CHEMICAL SENSORS: PROMISING TOOLS FOR THE ONLINE MONITORING OF FLUORIDES

Nausheen Ameer,a Ghulam Mustafa,a,* Imran Khan,a Muhammad Zahid,b,* Maimoona Yasinzai,a Surraya Shahab,a Nazia Asghar,a Ikram Ullah,a Afaq Ahmad,c Iqbal Munir,c Hamayoon Khan,d Saeed Badshah,e Imran Shahid,f Muhammad Nauman Ahmad,g Afia Zia,g Shakil Ahmadh

Islamabad, Pakistan

ABSTRACT: Online monitoring of environmental pollutants is of significant importance as it helps in controlling the pollution at source, in the formation of regulations and policies, and in checking of the compliance of industries. Numerous conventional techniques are in practice for the detection and analysis of fluorides in water samples. However, these techniques have limitations and disadvantages and are not applicable for real-time online monitoring. It is of substantial interest to develop miniaturized robust, precise, and accurate devices capable of real-time online analysis and sensor technology provides promising tools for this purpose. Traditional methods for the assessment of water quality parameters are being replaced by new concepts and techniques. This review considers the development of miniaturized devices like optical, electrochemical, and mass sensitive sensors, suitable for fluoride recognition in liquid in this modern era. These sensors are highly sensitive, selective, user friendly, and less time consuming with a quick response. The review highlights the available literature on the potential use of sensors for the accurate recognition of fluoride ions.

Key words: Analytical techniques; Electrochemical sensors; Fluorides; Mass sensitive sensors; Optical sensors; Receptors.

INTRODUCTION

Fluorine is the lightest and most reactive member of the halogen group elements. Its chemical conduct differs from that of the other halogen members and these variations are quite obvious, especially regarding the response to natural water.1 It is highly electronegative and is found in the form of the fluoride ion (F) in water.2 Fluorine gas yields hydrofluoric acid on reaction with most inorganic and organic substances.3 Fluorine consists of nine electrons and protons and thus seeks for an additional electron to be stable like the other halogen group members, e.g., iodine, bromine, and chlorine. Fluorine is highly reactive chemically, does not usually occur in elemental form, and is found in ionic form in combination with various chemical compounds in minerals, e.g., cryolite, fluorapatite, and fluorspar, etc. The fluoride ion can exchange with hydrogen and the replacement of fluorine for hydrogen in natural compounds yields a very large number of compounds. Fluorine contributes to approximately 30% of agrochemical compounds and 20% of medicinal complexes. If fluorine containing compounds are excessively present in the natural environment they cause pollution. These compounds mainly come from the commercial waste water used in the production of nickel, aluminum, and copper, steam producing...
stations, the processing of phosphate minerals, the use of phosphate fertilizers and the fluorine-based pesticides, and the production of cement, glass, adhesives, and glue. The pollution of water with F depends on the transport of fluorides due to presence of ion-variable substances, water hardness, and the pH of the water. Fluorides are found to a major extent as fluorspar (fluorite) \([\text{CaF}_2]\), sellite \([\text{MgF}_2]\), fluorapatite \([\text{Ca}_5(\text{PO}_4)_3\text{F}]\), and cryolite \([\text{Na}_3\text{AlF}_6]\). Fluorspar is also found abundantly in igneous and sedimentary rocks such as cryolite. These F minerals are usually insoluble in water but can be discharged to water reservoirs as a pollutant.4

F is not considered to be an essential trace element for human growth and development, and is not necessary for the development of healthy bones and teeth.5 Exposure to F may cause adverse health effects in both humans and animals which can affect bones (skeletal fluorosis), teeth (dental fluorosis) and the soft tissues in many organ systems (e.g., central nervous system including the pineal gland, gastrointestinal system, thyroid, reproductive system, and cardiac and skeletal muscle).6 Although the World Health Organization set, in 1984 and reaffirmed in 1993, a guideline of 1.5 mg F/L (1.5 ppm) as a “desirable” upper limit, it also allows countries to set Country Standards, their own national standards or local guidelines.7-9 The limit of 1.5 mg F/L has been seen to be unsuitable in some countries and lower Country Standards have been set in some countries. In India there is a requirement (acceptable limit) of 1.0 ppm (mg/L) and a permissible limit in the absence of an alternate source of 1.5 ppm.10-12 A rider to the Indian limit is that the “lesser the fluoride the better, as fluoride is injurious to health.”10 In Senegal, West Africa, the upper limit has been set at 0.6 mg/L.10 In the USA, the US Department of Health and Human Services Federal Panel on Community Water Fluoridation has now recommended an optimal F concentration in drinking water of 0.7 mg/L instead of the earlier recommendation of a range of 0.7–1.2 mg which was based on the outdoor air temperature of geographic regions.13-15

