

## Chapter 3

# Design of smartphone based optical sensor suitable for applications both in visible and near infra-red spectral regime

---

In this chapter, different aspects of photometric instrumentations and their limitations for in-field sensing investigations has been discussed. As an alternative, the usability of the smartphone ALS for development of a photometric sensor suitable for both visible and near infra-red spectral regime has been discussed. The designed optical platform is used to study the hazardous chemicals in water medium such as fluoride, iron and phosphate. Finally, important sensoristic parameters of the proposed sensor have been evaluated and its performance has been compared with that of a standard laboratory spectrophotometer.

---

### 3.1 Introduction

Light-matter interaction occurs in broad wavelength range and the investigation of these interactions defines different domains of spectrophotometry which has led to many chemical and biological sensing applications [1- 3]. In general, the spectrophotometric analysis is carried out by various photometric instruments where the electromagnetic radiation is allowed to interact with the analyte. The interaction of the impinging electromagnetic radiation with the sample can be evaluated from the changes of some optical parameter which is related to the concentration of the analyte present in the sample. Photometric analysis in the visible spectral range is also known as colorimetry. Colorimetric measurement process is based on the estimation of colored compound present in the solution [4]. The availabil-

ity of large number of chemical indicators working as a transducer for detection of various chemical species which cannot be possible previously by conventional optical means makes photometry an important scheme for many industrial and environmental monitoring applications [5]. More specifically, spectrophotometers and colorimeters have been rapidly used for detection of chemical contamination in drinking water resources which have direct impact in human health [6]. Photometric measurements are based on the Beer-Lambert's law of absorption which relates to the absorption of light passing through the sample and the intensity of the transmitted modulated signal varies with the concentration of the analyte in the sample.

### 3.1.1 Beer-Lambert's law of absorption and determination of concentration

The light-matter interaction in absorption spectrophotometry or colorimetry is evaluated in terms of the absorbance ( $A$ ) which is defined by Beer-Lambert's law as [7]:

$$A = \epsilon_{\lambda} \cdot b \cdot c \quad (3.1)$$

where,  $A$  is the absorbance,  $\epsilon_{\lambda}$  is the molar absorption coefficient,  $b$  is the optical pathlength in the absorbing medium, and  $c$  is the concentration concentration of the analyte in the sample.

The absorbance value can be determined experimentally. If a beam of monochromatic radiation with initial power  $P_0$  is allowed to propagate through an absorbing medium then the fraction of radiation transmitted is given by

$$T = \frac{P}{P_0} \quad (3.2)$$

where  $P$  is the power of the transmitted signal through the medium and  $T$  is defined as transmittance. Now, the absorbance ( $A$ ) can be measured from  $T$  as

$$A = -\log T = \log\left(\frac{P_0}{P}\right) \quad (3.3)$$

From equation 3.1 and equation 3.3, it can be concluded that for a fixed path-length and monochromatic radiation, the concentration of analyte in the absorbing medium can be determined from the absorbance value. In the present study, this

specific principle has primarily been followed for development of the smartphone platform photometric sensor.

### **3.1.2 Limitations of conventional photometric instrumentation**

Though photometric tools are ubiquitous for many environmental monitoring application but the massive size, significantly high cost, and need of external computational facility for data processing limits their applicability for in-field sensing applications. Again, the need of scientific expertise to operate such tools and requirement of communication facility to transfer field collected data is further a constraint for such systems for applications such as water quality monitoring. Due to nonavailability of proper monitoring facility, detection and estimation hazardous chemicals in water cannot be performed in many resource poor areas which results the epidemic of different water borne diseases annually [5].

Traditionally, the CMOS image sensor of the smartphone has been utilized to convert the smartphone into field-portable photometric tools [28,35,45]. Though in most of the spectrophotometric or colorimetric devices, the CMOS camera of the phone has been used as a detector, but due to the presence of the infra-red (IR) cutoff filter, the CMOS camera is sensitive only to the visible spectrum in the range between 400 to 700 nm. In many optical based sensing, it requires NIR spectral regime for detection of several important parameters in water. Therefore, the camera of the phone is not suitable for such purpose. The ALS of the phone is sensitive in the spectral range of 350 to 1000 nm. Thus, the use of ALS as a detector offers important advantage over CMOS camera in many sensing applications. In addition, the relatively high dynamic range 0 to 20000 Lux and good degree of resolution (0.01 Lux) offers the applicability of ALS for different sensitive analytical applications. In this chapter, the usability of ALS will be discussed as an alternative detection unit over the smartphone CMOS camera. Sensing modalities for development of the proposed sensor:

1. At first the in-built LED flash of the smartphone will be used as a light source and the wavelength selection for a specific sensing study has been accomplished by using an optical filter in the setup. The usability of the designed

sensor would be demonstrated for detection of fluoride level concentration in drinking water.

2. Since, the in-built LED flash has an emission spectral range in the visible regime only, therefore, to demonstrate the applicability of the ALS in the NIR spectral regime, an external LED has been used as an optical source and by using USB-OTG, the external LED is powered from the phone battery. The designed smartphone sensor will be demonstrated for detection of iron and phosphate concentration in water.

In this chapter, the development of the custom designed smartphone application has been discussed and its usability has been demonstrated in converting the smartphone into a standalone computational platform. The performance of the developed photometric platforms has been compared with a traditional laboratory grade spectrophotometer. Also the device characteristics will be compared with the existing field portable photometers.

### **3.2 Design of a field portable smartphone platform photometric tool for detection of fluoride level concentration in drinking water**

This section demonstrates the development of a low cost, robust, and field portable smartphone platform photometric tool for reliable and accurate estimation of fluoride level concentration in water. The presence of fluoride in drinking water within the controlled level can prevent dental caries which is important for human health [8,9]. Concentration of fluoride above the permissible limit may cause serious health hazard, such as dental fluorosis and skeletal abnormalities or damage [10,11]. The World Health Organization (WHO) has established the permissible limit of fluoride as 1 mg/L in drinking water [12]. The smartphone based photometric sensor has been designed by utilizing the ALS of the smartphone as light signal detector and its in-built LED flash as an optical source. Moreover, a custom designed android application- **FSense** has been developed so that detection, device calibration, data analysis and data transfer are possible within the phone itself. The proposed system is thus suitable for in-field sensing applications which

makes the developed platform as a standalone device. It is envisioned that the proposed platform can promote the de-centralized water quality monitoring capability so that effective fluoride removal program undertaken by governmental and nongovernmental organizations can be initiated on time which is an extreme need for many resource poor areas. The following subsections describes the various steps involved for development of the proposed smartphone photometric tool.

### 3.2.1 Material and methods

The detection scheme is based on the standard SPADNS colorimetric method for fluoride level detection in water in which fluoride reacts with the zirconium dye to form a colorless complex anion ( $ZrF_6^{2-}$ ) and the dye [13]. The fluoride concentration proportionately forms the complex anion in the solution. As the fluoride concentration increases, it tends to bleach the dye to make it progressively lighter in color. The chemicals used for the present experimental work have been procured from the following sources: SPADNS colorimetric reagent, and sodium fluoride (NaF) were procured from SRL, India. Zirconyl chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ) was procured from Sigma-Aldrich. Hydrochloric acid (HCl) was procured from Rankem Chemicals, India. All chemicals used in the present work are of analytical grade and were used as received without further purification. The deionized (DI) water used for preparing the sample solutions was obtained from a Milli-Q water purifying system.

### 3.2.2 Preparation of calibration standard solutions

958 mg of SPADNS has been dissolved in DI water and diluted to 500 mL to prepare the SPADNS solution. Zirconyl acid reagent is prepared by dissolving 133 mg of  $ZrOCl_2 \cdot 8H_2O$  in 25 mL of DI water. 350 mL of HCl is added to the solution, and the final volume was diluted to 500 mL with DI water. Equal volume of SPADNS solution and zirconyl acid have been mixed to produce SPADNSzirconyl acid complex reagent. Standard sodium fluoride solution has been prepared by dissolving 110.5 mg of NaF in DI water, and the final volume is diluted to 500 mL with DI water. The standard sample solution with known fluoride concentration (in the range 0 mg/L to 3.0 mg/L) has been prepared by diluting the specific volume of

the standard sodium fluoride solution with 50 mL of DI water. Figure 3.1 shows the photo image of the prepared samples that contains different concentration of fluoride.

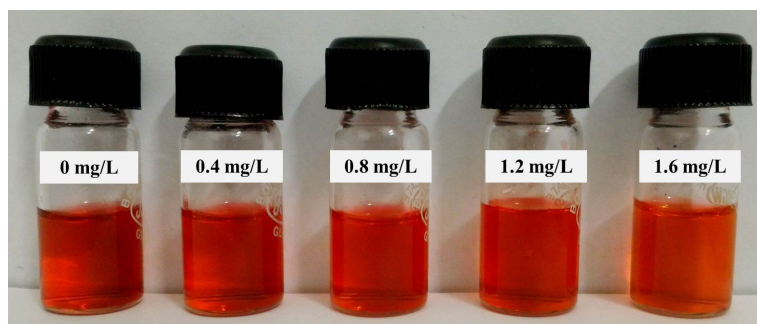


Figure 3.1: Photo image of the prepared samples that contain different concentration of fluoride level.

### 3.2.3 Spectrophotometric analysis of the test solution

To determine the peak absorption wavelength of the prepared samples, spectrophotometric analysis has been carried out with a standard laboratory grade spectrophotometer (UV-3600 Plus UV-Vis-NIR Spectrophotometer, Shimadzu).

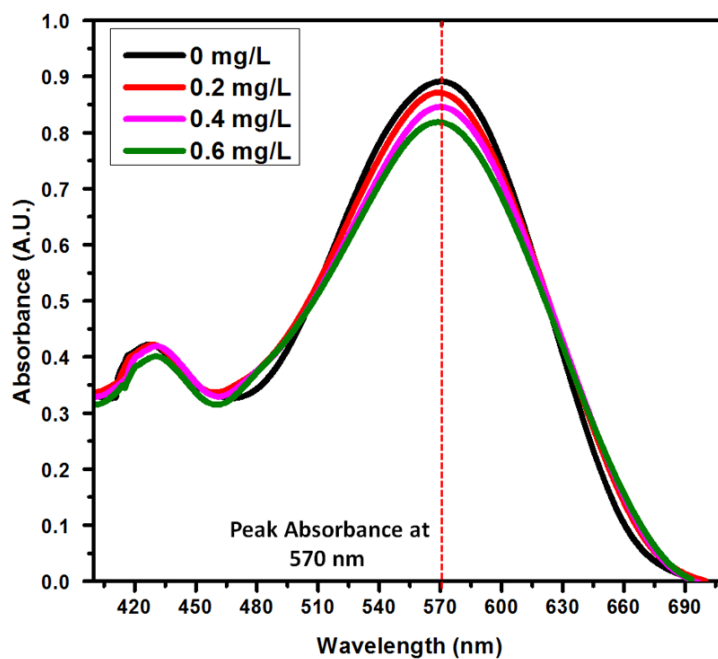


Figure 3.2: Absorption spectrum of zirconium–SPADNS dye mixed with water sample containing fluoride ion at different concentrations.

The peak absorption wavelength condition of SPADNS dye is found to be in the wavelength range of 560 nm to 580 nm. Figure 3.2 shows the characteristics absorption spectra for four different sample solutions. From the absorption spectra, it can be inferred that with the increase of fluoride level concentration there has been a gradual decrement of absorbance values of the transmitted light signal. This variation in modulated light signal intensity can be detected by the ALS of the smartphone. Subsequently, the concentration of fluoride in the medicine can be correlated with the measured signal intensity by the ALS of the phone .

### 3.2.4 Optical layout and device fabrication

The smartphone platform photometric system has been designed to perform as a self contained and standalone device. The readily available in-built optical components of the phone have been utilized for development of the sensor. A Sony Experia E3 smartphone is used to develop the required photometric platform. The flash LED of the smartphone covers a broad emission spectrum from 400 nm to 700 nm.

