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Rapid detection of fluoride in potable water using a novel fluorogenic compound 7-O-tert-butyldiphenylsilyl-4-methylcoumarin

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ABSTRACT

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

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1. Introduction

The development of fast, efficient and inexpensive methods for the detection of fluoride has been gaining significant attention in the recent years, particularly due to public awareness of harmful side-effects of fluoride. For example, for the first time, in more than 50 years, the United States Environmental Protection Agency (USEPA) has recommended to lower the mandated fluoride levels to be added in drinking water [1]. Fluoride is a mineral in water and soil. Almost 50 years back, through scientific studies, it was demonstrated that individuals whose drinking water naturally contained more fluoride had a fewer dental cavities [2]. This prompted dental products, like most of the toothpastes that are commercially available, to add additional fluoride and municipalities across the world started adding fluoride to their drinking water in limited concentrations [2]. The recommended level of fluoride in drinking water is 2 mg/L as directed by WHO [3]. On the other hand, an increase in fluoride concentration level leads to dental and skeletal fluorosis. Excess exposure to fluoride is also known to induce many endocrine effects such as decreased thyroid function and Type II diabetes. Fluorides are also known to cause

attention deficit hyperactivity disorder (ADHD) [4] and neurotoxicity there by resulting in lower IQs in children [2,3]. Hence, fluoride levels in drinking water have to be constantly monitored and precautions need to be taken to control the levels of fluoride in drinking water.

Although, fluoride sensing is of such great importance, there are challenges involved in the development of sensors with extreme sensitivity and specificity. There are several methods available commercially and in the literature for the detection of fluoride such as the ion selective electrode method [5,6], nuclear magnetic resonance spectroscopic (NMR) analysis [7], colorimetric (UV) [8–12] and fluorescence sensing [9,11–18]. Among these, ion selective electrode methods are most widely used. However, there are several disadvantages associated with this method such as the requirement for complex instruments, well-equipped laboratories and trained personnel. There are also other issues associated with these methods such as low specificity and inefficient performances at higher concentrations. Hence, neither the ion selective electrode nor the NMR approach can be used in minimally resourced communities. As a result, colorimetric and fluorescence sensing systems are emerging as an alternative to such complex systems due to their easy field deployment advantages along with high sensitivities and extremely low detection limits. These become more attractive for limited resource communities that cannot afford the establishment of well-equipped laboratories.

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Over the last decade, a large number of colorimetric and fluorescence sensing systems have been developed for detecting fluoride. Fluoride has the smallest ionic radius, highest charge density, and a hard Lewis basic nature [13]. Majority of fluoride sensing systems rely on fluoride interactions with Lewis acids wherein fluoride molecule acts as a participant or a disrupter, such as sensing systems based on F^- promoted cleavage reactions. A few examples of such systems include sensors based on boronfluoride interactions [7,19–22]; hydrogen-bond and $\pi-\pi$ interactions involving thiourea/urea [23], imidazoline/imidazole [24–26] and other groups serving as binding units; organometallic interactions involving metal ion binding sites [27]; and silyl ether-fluoride interactions. Systems based on silyl ether fluoride interactions have shown significant potential due to the great affinity of silyl groups towards fluoride arising from the large differences between the dissociation energies of Si–O (103 kcal/mol) and Si–F (141 kcal/mol) [28].

There are several examples of silyl based chromogenic or fluorogenic compounds available in the literature. Yamaguchi et al. [29] have developed a silyl ether based sensor (tri(9-anthryl)fluorosilane) which upon interaction with fluoride ions causes a change in its photophysical properties that can be detected using a spectrophotometer. Yang [30] designed and synthesized 4-methylumbelliferyl tert-butyldimethylsilyl ether (4-MUTBS) for fluoride ion detection. This 4-MUTBS is weakly fluorescent complex compound and was synthesized by reacting 4-methyl umbelliferone (4-MU) with tert-butyldimethylsilyl chloride. Fluoride ion in acetone-water solution cleaves this complex 4-MUTBS compound resulting in the release of the fluorogenic compound 4-MU. Kim et al. [31] have developed a tert-butyldiphenylsilane (TBDPS) based chemical compound, which releases resorufin through substitution by F^- at the silicon center thereby causing a major change in the color of the solution from yellow to pink. Kim et al. [32] have also synthesized another fluorometric fluoride sensor containing tert-butyldiphenylsiloxy group as the trigger and coumarin as the optical signaling group. Their sensor produces blue fluorescence upon interaction with fluoride and the fluorescence intensity of the solution increases with increasing concentrations of fluoride. Sokalingam et al. [33] have developed a coumarin-based sensor that is triggered by the F^- -promoted cleavage of the Si–O bond. Park et al. [34] have developed a fluorometric gel based sensor that results in the formation of a fluorescent gel upon interaction with fluoride in aqueous media. Ghosh et al. [35] synthesized O-tert-Butyldiphenylsilyl coumarin and tested for their anion binding properties with Fluoride ions in organic and aqueous organic solvents. They observed that a large amount of emission for samples tested in CHCl₃. In addition to the detection of fluoride ions in organic and aqueous mixture solutions, Ghosh et al. [35] and Kim et al. [32] used their developed compounds for imaging living systems. Although, all these sensors reported so far have great potential, there are several issues associated with them in terms of solubility in aqueous solutions and interference from other anions. There are several other colorimetric and fluorescence chemosensors that are based on the cleavage of the Si–O bond available in the literature [36–39].