Fluorosis is a burning global issue and is considered to be a serious problem in more than 25 countries around the globe. It threatens the human health and survival of approximately 200 million people around the globe. In many fluorotic areas, children face difficulties in mobility due to the damaging effects of skeletal fluorosis. The main cause of fluorosis is the intake of F through drinking water and high levels of F in water are a risk to human health.16 Since 1950, the opponents of fluoridation have argued that F exposure increases the risk of various diseases in humans including Down syndrome, bone fractures, and low intelligence.17 In waste waters fluorides can be present in the form of weak and highly toxic hydrofluoric acid (HF) whose toxicity can be seen in its characteristic of penetrating into tissue, because small molecules of HF quickly move through skin to tissue and damage it permanently.18 Therefore, the detection of F in water is of substantial importance due to its adverse effects on plants, marine life, animals, and humans.

**CONVENTIONAL METHODS FOR FLUORIDE DETERMINATION**

The various techniques and methodologies which are currently used for measuring the F levels in water are reviewed below.

*Spectrophotometric methods:* The spectrophotometric method is used extensively in practice for F determination because of its benefits and advantages like
reproducibility, accuracy, convenience, and the simplicity of the results. F determination by this method is carried out through the reaction of stained metal chelate complexes with F and as a response it produces a ternary complicated or substitute of the ligand F which give colorless fluoride steel CTPM dyes with groups that adhere to metal in a stable aggregate. Eriochrome cyanine R and S azurol are usually utilized as reagents for spectrophotometric detection of the fluoride complex. Aluminum complexes of triphenylmethane dyes, such as chrome azurol B and malachite green, have been used as reagents for spectrophotometric analysis of F and the determination of F using these aluminium complexes is possible, in the range of 0.0–2.0 mg/L for malachite green and in the range of 0.5 to 4.0 mg/L for chrome azurol B. The molar attenuation coefficient (molar absorption coefficient or molar absorptivity) for the complexes of chrome azurol B at 582 nm and of malachite green at 622 nm is $1.44 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $2.56 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, respectively (Figure 1).\textsuperscript{19}

Another spectrophotometric method based on the use of a zirconium oxide-xylenol orange (ZrO-XO) complex has been reported for the determination of F by the fusion of a sample with sodium hydroxide at 450–550°C and this method is simple, rapid and accurate due to there being no involvement of a distillation process.\textsuperscript{20} The reaction between zirconyl chloride and xylenol orange, catalyzed by the presence of stoichiometric amounts of F, provides a method for F determination in the range of 0.5 to 5 µg, in a final volume of 100 mL, which leads to an effective molar attenuation coefficient (molar absorptivity) of $2.0 \times 10^{-5} \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for the fluoride ion. The color changes are achieved within 90 minutes and remain stable.

**Figure 1.** Electronic spectra of chrome azurol B and its aluminium 1:2 complex in ethanol at $5 \times 10^{-5} \text{ M}$.\textsuperscript{19} Chrome azurol B is dark orange in ethanol. Its electronic absorption spectra displays 1 band with 2 heads at 280 and 296 nm in the UV region and a main broad band of greater intensity with heads at 444 and 580 nm in the visible region. The aluminium chrome azurol B ratio was determined as 1:2. The aluminium chrome azurol B 1:2 complex exhibits a dark pink colour in ethanol and displays 1 band in the visible region with 2 heads at 538 and 582 nm.
thereafter for 60 minutes when measured against a reaction system blank containing no F.\textsuperscript{21}

