

DETECTION OF FLUORIDE ION IN WATER: AN OPTICAL APPROACH AND REVIEW

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ABSTRACT

This paper presents the review on different concepts of fluoride detection techniques and technologies in water. At high concentration Fluoride is toxic to humans. When humans are exposed to fluoride-containing water, they can suffer from health problems, such as dental disease. Drinking water is the most consumed beverages. For humans beverages are significant sources of fluorides. Consistent evaluation of the element's content in the large variety of existing drinking water requires the small margin between suitable and overdose fluoride levels in the human body. Due to the collection of drinking water from public sources such as wells and tap-stands, also during its storage in the home, drinking-water can become polluted. There are various techniques to determine Fluoride ion in water such as Ion selective electrode, Colorimetric Technique, UV- Vis Technique, Fluorescence Technique. This paper gives comparative study of all these methods to detect Fluoride. This review will also give different study about optical approaches to detect Fluoride.

Keywords: Carbon Dots, Colorimetric Technique, Fluoride, Fluorescence Technique, Ion selective electrode, UV- Vis Technique.

1. INTRODUCTION

The major intimidation to human health is poor quality of drinking water. Minerals, toxic chemicals, effluent outfalls from industrial facilities, waste treatment plants, and are several possible sources which can pollute drinking water. In order to ensure the accessibility of uncontaminated and safe drinking water, its quality should be managed and examined carefully on a regular basis. The precise measurement of the fluoride concentration in water is an essential criterion to stay within the permissible dosing tolerances. Fluorides are the negatively charged ions of fluorine, which is the most reactive and the most electronegative of all elements. They are the major form of the element occurring in nature. The main mineral deposits of the element are soluble fluorite (CaF_2), cryolite (Na_3AlF_6), and fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). Villiumite (NaF), topaz ($\text{Al}_2(\text{SiO}_4)\text{F}_2$), micas, and some clays are also

fluoride-bearing minerals. Fluorine is one of the most abundant (0.06%) elements in the Earth's crust. Fluorides released from minerals are one of their natural sources in the environment [1]. Marine aerosols, volcanic gas emissions, and airborne dusts enriched in fluorine can also be sources of fluorides in the environment. Increased level of fluorides in various parts of the environment (water, soils, and plants) can originate from large industrial applications of the element, in particular, in the aluminum, glass, and electronic industries. Drinking water, both that naturally containing fluoride and fluoridated water, provides the main fluoride source for humans. Humans can also uptake fluorides from various food products; among them, tea infusions were found to be a potentially dangerous source of high amounts of Fluorides that can enter the human body. Tea trees absorb fluorides from soils and air and accumulate them (up to 98% of total amount) in leaves [2].

The World Health Organization (WHO) has restricted the maximum fluoride concentration which is suitable for safe drinking water to 1.5mgL^{-1} because of the adverse effects of fluoride. This paper mainly focuses on the Fluoride detection in water [3].

1.1. Global Status

High concentration of Fluoride in water occurs in huge and extensive geographical belts related with a) volcanic rocks, b) sediments of marine origin in mountainous areas and c) granitic and gneissic rocks. First spreads from Iraq and Iran through Syria and Turkey to the Mediterranean region and hence from Algeria to Morocco are the typical example. Some other major examples are southern Europe, the southern parts of the former USSR and the southern parts of the USA. East African Rift system, Ethiopia, Uganda, Kenya and the United Republic of Tanzania are well-known and documented areas related with volcanic activity. Various lakes of the Rift Valley system, especially the soda lakes have very high fluoride concentrations. In the Kenyan Lakes Elmentaita and Nakuru fluoride concentrations are $1,640\text{ mg/L}$ and $2,800\text{ mg/L}$ respectively and up to 690 mg/L in the Tanzanian Momella soda lake. The volcanic areas of the Nairobi, Rift Valley and Central Provinces had the highest concentrations, with extreme groundwater fluoride concentrations reaching $30\text{--}50\text{ mg/L}$. Drinking-water were being provided by the most of the sampled wells and boreholes and the problem of dental fluorosis was observed very high in affected areas.

A similar picture appears in the United Republic of Tanzania, where concentration of Fluoride in 30 % of drinking water is exceeded by 1.5 mg/L , concentration of Fluoride in the Rift Valley is up to 45 mg/L . In groundwater Concentration of Fluoride is very high due to igneous and metamorphic rocks such as granites and gneisses have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa. Endemic fluorosis has been reported in all 28 provinces, autonomous regions and municipalities excluding Shanghai in China. Both shallow and deeper ground waters are affected; in general the deeper ground waters have the higher concentrations. In Sri Lanka, the concentration of Fluoride is up to 10 mg/L in ground water in the Dry Zone, associated with dental and possibly skeletal fluorosis. In the Wet Zone, the severe rainfall and long-term leaching of fluoride and other minerals from the crystalline bedrock are possibly responsible for the much lower concentrations.

