Chapter 5

To design and develop a cradle (smartphone sensing system) for determination of spoilage

5.1. Introduction

Rapid advancements in the creation of innovative approaches to evaluate food quality features have resulted in the development of non-destructive and non-invasive instrumental methods including biosensors, electronic nose, texture meters, image analyzers, colorimeters, and spectroscopic methods (Rezaei et al., 2018; Morsy et al., 2016). To detect fish spoilage, several methods and techniques using optical spectroscopy, visible spectroscopy, and hyperspectral imaging have been developed (Zhu et al., 2013; Cheng et al., 2013; Cheng et al., 2014; Zhao et al., 2019; Wu et al., 2021; Franceschelli et al., 2021). Spectral analysis as in hyperspectral imaging is one of the methods for measuring the quality of fresh fish for identifying and quantifying physical, and chemical processes and contaminants that indicate spoilage. Few hyperspectral imaging was carried out to evaluate the fish quality like the differentiation between fresh and frozen-thawed halibut (Zhu et al., 2013), measurement of the color of grass carp (Cheng et al., 2014), predicting meat quality (Pérez-Santaescolástica et al., 2019), real-time quality control of food product, etc. (Khan et al., 2020). Despite their high performance, such techniques are not widely used in the food industry due to the high equipment cost, the large amount of information generated during analysis, and the need for complicated data analysis and algorithms. Spectral smoothening is one of the main machine design choices. Improper selection or application of data processing techniques can cause the loss of important information (Khan et al., 2020). The previously mentioned spectroscopic or non-destructive techniques were also not suitable for field analysis. A smartphone device that is equipped with a high-resolution CMOS sensor and has computation capability may be an alternative to tedious and time-consuming techniques. Globally, researchers have recently become increasingly interested in converting smartphones into usable sensing tools.

Therefore, keeping this in view, we reported for the first time a feasible, cost-effective sensor based on a smartphone for monitoring the freshness of fish. To monitor the deterioration of fish during storage, we created a smartphone-based sensor in which the change in color of the PANI label was observed through the designed cradle and the rear camera of the smartphone. We focused on the steps for embedding optical components as an alternative to a spectrophotometer onto a mobile phone. Utilizing a 3D printed compartment, it is possible to use the broadband light source without depending on the availability of ambient light and it minimizes the cost as compared to the benchtop commercial instruments. Subsequently, we created a financially feasible scaled-down sensing system that can be coordinated with a smartphone for more extensive use by individuals in the food production network, particularly for affirming the quality and freshness of fish. In the present investigation, we designed a cradle attached to the rear camera of the smartphone (Redmi K20, Mi India). The designed setup integrated with the PANI label was utilized for the observation of fish spoilage. the performance, LOD, and LOQ of the designed sensor with the PANI label were also evaluated.

5.2. Materials and Methods

All the optical components namely LED, N-BK7 Plano-Convex lens were purchased from Edmund Optics, India, Pinhole was purchased from Thorlabs, US, Polylactic acid (PLA), and red and blue laser light was purchased from Amazon. Fresh fish samples were procured from Tezpur's local market near Tezpur University.

5.2.1. *Design and development of cradle for sensing using a smartphone*

A schematic illustration of the smartphone sensing system is shown in **Fig. 5.1**. The optical system was made up of four parts: an LED light source (610 nm), a pinhole (100 µm), a collimating lens (f/l 11mm), and a diffraction grating (1200 lines/mm). A 3D design drawing of the cradle set up using Google SketchUp 2020 is presented in **Fig. 5.2**. To combine all the optical components, the whole chamber was produced using a 3D printer (Raise 3D N2) and a biodegradable polymer (polylactic acid (PLA)) (**Fig 5.3a**). The diameter of the label holder was kept at 22 mm so that the PANI label could be inserted easily. The overall dimension of the designed optical setup was (9×4×4) cm in length, width, and height. 3D printed parts and cradle setup are illustrated in **Fig. 5.3b**. The approximate cost required for raw material for development of cradle was in the range of less than Rs 12,000 which was significantly less than the double or single beam UV vis spectrophotometer or colorimeter. A Plano-convex lens with an 11 mm focal length and 6 mm diameter was used to collimate and focus the emitted light from the label to the grating, and then over the rear camera of the smartphone, which was mounted at a 45° angle to allow the first-order diffracted output from the grating to illuminate the sensor (McGonigle et al., 2018). Mounting the rear camera of the smartphone at a 45° angle ensures that the first-order diffracted light from the grating effectively reaches the sensor. This position optimizes the capture of detailed spectral information, important for analyzing light properties like wavelength and intensity. The camera of the smartphone (Redmi K20, Mi India) captured the spectrum of the light signal, and the spectral information from the digital image was obtained using Image-J software (Dutta et al., 2014). The software transforms the optical spectrum image into a grayscale intensity Vs pixel value. While capturing the image, the parameters of the camera were set at 100 ISO, its aperture at f/1.75, and the focal length of the camera was 4.77 mm. The developed smartphone sensor coupled with the PANI label was respectively used to monitor the fish spoilage during storage at room temperature.