In order to measure very small amounts of F a simple and convenient method was developed based on the reduction of the optical absorbance of a solution of the zirconium-chrome azurol complex on the addition of F to it. The measurement of minute quantities of F in micrograms (about 2 µg), is possible with this method with high precision.\textsuperscript{22} In natural water, a novel extraction spectrophotometric approach involving a chemically associated octyl solid phase extraction (SPE) cartridge can be helpful for the quantification of fluoride ions in which the aluminum oxinate chelates are absorbed onto the SPE cartridge and then the water sample (containing fluoride ions) through the SPE control tool. In this process the excessive oxine sorbent is washed with acetate buffer and subsequently the various aluminum oxinate chelates on sorption are turned into elute by ethanol and their absorption spectra can be recorded by using a 375 nm light beam.\textsuperscript{23} The decline in adsorbed aluminium-oxinate chelate on sorbent can be correlated to the fluoride ion concentration in the samples. It only detects F concentrations up to 80 ng/mL but this method is highly sensitive with high quality and has an absorbance variant for every single mg/mL fluoride ion of 0.6.\textsuperscript{24}

Stopped-flow reagent-injection technique (Figure 2)\textsuperscript{25} is also used in practice for the detection of F in water samples in which the amount of F can be determined with lanthanum /alizarin fluorine blue in the presence of sodium dodecyl sulphate at a pH 4.6. This method produces a linear calibration graph for the F range of 0.08–1.2 mg/L with a relative standard deviation (n=10) of 0.2\% at 0.60 mg F/L. This method is comparatively fast and efficiently suitable for a large number of samples such as sea water and bottled mineral waters.\textsuperscript{26}

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{stopped_flow_system.png}
  \caption{The diagram illustrating the stopped flow system.\textsuperscript{25}}
\end{figure}
determination and reaction with F; (ii) indirect spectrophotometry based on the determination of the reduced absorbance via F or estimation of a compound that is released by F; (iii) direct extraction spectrophotometry which is primarily based on the formation of a complex with F; and (iv) indirect extraction spectrophotometry based on the determination of the extra reagent and the formation of a fluoride-reagent complex. It is very fast method and the sensitivity is very close to the Eriochrome cyanine R-zirconium standard technique. Another highly sensitive spectrophotometric quantification of F in tap water is carried out through aluminum complexes of triphenylmethane dyes (chrome azurol B and malachite green) that are used as spectrophotometric reagents. This technique, where an Al-xylenol orange (XO) complex has a very important role, gives the most consistent and trusted detection of F in a variety of samples for malachite green and chrome azurol B, for F ranges of 0.0–2.0 mg/L and 0.5–4.0 mg/L, respectively. In such spectrophotometric techniques an Al-xylenol orange complex is used as a coloring reagent for the determination of smaller amounts of fluorides in sample matrices. This method relies on the decolourization of a complex of Al with xylenol orange (XO) as an ultra-sensitive colored reagent and is preferred for analyzing relatively larger numbers of samples such as drinking water samples.

The ion specific selective electrode is a breakthrough in the analysis of F in water samples and the interference effect is less than during chemical analysis. During analysis, TISAB solution containing cyclohexylenedinitrilotetraacetate (CDTA) is used as an improved ionic buffer containing CDTA to control Al interference while it is trustfully applicable for samples with a F content of 5mg/L. An Orion fluoride ion electrode has been used to quantify the F ions by using a saturated calomel electrode as the reference electrode. A fluoride-sensitive electrode which makes use of the measurement of potential has been fabricated to develop activities across lanthanum fluoride crystals which depend on the ratio of fluoride on every facet of the crystal. Since the fluoride internal activity for all realistic purposes is regular, the potential developed depends on the value of fluoride’s activity in the external solution while the external reference electrode is usually calomel electrode.