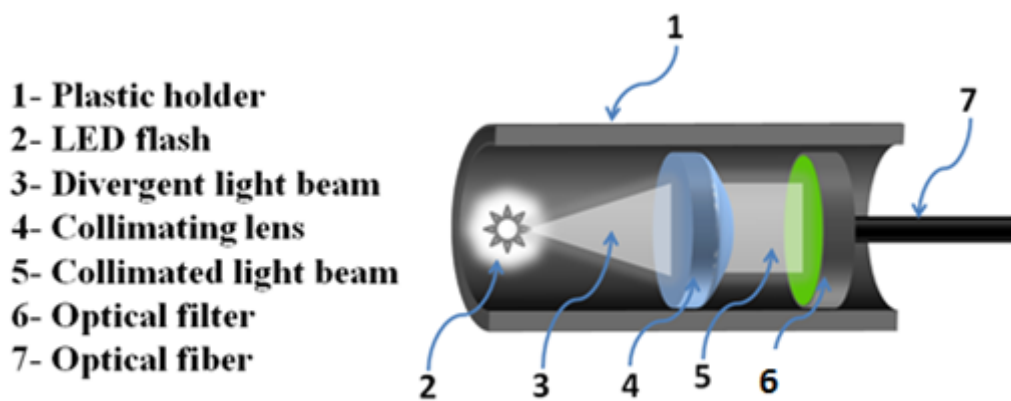


Figure 3.3: schematic view of the optical configuration for wavelength selection from the LED flash of the smartphone.

By using an optical filter, selective wavelength extraction can be possible so that the LED flash can be used as a light source for development of the sensor. In the present sensing design, the wavelength selection has been accomplished through a custom designed optical configuration shown in figure 3.3. A plano-convex lens (7 mm diameter, focal length 11 mm, Edmund Optics 32404) has been used to

collimate the diverging light beam from the LED flash and the collimated light beam is then allowed to pass through a narrow-band optical filter (Product id. 7–0302, Spectrogon) with peak transmission wavelength of 568 nm which matches the peak absorption wavelength of the reagent treated standard samples. As shown in figure 3.3, a multimode optical fiber (980/1000 m and NA = 0.37, Product id. 02534, Edmund optics) is used to collect a fraction of the filtered light beam. The light signal from the output end of the optical fiber is fetched to the light coupling and sample handling mount as shown in figure 3.4. Then the divergent light beam from the output end of the optical filter has been collimated by a collimating lens (7 mm diameter, focal length 11 mm, Edmund Optics 32404) and allowed to propagate through the sample solution as shown in figure 3.4.

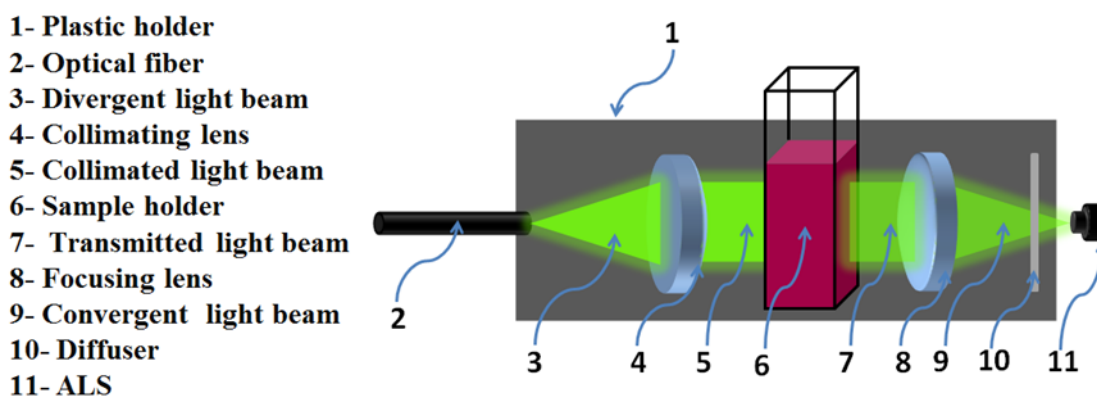


Figure 3.4: schematic view of the compact optical attachment used for light coupling and sample handling.

A quartz cuvette (Product id.21Q-5, 5 mm path length, Spectrosil Quartz) has been used as for sample holder. Due to absorption, intensity modulation takes place in the transmitted light beam that depends on the analyte concentration in the sample. Thus, the measurement of intensity of the transmitted modulated light signal is correlated to the analyte concentration. A Planoconvex lens (7 mm diameter, focal length 11 mm, Edmund Optics 32404) is used to focus the transmitted modulated light beam to the ALS of the smartphone. Figure 3.5 (a) shows the 3D schematic of the developed optical platform. The plastic holder used for optics holding has been fabricated in a computer numerical control (CNC) machine using nylon as a material. It has been observed that, for the designed



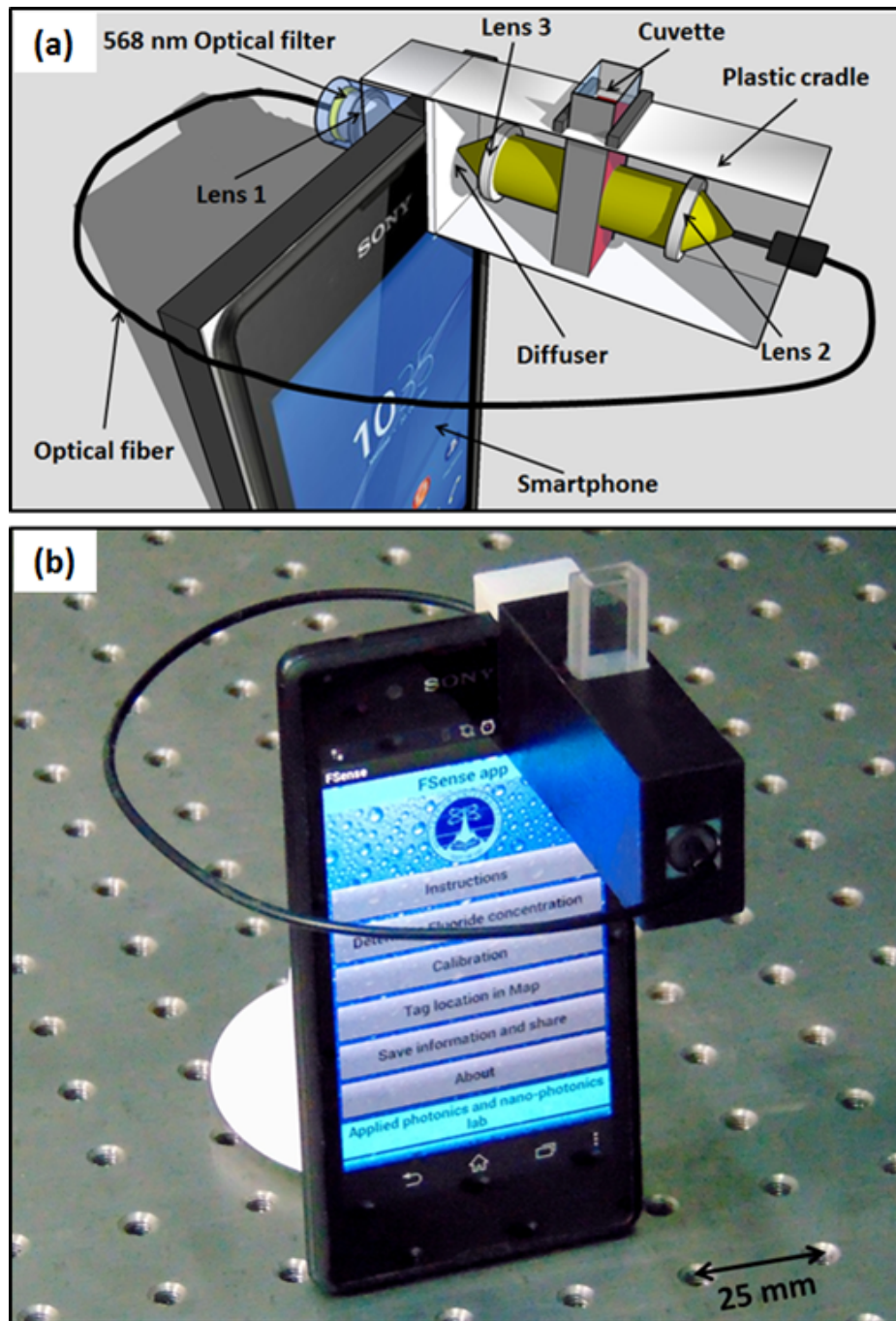


Figure 3.5: (a) Schematic of the smartphone based photometric platform and (b) photograph of the designed platform.

optical platform, when the distance between the ALS and the output end of the optical fiber is 60 mm, then the ALS measures the intensity of the light beam as high as 1150 Lux when the sample holder is filled with DI water. A high intensity value of the light signal may cause unwanted fluctuations in the ALS reading. To mitigate this issue, a thin nylon sheet is used as a diffuser which is placed between

the focusing lens and the ALS of the smartphone to further reduce the intensity of the light beam. It has been observed that, with the incorporation of the diffuser, the intensity of the light beam was decreased by a factor of 0.25. With this low intensity, value the ALS gives desirable stable readings and low measurement error. Figure 3.5 (b) shows the photo image of the designed smartphone photometric system. All optical components have been mounted on a custom developed plastic cradle which can be attached to the smartphone as a plug-and-play device. The inner wall of the plastic cradle is completely blackened and a black cap is used to cover the sample in the cuvette. This would reduce any possible interference due to external radiation in the de- signed optical device. The dimension of the plastic cradle is measured to be 75 mm length, 30 mm breadth, and 20 mm in width, and its weight is approximately 180 g excluding the weight of the smartphone.

### 3.2.5 Development of the **FSense** smartphone application

Along with the designed hardware system for photometric investigations, a smartphone application **FSense** has been developed for simultaneous data recording, processing, and transfer which is a essential for various in-field sensing applications. The application has been developed using MIT app inventor 2-a cloud based software platform for android application development. Detail analysis of the android based application development has already been provided in chapter 2. Figure 3.6 shows the process flow of the application with the required screenshots. Upon clicking the **FSense** application, it will pop-up a new window shown in Figure 3.6 (b) which will contain all the options for the required computation. This window includes the following buttons: ‘Instructions’, ‘Determine Fluoride concentration’, ‘Calibration’, ‘Tag location in Map’, and ‘Save information and share’. As shown in figure 3.6 (c), all necessary informations required to operate the designed sensor has been outlined. This can be accessed by clicking the ‘Instruction’ button. On clicking the ‘Determine Fluoride concentration’ button in the home screen the user can access the window which has been developed for detection as shown in figure 3.6 (d). Upon inserting the sample in the holder and with the LED flash on, the ALS will measure the corresponding modulated light intensity in Lux units. On clicking the ‘Find Fluoride concentration’ tab in this



Figure 3.6: Process flow of the custom designed smartphone application.

window, fluoride level concentration of an unknown sample can be measured by fitting the data in the pre-loaded calibration equation. For the preliminary investigation, the application has been calibrated with standard samples in the range 0 mg/L to 2 mg/L. The application has been incorporated with symbolic indications

as shown in figure 3.6 (d). After estimation of the fluoride content, the application will automatically inform the user symbolically regarding the concentration level of fluoride in the drinking water. In the present study the threshold level has been set as 1 mg/L, which is the permissible limit defined by World Health Organization (WHO). The sensing investigation may be affected due to different ambience parameters which eventually leads to measurement error. For in-field applications, on-site calibration of the device is required. A provision for recalibration of the sensor has been included in the designed application. All the necessary statistical algorithm for calibration such as least square fitting has been incorporated in the application which has been discussed below.

