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Monitoring of fluoride in water samples using a smartphone

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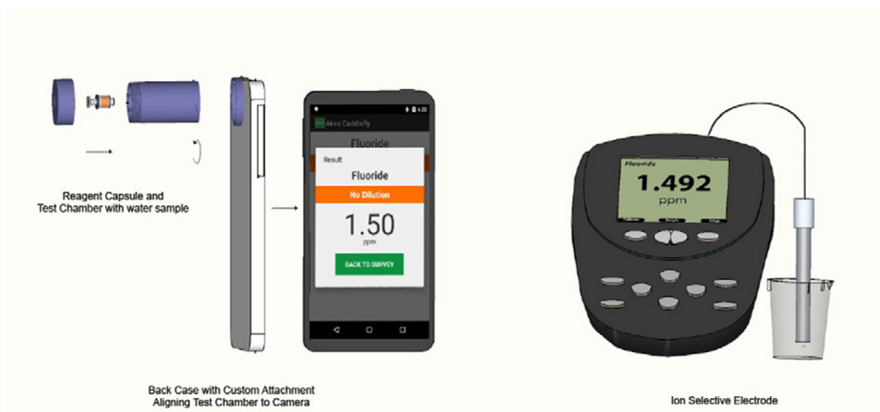
HIGHLIGHTS

- Fluoride is an inorganic pollutant in ground water, affecting human health.
- A colorimetric method for measurement of fluoride in drinking water with smartphone
- Measurement is by mixing water with zirconyl xylenol orange complex reagent.
- Results are comparable with laboratory-based ion selective fluoride electrode method.

GRAPHICAL ABSTRACT



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ABSTRACT

In several parts of India, groundwater is the only reliable, year round source for drinking water.
Prevention of fluorosis, a chronic disease resulting from excess intake of fluoride, requires the screening of all groundwater sources for fluoride in endemic areas. In this paper, the authors present a field deployable colorimetric analyzer based on an inexpensive smartphone embedded with digital camera for taking photograph of the colored solution as well as an easy-fit, and compact sample chamber (Akvo Caddisfly). Phones marketed by different smartphone makers were used. Commercially available zirconium xylenol orange reagent was used for determining fluoride concentration. A software program was developed to use with the phone for recording and analyzing the RGB color of the picture. Linear range for fluoride estimation was 0–2 mg l^{-1}. Around 200 samples, which consisted of laboratory prepared as well as field samples collected from different locations in Karnataka, India, were tested with Akvo Caddisfly. The results showed a significant positive correlation between Ion Selective Electrode (ISE) method and Akvo Caddisfly (Phones A, B and C), with correlation coefficient ranging between 0.9952 and 1.000. In addition, there was no significant difference in the mean fluoride content values between ISE and Phone B and C except for Phone A. Thus the smartphone method is economical and suited for groundwater fluoride analysis in the field.

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1. Introduction

Consumption of drinking water with an elevated level of fluoride leads to a chronic disease, which manifests as dental and skeletal fluorosis (Ozsvath, 2009). Based on health hazards estimates, the World Health Organization (WHO) has established a guideline value of 1.5 mg l^{-1} for fluoride in drinking water (World Health Organization, Guidelines for Drinking-water Quality, Fourth Edition; 2011). Bureau of Indian Standards are 1.0 mg l^{-1} as permissible and 1.5 mg l^{-1} as the maximum permissible limit in the absence of alternate source (Bureau of Indian Standards, Drinking Water - Specification, IS 10500 Second Revision, 2012). It is estimated that around 200 million people, from among 25 nations, may be affected by fluorosis (Brindha and Elango, 2013). In India, around 20 states have been identified as endemic for fluorosis. More than 25 million people are affected and approximately 66 million people are at the risk of being affected (Susheela, 1991). Groundwater is used for potable purposes by over 50% of the global population whereas in India, it is the drinking water source in ~80% rural and ~50% urban dwellings (Jadhav et al., 2015). Young children appear most susceptible, given that dental enamel and skeletal formation is most active during early childhood (Kravchenko et al., 2014).

Extensively used laboratory methods for determination of fluoride in water include potentiometry using a fluoride selective electrode and colorimetry (Eaton et al. "APHA: Standard Methods for the Examination of Water and Wastewater." *Centennial Edition., APHA, AWWA, WEF, Washington, DC* (2005).). Latter methods generally use zirconium dye complex (SPADNS and Alizarin red) reagents (Bellack and Schouboe, 1958; Megregian and Maier, 1952). Zolgharnein et al. (2009) reported the use of Al-xylenol orange complex as a reagent for determining trace amounts of fluoride in water. Field based methods (Strip format or liquid reagent) for fluoride determination have also been developed using Zirconium SPADNS, Zirconium xylenol orange and aluminum quinalizarine (Barghouthi and Amereih, 2013; Rao et al., 2002; (http://www.hach.com/pocket-colorimeter-ii-fluoride-spadns-ii-arsenic-free/product-details?id=7640445206).