**Chromatographic and flow injection analysis methods:** A practical method for ion exchange chromatography of cations and anions is reported in which the conductivity cell is used as a detector. In this method the resins split the ions of interest and strip the eluent from the background. Ion chromatography is carried out with the pulse electrochemical detector in conductivity mode. A potentiometric flow injection analysis system has been developed for the determination of fluorides in drinking water and other fluoride containing matrices. Sample analysis at the rate of 360 samples per hour through an electrode polished with slurried alumina is feasible with ion injection method. In this technique the stopped-flow mode is applied in manifolds, both in the regular and the opposite directions by synchronizing the propulsion gadgets and injections. The reacting plug is halted at the reactor to affirm the most efficient enhancement of the response without increasing the dispersion (non-kinetic stopped-flow mode) or the flow cell to detect the change in response via collecting signal-time information pairs (kinetic stopped-flow mode).

**Titration method:** A number of reports are available in the literature about the quantification of fluorides in water by using titration methods. For instance, thorium
nitrate titration test solution has been utilized to produce a permanent pale pink color in the presence of red alizarin as an indicator. A titrant of an equal amount can be used to a comparison solution which will be more pinkish than the test solution. After this, the final titration can be done with the standard solution of fluoride with the production of color in the solution to the comparison point. The results vary in the range of 100 to 102% with a standard deviation of about 3% and normal recovery rates after spiking the samples with natural water.

**Colorimetric methods:** In colorimetric analysis the concentration of a chemical compound or chemical element in a solution can be quantified with the help of a colored reagent and can be used equally for both inorganic and organic sample matrices. This method was developed by selective ligand-exchange between fluoride and a catechol type hemicyanine dye. In addition, to its high ability for specificity and sensitivity, the quantification is possible by naked-eye detection. Another high divorce colorimetric method has been reported to detect F in the water. Reagent for this method is cyanide colorant (C1), on which an hydroxyl group has been protected by reaction with tert-butildimethylilsilan (TBS) to form C2 silanated dye. C2 is fluoride ion selective and is attacked by the fluoride ion to form C1. C1 has an absorption capacity at the power 600 nm with a molar attenuation coefficient (molar absorptivity) of about 200,000 L•mol⁻¹•cm⁻¹. Under optimal conditions, the optical density at 600 nm is directly proportional to the amount of fluoride ion and the method has been successfully applied to the quantitative analysis of F in rain water. Mostly the colorimetric techniques for detection of fluoride ions rely on the colorizing action of fluoride anions with certain organometallic complex dyes. The reaction of zirconium-alizarin Lake with F is the basis for most colorimetric techniques for the determination of F concentration in water.

**Electrochemical technique:** The electro-analytical technique for the quantification of F in water samples is based on synergistic reaction electrochemistry with a bare boron-doped diamond electrode. This method has been evolved as a variation which depends on the dynamic electrochemistry of ISE and relies on a diffuse current of unfastened metal with a boron doped diamond electrode. Due to the low background signal of the boron-doped diamond electrode this sensor bears substantially low limits of detection up to 106 mol/L with the linear sweep voltammetric method and 107 mol/L with the rectangle version of approach. The linear sweep voltammetric method based on [CeF₆]²⁻ complex formation showed relatively low sensitivities and was therefore more suitable for those samples containing higher content of fluorides. A simple method to determine the F concentration in water by using homemade fluoride reagent paper saturated with aluminum quinalizarin complex has been designed. F reacts with reagent impregnated paper free ligand with orange colors different from those with other complexes. Color changes, related to the F concentration, can be measured using an arsenator. The arsenator functionality is based on photometric measurement spots on the paper expanded reagent for analyzing the F. The method can reliably determine fluoride in the range of 0.0–2.0 mg/L.