**Implementation of algorithms for regression analysis:** In the present study, linear regression model has been used for implementing device calibration for the custom designed application. The linear regression equation [14]

$$y = a.x + b \quad (3.4)$$

has been used as a calibration model where  $a$  is the slop and  $b$  is the intercept value which can be determined as

$$a = \frac{(\sum y).(\sum x^2) - (\sum x).(\sum xy)}{n(\sum x^2) - (\sum x)^2} \quad (3.5)$$

and

$$b = \frac{n(\sum xy) - (\sum x).(\sum y)}{n(\sum x^2) - (\sum x)^2} \quad (3.6)$$

the application has been configured to determine the correlation coefficient ( $r$ ) of the calibration model which can be define as

$$r = \frac{n(\sum xy) - (\sum x).(\sum y)}{\sqrt{n(\sum x^2) - (\sum x)^2} \cdot \sqrt{n(\sum y^2) - (\sum y)^2}} \quad (3.7)$$

All the parameters have been implemented as block codes in the MIT app inventor interface. Figure 3.7 shows the block codes used for implementing the regression model in **FSense** application. As shown in this figure block 1 is used for implementing equation 3.5, block 2 for equation 3.6 and block 3 for equation 3.7. After determining slop  $a$  and intercept  $b$ , the regression equation can be modeled as shown by block 4 in figure 3.7.

On clicking the ‘Calibration’ button, the application will provide two options as shown in figure 3.6 (e). Upon selecting ‘Yes’ button, the application will pop-up

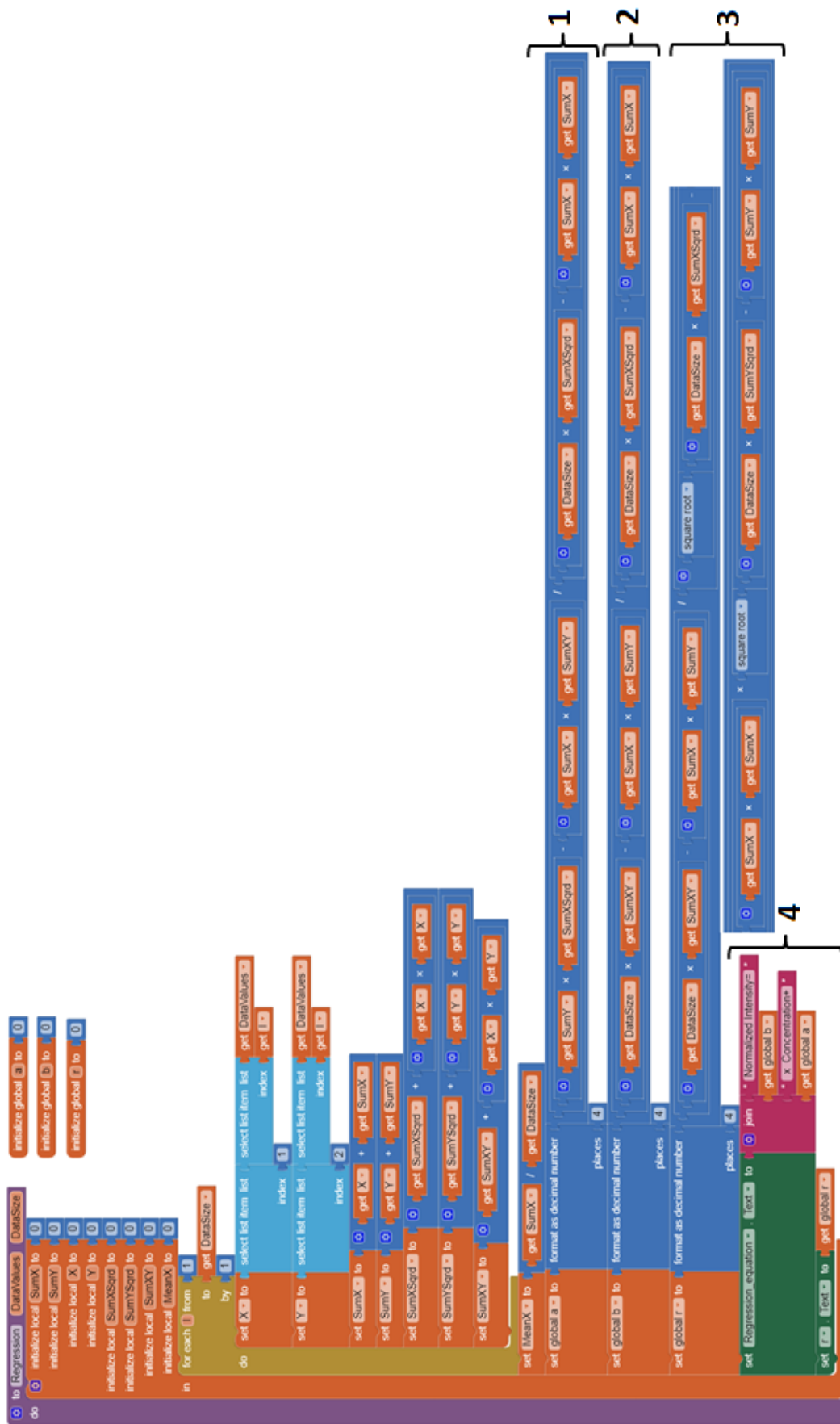


Figure 3.7: Screenshot of the block codes developed with the MIT app inventor interface for implementing regression analysis.

a new window for device calibration as shown in figure 3.6 (f). In this window, the user needs to record the intensity values for the considered standard samples and on clicking the ‘Normalize’ button the recorded data can be normalized. Again on clicking the ‘Plot calibration Curve’ button, the developed application generates a new set of calibration curve as shown in figure 3.6 (g). In-field data sharing and reporting are often required for various field sensing investigations. Therefore, provision for localization of the area where sensing studies have been performed is included using the in- built GPS facility. The real-time reporting is thus possible using the in-built communication facility. By clicking the ‘Tag location in Map’ button, the user can mark the place region in Google map for further use as shown in figure 3.6 (h). On clicking the ‘Save information and share’ button, the application will pop-up a new window, where one can write comments and information about the sensing data which will be stored as a text file in the phone as shown in figure 3.6 (i) and figure 3.6 (j). Using the communication facility, in-field sensing data can be shared in a social network platform or by individual mailing. When the ‘Share’ button is clicked, it will show all the communication applications present in the phone. Here, the Gmail application from Google has been utilized as a communication platform as shown in figure 3.6 (k).

### 3.2.6 Device calibration

After setting up the instrumental parameters of the developed photometric platform, the device has been calibrated to estimate the fluoride level concentration in unknown water sample. The designed sensor has been calibrated with the prepared standard samples in the range 0 mg/L to 3 mg/L with step incremental value of 0.2 mg/L. The standard samples have been inserted in the holder and corresponding ALS response has been recorded. Figure 3.8 (a) shows the characteristic response curve of the considered sample solutions. It has been observed that the response of the designed platform is linear when the fluoride concentration in the sample varies in the range 0 mg/L to 2.6 mg/L and becomes nonlinear beyond this level. A calibration curve has been obtained through the **FSense** application and stored in the application database for further use. Figure 3.8 (b) shows the calibration curve for standard solutions in the range 0 mg/L to 2.0 mg/L. The

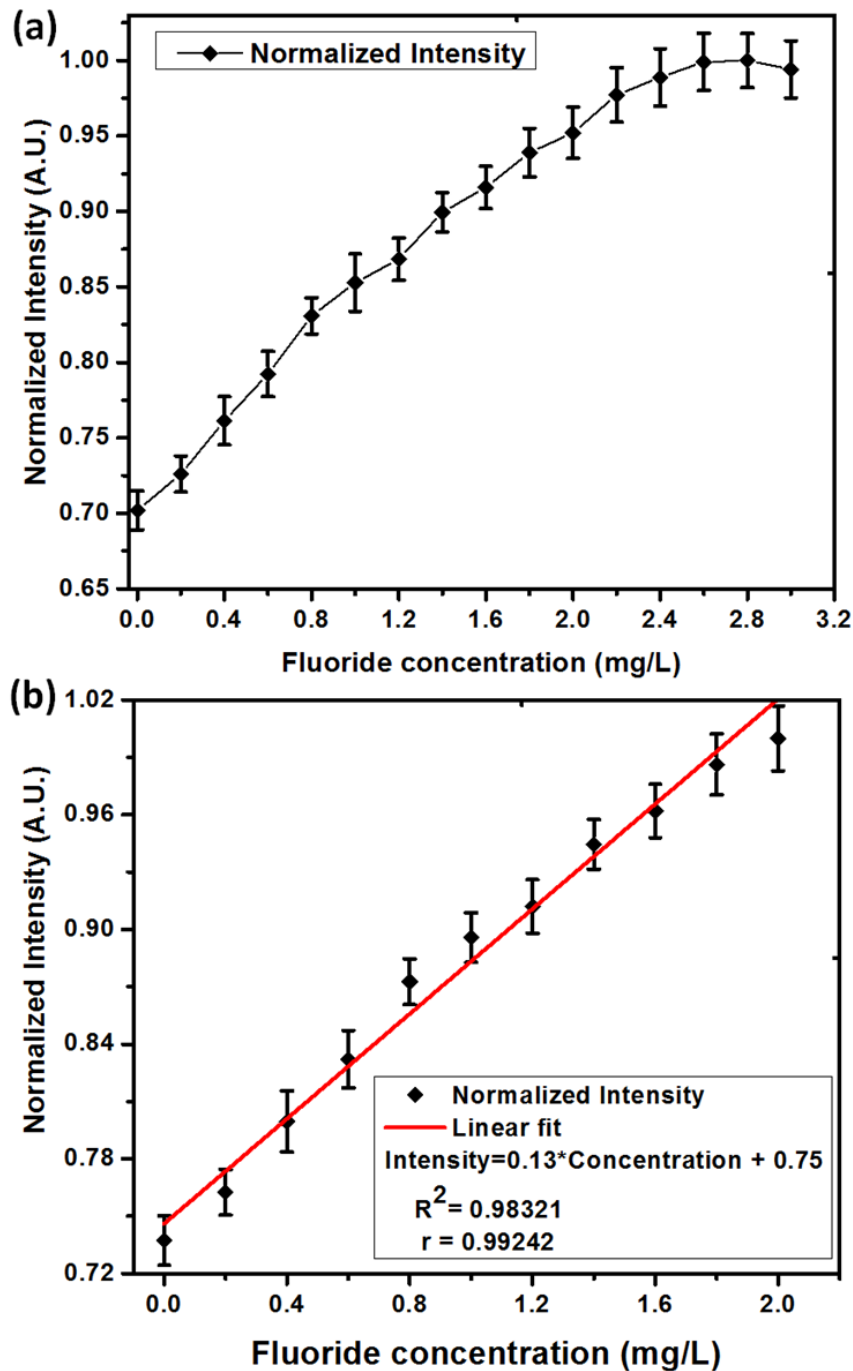


Figure 3.8: Response characteristics of the designed smartphone based photometric platform. (a) response curve for the range 0 mg/L to 3 mg/L and (b) Calibration curve prepared for 0 mg/L to 2 mg/L.

error bars signify the standard deviations yielded for five consecutive measurements of each sample recorded by the smartphone photometric system. The value of the correlation coefficient  $r = 0.992$  and coefficient of determination  $R^2 = 0.983$  signifies a good degree of linearity linearity of the detection schemes in measuring

of fluoride level concentration in water. From the regression analysis, the following equation has been modeled, which can be used to estimate the concentration from unknown sample:

$$\text{Unknown fluoride concentration} = \frac{\text{Normalized Intensity} - 0.75}{0.13} \quad (3.8)$$

The above equation has been used within the **FSense** application to determine the fluoride level concentration in unknown water sample. Estimation of fluoride concentration above the calibration range can be done through successive dilution with distilled water.