Prevention of fluorosis requires the screening of all groundwater sources for fluoride in endemic fluorosis areas. Further small-scale defluoridation units are being increasingly used at household or community level, which requires periodic monitoring. Laboratory testing of all sources, especially in rural areas, would require proper sample collection, preservation and transportation to the laboratory of large number of samples, which would be time consuming and prohibitively costly. Reliable field testing methods offer a cost effective solution for the mass screening of sources as it can be completed in an acceptable time scale. Furthermore, testing can be performed in the presence of consumers and thus becomes an important communication tool. Many field test kits are commercially available in India. They include strip formats as well as liquid reagents. Many of these are based on the colorimetric principle; Fluoride present in the water sample reacts with the colored reagent leading to the dissociation of a portion of the Zr-dye into a colorless complex anion and the dye. Decolorization or discoloration or color change is proportional to the concentration of fluoride in the sample (Bellack and Schouboe, 1958; Megregian and Maier, 1952).however, they generally rely on color comparators for detecting the change. The results may therefore be subject to high individual variation. Evaluation of these commercial kits was carried out by Shriram Institute for Industrial Research in collaboration with UNICEF, showed the BARC developed method based on zirconium xylenol orange reagent as one of the best. (Rao et al., 2002; http://www.indiawaterportal.org/sites/indiawaterportal.org/files/Field%20Test%20Kits_2nd%20Feb%2006_PRINT.PDF).

Dahi et al. (2004) evaluated Pack test kit marketed by Kyoritsu Chemical-Check Lab Corporation, Japan, which is based on a Lanthanum–Alizarin Complexon Visual Colorimetric Method. They concluded that the Pack test kit, with few limitations taken into consideration, provides a very handy, rapid and quite reliable tool for decision on whether a given water is fit for drinking or not or whether a defluoridator in operation should be discontinued or not. This method has measurement range of 0.2–3 ppm with minimum detection limit of 0.2 ppm. A simple field method for determination of fluoride in drinking water using handmade fluoride reagent paper impregnated by aluminum quinalizarin complex was reported by Barghouthi and Amereih (2013). Fluoride reacts with the impregnated reagent paper to release the free orange dye. The change in the color from pink to orange was proportional to the amount of fluoride and was measured using an arsenator (Wagtech, UK), which is a portable digital photometer driven by a battery, blue diode as a source of light, and photodiode detector. The method gave a reliable determination of fluoride in the range 0.0–2.0 mg L^{-1}. Hach is marketing a lightweight and battery operated Pocket Colorimeter™ II for fluoride, suitable for quick, on-the-spot fluoride monitoring in the field. The colorimeter is precalibrated and thus it can be used only with their SPADNS reagent and it has measurement range of 0.1–2 ppm with minimum detection limit 0.1 ppm.(http://www.hach.com/pocket-colorimeter-ii-fluoride-spadns-ii-arsenic-free/product-details?id=7640445206). The analysis cost will therefore be high. Recently (Jyoti Boken et al., 2015) have demonstrated fluoride selective aggregation of thiobarbituric acid-capped gold nanoparticles is rapid, selective and sensitive. This is associated with dramatic color change in an aqueous solution, which can be used as a method for visual detection.

Smartphones are popular devices frequently equipped with sensitive sensors and high computational ability. According to a recent report from the World Bank (Bank, W, Information and Communications for Development, 2012), there are currently more than 6 billion cell phone subscriptions, with nearly 5 billion in the developing world, and more than 35 billion apps (App Store and Google Play-Android) have been downloaded. Extensive research is being focused on the use of a smartphone as an optical sensing tool for different applications for monitoring pH (Sicard et al., 2015) metal pollutants (Wei et al., 2014) and pesticides (Mei et al., 2016) in water. In this study, we report the development of a testing chamber which can be aligned to the camera and flash of a smartphone and its application for quantification of fluoride using a commercially available field test reagent. In addition, the fluoride concentration of a specific sample can be logged along with the location on a publicly accessible map. According to our knowledge, this is the first such report for fluoride analysis. Advantages and drawbacks of the test kits are given in Table 1. Evaluation of different fluoride test kits has been carried out by Shriram Institute for Industrial Research in collaboration with UNICEF (http://www.indiawaterportal.org/sites/indiawaterportal.org/files/Field%20Test%20Kits_2nd%20Feb%2006_PRINT.PDF).

In the designed fluoride assay kit, the smartphone camera is used as colorimeter which is portable, battery powered and widely available in the market. This allows accurate testing to be performed inexpensively on the field. Test chamber and reagent capsule is designed to ensure accurate mixing of sample and reagent while being simple enough to be used by a layman. Android app developed allows much greater accuracy in the measurement of color as compared to visual judgment. Results obtained are comparable with the laboratory based expensive Ion Selective Electrode method and does not need any technical expertise for interpretation of results.

2. Materials and methods

2.1. Reagents

The field fluoride testing kit was purchased from Orbit Technologies Pvt. Ltd. Hyderabad. Each bottle contains 75 ml of zirconium xylenol orange reagent. Fluoride estimation is based on the bleaching of zirconium xylenol orange complex and is developed at Bhabha Atomic Research Centre, India. The kit also provides a color chart of range 0–3 ppm. To perform the test, the user must mix a 4 ml water sample and 1 ml zirconium xylenol orange reagent. The color changes from pink to yellow depends