**LIMITATIONS OF CONVENTIONAL METHODS**

If identical chemical species exist in a sample then selecting a potentiometric method is limited and neutral samples have other limitations such a need for time
consuming conditioning of the electrode surface and the potentiometric method not being precise. The distillation technique has limitations such as toxicity, being time consuming, and requiring operation by skilled personnel. Colorimetric methods are generally used for the analysis of fluorides but cannot be preferred due to the time consuming multiple steps involved and the requirement of tested equipment furthermore; these methods are also not feasible for large number of samples. Fluorotelomer alcohols and fluorotelomer acids have been proposed as a source of the perfluorinated carboxylic acids found in remote marine locations and a method has been developed to measure a suite of neutral and acidic fluorochemicals including, fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids, in water and biological samples. The method involves solid-phase extraction with weak anion exchange (WAX) cartridges, followed by sequential elution with sodium acetate buffer, methanol, and 0.1% NH₄OH in methanol. For biological samples, prior to solid-phase extraction, tissues are digested in 0.5 N potassium hydroxide/methanol, diluted in water, and passed through the WAX cartridge. Neutral compounds and telomer alcohols are separated from other poly- and perfluorinated acids. The method is robust (i.e., capable of measuring neutral and acidic compounds), and can be applied for the analysis of a range of poly- and perfluorinated acids, including telomer alcohols, telomer acids, perfluoroalkylcarboxylates, and perfluoroalkylsulfonates in water and biota. With the use of high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS), a method detection limit in the range of several tens to hundreds of parts-per-quadrillion (pg/L) in water and at a few tens to hundreds of parts-per-trillion (pg/g) levels in biological matrices can be achieved. However, only limited quantities of fluorotelomer alcohols and acids can be detected by using ion chromatography (IC) techniques and this method is not feasible in aqueous media as PFCs are present at parts-per-trillion (ppt) or parts per quadrillion (ppq) levels and the limitation of this method has been in the high parts-per-billion (ppb) levels. The requirement for complex instruments, trained personnel, and well-equipped laboratories are the limitations of the ion selective electrode method. This method also shows ineffective performance and low specificity at higher concentrations. Anions play important roles in environmental, chemical, and biochemical processes and hence their recognition is important. Thus precise and sensitive tools and methods for real-time online monitoring of fluorides in waters are of substantial interest and in key demand.

CHEMICAL SENSORS

Chemical sensors are the analytical devices, constituting a recognition element (analyte) that is in direct connection with some physical or chemical transducer and which upon contact with the analyte produces a response in the form of signal showing the exact concentration of analyte of interest in the given sample. In the absence of that specific analyte the sensor would not show any response, even if competing agents bearing a close resemblance to the analyte of interest are present in simple or complex media. When the analyte of interest interacts with the receptors, the transducer inhibits the change in any of its physical properties, whether it is an optical, electrochemical, or mass change, etc. and converts it into an electrical signal. Chemical sensors are divided into three major classes on the basis of the transducers: (i) mass sensitive sensors, (ii) electrochemical sensors, and (iii) optical sensors.
signal produced by a transducer is usually very small and unable to be analyzed. The amplifiers are used to detect a small input signal coming from the transducer which is then amplified to become a large output signal containing the important waveform features of the input signal. The amplified signal is then processed through the signal processor where it can be displayed, stored, or analyzed further. A number of transduction methods have been developed in the past decade for the sensing of an analyte of interest. Though new types of transducers are constantly being introduced for their use in biosensors, the mass based (piezometer) transduction method is of substantial importance because it is the easiest, cheapest, and most popular method. Chemical sensors always require a recognition receptor layer which is sensitive to the chemical changes taking place in the surrounding environment and transmits these changes to the physical sensor at its core, which transduces the signals into useful analytical information. The sensor layer plays a crucial role in the effectiveness of a chemical sensor because the sensitive layer is responsible for the sensitivity, selectivity, response time, and lifetime of a chemical sensor. This sensor layer may be composed of polymer thin film, nanoparticles, selective membranes, biomacromolecules, or composite materials. Chemical sensors are usually designed for the detection of low concentrations of chemical species and could not reach to the detection limits of modern analytical instruments but still have many desirable advantages over them due to their small size, low cost, ease of operation, and their manufacture by established technological methods. Chemical sensors have a small size compared to other analytical instruments and because of their small size and ruggedness they can be used for remote measurements. These devices do not require too much maintenance because of their simplicity in design and can be easily operated by a nonprofessional. Chemical sensors are a promising candidate for the on-line in-time monitoring of specified analytes and are highly suitable for all kinds of applications. The fabrication of highly specific and simple receptors capable for sensing fluoride anions has gained significant interest and a number of receptors with high specificity have been reported that can sense and recognize important anions through electrochemical and optical responses in simple and complex media.

