

Fluoride Detection in Drinking Water: A Comparative Review of Traditional Methods and Sensor-Based Technologies

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ABSTRACT - Fluoride contamination in drinking water has become a major global problem and is still an invisible killer of public health, which is affecting people, especially in those areas where they are dependent on groundwater that is not treated. Dental and skeletal fluorosis can result from prolonged exposure to even minimal traces of fluoride in drinking water. If not properly treated or prevented, these conditions can worsen over time, potentially leading to disability. That is precisely why the detection of this harmful agent in the water must be accurate, rapid, and affordable. The detection methods and technologies have been progressing from basic chemical analysis to advanced platforms that combine nanomaterials, photonic structures, and intelligent devices. This survey gives full coverage of the developments of fluorine detection technology from conventional methods to modern electrochemical, fluorescence, paper, and photonic crystal sensor systems, with the elucidation of mechanisms, advantages, and disadvantages. The comparative survey not only deals with analytical efficiency but also scalability, eco-friendliness, and the practicality of deployment in field conditions. The review defines the elements necessary to design next-generation fluoride sensors by presenting latest trends like the use of smart devices for reading and IoT-based continuous monitoring of sensed parameters. Finally, it highlights the necessity of low-cost, portable, user-friendly, and highly selective sensors that have the potential to decentralize fluoride monitoring for broad community application, particularly in areas that are unserved and difficult to reach.

Keywords - Drinking water contamination, Electrochemical sensors, Nanomaterials, Environmental monitoring, Portable water testing, Heavy metals.

I. INTRODUCTION

Fluoride is beneficial in a safe concentration for a healthy tooth, but it can become a dangerous environmental pollutant if its quantity is above the acceptable limit. The World Health Organization gives a permissible level of 1.5 mg/L fluoride in drinking water; however, an enormous number of people around the world are still overexposed to it without even realizing it. Fluoride has been proven scientifically to be the main cause of fluorosis, which affects the dental and skeletal systems after a person has taken in fluoridated water, alongside other health problems. Besides, fluoride is not only a cause of skeletal system disease, but it is also considered a factor of neurotoxicity that can deteriorate children's cognitive growth, lower their IQ, and make learning difficult. In this case, as the studies show, fluoride also becomes a problematic hormone that is overproduced and depleted due to thyroid dysfunction, secretion of hormones in the endocrine system goes awry, and at the same time, reproductive disorders take place, like loss of sperm motility, and the risk of stillbirth increases. Vulnerable populations such as children, pregnant women, and the elderly are the ones who suffer the worst from this, often without even noticing their health issues at the beginning, as the symptoms are not very visible.

Besides natural leaching from fluoride-bearing rocks, another big reason for the increase in fluoride levels in the water table, caused by humans, is the use of phosphate-based fertilizers and certain pesticides in agriculture without any restrictions. These agrochemicals often contain fluoride compounds as additives or by-products. Over time, rainfall and irrigation facilitate the leaching of these chemicals into the soil, from where they contaminate surface and groundwater reserves. This is especially worrying in semi-arid areas where drainage is poor, as here water tends to stagnate, and therefore fluoride deposition is increased. Moreover, in rural agrarian belts, there is usually insufficient water purification infrastructure, and, hence, such contamination directly translates to long-term exposure for both humans and livestock. To minimize those health hazards, many detection methodologies have been developed. These techniques are based on the colorimetric and complexometric assays, or they use ion-selective electrodes (ISEs), fluorescence sensors, electrochemical devices, and paper-based diagnostic kits. The performances corresponding to these techniques' analytical, cost, and field application features differ widely. Nevertheless, to truly realize the potential of fluoride monitoring at the grassroots level, the technology should go beyond the laboratory. Detection

systems have to be cheap, simple, mobile, and preferably digital or smartphone-integrated to be able to disseminate results quickly.

The latest developments in IoT-connected electrochemical sensors, paper-based colorimetric platforms, and molecularly imprinted polymer systems are therefore very promising. This review is, on the one hand, a complete overview of the existing technologies for fluoride detection and, on the other hand, it gives the basic features of the next-generation low-cost and user-friendly sensor, which is made for easy accessibility of laypeople and obtaining their health benefits.