Our primary target is to develop a low-cost sensor to monitor water contamination. In the past, we have developed a Mobile Water Kit to monitor pathogen contamination in potable water [40,41]. The great affinity and selectivity of silyl ethers towards fluoride has inspired us in designing and synthesizing a novel coumarin based fluorogenic compound - 7-O-tert-butyldiphenylsilyl-4-methyl coumarin (TBDPSC) compatible with aqueous solutions. Moreover, the compound has been synthesized to attain great specificity towards fluoride and primarily targeted towards rapid, low-cost and portable water testing. This new development

will allow us to increase the versatility of MWK towards detecting toxic contaminants in water. A detailed description of the synthesis and characterization of the compound, testing with sodium fluoride (NaF) and interference testing from other anions has been presented. The selectivity and specificity of the compound towards fluoride has been investigated in water and the potential applications of the compound for fluoride sensing in the environmental monitoring have been described.

2. Experimental section

2.1. Materials

All the chemicals and commercial reagents required for the synthesis and testing of TBDPSC were purchased from Sigma Aldrich, Canada and used without further purification unless otherwise mentioned.

2.2. Physical measurements

NMR spectra were recorded at 400 MHz, using Agilent/Varian Inova two-channel spectrometer (Agilent Technologies, CA, USA). Proton chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS) or in reference to the solvent CDCl₃ (δ 7.26). Coupling constants (J) are reported in hertz (Hz). Electrospray Ionization (ESI) mass spectra (MS) were obtained on Agilent single quadrupole mass spectrometer. Thin layer chromatography (TLC) was performed on EMD-Merck silica gel GF254 plates (Merck, Darmstadt, Germany) and detections were achieved by charring with phosphomolybdic acid/EtOH or cerium sulfate/ammonium molybdate/H₂SO₄/H₂O solution. Column chromatography was performed using silica gel F60 purchased from Silicycle, Canada. Molecular sieves were dried under high vacuum at 170–180 °C for 6–10 h immediately before use. Fluorescence measurements were conducted using Agilent Varian Cary Eclipse Spectrofluorometer.

2.3. Methods

2.3.1. Synthesis of 7-O-tert-butyldiphenylsilyl-4-methyl coumarin

7-Hydroxy-4-methyl coumarin (5 g, 28.38 mmol) and imidazole (3.9 g, 56.76 mmol) were dissolved in 100 mL of dry dichloromethane (DCM)-Tetrahydrofuran (THF) solvent mixture (3:1). The mixture was stirred under nitrogen atmosphere till a clear solution was obtained. Tert-butyldiphenylsilylchloride (TBDPS-Cl, 8.1 mL, 31.22 mmol) solution in 10 mL of DCM was then added slowly dropwise for over a period of 1 h. The reaction was then allowed to stir for 2 h under nitrogen at room temperature. The reaction mixture was then filtered through a short bed of celite and was washed with 200 mL water and 100 mL brine. The organic layer was dried with anhydrous sodium sulphate, filtered and concentrated under reduced pressure to give the crude product. The crude residue was purified by column chromatography using hexane ethylacetate as eluent. The product was obtained as a colorless oily compound, which was only 70% pure by ¹H NMR. The product was again subjected to a second column using hexane-ethylacetate solvent system. The column was run very slowly this time and only the middle fractions were collected. After concentrating the product under reduced pressure and prolonged drying under high vacuum, the product was obtained as a colorless solid, 5.5 g (47% yield). ¹H NMR is in accordance with the structure. ¹H NMR (400 MHz, CDCl₃): 7.70–7.74 (m, 4H, Ar–H); 7.44–7.49 (m, 2H, Ar–H); 7.37–7.43 (m, 4H, Ar–H); 7.34 (d, J = 14 Hz, 1H, Ar–H), 6.70–6.76 (m, 2H, Ar–H), 6.10 (d, J = 2 Hz, 1H, =CH–CO); 2.35 (s, 3H, CH₃); 1.15 (s, 9H, (CH₃)₃). A schematic of the synthesized compound is presented in Fig. 1.