### 3.2.7 Evaluation of different sensoristic parameters of the designed smartphone based photometric sensor

All important sensoristic parameters of the designed sensor have been evaluated and discussed as follows:

**Sensitivity** of an instrument is defined as the change of its characteristic response per unit change of input stimulus. The sensitivity of the designed photometric platform has been estimated by measuring the response characteristic of standard sample solutions that contain fluoride concentrations of 0 mg/L, 0.02 mg/L, 0.04 mg/L, 0.06 mg/L, 0.08 mg/L, and 0.10 mg/L and the corresponding response characteristic is shown in figure 3.9. The correlation coefficient for the considered investigations is observed to be  $r = 0.994$  and coefficient of determination as  $R^2 = 0.983$  respectively. The error bars in figure 3.9 indicate the standard deviations obtained for ten consecutive measurements for each sample solution. Considering the linearity in sensor response, the sensitivity can be determined using the following equation [15] :

$$\text{Sensitivity}(s) = \frac{\Delta S}{\Delta C_F} \quad (3.9)$$

where,  $\Delta S$  is the change in sensor response and  $\Delta C_F$  is the change in concentration of the standard fluoride solutions. The sensitivity for the designed sensor is found to be  $0.86 \text{ A.U./mgL}^{-1}$ .

**Resolution** of an instrument indicates the smallest magnitude of input stimulus required to produce an observable change in its response. The resolution of the



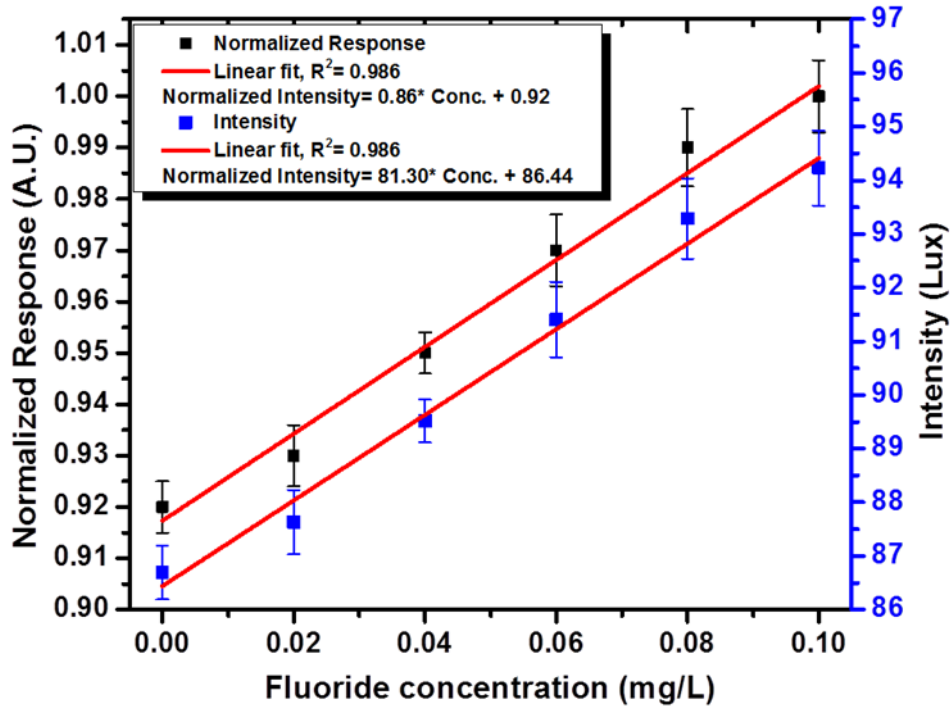


Figure 3.9: Response characteristic of the designed photometric platform for standard samples with a lower level of fluoride concentrations in the range 0 mg/L to 0.1 mg/L.

designed smartphone based photometric platform depends on the resolution ( $R$ ) of the embedded ALS which is given by 0.01 Lux. The resolution of the proposed sensor can be estimated as [15] follows:

$$Resolution(R) = \left(\frac{1}{S}\right)R_{ALS} \quad (3.10)$$

where,  $R_{ALS}$  is the resolution of the ALS and  $S$  is the sensitivity of the designed platform. Using this equation, the resolution of the sensor is estimated to be  $1.23 \times 10^{-4}$  mg/L.

**Limit of detection (LoD)** is defined as the lowest amount of analyte present in a sample, which can be detected but not necessarily quantitated under stated experimental conditions. The ICH guidelines has been used to estimate the LoD, according to which the LoD in an analytical measurement is given by [16]

$$LoD = \frac{3.3\sigma}{S} \quad (3.11)$$

where,  $\sigma$  is the standard deviation of y-intercepts and  $S$  is the slope of the response characteristic of the designed photometric platform in the low concentration range

as shown in Figure 3.9. Using equation 3.11, the LoD of the designed photometric platform is found to be 0.0256 mg/L.

**Accuracy** is defined as the closeness of agreement between a test result and the accepted reference or true value of the property being measured. Accuracy can be estimated in terms of %bias which is given by [17]

$$\%Bias = \left( \frac{Knownconc. - Meanconc.}{Knownconc.} \right) \times 100 \quad (3.12)$$

**Precision** expresses the closeness of agreement or degree of scatter between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions. Precision may be considered at three levels: repeatability, intermediate precision and reproducibility. For the present work, the precision has been evaluated in terms of repeatability which expresses the precision under the same operating conditions over a short interval of time. It can be evaluated in terms of % residual standard deviation (%RSD) and is given by [17]

$$\%RSD = \left( \frac{SD}{Mean} \right) \times 100 \quad (3.13)$$

To evaluate the accuracy and precision (repeatability) of the designed photometric platform, five standard samples are prepared with concentrations 0.2 mg/L, 0.4 mg/L, 0.8 mg/L, 1 mg/L, and 1.4 mg/L. The considered samples cover the low, medium and high concentration values within the calibration range. The concentration of the sample solutions have been measured by the proposed tool within the same day. Each solution has been measured for 5 times and the mean

Table 3.1: Accuracy and precision data for concentrations of standard fluoride solutions(n = 5)

Standard concentration (mg/L)	Mean	SD	Accuracy (% Bias)	Precision(%RSD)
0.2	0.2	0.02	0.00	10.00
0.4	0.41	0.03	2.50	7.32
0.8	0.8	0.04	0.00	5.00
1	0.99	0.03	1.00	3.03
1.4	1.43	0.05	2.14	3.50
			Mean % Bias =	1.13%
			Mean % RSD =	5.77%

concentration and corresponding standard deviation (SD) have been determined. Table 3.1 summarizes the accuracy and precision data of the designed photometric platform for the considered samples. The mean bias of accuracy is found to be 1.17% while mean RSD in precision for the analyte has found to be 5.77%. The lower value of % RSD signifies greater precision of the designed tool.

### 3.2.8 Comparison of the designed smartphone based photometric platform with a laboratory grade spectrophotometer

The performance of the developed smartphone photometric platform as an alternative over its sophisticated commercial counterparts has been evaluated by comparing the results with a laboratory grade spectrophotometer. In general, fluoride contamination is found in ground water resources in Assam due to its natural abundance in many regions. Therefore, ground water samples from

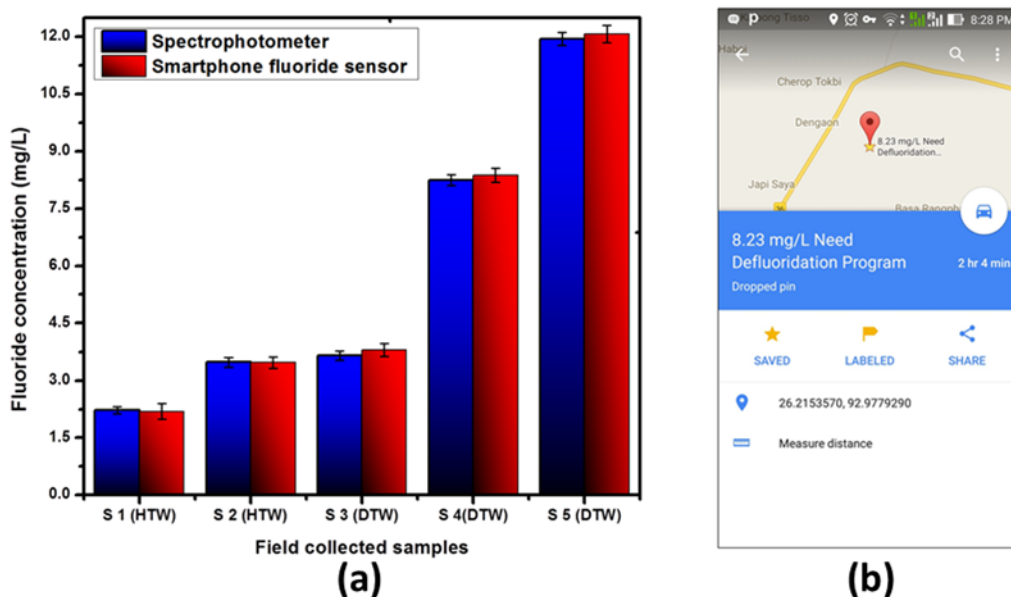


Figure 3.10: Fluoride concentration measurement for field collected water samples. (a) Histogram representation of the fluoride concentration estimation by a commercial spectrophotometer and by the designed sensor. (b) A screenshot image of one of the considered areas (Hamren, Karbianglong) shown in a Google maps application, Google Inc. (used with permission), to demonstrate the in-field data sharing ability of the designed sensor.

five different fluoride affected locations of Assam, namely Sixmile (Guwahati) (S 1), Kacharigaon (Nagaon) (S 2), Birkuchi (Guwahati) (S 3), Hamren (Karbi-anglong) (S 4), and Ramsapathar (Karbi-anglong) (S 5) have been collected from both hand tube well (HTW) and deep tube well (DTW) for analysis. Since, turbidity can affect the photometric measurements, the field collected samples are initially filtered to remove particulate residue. After proper sample treatment, Zirconium-SPADNS reagent is added to the water samples and the characteristic photometric response has been measured by both with the laboratory grade spectrophotometer (Systronics Visible spectro 104; Systronics India) and the designed smartphone based photometric tool. A histogram representation of the fluoride concentration measurement by both standard spectrophotometer and the smartphone based photometer is shown in figure 3.10 (a). The error bars represent the standard deviations for five consecutive measurements of each sample recorded by the two devices. A screenshot of Google map application is shown in Figure 3.10 (b) to indicate the location from where the water samples have been collected. The developed **FSense** application can be used to tag the location of the fluoride affected region which can be shared directly to a distant central water quality monitoring laboratory to initiate effective removal programme on time.

### **3.2.9 Sensor performance evaluation of the proposed tool with different smartphones**

The ALS is found in all modern smartphones. The performance of the designed photometric platform has been investigated for two other smartphones: Asus Zenfone 2 (android OS version 4.4.2) and Moto G xt1033 (android OS version 5.0.2). Using double sided tape, the plastic cradles containing the optical components and the light coupler have been attached to these and the corresponding responses for standard sample solutions have been measured. Figure 3.11 shows the corresponding response characteristics of the designed photometric platform for these two smartphones. Asus Zenfone 2 contains a cm36282 light sensor from capella microsystems, which has a dynamic range of 0-10240 Lux, and Moto G xt1033 contains a CT406 light sensor from TAOS and has a dynamic range of 0-27000 Lux [18]. It has been observed from figure 3.11 that the response is fairly linear for

both the smartphones while estimating the fluoride level concentration in water samples. Thus, it can be concluded that the proposed photometric platform is compatible with any other variant smartphone for such studies.