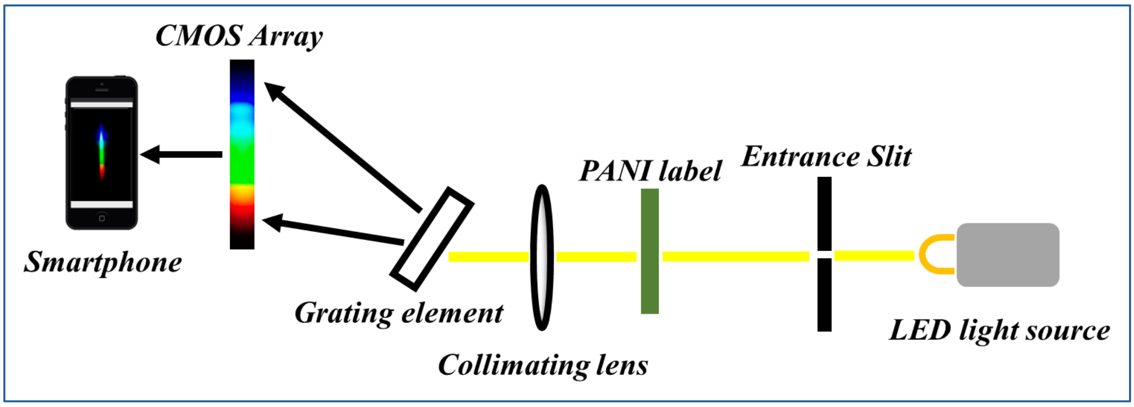


Figure 5.1. Schematic diagram of smartphone sensing system.