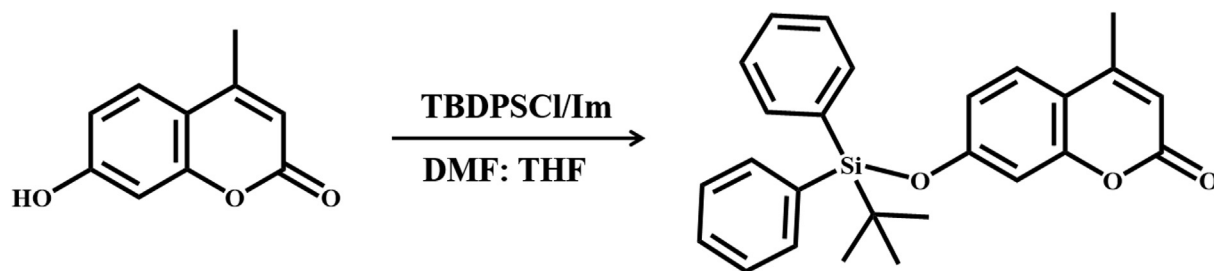


Fig. 1. Schematic of TBDPSC synthesis.

2.3.2. Fluoride testing

A series of test samples with varying concentrations of fluoride ranging from 0.1 to 100 mg/L were prepared by dissolving 0.2210 g of NaF in 1 L of de-ionized (DI) water and diluted as per the required concentration. 40 μ L of 4% TBDPSC solution prepared in THF was then added to 1 mL of each of these solutions. Fluorescence spectra was obtained for each of these solutions with corresponding excitation and emission wavelengths of 360 nm and 450 nm, respectively. Several replicates were tested for each of these samples.

2.3.3. Interference testing

A series of test samples were prepared with different anions that include F^- , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} and CH_3COO^- . Each of the anion solutions were prepared in DI water and maintained at a specific concentration of 5 mg/L. 40 μ L of 4% TBDPSC solution prepared in THF was then added to 1 mL of each of these solutions. Fluorescence spectra was obtained for each of these solutions with corresponding excitation and emission wavelengths of 360 nm and 450 nm, respectively.

3. Results and discussion

Addition of TBDPSC to fluoride samples results in the dissociation of TBDPSC into TBDPS-F and coumarin. Coumarin emits a blue fluorescence that confirms the presence of fluoride in solution. A schematic of the TBDPSC and fluoride interaction is presented in Fig. 2. The fluorescence emitted by the solution can be visualized under a simple hand-held ultraviolet (UV) lamp. The effect of fluoride concentration on the fluorescence intensity was studied by

adding 40 μ L of 4% TBDPSC solution prepared in THF to 1 mL of different fluoride samples with concentrations ranging from 0 to 10 mg/L. The resulting fluorescence was then observed under a UV lamp at a wavelength of 360 nm after a few seconds and the increase in fluorescence intensity with increasing concentrations of fluoride is represented in Fig. 3(a). It can be observed that fluorescence is absent in sample with no fluoride ions and considerably visible fluorescence is observed in samples with concentrations as low as 0.2 mg/L. Fig. 3(a) clearly demonstrates that TBDPSC is highly sensitive towards fluoride capable of detecting extremely low concentrations and also the time required for sensing is very fast (5–10 s).

The fluorescence intensity of the samples was quantified using a Varian Cary Eclipse spectrofluorometer at excitation and emission wavelengths of 360 and 450 nm, respectively. Fig. 3(b) represents the increase in fluorescence intensity with the increase in the concentration of fluoride ion. This plot is based on readings taken from several replicates of fluoride samples. It can be observed from the figure that the fluorescence intensity linearly increases with fluoride concentration indicating a 1:1 stoichiometric ratio between fluoride ions and TBDPSC. It should be noted that no fluorescence is observed in samples with DI water (no fluoride ions).