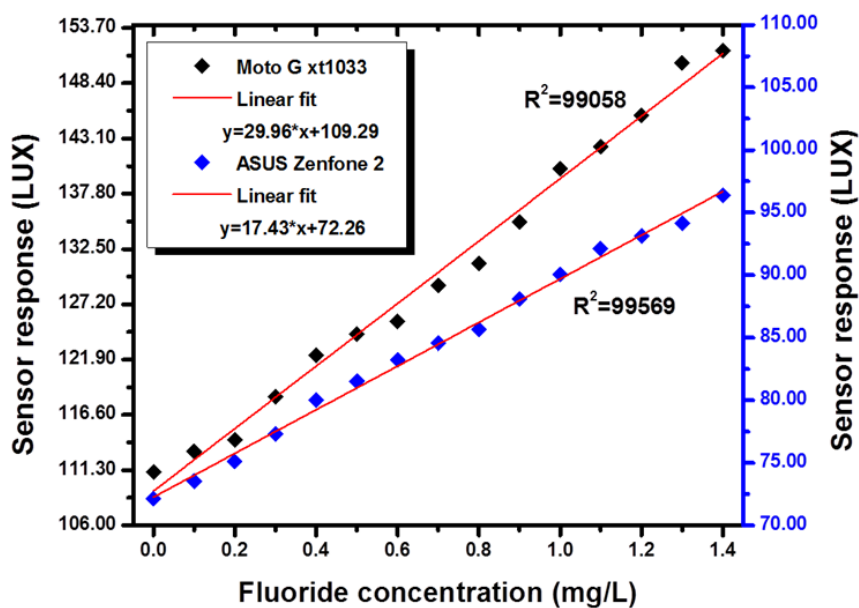


Figure 3.11: Response characteristics of the designed photometric platform for two different smartphones.

### 3.2.10 Comparison of the proposed smartphone photometric platform with the existing portable spectrometers

Many sophisticated analytical tools such as ion selective electrodes (ISE) and portable spectrophotometers are commercially available for similar applications. ISE is target specific, for example, to determine other contaminants, such as nitrate, chloride, and pH, specific electrode will be required, which is a costly process for resource poor regions. Portable spectrophotometers such as DR 1900 from Hach and i-LAB from MicrOptix are being extensively used for in-field studies. The designed smartphone based photometric system however offers several important advantages over its commercial counterparts in terms of size, weight, cost, ability to do data transfer, and storing of in-field sensing data for further use. Moreover, the easy to use graphical interface and visual indications make the device easy to operate by any individual. Table 3.2 summarizes the performance

comparison of the designed system with two commercially available and widely used portable spectrophotometers used for similar purposes.

Table 3.2: Comparison of the smartphone based photometric platform with the existing portable spectrophotometers

Figure of merits	DR 1900 spectrophotometer from Hach	i-LAB spectrophotometer from MicroOptix	Designed smartphone based photometer	Remarks
Size (Height × Breadth × Width)	267 mm × 98 mm × 178 mm	127 mm × 69.85 mm × 44.45 mm	75 mm × 30 mm × 20 mm (With-out the smartphone)	Excluding the smartphone size; the size of the plastic attachment is relatively small
Weight	1.5 kg	0.2 Kg	0.25 kg (Including the smartphone)	The weight of the plastic cradle is 0.15 kg which is negligible if we exclude the weight of the phone
Optical source	Xenon lamp	LED array	LED flash of the phone	Use of LED flash of the phone makes the device cost-effective
Power supply	4 AA batteries	3 AA Batteries	Smartphone battery	Use of smartphone battery makes the device self-powered
Data Storage	500 measured values	100 measured values	Unlimited	Gigabyte storage of phone memory provides unlimited data storage
Real time data transfer	Not applicable	Not applicable	Yes	In-built mobile network facility makes it possible to real time and in-field data transfer to anywhere in the world
Cost	\$3,160.00	\$1,410.25	\$ 206.23	If we consider disposable plastic cuvettes (price \$ 0.15) then the price will be around \$ 94.23 which becomes cost effective and is suitable for resource poor regions

### **3.3 Extending the applicability of the smartphone photometer to visible and NIR spectral regime**

In the previous section, the usability of the smartphone has been demonstrated as a low cost and field portable photometric tool where the in-built LED flash of the smartphone has been used as an optical source. The developed platform has been utilized to determine fluoride level concentration in water samples. The optical filter used in the demonstrated work has been chosen so that it matches the peak absorption wavelength of the analyte to be quantified. Different photometry based analytical methods may require different absorption wavelength which will eventually require specific optical filters. The use of filters in the proposed tool would significantly increase the overall fabrication cost. For instance, in the previous demonstration the overall fabrication cost of the device is \$94.23 where the optical filter cost was \$38.23. The primary motive of this thesis work is to find technological solutions which is meant to be used for resource poor region. Therefore, further investigations would be required to achieve the desired goals. The LED flash has an emission wavelength within the visible region, therefore, it is not possible to use the same for analytical investigations where UV or IR source is required. Due to the rapid advancement in the semiconductor technology, now a days, LEDs of any specific peak wavelength are available at significantly low cost (\$1). The micro USB port of the smartphone has been used to connect peripheral devices such as external data cards. The same micro USB port can be used as a host device with the help of newly developed USB-OTG technology. The same can be used to power an external LED from the battery of the phone [19]. This section will demonstrate the development of an optimized version of the already developed smartphone based photometric platform in terms of cost effectiveness, usability and better data processing algorithms.

Herein, an external LEDs has been used as optical sources which is powered by the smartphone battery. The external LED can be powered through the micro USB port of the phone. Previously, no statistical algorithm has been introduced in the smartphone application so as to reduce the measurement error. In the present work, proper data averaging algorithm has been implemented to reduce the measurement error. Also, in the present work, the android application has

been configured to determine the exact absorbance value. The usability of the photometer has been demonstrated to measure different analyte which are sensitive in visible and NIR regime. The usability of the designed photometric platform has been realized for quantification of total iron and phosphate concentrations in water samples. The performance of the designed platform has been evaluated with of a commercially available laboratory grade spectrophotometer. The details about the methodologies used in developing the photometric system has been described in the following subsections.

### 3.3.1 Material and methods

**Synthesis of standard iron (II) sample solutions:** The standard phenanthroline colorimetric method is used for detection and estimation of total iron concentration in water samples [20]. In this method, iron present in water sample in ferric state is first reduced to ferrous state and then the sample is treated with 1, 10-phenanthroline reagent to develop an orange-red complex in water sample. With the increase in iron concentration, the color of the solution gradually changes from light to dark orange which results in increasing of absorbance value of the transmitted light signal through the sample solutions. Therefore, by measuring the absorbance value, the concentration of total iron present in the water medium can be estimated. The chemicals used for the present experimental work are obtained from the following sources: concentrated hydrochloric acid (HCl) (37.2 w/w %), ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ), 1, 10 phenanthroline monohydrate ( $\text{C}_{12}\text{H}_8\text{N}_2\cdot\text{H}_2\text{O}$ ) and glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) (99.8 w/w %), have been procured from SRL, India. hydroxylamine ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) and ferrous ammonium sulphate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ ) have been procured from Qualigens Fine Chemicals, Mumbai, India. The de-ionized (DI) water used for preparing of the sample solutions was obtained from a Milli-Q water purifying system.

Following standard synthesis protocol [20], iron (II) samples are initially prepared in the laboratory. The details about the reagent preparation process are given below:

1. **Ammonium acetate buffer:** Dissolve 125 g  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in 75 mL in distilled water and add 350 mL  $\text{CH}_3\text{COOH}$ .



2. **Phenanthroline solution:** Dissolve 100 mg  $C_{12}H_8N_2 \cdot H_2O$  in 100 mL distilled water and then add 2 drops of conc. HCl.
3. **Stock iron Solution:** Add 10 mL conc. HCl to 25 mL of distilled water and dissolve 0.702 g of  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ . Dilute the final volume to 500 mL. Now, 1 mL of stock iron solution would obtain 200  $\mu g$  Fe.

The reagents, and the stock iron solution are mixed in a certain ratio to prepare the standard iron(II) solutions. 23 standard iron(II) solutions were mixed in a certain ratio to prepare different sample solutions: 0.01 mg/L to 0.09 mg/L in steps of 0.01 mg/L, 0.1 mg/L to 0.9 mg/L in steps of 0.1 mg/L, and 1 mg/L to 5 mg/L in steps of 1 mg/L. Figure 3.12 shows the photo image of four such prepared iron(II) sample solutions. The figure clearly indicates the variation of color with the increase in iron concentration in the sample.

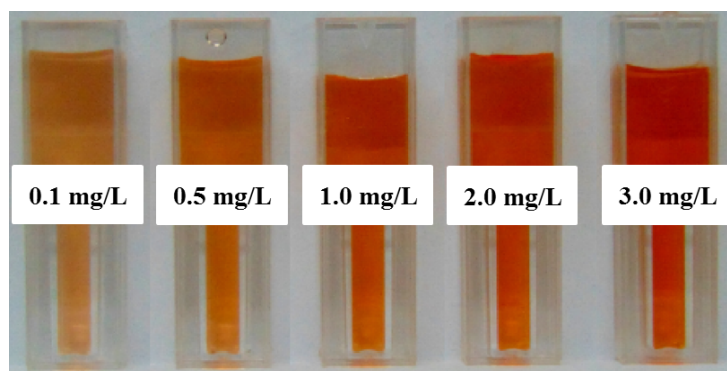


Figure 3.12: Photo image of the prepared iron(II) standard solutions.

**Synthesis of standard phosphate sample solutions:** The standard ascorbic acid method has been used for detection and estimation of phosphate concentration in water samples [21]. In this method ammonium molybdate and potassium antimonyl tartrate react in acidic medium with orthophosphate to form a heteropoly acidphosphomolybdic acid which is reduced to molybdenum blue upon treatment ascorbic acid. With increase in the concentration of phosphate, the color of the solution increases gradually from lighter to darker blue. By measuring the absorbance value at its peak absorption condition of the sample, the concentration of phosphate in the water samples can be estimated. The chemicals used for this analytical method has been procured from the following sources: concentrated sul-

furic acid ( $\text{H}_2\text{SO}_4$ ), anhydrous mono-potassium phosphate ( $\text{KH}_2\text{PO}_4$ ), and potassium antimonyl tartrate ( $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2\cdot 3\text{H}_2\text{O}$ ) are procured from SRL, India and ammonium molybdate ( $((\text{NH}_4)_6)\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) and ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ) are procured from Qualigens Fine Chemicals, Mumbai, India.

Standard solutions of phosphate has been prepared by following the standard protocol [21]. Steps involved for the preparation of the sample process are given below:

1. **5N sulfuric acid solution:** Dissolve 70 ml of conc.  $\text{H}_2\text{SO}_4$  with 500 mL with distilled water.
2. **Potassium antimonyl tartrate solution:** Dissolve 0.685 g of  $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2\cdot 3\text{H}_2\text{O}$  to 50 mL distilled water.
3. **Ammonium molybdate solution:** Dissolve 2 g of  $((\text{NH}_4)_6)\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  to 50 mL of distilled water.
4. **Ascorbic acid (0.1M):** Dissolve 1.76 g of  $\text{C}_6\text{H}_8\text{O}_6$  to 100 mL distilled water.
5. **Combined reagent:** 100 mL of combined reagent has been prepared by mixing the above reagents in the following proportions: 50 mL  $5\text{NH}_2\text{SO}_4$ , 5 mL  $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2\cdot 3\text{H}_2\text{O}$ , 15 mL  $((\text{NH}_4)_6)\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , and 30 mL  $\text{C}_6\text{H}_8\text{O}_6$ . All the solution are mixed in the given order at normal room temperature condition.
6. **Stock phosphate solution:** 219.5 mg of anhydrous mono-potassium phosphate is dissolved in 1000 mL where 1 mL of stock phosphate solution gives  $50\mu\text{g PO}_4^3$ .

The final combined reagent solution and the stock phosphate solution are mixed in a specific proportion to prepare the standard phosphates solutions. 23 standard phosphate samples are prepared in the concentration range similar to that of iron(II) solution. Figure 3.13 shows the photo image of some of the prepared standard sample solutions. The figure clearly indicates the variation of color with the increase of phosphate concentration in the samples.