II. LITERATURE SURVEY

Fluoride (F^-) contamination in drinking water is a significant environmental and public health concern, especially in regions where naturally high fluoride levels or agricultural runoff elevate its concentration beyond safe limits. Prolonged ingestion of fluoride-rich water can result in dental and skeletal fluorosis, thyroid dysfunction, and neurological issues in both humans and animals. Over the past several decades, researchers have developed a range of detection techniques to monitor fluoride levels effectively. The methods for detecting fluoride ions have developed from early colorimetric techniques and ion-selective electrodes toward more complicated platforms like electrochemical sensors, probes based on nanomaterials, or microfluidic-based systems. Each technology provides its own advantages in terms of sensitivity, selectivity, cost, or in-situ field usability, which only amplifies the growing toolkit options for near real-time detection of fluoride in drinking water.

Colorimetric detection of fluoride was one of the earliest available fluoride detection methods, dating back to the 1930s when F. E. Smith was at the U.S. Public Health Service. This detection method relies on the reaction of fluoride ions with a red zirconium-dye complex, where fluoride ions act as a reducing agent that fades the color of the dye. This is ultimately quantified using the concept of spectrophotometry. This has significant implications for testing municipal water due to its low costs and simplicity of use. While this testing did initially have some limitations due to interference from ions such as phosphate or sulfate, fluoride detection methods have recently taken hold both sensitivity and selectivity. For example, Alqahtani et al. [1] used a fluorometric carbon-dot-based method utilizing zirconium-alizarin complexes for dual water and saliva testing. Also, Jha et al. [3] designed a green, water-dispersible photoluminescent probe, which provides improved environmental compatibility. These changes, keeping with the method's low-cost characteristic, open up new opportunities for the use of this technique in the field while improving the accuracy of the measurements, especially in remote areas or areas with limited resources.

Subsequently, in 1966, Frant and Ross furthered previous work on fluoride measurements by establishing fluoride-selective electrodes using a LaF_3 crystal. ISEs measure ion activity by a direct measurement of potential difference. Therefore, readings were measurable. ISEs as a lab method obtain real time, accurate results and measure the range of concentrations. These subsequently became the standard laboratory methods for fluoride analysis. Recent improvements in instrumentation have improved the robustness and sensitivity of the analysis to date, Dey and Sarkar [4] added amendment to mesoporous silica membranes to the membrane properties. Barreto and Sartini [5] created lanthanum fluoride solid-state membranes that assisted in the stability of ion sensors. Meyer et al. [6] even created screen printed FISE and spaces, thus contributing to decentralization. Ion chromatography (IC), developed by Small and his colleagues at Dionex in 1975, is still the most practical used method to date, making it the most accepted fluoride method. It is based on the principle of anion-exchange, where the anion-exchange column separates the fluoride ions from a water sample, which is then followed by conductivity detection. IC offers high selectivity, minimal detection limits, and the capability of detecting several anions simultaneously in one run. Zhang et al. [7] demonstrated its application in natural waters, while Yan et al. [8] emphasized its regulatory function in drinking water testing. Packer and Foss [9] proved its solidness throughout various aqueous matrices. Even though the equipment is expensive and skilled personnel are required, IC is still the best choice in regulatory and industrial environments.

In the 1950s and 1960s, spectrophotometric fluoride detection came into existence by way of fluoride reduction of cerium (IV) to cerium (III), which was detected by a change in absorption. This method was the foundation for early fluoride quantification, but it had a limited selectivity problem. The new versions of this method have solved these problems. Wang et al. [11] produced a sensor based on a graphene oxide-supported composite to detect samples from food and water. In an extensive review, Khatkar et al. [12] gave details about the different

spectrophotometric systems and reagents. The method's pros and cons have been described by Nair et al. [10] in the case of both biotic and abiotic media. Even though it is now often replaced by IC or electrochemical sensors, spectrophotometry still has its role in labs with limited budgets, as it is affordable and moderately sensitive. Electrochemical sensors are a new generation of fluoride detectors that use electrode materials in advanced configurations for real-time, sensitive, and selective detection. Such sensors are introduced in the work of Wang et al. (2022), who realized a multilayer electrode modified with conducting polymer of boronic acid and reduced graphene oxide that enabled the amplification of signal drastically even in complex matrices [14]. A study by Ma et al. (2021) aimed to construct a sensor based on an electrode modified with gold nanoparticles, which allowed for a speedy and sensitive fluoride determination [15]. Due to their scalability, miniaturization, and the ability to communicate with smartphones or IoT systems, such devices are highly appreciated. These authors [13] also mentioned the potential of paper-based electrochemical sensors for use in decentralized diagnostics via the electrolyte conductivity of a liquid and highlight their importance in real-time and portable fluoride testing herein. Given their sub- μM detection limits and compatibility with remote monitoring platforms, electrochemical sensors are the most promising technologies for next-generation environmental surveillance.