In order to test the specificity of TBDPSC towards fluoride, several anion solutions were prepared with standard concentrations of 5 mg/L that included Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} and CH_3COO^- . 40 μ L of 4% TBDPSC solution prepared in THF was then added to 1 mL of each of these solutions to check for interference from either of these compounds towards fluoride testing. The resulting fluorescence was then observed under a UV lamp. Fig. 4(a) represents

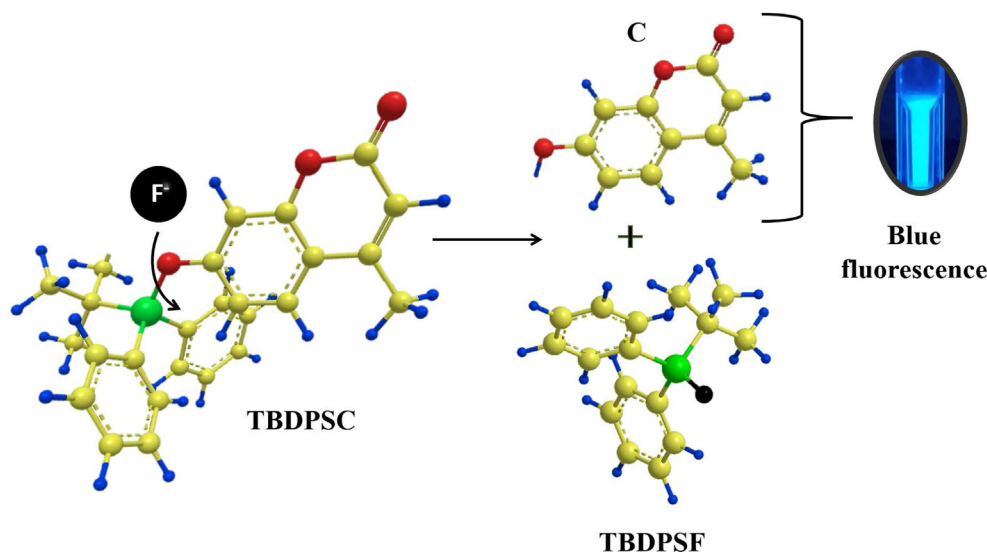
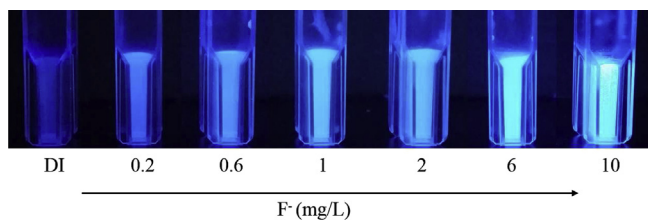
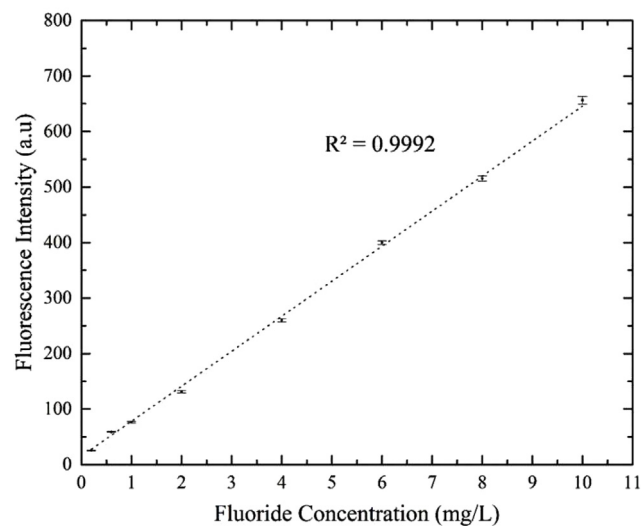


Fig. 2. Schematic of TBDPSC-fluoride interaction.