DETECTION OF FLUORIDE WITH SENSORS

The change in optical properties on receptor-analyte interaction can be utilized for the quantitative sensing of fluorides in a complex matrix by measuring the change in light related phenomenon namely: transmittance, reflection, absorbance, fluorescence, and chemiluminescence, etc. A fluorescence chemical sensor for the detection of F in water has been reported by Wie et al. This sensor experiences high selectivity towards the analyte of interest (fluoride ions) and the change in color can be distinguished and visualized by the naked eye up to a F concentration of 1.5 mg/L which is close to the upper limit set by the WHO for F in drinking water. This fluorescent probe showed high sensitivity with limit of detection for F of 0.38 mg/L. The specific interactions between silicon and fluoride ions may be a promising strategy for the generation of highly specific receptors and signal transduction can be carried out in two independent modes based on fluoride–fluorescence color (colorimetric mode) and dependent changes of intensity, respectively. This sensor system has high sensitivity ranging to the ppb level by using the power-metric mode.
The concentration of fluoride ion is converted to a fluorescent color signal in the colorimetric mode. The fluorescence color signal is also observable with the naked eye and this property of being able to distinguish changes with the naked-eye color is excellent for F levels less that the WHO upper limit for F of 1.5 mg/L. The sensing process of this sensor is quite fast in both modes, takes only 20 seconds, and is convenient for the detection of fluoride ions in daily applications.54

The detection of F at pico molar levels in water can be achieved by Schiff bases based chemosensor and fluorescent organic chemo receptors, e.g., hydrazine which is highly selective, sensitive, and relatively easy to formulate for the recognition of F in the aqueous environment.55 The transfer of protons from the quinone hydrazine tautomer to fluoride anions results in the creation of an azophenol tautomer and causes a considerable alteration in color (blue-violet from orange) with a limit of detection of approximately 10 ppm. This probe based sensing system having Ru-bipy based quinone hydrazone, is cheap, and can be substantially useful for developing and third world countries for the prevention of fluorosis.56 A Schiff base fluorescence chemosensor for the detection of F in water samples at the pico molar level has also been reported. There are some fluorescent organic chemo receptors, such as the hydrazine based ones, with various changeovers in their salicylaldehyde wing, which acts as a highly sensitive receptor for the analyte of interest and has tailored receptors which play a vital role in tuning the acidity. This system has the potential to be utilized as a promising material for the sensitive recognition of F. It may be used for measuring picomolar concentrations of F in tap water (Figure 3).56

Figure 3. The image highlights the changes in the color of the test papers for sensing the fluoride ion in neutral liquid solution with various fluoride concentrations.56

The colors illustrated are:
- 1000 mg F/L = blue-violet
- 100 mg F/L = greenish brown
- 10 mg F/L = yellow
- 0 mg F/l = pale orange

A strong interaction between graphene oxide (GO) and aluminum micro-interdigitated electrodes (Al-µ-IDEs) with fluorides can be utilized as a recognition strategy for the detection of F in aqueous solution in the range of 0.1–10 ppm. The GO is synthesized using the chemical oxidation of graphite and lithography patterned
Al-µ-IDEs on p-Si. The aqueous fluoride ions are adsorbed on the hydrophilic functional sites (hydroxyl, carbonyl, carboxyl, epoxy) available in GO which causes the increase in sensitivity. This strong interaction and sensitivity has resulted in a cheap and easily processable tool for F quantification and, with its selectivity, this real time sensor has a great potential to be a sensor at the forefront for detecting aqueous F in natural drinking water.57

Electrochemical sensor set-ups are usually very energy efficient due to their low power requirement to operate. Numerous innovative sensor technologies have been developed for the recognition of analytes of interest with substantial sensitivity and many electrochemically active materials are suitable candidates for utilization as efficient receptors for electrochemical sensors. Calyx pyrrole can be used in polyaniline matrix as a receptor for the detection of fluoride ions in aqueous solution. Using electrochemical deposition, the polyaniline was deposited inside the pores, up to 1.2 µm in diameter, of isoporous polycarbonate membranes. F binds compactly to the calyx pyrrole and the sensor gives a quick response at –0.2 V and +0.2 V gate voltage because the sensor’s receptor is immobilized at +0.2 V efficiently. This device has the ability to detect minute amounts of fluoride, in nM concentrations, and, in terms of molarity, at the WHO limit of 1.5 ppm where the curve has a nearly linear reaction on the either side of the limit (Figure 4).58