Nowadays, fluorescence-based probes are the most promising tools for the recognition of fluoride ions in water due to their extraordinarily high sensitivity and selectivity. These sensors work on the principle of fluorescence quenching or enhancement of certain functional groups or nanomaterials upon interaction with the fluoride ion. For instance, Jha et al. (2017) [16] synthesized fluorescent dots of carbon to be water-dispersed that performed the on-off-on behavior with the presence of fluoride and showed the high selectivity and reusability of the sensor. The latest effort from Wang et al. (2024) [17] is a fluorescent probe that can be ratiometrically based on urolithin derivatives and offers real-time quantitative analysis supported by theoretical calculations. The latter demonstrated high brightness and corrosion resistance in environmental matrices. Adding to the selectivity, Chen et al. (2024) [18] proposed a silica-protected carbon dot phosphorescent probe that allows for autofluorescence interference-free detection of fluoropyrimidine, ensuring good sensor performance even in turbid or complex water. These fluorescent sensors are being more integrated into point-of-care or field-testing systems, due to their label-free detection, miniaturization potential, and compatibility with smartphone-based platforms. To summarize, the fluorescence-based fluoride probes are very promising sensors, which have the unique ability to detect flaws at the nanomolar range that are the key driving factor for decentralized and user-friendly environmental monitoring solutions.

PADs are simple, quick, and cheap instruments for bulk screening of fluoride that can be applied in field settings, especially in low-resource communities. The same devices are made of filter paper impregnated with colorimetric reagents, which change their color visually when they encounter fluoride. Zhou et al. (2021) illustrated a strong and economically feasible PAD system for fluoride detection in potable water, which could provide easily understandable visual signals [21]. Qiu et al. (2023) presented a PAD synchronized with a smartphone that is based on the aggregation-induced emission (AIE) carbon dots, and this allowed the ratiometric and quantitative analysis to be conducted through the imaging on the smartphone [20]. Currently, although PADs have lower sensitivity than laboratory techniques, they are perfectly suited for initial screening, instructional purposes, and citizen science applications due to their cheapness, disposability, and overall easy use. Sensors based on novel nanomaterials are at the forefront of advances in fluoride detection because of their unique physicochemical features, large surface area, high affinity/ reactivity, and good signal transduction capability. Alqahtani et al. (2024) introduced a carbon dot sensor regulated by a zirconium-alizarin complex that provided double-visual and fluorescence detection of laboratory and real-world samples such as the Nile River water [22]. In the same way, Roy (2024) used carbon dot-based probes for the overwhelming detection of fluoride with low detection limits in biological and environmental matrices [23]. Kaur et al. (2022) searched for the materials that make up sensors based on graphene oxide that demonstrated good fluoride affinity, minimum interference, and stability under the various water sources [24]. Although they are quite novel, they are already demonstrating their usefulness in places where there is hardly any centralized testing infrastructure.

Polymers imprinted on the molecular level are synthetic substances aimed at the recognition of fluoride ions. Such materials have several molecular recognition sites that are specific to fluoride ions; therefore, they are going to natural receptor-ligand binding and are used in sensors more because of their chemical stability, reusability, and specificity. Kaur et al. (2021) created systems that combined MIP capable of detecting fluoride ions in aqueous matrices with high affinity and reproducibility [25]. Su et al. (2021) furthered the idea in the field of environmental monitoring, showing that MIPs are still strong even in such complicated matrices as river or industrial water [26]. Wang et al. (2021) presented an electrochemical MIP sensor with high sensitivity and good linearity throughout the fluoride concentration range of interest, which accessed [27]. The synthesis procedure, however, consumes a lot of time, and it is frequently necessary to optimize it if one intends to apply it in the field. Surface-enhanced Raman

scattering is a sensitive optical detection technique that exploits localized surface plasmon resonance (LSPR) phenomena of metal nanostructured materials to significantly increase the Raman signals of molecules present at the surface. For fluoride detection, target recognition is most often realized through the functionalization of silver or gold nanoparticles, which react to the presence of fluoride by the change of their surface charge or by the binding of fluoride-specific ligands to them. Ye et al. (2021) prepared silver nanoparticle substrates for domestic water purposes and verified that they have exceedingly high enhancement factors and low detection limits [28]. Xu et al. (2021) implemented a strategy free from labels by employing gold nanostars, thus allowing easy and accurate monitoring without the need for complicated tags [29]. Li et al. (2021) introduced a SERS paper-based system that merges portability with an extremely low detection limit that makes field-based Raman fluoride diagnostics possible [30]. Nevertheless, SERS still has the highest sensitivity, yet it has a limited nature in terms of price, complexity, and reproducibility.