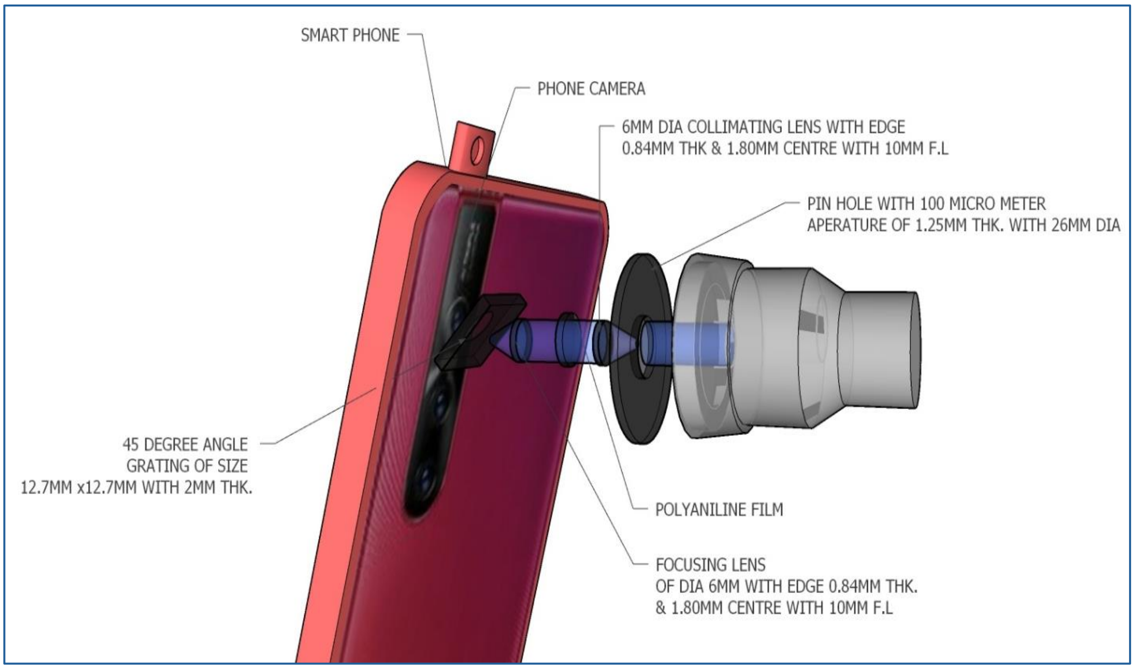
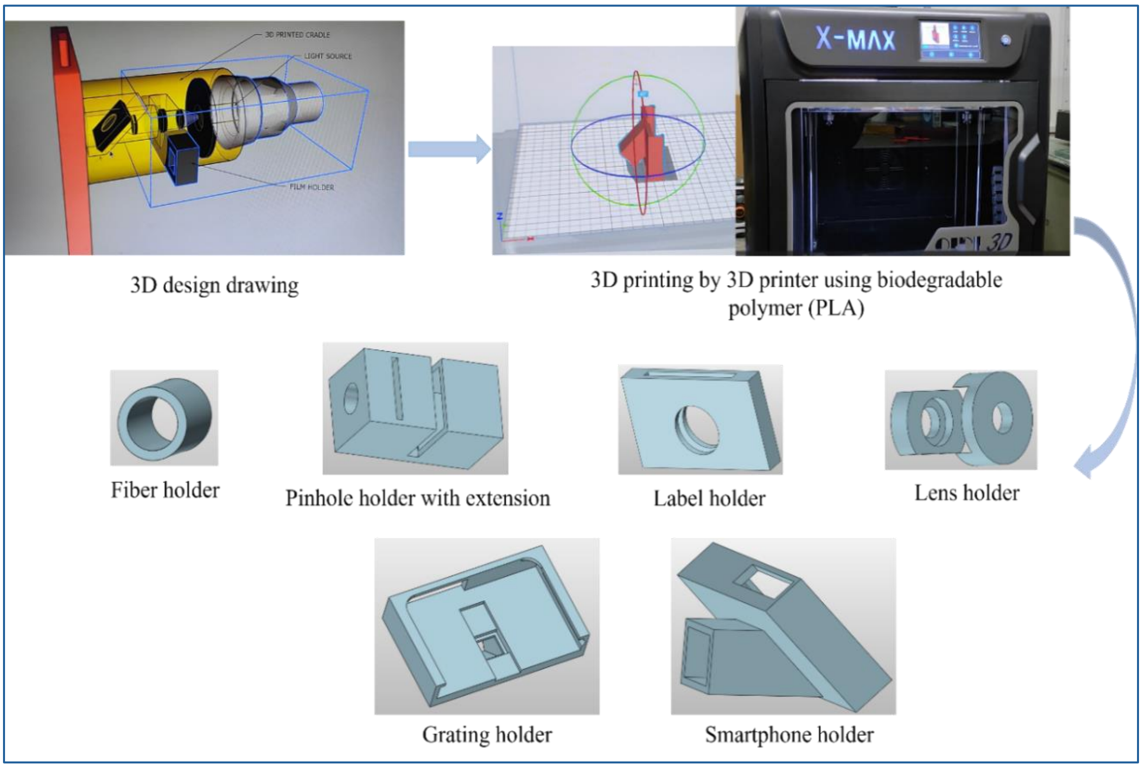
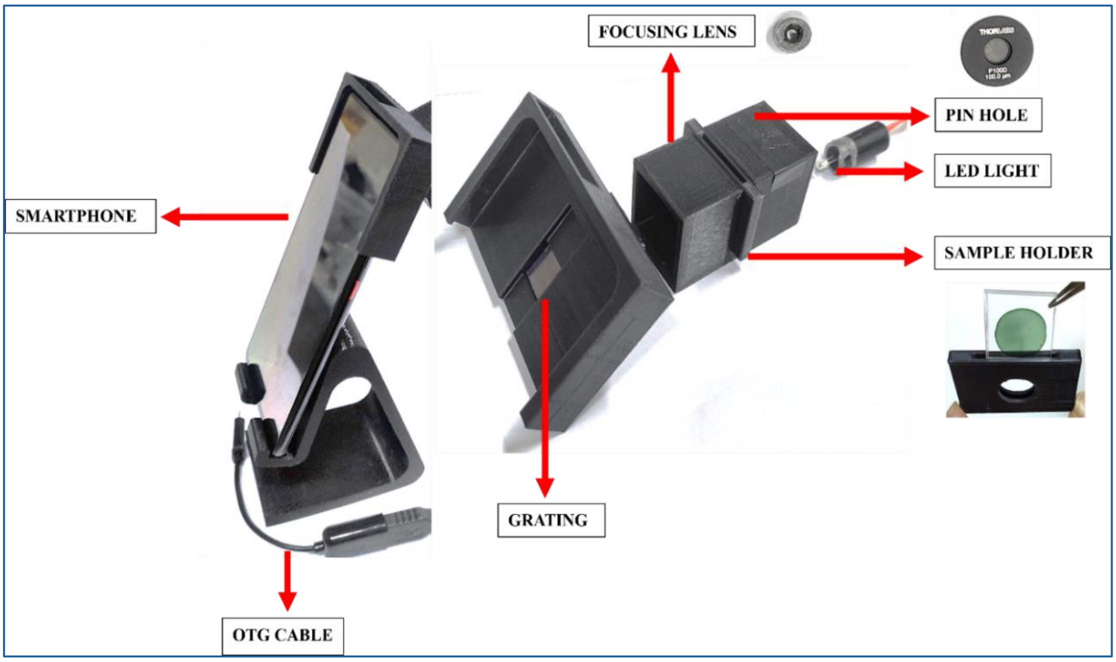