1.2. National Status

Endemic fluorosis remains a challenging and widely studied national health problem in India. In 1991, 13 of India's 32 states and territories were reported to have naturally high Fluoride concentrations in water, but this had risen to 17 by 1999. The most extremely affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh. The highest concentration observed in India is 48 mg/L in Rewari District of Haryana. The high concentrations of Fluoride in ground water are consequence of dissolution of fluorite, apatite and topaz from the local bedrock. Efforts to address the problem of fluoride in rural water supplies in India have been managed by the Rajiv Gandhi National Drinking Water Mission, with substantial support from external agencies, particularly UNICEF. However, even with the great interest in fluoride in India, it is not easy to arrive at a reliable approximation of the number of people at risk. This is due to the difficulty of sampling groundwater from India's many millions of hand pumps.

1.3. Harmful Effects In Body

Excess fluoride consumption affects the following body parts of human:

BRAIN

In a meta-analysis on 27 epidemiological studies, it was found that excess consumption of fluoride in childhood reduces the IQ. The authors noted that this research is not appropriate to the safety of artificial water fluoridation because the adverse conclusion on IQ was found with fluoride levels that were much higher than typically found in artificially fluoridated water [4]. However, they conclude that more research is required to assess the adverse effects on children's neuro development [5] [6]. The Meta analysis has been criticized for failing to account for confounding factors.

For example, in some of the studies fluoride exposure came from the burning of high fluoride content coal, and used a control group from an area in which wood was used as fuel [7].

BONES

Water contains fluoridated is associated with reduced levels of fractures in a population, toxic levels of fluoride was found as a major cause of weakening of bones and increase in wrist fractures. It was concluded that fractures with fluoride levels 1–4 mg/L, suggesting a dose-response relationship by U.S. National Research Council. Excess consumption fluoride for a long period causes skeletal fluorosis. In some areas like Asian subcontinent, skeletal fluorosis is endemic.

KIDNEY

High toxic levels of serum fluoride introduce some kidney injury like nephrotoxicity. It is commonly occurs due to release of fluoride from some drugs, like methoxyflurane which contains fluorine. If we take proper dose, no effects are accursed .An chronic ingestion in excess of 12 mg/day shows adverse effects. Inorganic fluoride inhibits adenylatecyclase activity essential for antidiuretic hormone effect on the distal convoluted tubule of the kidney.Internal vasodilation is also stimulated byfluoride which improved medullary blood flow and improved medullary blood flow interferes with the counter current mechanism in the kidney essential for concentration of urine. The kidney damage is due to failureto concentration of urine.

Table 1: Different Fluoride Concentrations and Their Effects onHuman Body

Fluoride (mg/l)	Effects on Human Body
Below 0.5	Dental Caries
0.5 to 1.0	Protection against dental caries. Takes care of bone and teeth
1.5 to 3.0	Dental fluorosis
3 to 10	Skeletal fluorosis (adverse changes in bone structure)
10 or more	Crippling skeletal fluorosis and severe osteoclerosis

II FLUORIDE

Fluoride ions basically come from fluorine atoms. Due to their high reactivity fluorine atoms occurs in the form of fluorides in many minerals, for e.g. cryolite, fluorspar,fluorapatite and it covers about 0.3 g/kg of the Earth’s crust [8]. In 1994, WHO has given the permissible limit of Fluoride in water is 1.5 mg/litre (i.e. 1.5 ppm) and reaffirmed in 1993. The fluorides ions are not harmful if their concentration is 1.5 ppm or lesser. Millions of people are encountered by the lethal effects of fluorides around the world.

Fluorine (F) is an element of the halogen family. It also comprises chlorine, bromine and iodine. It forms inorganic and organic compounds called fluorides. Living organisms are mainly exposedto inorganic fluorides through food

and water. Hydrogenfluoride (HF), calcium fluoride (CaF_2), sodium fluoride (NaF), sulfur hexafluoride (SF_6) and silicofluorides are the most appropriate fluorides. Fluorides represent about 0.06-0.09% of the earth's crust.

III VARIOUS METHODS FOR FLUORIDE ION DETECTION

3.1. Ion Selective Electrode method

ISE is a sensor (or transducer) that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a multimeter. An ion-selective electrode (ISE) is also known as a specific ion electrode (SIE). Now days, carbon paste electrodes are used for different metal ions detection.