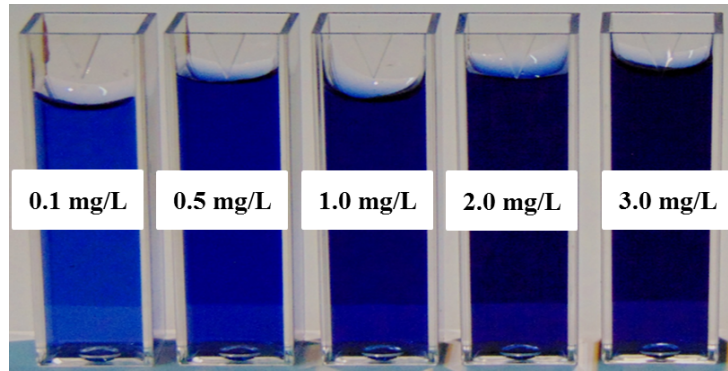


Figure 3.13: Photo image of the prepared phosphate standard solutions.

### 3.3.2 Spectrophotometric analysis of the standard iron(II) and phosphate solution

The peak absorption wavelength condition of both standard iron(II) and phosphate samples have been determined with a standard laboratory grade spectrophotometer (UV-3600 Plus UV-Vis-NIR Spectrophotometer, Shimadzu). The characteristics absorption spectra of some of the prepared samples are shown in figure 3.14 (a) and (b).

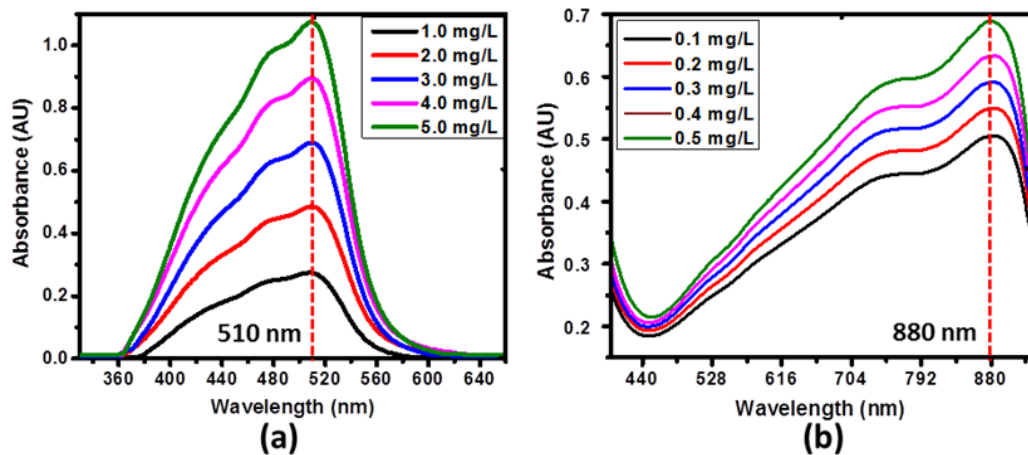


Figure 3.14: (a) Absorption spectra of the reagent treated standard iron(II) and (b) phosphate solutions.

The peak absorption wavelength conditions for standard iron(II) and phosphate sample are found to be 510 nm and 880 nm respectively. For designing of the photometric platform, the emission wavelength of the LEDs have been chosen

such that its the peak emission wavelength matches with the peak absorption wavelength conditions of analyte in the sample.

### 3.3.3 Optical layout and device fabrication

The optical layout of the current photometric platform is similar to that of the already developed platform where LED flash has been used as a light source. In the present study, the optical source (LED flash, optical filter, lens and optical fiber configuration) has been replaced by low cost external LEDs which has been powered by the smartphone battery. Figure 3.15 shows the schematic diagram and photograph of the designed smartphone based photometric platform. Based on the spectrophotometric analysis, two separate LEDs having peak emission wavelength 510 nm (Product no. MCDL-5013BGC-TL, Jameco Electronics) and 880 nm (Product no. SFH485, Osram Opto) have been used as light sources for estimation of iron(II) and phosphate condition in water samples respectively. An USB- OTG cable has been used to power the LED through the internal battery of the smartphone. The output current rating of the smartphone USB port at 5V is 500 mA, therefore a 250 resistor has been used to limit the current passing though the LED. In developing the present photometric platform, the optical fiber mount which has been used previously in the plastic holder was removed and the external LED has been placed at the focus of the collimating lens. Same plastic holder, optical layout and optical components have been used for light beam collimation and focusing of the transmitted modulated light beam to the ALS shown in figure 3.4. The intensity of the transmitted beam varies with the analyte concentration and this variation occurs in accordance with Beer-Lambert law of absorption. In the present optical platform, Sony Xperia E3 smartphone (Android 4.4.3 lollipop) has been used. As described in the previous section, same diffuser has been used to reduce the fluctuation in the signal readings received by the ALS. Besides the hardware design, effort has been made to reduce the measurement error computationally by implementing proper algorithms in the newly developed PhotoSense smartphone application. While describing the present photometric platform, the sampling time of the ALS has been set at 1 second and intensity data for a sample has been recorded for 20 seconds. Finally, the average of the 20 acquired signal

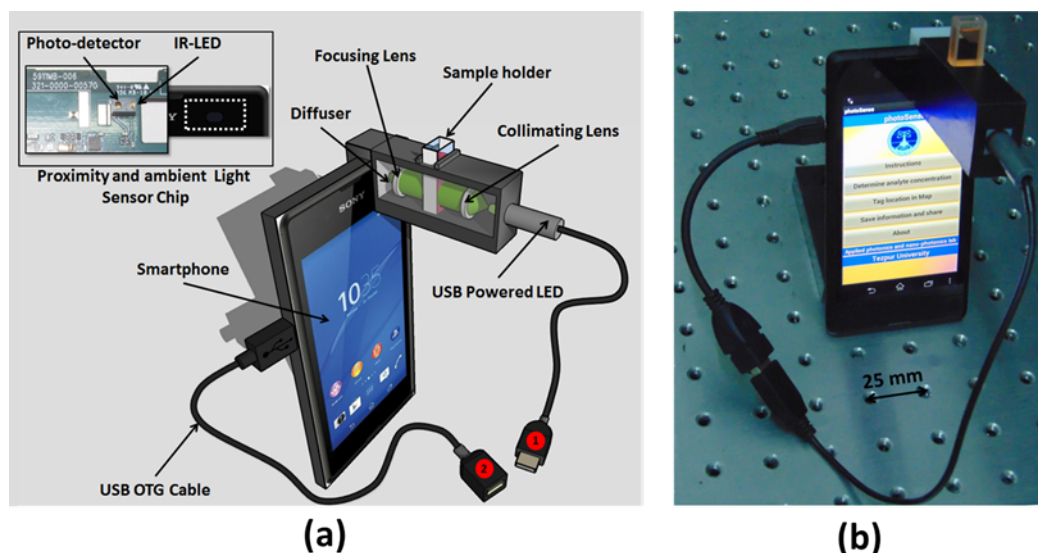


Figure 3.15: (a) Schematic of the smartphone based photometric platform and (b) photograph of the designed platform.

readings have been used to determine the required analyte concentration. This process will significantly reduce the random error that may occur in any experimental investigation. In the present case, the developed application has been configured to compute directly the absorbance value, and subsequently has been used to estimate the analyte concentration of unknown samples by using an internally developed calibration curve. The details about the development of PhotoSense application has been discussed in the next subsection.

### 3.3.4 Development of PhotoSense smartphone application

The **PhotoSense** application developed for the current work is a modified version of the already developed **FSense** application already discussed in section 3.2.5. Figure 3.16 shows the process flow of the custom designed application with the screenshot image of each window. On running the application, it will provide the same sets of options which has been used in the **FSense** application. The algorithms used previously for device calibration, data sharing, reporting and tagging locations in the Google maps have been reused for development of the **PhotoSense** application without any modification. Therefore, in this section, we will discuss mainly about the optimization that has been done to enhance the device performance. On clicking the ‘Determine analyte concentration’ button, it

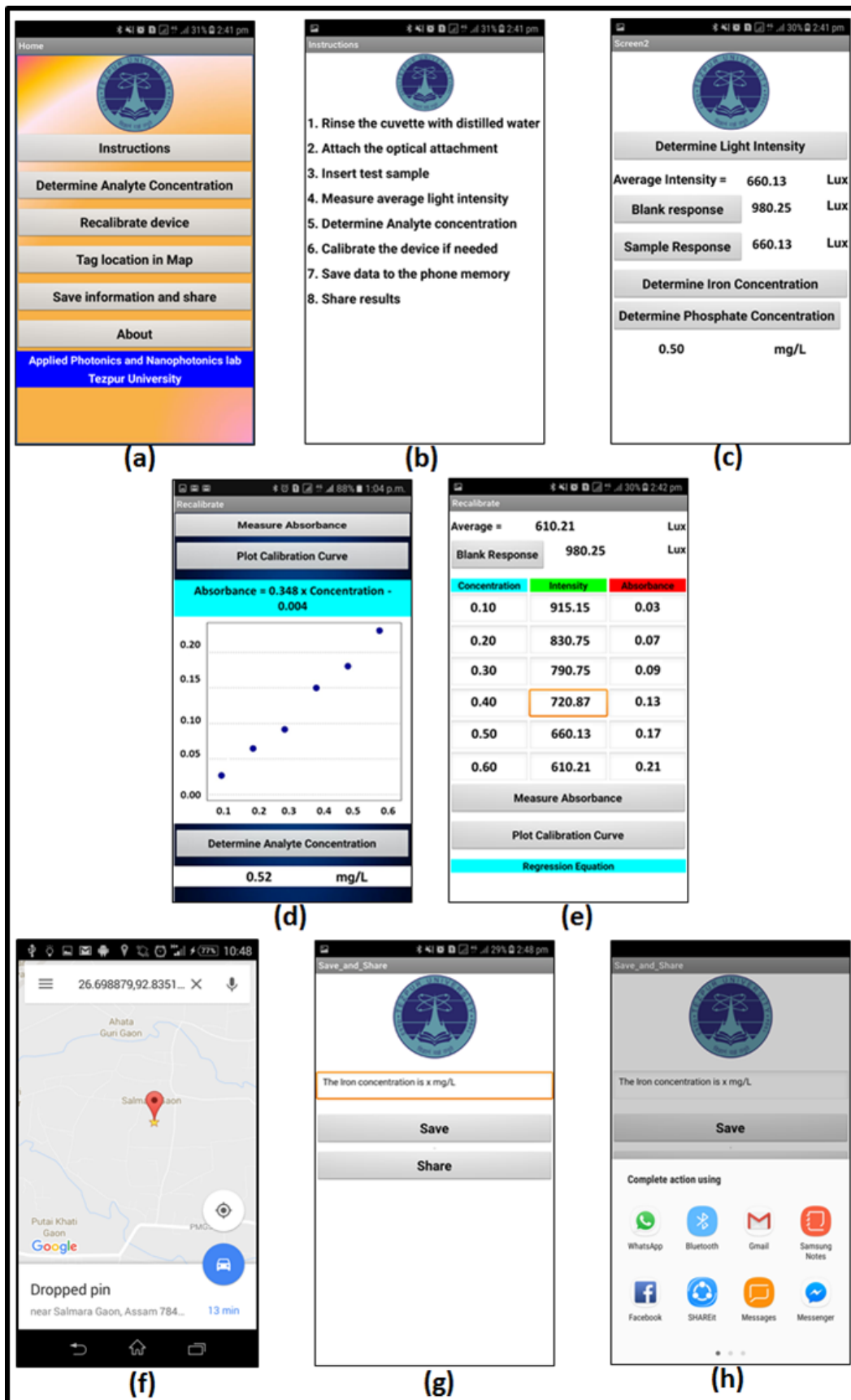


Figure 3.16: Workflow of the designed **PhotoSense** smartphone application.

will pop-up the main detection window shown in figure 3.16 (c). In this window, on clicking the ‘Determine Light Intensity’ tab, the application will record the intensity data detected by the ALS for 20 seconds with a sampling time of 1 second and compute the average intensity value. This step will reduce the measurement error which may occur due to intensity fluctuations of the optical source. Moreover, in the present application, an algorithm has been used to determine the absorbance value which can be used to estimate the analyte concentration directly from Beer-Lamberts equation. Detail about implementation of the algorithms for data averaging and determination of absorbance value is discussed as follows.