Photonic crystal sensors are around the corner as an innovative means of fluoride detection in water via the optical method. These sensors fundamentally depend on a periodic nanostructure that works on the light, fluoride ions bring to the structure, or the refractive index changes of the photonic hydrogel matrix; hence, a colour change is seen. A method that was brought about by Zhang et al. (2022), who launched a photonic crystal sensor with a fast response and high selectivity as well as stability for the fluoride in the aqueous environment, was discussed [31]. Wu et al. (2020) have indicated that hydrogel-based photonic crystals became tunable for the exact detection of fluoride ions if cross-linking densities and pH-responsive elements were adjusted [32]. Huang et al. (2021) named a hydrogel swelling process as a detection method, where the fluorine-stimulated swelling changed the photonic band gap to make the sensor’s reflected colour different from one [33]. These are still under development, and the fact that they are compatible with portable readers as well as visual interpretation tools indicates that they have high potential for low-cost fluoride monitoring both in the developed and developing regions.

The development of fluoride detection technologies reflects the world-wide imperative of grappling with water safety issues, especially in endemic fluorosis settings. Earlier, classical methods in fluoride monitoring test like titrimetric, colorimetric tests, for instance, were the first practical methods of fluorine monitoring, but were limited in regards to sensitivity and specificity. Techniques like optical spectroscopy, ion chromatography and fluoride ion selective electrodes enhanced fluoride monitoring, but still the water sample needed to be tested in laboratories and well-trained users were required to use them. Recently, the development of portable, low-cost electrochemical, and nanomaterial-enhanced fluoride sensors offered real-time, in-field fluoride detection. Other recent developments are huge time savers and offer non-trained people the opportunity to test their water in a timely manner and to assess water safety issues. This is consistent with WHO guidelines and public health goals. As outlined in this survey, the future direction of fluoride detection will be experienced accuracy, affordability, adaptability to local environmental conditions, and socioeconomic mitigation. As such, it is important to search for a technology route towards safe, affordable and adaptable to local environmental conditions.

Decade	Detection Method	Inventor / Author	Principle
1930s	Colorimetry with SPADNS Dye	Bellack & Schouboe	Fluoride forms a complex with zirconium–SPADNS dye, causing a measurable color change.
1960s	Ion-Selective Electrode (ISE)	Frant & Ross	Fluoride-selective membrane develops potential proportional to F [−] concentration.
1980s	Flow Injection Analysis (FIA)	Ruzicka & Hansen	Automated injection of sample with reagent for continuous colorimetric or potentiometric detection of fluoride.
1990s	Spectrophotometry with Alizarin Complexone	Suzuki et al.	Fluoride displaces dye from metal-dyed complex, causing a measurable change in absorbance.
2000s	Luminescence-Based Sensors	Nakamura et al.	Fluoride quenches or enhances luminescent signal in lanthanide complexes.
2010	Electrochemical Sensor (Al ₂ O ₃ /ZnO Coating)	Singh et al.	Surface-modified electrodes change impedance when fluoride binds.
2015	Optical Fiber Sensors	Gupta et al.	Fluoride alters the refractive index of a sensing film on an optical fiber.
2020s	Nanomaterial-Based Electrochemical Sensors	Sharma et al.	Graphene/ZnO nanocomposites amplify electrochemical response upon F [−] binding.

Table 1 - Comparison of various methods used for fluoride detection

III. CRITICAL ANALYSIS

Despite the advent of many different analytical techniques for fluoride detection, whether established or promising, there are usually limitations in each and thus they cannot be universally applicable. Old colorimetric and spectrophotometric techniques like SPADNS and the cerium (IV)–cerium (III) reduction method are still very inexpensive and easy to apply, but selectivity, instability of the reagents, and anion interferences (phosphate, sulfate, or silicate) limits their reliability. Even recently developed fluorescent detection reagents using carbon dots or a zirconium–dye complex indeed draws on spectrophotometry, testing, and does not offer automation or digital quantification. The next logical step for this area of research would be to use colorimetric chemistry in conjunction to microfluidic or in -situ- 3D printed platforms to enable smartphone-based optical readouts for ephemeral, real-time analysis and out in the field where appropriate. While we discussed ISEs, especially LaF_3 membranes, which offer high accuracy and wide dynamic range, they all face limitations in terms of membrane fouling and drainage over time, sensitivity to pH, and need for frequent calibration. Options for improving ISE performance include the creation of solid-state or nanocomposite membranes that also have had promising increased sensitivity and stability. However, monitoring real matrices is still difficult, and there is a need for more work designing self-cleaning, anti-foul ISE coatings