(a)

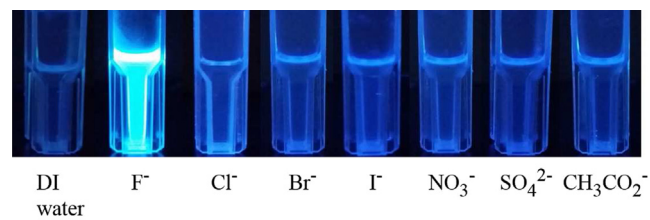


(b)

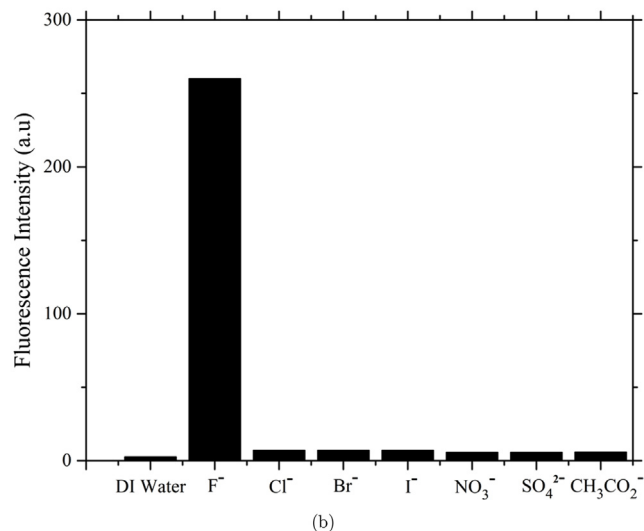
Fig. 3. (a) Development of blue fluorescence in samples with increasing concentrations of fluoride within few seconds after the reaction with TBDPSC; (b) Variation in fluorescence intensity of samples with increasing fluoride concentrations in DI water.

the fluorescence emitted by each of these solutions under a UV lamp. It can be observed that no discernible fluorescence can be visualized for any other ions other than fluoride indicating the highly specific nature of TBDPSC. The corresponding fluorescence intensities for each of these solutions were quantified using a spectrofluorometer. Fig. 4(b) represents the fluorescence emitted by each of the compounds at excitation and emission wavelengths of 360 nm and 450 nm, respectively. It can be observed that quite negligible fluorescence is produced by other anions other than fluoride even at such high concentrations. The figure indicates that no discernible fluorescence is observed for other anions at low concentrations thereby demonstrating the extreme specificity of TBDPSC towards fluoride. These observations are in concordance with the fact that silyl ethers have great affinity towards fluoride. We also tested for samples containing other ions in the presence of fluoride. It is observed that there is not much difference in the fluorescence intensity for the samples containing fluoride with and without other ions. It is a good indication that the new compound TBDPSC is working fine with complex water samples and there is no interference with other ions.

The fluoride samples were also tested with commercial fluoride test kits (Quantofix) obtained from Sigma Aldrich, Canada in order to validate the results. Quantofix test kit is a rapid test kit for semi-quantitative determination of fluoride ions in surface and ground water. This kit is manufactured by Macherey–Nagel GmbH & Co., KG (Duren, Germany) and supplied by Sigma–Aldrich, Canada. The Quantofix test kit comes with test discs, a beaker, needle, 6 % hydrochloric acid, and color scale. The pink test disc in the test kit is bleached with fluoride ions containing hydrochloric acid solutions. The size of the bleached area correlates with the concentration of



(a)



(b)

Fig. 4. (a) Optical changes in fluorescence emission of several anion solutions after reacting with TBDPSC at 25 °C for 1 h; (b) Comparison of fluorescence intensity values of several anion solutions after reacting with TBDPSC at 25 °C for 1 h. Tested samples were excited by UV light at 360 nm and emission intensities were measured at 460 nm. Left to right: DI water, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, SO₄²⁻ and CH₃COO⁻.

fluoride ions. The test procedure is as follows: The contaminated water sample of 10 mL was collected in a beaker and then added 20 drops of hydrochloric acid. The pH value of the sample should be maintained below 1. A hole was pierced at the center of the test disc with the help of needle and the test disc was submerged into the water sample containing hydrochloric acid. The test disc was saturated with solution after 5–7 min, i.e., it does not absorb any more sample. The test disc was then removed from the sample after 2 min and then compared the size of the bleached zone with the color chart provided. The concentration of fluoride is measured in mg/L. Fig. 5 in the revised manuscript shows the comparison results of the present method and Quantofix fluoride test kit. It is observed that the results obtained with TBDPSC (present method) are in 100 % concordance with the ones obtained with the Quantofix test kit.