Optical chemical sensors employ a transduction mechanism that transduces a particular analyte recognition event into an optical sign. The phenomenon of fluorescence on the interaction of sensor receptors with fluoride ions can be used for the quantification of fluorides. The relationship among the fluoride ion and the C-H bond was studied by way of fluorescence spectroscopy and NMR titration. The
interactions were verified by monitoring the change in fluorescence intensity and were utilized to determine the F in aqueous media at concentrations down to 1.9 ppm. This fluorine-based fluoride sensor consists of two triazolium groups and the sensor is based totally on the deprotonation of a C-H bond. The combination of triazolium and fluoride units offers a highly selective fluorescence turn-on prototype sensor with a very high sensitivity for the detection of F (Figure 5).59

A strong fluorescent turn-on sensor for detecting the fluoride ion in a totally aqueous environment has been reported by utilizing the biocompatible hydrophilic polymer poly(ethylene glycol) (PEG). Tert-Butyldiphenylsilyl (TBDPS) groups are covalently introduced onto the fluorescein moiety that appeared in the successful quenching of the fluorescence into the sensing set-up. On exposing the sensor to the fluoride ion, the selective fluoride-mediated cleavage of the SiO bond leads to the healing of the fluorescein moiety resulting in an intense increase in fluorescence intensity underneath visible light excitation. This sensor produces a quick response and is quite selective towards the fluoride anion in the presence of other competing anions with a limit of detection about 19 ppb. In addition, this sensor can be applied to a real sample, e.g., running water for the determination of fluoride ions (Figure 6).60
A number of reports are available about the optical sensing phenomenon based detection of fluorides in aqueous and non-aqueous media. A new idea has been reported for detecting the fluoride ion where a porous crystalline structure assists fluorescence. The quantification and interaction phenomenon is carried out by the decomposition of the host scaffold which causes the discharge of the fluorescent dye molecules. Through this relatively new approach, the optical-phenomenon based sensing of fluoride is highly selective even in the presence of various competing anions. Another approach based on metal-organic frameworks (MOFs) can be a powerful way of quenching of fluorescent guests upon incorporation into the porous framework and the subsequent dequenching upon analyte-specific degradation of the host material. This sensing phenomenon was confirmed by the dye-loaded MOF NH$_2$-MIL-101(Al), and it resulted in an incredibly selective and sensitive fluoride sensor highly suitable for aqueous solutions (Figure 7).
Another effort have been made by Wie et al. for the detection of F (Na⁺ and TBA⁺ salts) by using a fluorescent probe which was primarily based on a desilylation induced chromogenic response in water. The fluorescent detection of F depends on a fluoride-mediated selective cleavage of a Si–O bond, resulting in the formation of a fluorescent intermediate with a strongly improved fluorescence intensity. This method is highly selective towards F with, in addition, noteworthy color changes visible to the naked eye at the concentration of 1.5 mg/L, the upper limit set by the WHO for F in drinking water (Figure 8).62

CONCLUSIONS

A high concentration of fluoride in ground drinking water may result in adverse health effects involving dental fluorosis, skeletal fluorosis, and non-skeletal fluorosis. Alternative new concepts and techniques are required to replace traditional methods for the measurement of water quality parameters. The modern sensing options for the detection of fluoride in water include the use of optical sensors, electrochemical, and chemical sensors. The use of sensor technology, as an alternative solution for the detection of fluorides in water, is due to its high sensitivity, selectivity, user friendliness, rapid response, and it being less time consuming as compared with the traditional sensing methods. These modern tools will have to undergo a transition from the laboratory scale to a form applicable for real-time use and mass industrial manufacturing in order to meet the current key challenge for commercialization.

REFERENCES

Chemical sensors: promising tools for the online monitoring of fluorides

Ameer, Mustafa, Khan, Zahid, Yasinzai, Shahab, Asghar, Ullah, Ahmad, Munir, Khan, Badshah, Shahid, Ahmad, Zia, Ahmed