coal (Coal ash). These may cause increase in fluoride concentration in soils which on leaching results in enrichment of fluoride in ground water. Fluoride shows a positive correlation with bicarbonate ion and negative correlation with calcium ions. (Kakar et al; 1988)  

**Fluorine in Food Stuffs:**- Fluoride in foodstuffs depends on the nutrient uptake from the soil. Nutrient uptake in plants depend upon the composition and pH of soil. Nutrient uptake in plant is not dependent upon the concentration of mineral in soil but rather depends on the leachability/ solubility of the particular mineral under contemporary pedological environment (Pande et al; 1993). Natural or marginally alkaline pH of the soil facilitates nutrient uptake in plants (Govinda rajan and Gopalarao 1978). Tea plants (Camellia Sinesis) accumulates and stores more fluoride by absorption from air and soil than any other plant. Up to 98% of fluoride in tea plants is stored in leaves (Cao et al; 2006; Malinokuska et al; 2008). Concentration of fluoride in black and green tea leaves was determined by Zerabruck et al (Zerabruck et al; 2010). Fluoride is widely used in various branches of industry and some fluoride compounds are formed as by products in certain processes. Excessive amounts of fluoride in the form of different compounds can enter the human body by means of polluted air, water and food chain. Fluoride prevents tooth decay at 1-mg/lt concentration but causes mottled teeth (dental fluorosis) and bone damage (Skeletal fluorosis) at about 5-mg/lt concentration (Huang and Jackson 1997; Nancy et al; 2003; Pamela et al; 2006; Bossin E.B et al; 2006; David et al; 2004; Tokalioglu et al, 2001; Dozal et al; 2005; Kim et al; 2011).
Conclusion
About 150 fluorine bearing minerals are known. Some are silicates some halides and some are phosphates. Granite, Gabbro, Pegmatite Quartz and Kimberlite are fluoride bearing Igneous rocks. Fluorite Apatite Mica, Illite and Montmorillonite are the fluoride bearing sedimentary rocks. Fluoride ion because of similarity of ionic radius with OH\(^-\) ion and high electro negativity, replaces OH\(^-\) ion completely from the rocks. Concentration of fluoride in sedimentary rock is determined by the kind and distribution of fluoride bearing minerals. Fluorspar (Fluorite) Apatite (Fluorapatite) and Phosphorite are generally the main minerals contributing to the presence of fluoride in the soil and water. In ground water sample fluoride shows a positive correlation with pH, Sodium, bicarbonate ion and negative correlation with Calcium, Magnesium ion. Concentration of fluoride in foodstuffs does not depend on the fluoride bearing mineral concentration in the soil but depends on the nutrient uptake, which in turn depends upon the pH of soil and environment. Fluoride prevents tooth decay at lower concentration but at higher concentration it causes a disease called fluorosis. World health organization (WHO) recommended a guide line maximum fluoride value of 1.5mg /l as a level at which fluorosis should be minimal. Fluorosis is of four types (1) Dental fluorosis (2) Skeletal fluorosis (3) Osteoporosis or genuvalgum (4) Dental carries. Several defluoridation techniques are used to maintain the concentration of fluoride in ground water within permissible limit. Out of the four method used to characterize fluoride in different types of samples, ion selective electrode method is most frequently used for environmental and biological samples.

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[74] Kakar Y.P., V Sikka V.M., Das Janeshwar and Bhatnagar N.C.; 1988, Hydrochemistry and pollution of ground water in Faridabad area Haryana, Central ground water board, North west region, Chandigarh; p-32.
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