4. Conclusion

We have designed and synthesized a novel fluorogenic compound - 7-O-tert-butylidiphenylsilyl-4-methyl coumarin (TBDPSC) in order to develop a simple, rapid and inexpensive test method for fluoride testing in potable water. A detailed procedure for the synthesis and characterization of the compound has been presented. We have tested the compound with different concentrations of fluoride in water and validated the results with commercially available test kits. We have also tested the compound with other anions in order to study the selectivity of the compound towards fluoride. Excellent selectivity and specificity of TBDPSC towards fluoride has been demonstrated in water. The current TBDPSC based test method involves adding a few drops of TBDPSC solution to 1 mL of sample and visualizing the sample under a

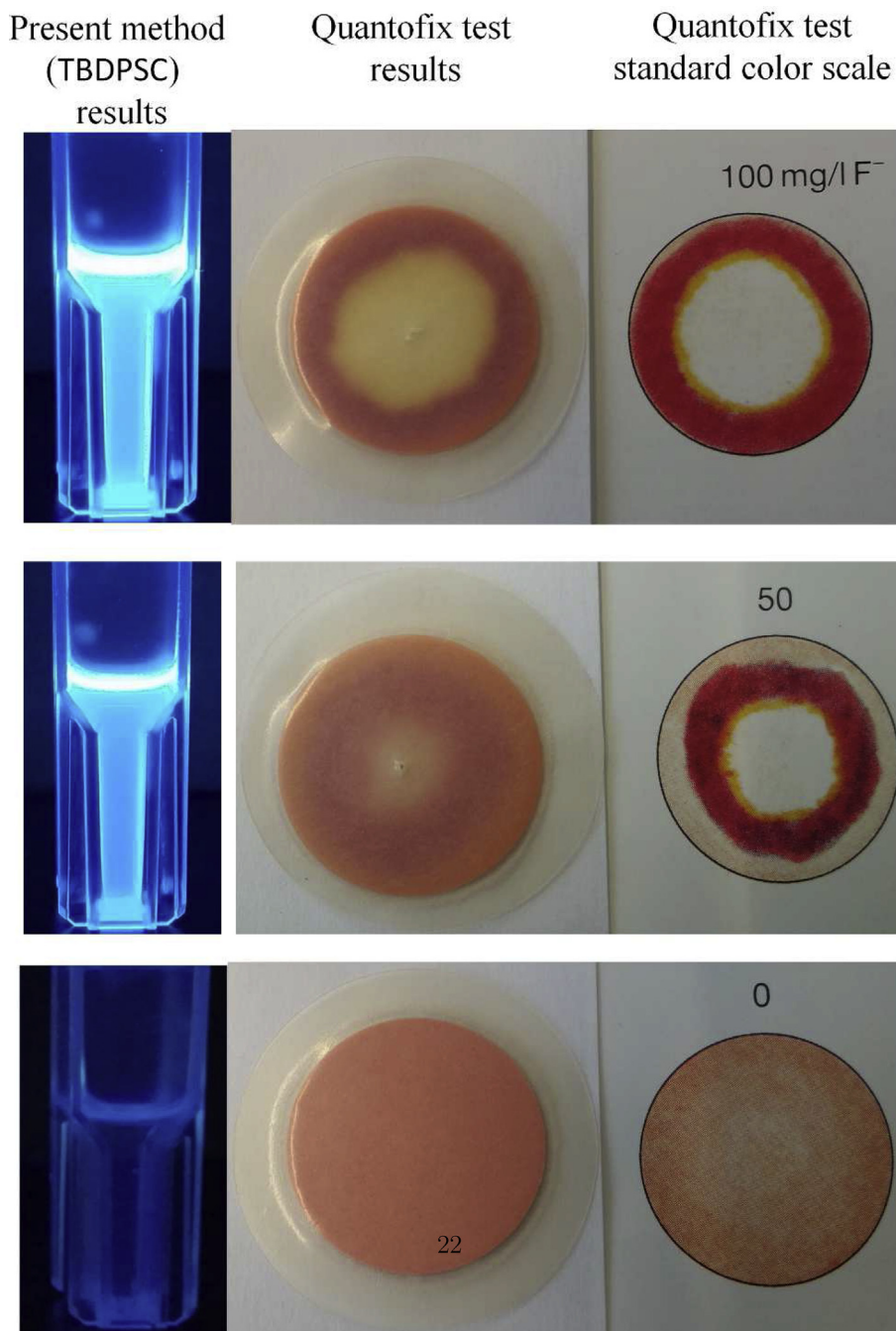


Fig. 5. Comparison of present method (TBDPSC) results with Quantofix test results for the detection of fluoride.

simple handheld UV lamp. Such ease of the test method would allow any untrained user to conduct the test and assess the quality of water. Hence, this test method has a great potential to be used as a portable fluoride test kit for water quality monitoring and endeavors are in place to integrate this simple testing method with the already field-deployed Mobile Water Kit [42].

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