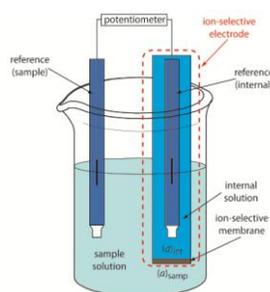


Fig. 1 Experimental setup of Ion Selective Electrode

Fluoride selective membrane electrode for measuring fluoride ions concentrations in terms of F^- , HF, and HFP^- species is implemented [9] [10]. This electrode comprises of a single crystal of doped lanthanum fluoride cemented into a plastic tube containing an internal reference solution. The determination of fluoride ions were done in acidic medium by fluoride-selective membrane electrode. There are also similar reports based on fluoride-selective membrane electrode [11, 12, 13].

3.2 Colorimetric method

With the aid of a color reagent, Colorimetric study is a method of determining the concentration of a chemical element or compound in a solution.

Based on adsorption of analyte as Fe(III) fluoride complex on MIONs (magnetic iron oxide nanoparticles) and desorption by NaOH solution, Fluoride ion is determined. After neutralization of the alkalinity, the removed fluoride ions react with colored Fe^+SCN complex and form FeF_6^{3-} colorless anionic complex which causes discoloration of Fe-SCN complex. The color of the reaction mixture converts progressively lighter as the quantity of fluoride ions increases. For determination of fluoride in water samples, this technique offers a selective, sensitive, simple, rapid and low cost colorimetric method [14].

An imidazole based sensing probe to detect fluoride ions is discovered [15]. In their system, the color 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 [16]. 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 fluorescence signals is enhanced. Dipyrrolyl derivatives and di cyano functionalities for detection of fluoride ions based on color change which can be determined visually as well as with some spectroscopy techniques are also used [17]. Here color is changed from red to green and yellow to red with addition of fluoride ions. There are also similar reports based on ratiometric change in the colour of the sensor with fluoride interaction [18, 19]. But the main drawbacks of these methods are toxicity, complexity and interference of other ions.

3.3 UV-Vis method

This technique is based on the principle of Beer-Lambert law. According to the Beer-Lambert law "The absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the pathlength".

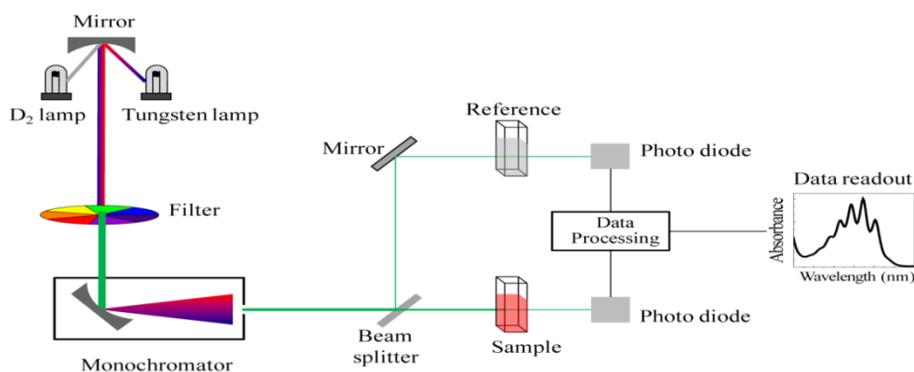


Fig. 2 Experimental setup of Ultra Violet Spectrophotometer

Holder for the sample, a light source, a diffraction grating in a monochromator or a prism to distinct the different length of light, and a detector are the basic part of a Spectrophotometer. There are two type of source one is Tungsten filament and another is Deuterium arc lamp. Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength extents the detector at a time. The spectrometer can be single beam or double beam. In double-beam instrument, the light is divided into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% transmission, and the measurement displayed is the ratio of the two beam intensities. Samples are typically sited in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1cm. Test tubes can also be used as cuvettes in some instruments. The type of sample container used must permit radiation to pass over the spectral region of

interest. The most widely applicable cuvettes are prepared by quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions [20].

3.4 Fluorescence method

Fluorescence is a method of analysis where the ions and molecules of solution excited by irradiation at a certain wavelength and emit radiation of dissimilar wavelength.

A fluorescent probe based on $Zr(CDs-COO)_2EDTA$ complex for detection of fluoride ions is synthesized [21]. When F^- coordinated to $Zr(H_2O)_2EDTA$, the strong fluorescence quenching of the probe was done as a result of the formation of the non-fluorescent complex $Zr(F)_2EDTA$, due to the stronger affinity of F^- than the $-COOH$ in the CDs to Zr(IV) [22].