Ion chromatography (IC) continues to be the standard method for PFAS analysis because of its selectivity as well as its ability to detect multiple ions. The downside to using IC in the field is its cost and use of up-concentration and power, as well as personnel expertise. Miniaturized IC or chip-integrated IC systems could fill that gap, especially for point-of-use testing in rural or resource-limited settings. There have been more recent advances in electrochemical- and fluorescence-based probes, which demonstrate sensitivity limits at sub-micromolar levels and are compatible with digital display technologies. However, common issues such as degradation (electrode surface), photobleaching, and signal drift have not yet been addressed. Work on ratio metric and time-gated fluorescence systems or hybrid electrochemical–optical systems may progress work on stability, selectivity, and error correction. Paper-based analytical (PADs) devices have gained more acceptance as low-cost technology that can be used to identify fluoride on site; however, they are not yet quantitative and are not very close to providing long-term stability or precision. Future advances could help integrate PADs with smartphone imaging or machine-learning algorithms, which may improve the precision and accuracy of analytical results on integrating ISEs into IoT nodes for autonomous, long-term monitoring period

IV. CONCLUSION

Fluoride contamination in drinking water is far from over and remains a danger to global public health, especially in developing regions where access to safe water is limited. The chronic intake of fluoride has been proven to be the direct cause of irreversible conditions like dental and skeletal fluorosis, as well as more general symptoms of the nervous system, the thyroid gland, and organ failure. Although the awareness about the issue has grown, the lack of affordable and easily accessible detection technologies has impeded the accomplishment of the mitigation of this problem. Over the decades, there have been changes in fluoride detection methods from early colorimetric and titrimetric assays to the latest tools such as ion-selective electrodes, ion chromatography, electrochemical sensors, and nanomaterial-enhanced platforms. Those provide higher sensitivity and selectivity, but their wide-range application is very often limited due to soaring prices, reliance on labs, or complicated operation. The paper highlights the urgent demand for low-cost, mobile, and instant detection equipment that users can operate without specialized training. The advent of these technologies, such as PADs, smartphone-enabled sensors, and MIPs, is significantly contributing to the decentralization of water monitoring. At the end of the road, a perfect fluoride sensor will be a precise, cost-effective, and versatile one, thus enabling ordinary people, students, and health workers to be able not only to monitor water safety but also to take proactive health measures. Getting back and forth between science and social needs is the main game in achieving water security and public health.

V. FUTURE SCOPE

Even though there have been huge improvements in the technology that can detect fluoride, the limitations that are significant are restricting its wide usage to continue. This is especially so in places that are rural and have very few resources. High-tech methods like ion chromatography, surface-enhanced Raman spectroscopy, and fluorescence-

based sensing possess a high sensitivity and selectivity, which are perfect, but their use is limited to laboratories only due to the high cost, complexity, and the need for the personnel that are trained. On the other hand, the low-cost options are represented by colorimetric strips and basic potentiometric tools; it is often the case that they sacrifice some aspects, such as accuracy, selectivity, or usability. The road to the future of fluoride surveillance is lined with creating low-cost, easy-to-use, and mobile sensing systems that can be operated in the field without any help from a specialist. The breakthroughs in nanomaterial-functionalized electrodes, molecularly imprinted polymers, and the graphene/carbon-dot composite, among others, will be the main players that make it possible to obtain high sensitivity and selectivity in the most convenient formats. The collaboration with the smartphone-based interfaces, IoT modules, and AI-powered calibration in the case of real-time data collection, facilitates the automated interpretation, and the provision of predictive analytics for the early warning of the disaster will be at your fingertips.

In summary, there is an urgent and rising need for next-gen fluoride detection systems that are inexpensive, and deployable in the field for non-experts. We cannot ignore the extent of fluoride contamination of groundwater, primarily in rural and agricultural areas. Future fluoride detection technology needs to occupy the space in between high-end laboratory accuracy and real-life utility. A fluoride sensing system of any significance must allow for routine testing of water safety by non-experts, plus allow communities to mobilize into action. Innovations should seek to make verifying the drinking water status for fluoride safety, a right for all, and not just a few privileged communities.

VI. ACKNOWLEDGEMENT

The authors would like to express their sincere gratitude to the Department of Electronics and Telecommunication, Vidyalankar Institute of Technology. We would also like to thank Dr. Sheetal Mapare for providing the necessary facilities and support during this research work. We are especially thankful to Soham Pal for his valuable guidance, encouragement, and continuous support throughout the study.

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