**Implementation of data averaging algorithm:** Figure 3.17 shows the block codes developed in MIT app inventor interface for implementing data averaging algorithm. The first three blocks has been used to create three variables ‘counter’ for data sampling, ‘listData’ to store the detected intensity values and a variable

```

initialize global counter to 0
initialize global listData to create empty list
initialize global sum to 0

when Determine_Light_Intensity .Click
do
  set global counter to 0
  set global sum to 0
  set global listData to create empty list
  set Average_Intensity .Text to ""
  set Clock1 .TimerEnabled to true

when Clock1 .Timer
do
  if get global counter ≤ 20
  then
    set global counter to get global counter + 1
    initialize local illumiance to round Light1 .Illuminance
    in add items to list list get global listData
    item get illumiance
    set global sum to get global sum + get illumiance
    set Intensity_data .Text to replace all text list to csv row list get global listData
    segment ""
    replacement ""
  else
    set Clock1 .TimerEnabled to false
    set Average_Intensity .Text to join "average="
    get global sum / get global counter
  
```

Figure 3.17: Screenshot of Block codes developed with the MIT app inventor interface for averaging intensity data for 20 seconds.

‘sum’ to compute the summation of the stored intensity data. The fourth block is used for user interaction; when the user clicks the ‘Determine Light Intensity’ button, it will set the three variable to zero and enable a clock. The clock used here as a timer which starts from zero and forwarded with an increment of 1 second. After starting the timer as shown in fifth block, the ‘listData’ variable stores the illuminance (Intensity value) measured by the ALS for each count till the timer goes to 20 seconds or the counter counts 20 events. Then the ‘sum’ variable stores a value which is the summation of the 20 intensity values stored in the list. After the clock stops at 20 seconds, the application will automatically determine the average value by dividing the summation of 20 intensity values stored in the ‘sum’ variable by the total counts (20) stored in the ‘counter’ variable which is shown in the last two lines of the fifth block code. The calculated average intensity value for a particular sample is stored in the application which can be used for further use as shown in figure 3.16 (c). The implementation of data averaging algorithm in this **PhotoSense** application significantly enhance the device performance in terms of its reduced error compared to the previously developed **FSense** application.

**Determination of analyte concentration from absorbance value:** After configuring the application for determination of average intensity value, the next task is to determine the absorbance ( $A$ ) for for a particular sample. The absorbance value and correspondingly the analyte concentration can be determined in the following steps:

1. Insert the reagent blank used for the particular method and click the ‘Determine Light Intensity’ button. This will determine the average intensity value for the reagent blank. Now, the user needs to click the ‘Blank response’ button to record the average value for further use which is shown in figure 3.16 (c).
2. Next, insert the particular test sample and record the average intensity value by clicking the ‘Sample response’ button.
3. Upon determining the intensity value for reagent blank ( $I_0$ ) and sample response ( $I_T$ ), the application will determine the absorbance value internally



by implementation the following relation

$$A = \log\left(\frac{I_0}{I_T}\right) \quad (3.14)$$

The block code used for above step is shown in figure 3.18. After determining the absorbance value internally for a particular analyte solution, the application will insert the corresponding absorbance value in an internal calibration curve developed within the application itself to determine the analyte concentration. For example, the implementation of calibration equation for determination of iron concentration has been defined in the bottom lines of the block code as shown in figure 3.18.

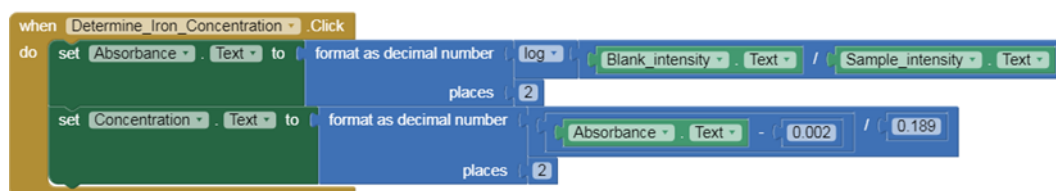


Figure 3.18: . Screenshot of Block codes developed with the MIT app inventor interface for evaluation of absorbance value.

The designed **PhotoSense** application has been also configured for on-site calibration as indicated by the corresponding windows shown in figure 3.16 (d) and figure 3.16 (e).

### 3.3.5 Device calibration

The designed smartphone photometric tool in the present study has been initially calibrated with prepared standard iron(II) and phosphate solutions. For both the analyte 0 mg/L of iron(II) and phosphate samples is considered as the reagent blank. In the present study, the experimental data has been recorded for five consecutive times (n=5) for each sample and the average value has been considered for obtaining the calibration curve. The characteristic plot of the absorbance values measured by the developed platform for both the standard solutions samples are shown in figure 3.19. The error bars in the figure indicates the standard deviations yield for five consecutive measurement of each sample. The linearity is well maintained throughout the concentration range 0.01 mg/L to 5 mg/L for

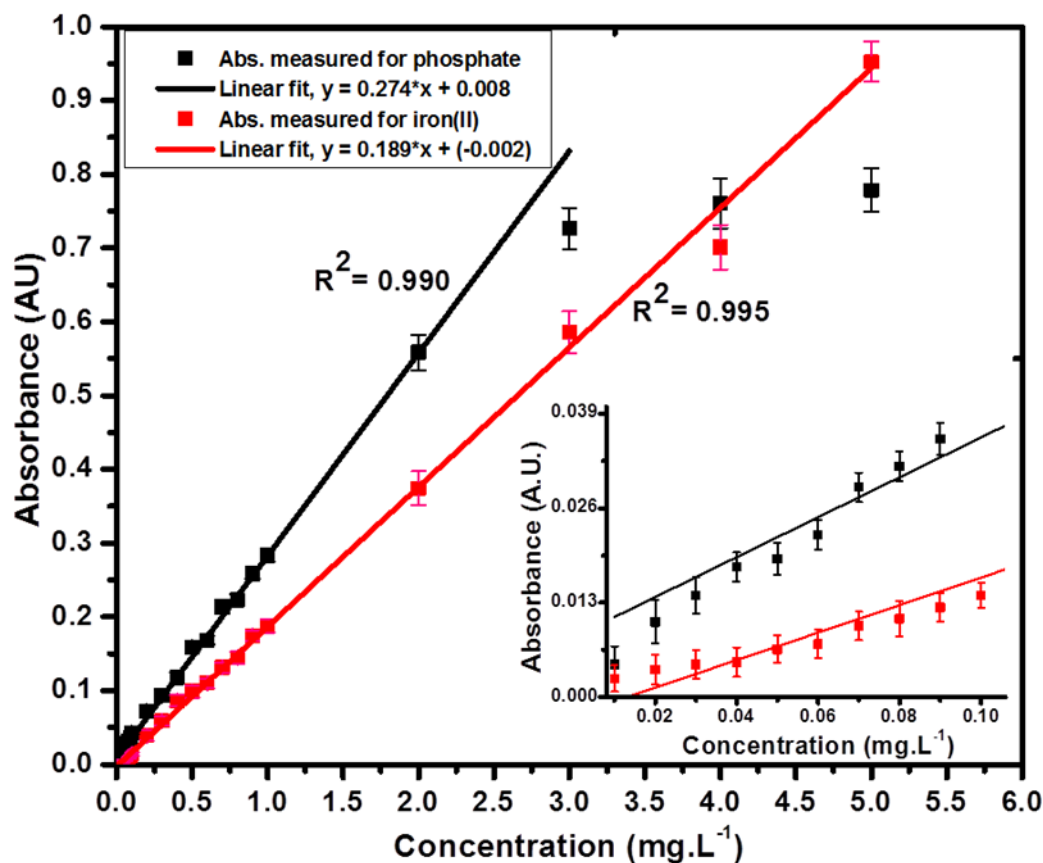


Figure 3.19: Characteristic plot of absorbance measured with the sensor for the concentration range 0 mg/L to 5 mg/L of the prepared standard solutions.

iron(II) standard solutions with a coefficient of determination  $R^2 = 0.995$ . The developed photometric platform has been calibrated for this concentration range and the corresponding calibration equation is given by

$$C_I = \frac{A_I + 0.002}{0.189} \quad (3.15)$$

where,  $A_I$  is the measured absorbance value and  $C_I$  is the concentration of the iron(II) present in the standard solution. This calibration equation has been implemented in the **PhotoSense** application as shown in figure 3.18. From figure 3.19, it has been observed that the characteristic absorbance values gets saturated for higher concentrations values of the standard phosphate solutions. This is a limitation of the chemical method used for detection of phosphate concentration in water sample. With coefficient of determination  $R^2 = 0.990$  in the concentration range 0.01 mg/L to 3 mg/L, the calibration equation for phosphate concentration

in water sample is given by

$$C_P = \frac{A_P - 0.008}{0.274} \quad (3.16)$$

where,  $A_P$  is the measured absorbance value and  $C_P$  corresponding concentration of the phosphate present in the standard solution. As shown in the inset of figure 3.19, the designed photometric platform yields fairly good linearity between the measured absorbance values with the change in concentration of both the analyte even at low concentrations. In the present study, the same calibration curve has been used for detection of low concentration levels.

### 3.3.6 Evaluation of different sensoristic parameters of the designed smartphone optical platform

Similar to the earlier study of fluoride level detection in water, all the necessary sensoristic parameters have been evaluated for the designed smartphone photometer.

**Evaluation of sensitivity, limit of detection, and resolution:** Since, the single characteristic calibration curve has been used to determine analyte concentration both in low and high concentration range, the sensitivity of the proposed platform has been estimated from the slope of the respective calibration curves developed for iron(II) and phosphate standard solutions. The sensitivity of the designed photometric platform for iron(II) sample is found to be  $0.189 \text{ AU/mgL}^{-1}$  and for phosphate sample this value is found to be  $0.274 \text{ AU/mgL}^{-1}$  respectively. Similar to the sensitivity, the same calibration curve has been used for determination of limit of detection. Equation 3.11 has been used to determine the LoD for the present study. Here  $\sigma$  has been considered as the standard deviation of y-intercepts of the calibration curves developed for both iron (II) and phosphate standard solutions as show in figure 3.19 and  $S$  as the corresponding slope or sensitivity determined above. By inserting the corresponding values of  $\sigma$  and  $S$  for both the analyte, the LoD has been calculated, and the value is found to be  $0.053 \text{ mg/L}$  for iron(II) and  $0.069 \text{ mg/L}$  for phosphate respectively.

In the next step, the resolution of the designed smartphone photometer has been evaluated. This has been done by investigating the device performance in the

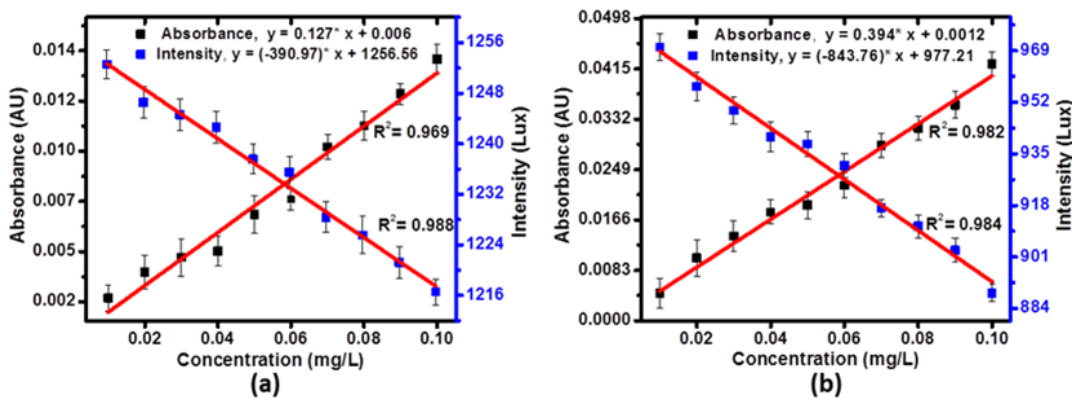


Figure 3.20: Characteristic plot of absorbance measured with the sensor for the concentration range 0.01 mg/L to 0.10 mg/L of the prepared standard solutions.

lower concentration range 0.01 mg/L to 0.10 mg/L in terms of intensity units. Figure 3.20 shows the corresponding characteristics response curves in the considered range in terms of intensity units. The corresponding absorbance values are shown as a reference. In the present study, the slopes of the characteristic plots have been considered as sensitivity which is given by  $390.97 \text{ Lux}/\text{mgL}^{-1}$  for iron(II) and  $843.76 \text{ Lux}/\text{mgL}^{-1}$  for phosphate standard solutions respectively. The corresponding resolution has been determined by inserting the respective values of sensitivities for both the analyte in equation 3.10. The calculated values of resolution of the developed platform while measuring iron(II) and phosphate concentrations are found to be  $2.55 \times 10^{-5} \text{ mg/L}$  and  $1.88 \times 10^{-5} \text{ mg/L}$  respectively.