A fluoride-sensing system, consisting of polymer membrane in which Si-O bond cleavage by triggering fluoride ions results in the formation of a highly fluorescent coumarin. It was reported that coumarins are laser dyes with high radiative quantum yields [23]. Polymer membrane and Coumarin consists of tert-butyldimethylsilyl (TBS) group which was protecting group for the phenols which were found to be more selective to fluoride with less interference from other ions. For detection of fluoride ions through intramolecular energy transfer from conjugated polymers uses Fluorescence resonance energy transfer (FRET).

For detecting fluoride ion fluorogenic probe are used by fluoride-induced cleavage of tert-butyldimethylsilyl ether [24]. Probe was made of 4-methylumbelliferyl tert-butyldimethylsilyl ether (4-MUTBS), with addition of fluoride ion in acetone-water solution, the Si-O bond of 4-MUTBS was broken and highly fluorescent 4-methylumbelliferone (4-MU) was released. Similar method was used in which metal-organic framework $NH_2-MIL-101(Al)$ with some fluorescent molecule trapped in MAF and detection is based on the decomposition of the MOF and the release of the trapped fluorescent molecule, when this MOF comes in contact with fluoride ions [25] [26].

IV OPTICAL APPROACH

4.1. Carbon Dots

Quantum dots (QDs) are minute particles formed by grouping 10-50 atoms of a semiconducting material having diameters in the range of 2-10 nanometers. Quantum Dots which are having carbon as their core material are known as Carbon Dots. Carbon Dots are new kind of fluorescent carbon nanomaterials, with the size below 10 nm have been synthesized by using carbon-based materials as carbon resources [27, 28]. High fluorescence is main reason of attraction of CDs.

Strong Luminescence, High Solubility, Broad excitation wavelength, Robust chemical inertness, High resistance to photo bleaching, size-tunable emission, Low toxicity, Good bio-compatibility, narrow emission spectrum, are some of the unique optical properties of Carbon Dots [29]. By using energy transfer between QDs many of the applications utilizing QDs are based on the fluorescence quenching phenomenon occurs [30, 31].

Table 2: Different sources and methods by which Carbon Dots can be made

Sources for CDs preparation	Methods of CDs preparation
Citric acid and with various amine	Microwave-Assisted Pyrolysis
Graphene Quantum Dots	Solvothermal Process
Citric Acid And Urea Route	Microwave Synthesis
Graphite	Laser Ablation
Food-Waste-Derived Sources	Hydro Thermal Process
Gelatin	Hydro Thermal Process
Sucrose	Carbonization
TrapaBispinosa Peel	Hydro Thermal Oxidation process
Orange Juice , Jaggery, Bread And Suga	Hydro Thermal Process

Carbon Dots have application in Biological Labeling, Bioimaging, Bio- sensors, Photo catalysis, Photovoltaic devices, etc. They are also used as Nanoprobes for Sensitive Ion Detection such as Fluoride.

Table 3: Comparison of Different Techniques

S. No.	Techniques	Limitations	Advantages
1	Colorimetric Method	<ul style="list-style-type: none"> Different membranes required for detecting different metals. Time consuming 	<ul style="list-style-type: none"> Simple preparation method As little as 65 ppb of heavy metals were detected by naked-eye color test

2	Optical Method	<ul style="list-style-type: none"> • Very few molecules are naturally luminescent • More complicated equipment required 	<ul style="list-style-type: none"> • More sensitive • More specific
3	Fluoride-selective Membrane/ Electrode	<ul style="list-style-type: none"> • Interference from others ions present • Less sensitivity 	<ul style="list-style-type: none"> • Easy to use • High speed • process

Table 4: Comparison on Basis of Some Technical Specifications

S. No.	Techniques	Limits of Detection	Precision	Selectivity	Cost
1	Colorimetric method	65ppb	Average	High	Low
2	Optical method	1-100ppb	High	Average	Low
3	Fluoride-Selective Membrane/Electrode	1-100ppm	low	low	Low

V SUMMARY

Global occurrence of Fluoride in water is considered to be a major risk factor, affecting human health. In this review, several detection techniques including Ion selective electrode, Colorimetric Technique, UV- Vis Technique and Fluorescence Technique are described in their great potentials in quality of water. Fluorescence Technique for Fluoride determination provides simple, cost effective, good sensitivity and selectivity. Table 3 summarizes the merits and demerits of different methods used to determine Fluoride ion in water. By these methods Fluoride ions in water is detected and safe drinking water within its permissible limit is provided. Table 4 gives the comparison of different technique based on its technical specifications. Now days, Carbon Dots are getting more attraction due to its high fluorescence property and many other unique properties for Fluoride determination in water. Table 2 gives

different method to make Carbon Dots. This paper gives overall information about different techniques for fluoride determination in water and comparison between them.

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