**Evaluation of accuracy and precision:** As defined previously by equation 3.12 and equation 3.13, the accuracy and precision for the present platform have been determined in terms of %bias and %RSD. The accuracy and precision have been evaluated with five standard sample solutions with concentrations 0.05 mg/L, 0.1 mg/L, 1 mg/L, 2 mg/L, and 3 mg/L of both the analytes separately. The concentration of the considered standard solutions with known concentration values have been measured within the same day. Each solution has been measured for 5 consecutive times and the mean concentration and corresponding standard deviation (SD) has been determined. Table 3.3 summarizes the accuracy and precision data yielded in the present investigation. The mean bias of accuracy in measuring iron(II) and phosphate concentration are found to be 0.93% and 0.73% respectively while mean RSD in precision for the analytes were found to be 3.44%

Table 3.3: Accuracy and precision data for concentrations of standard solutions of iron(II) and phosphate (n=5)

<b>For standard iron(II) solutions</b>				
<b>Standard concentration (mg/L)</b>	<b>Mean</b>	<b>SD</b>	<b>Accuracy (% Bias)</b>	<b>Precision(%RSD)</b>
0.05	0.05	0.00	0.00	0.00
0.10	0.10	0.01	0.00	10.00
1.00	1.02	0.04	2.00	3.92
2.00	2.02	0.04	1.00	1.98
3.00	3.05	0.04	1.67	1.31
Mean % Bias =				0.93%
Mean % RSD =				3.44%
<b>For standard phosphate solutions</b>				
<b>Standard concentration (mg/L)</b>	<b>Mean</b>	<b>SD</b>	<b>Accuracy (% Bias)</b>	<b>Precision(%RSD)</b>
0.05	0.05	0.00	0.00	0.00
0.10	0.10	0.00	0.00	0.00
1.00	1.02	0.03	2.00	2.94
2.00	2.02	0.04	1.00	1.98
3.00	3.02	0.04	0.67	1.32
Mean % Bias =				0.73%
Mean % RSD =				1.25%

and 1.25%. The lower value of % RSD signifies greater precision of the designed tool.

### 3.3.7 Comparison of the designed smartphone based photometric platform with a laboratory grade spectrophotometer

The applicability of the designed photometric platform has been evaluated as a low cost alternative by comparing the sensing data with that of a laboratory grade spectrophotometer (UV-3600 Plus UV-Vis-NIR Spectro-photometer, Shimadzu). Five standard sample solution of concentration 0.1 mg/L, 0.5 mg/L, 1.0 mg/L, 2 mg/L, and 3 mg/L of both the iron (II) and phosphate have been analyzed by the designed platform and the commercial spectrophotometer. Before any measurement, the spectrophotometer has been calibrated to the same calibration

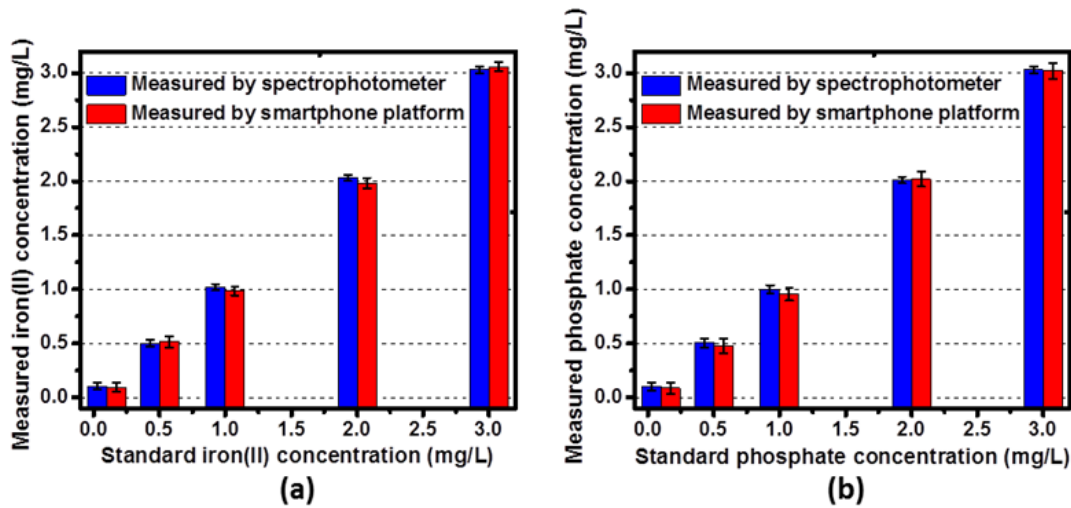


Figure 3.21: Comparison of the designed sensor with a laboratory grade spectrophotometer in measuring (a) iron(II) and (b) phosphate in water.

range as considered for the designed platform. The histogram representation of concentrations measured by the designed smartphone platform and that by the laboratory grade spectrophotometer are shown in figure 3.21 (a) and figure 3.21 (b). It has been observed that the maximum difference in concentration measured by the proposed smartphone based platform is less than 4% to that of the standard laboratory grade spectrophotometer. This signifies that the developed smartphone based photometric platform yields nearly similar results as that of the laboratory grade spectrophotometer.

### 3.4 Summary

In summary, the usability of a modern smartphone has been demonstrated as a low cost alternative for photometric sensing investigation which is operational both in visible and NIR spectral regime. Two optical configurations have been demonstrated to make it truly cost effective, robust and portable. At first, the embedded ALS and the LED flash of the smartphone have been used to convert the phone as a photometric platform and its usability has been demonstrated by measuring fluoride level concentration in water samples. Also, an application, **FSense** has been developed for detection, calibration, data analysis and data transfer, which significantly reduces the computation cost. The performance of

the device has been compared with that of a laboratory grade spectrophotometer for field collected water samples. Moreover, the performance of the developed optical platform has been evaluated with different smartphones which shows reliable results. Due to the use of in-built LED flash makes the device self contained. The main objective of this thesis is to find technological solutions which is meant to be used for resource poor region which should be low cost, user friendly so that it can have access to everyone in future. The LED flash of the phone has an emission wavelength within the visible region, therefore, it is not possible to use in analytical investigations where UV or IR source is required. Low cost LEDs of any specific wavelength is commercially available. The external LED can be easily powered by the smartphone battery by using the USB-OTG protocol. Therefore, in the second phase of the present study, a truly cost effective, user-friendly and robust photometric platform has been demonstrated. The designed platform has been used for photometric investigation both in visible and near-IR spectral regime by measuring iron concentration in the visible domain (510 nm) and phosphate concentration in the NIR domain (880 nm) in water samples. The developed **PhotoSense** application has been configured with data averaging algorithm which helps to reduce the measurement error. The performance of the developed platform has been compared with a laboratory grade spectrophotometer which shows nearly similar results. Due to the vast availability of smartphones both in rural and urban areas of India, it is envisioned that the developed smartphone based photometric tool may find its applicability as an affordable alternative for water quality parameter monitoring in resource limited regions which is now considered as a global challenge. The performance of the proposed tool has been optimised through optimally designing its hardware and software part of the system.

## References

- [1] Cazes, J. Analytical instrumentation handbook. CRC Press, 2004.
- [2] Narayanaswamy, R. and Wolfbeis, O. S. Optical sensors: industrial environmental and diagnostic applications, volume 1. Springer Science and Business Media, 2013.
- [3] Thomas, O. and Burgess, C. UV-visible spectrophotometry of water and

- wastewater. Elsevier, 2017.
- [4] Perkampus, H.-H. UV-VIS Spectroscopy and its Applications. Springer Science and Business Media, 2013.
- [5] Ohta, N. and Robertson, A. Colorimetry: fundamentals and applications. John Wiley and Sons, 2006.
- [6] Onishi, H. Photometric determination of traces of metals. 1986.
- [7] Ricci, R. W., Ditzler, M., and Nestor, L. P. Discovering the beer-lambert law. *Journal of chemical Education*, 71(11):983, 1994.
- [8] Kotoky, P., Barooah, P., Baruah, M., Goswami, A., Borah, G., Gogoi, H., Ahmed, F., Gogoi, A., and Paul, A. Fluoride and endemic fluorosis in the karbianglong district, assam, india. *Fluoride*, 41(1):72, 2008.
- [9] Majumdar, K. K. et al. Health impact of supplying safe drinking water containing fluoride below permissible level on fluorosis patients in a fluoride-endemic rural area of west bengal. *Indian journal of public health*, 55(4):303, 2011.
- [10] Kirkeskov, L., Kristiansen, E., Bggild, H., Platen-Hallermund, V., Sckerl, H., Carlsen, A., Larsen, M. J., Poulsen, S., et al. The association between fluoride in drinking water and dental caries in danish children. linking data from health registers, environmental registers and administrative registers. *Community dentistry and oral epidemiology*, 38(3):206-212, 2010.
- [11] Ozsvath, D. L. Fluoride and environmental health: a review. *Reviews in Environmental Science and Bio/Technology*, 8(1):59-79, 2009.
- [12] Kumar, M. and Puri, A. A review of permissible limits of drinking water. *Indian journal of occupational and environmental medicine*, 16(1):40, 2012.
- [13] Bellack, E. and Schouboe, P. Rapid photometric determination of fluoride in water. use of sodium 2-(p-sulfophenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulfonate-zirconium lake. *Analytical Chemistry*, 30(12):2032-2034, 1958.
- [14] Montgomery, D. C., Peck, E. A., and Vining, G. G. Introduction to linear regression analysis, volume 821. John Wiley and Sons, 2012.



- [15] Nakra, B. and Chaudhry, K. Instrumentation, measurement and analysis. Tata McGraw-Hill Education, 2003.
- [16] Guideline, I. H. T. Validation of analytical procedures: text and methodology q2 (r1). In *International Conference on Harmonization*, Geneva, Switzerland, 11-12. 2005.
- [17] Gonzalez, A. G. and Herrador, M. A. A practical guide to analytical method validation, including measurement uncertainty and accuracy profiles. *TrAC Trends in Analytical Chemistry*, 26(3):227-238, 2007.
- [18] Android device specifications. Retrieved on 24 June, 2016 from <http://specdevice.com>,2016.
- [19] Doeven, E. H., Barbante, G. J., Harsant, A. J., Donnelly, P. S., Connell, T. U., Hogan, C. F., and Francis, P. S. Mobile phone-based electrochemiluminescence sensing exploiting the usb on-the-go protocol. *Sensors and Actuators B: Chemical*, 216:608-613, 2015.
- [20] Clesceri L. S., Greenberg A. E., and Eaton E. D. Method 3500-Fe B: Phenanthroline method. In *Standard Methods for the Examination of Water and Wastewater*, pages 472-477, American Public Health Association, 1999.
- [21] Clesceri L. S., Greenberg A. E., and Eaton E. D. Method 4500-P E: Ascorbic acid method. In *Standard Methods for the Examination of Water and Wastewater*, pages 823-825, American Public Health Association, 1999.