Figure 5.2. 3D design drawing of the cradle set up using Google SketchUp 2020.



(a)



(b)

Figure 5.3 (a) Process diagram of the optical-based smartphone sensing system, and **(b)** Cradle setup with optical component integrated into the camera of the smartphone.

5.2.2. *Wavelength calibration for the developed smartphone sensor*

The developed sensor has been calibrated using a three-diode laser source so that the light spectrum captured through the camera can be measured on a wavelength scale. Red, green, and blue laser light of wavelength values 629 nm, 532 nm, and 405 nm respectively were used for wavelength correction as per the method of Dutta et al. (2014) (**Fig. 5.4**). Wavelength calibration was carried out before the experimentation to match the pixel position of the CMOS sensor of the smartphone to the wavelength of the spectrophotometer (Ding et al. 2018) and it was converted by **Eq. 5.1** (de Oliveira et al. 2017):

$$\text{Wavelength} = \text{MF} \times \text{PV} + \text{Constant} \qquad (5.1)$$

Where MF represents the multiplying factor that is the wavelength (nm) resolution per pixel and PV is the pixel value recorded from the optical image.
The corrected wavelength is further used to plot the response between intensity Vs wavelength for the determination of fish freshness.

Figure 5.4. Spectral image of red and blue laser light obtained using the developed sensor.

5.2.3. *Calibration of the sensor, and Measurement of Uncertainty (MOU) of the developed label*

The developed sensor was calibrated by exposing the PANI label to a standard ammonia solution (20 mL) with concentrations ranging from 0-400 ppm five times. The exposure occurred for a duration of 5min while maintaining a relative humidity of 40-60 %. The volume and relative humidity were kept constant for each measurement. The spectrum of the exposed PANI label was obtained and spectra were corrected from pixel values to wavelength scales as discussed in section **5.2.2** (**Fig. 5.5**). A calibration curve between the grayscale intensity versus ammonia concentration was plotted. The linear equation obtained was used for monitoring the volatile amines released from the stored fish sample **(Eq. 5.2)**:

$$\text{Ammomia Concentration} = \frac{(\text{Intensity} - \text{b})}{\text{S}} \tag{5.2}$$

Where b and S represent the intercept and slope of the calibration curve. The obtained value using a developed smartphone device was further evaluated for performance before sample detection.

The uncertainty of the concentration of the test result for each parameter was given in standard deviation values. Calculated statistics include slope (s) and standard deviation slope (SDs), intercept (i) and standard deviation intercept (SDi), coefficient determination (R^2), and standard deviation regression (SDr) (Irnawati et al., 2021).

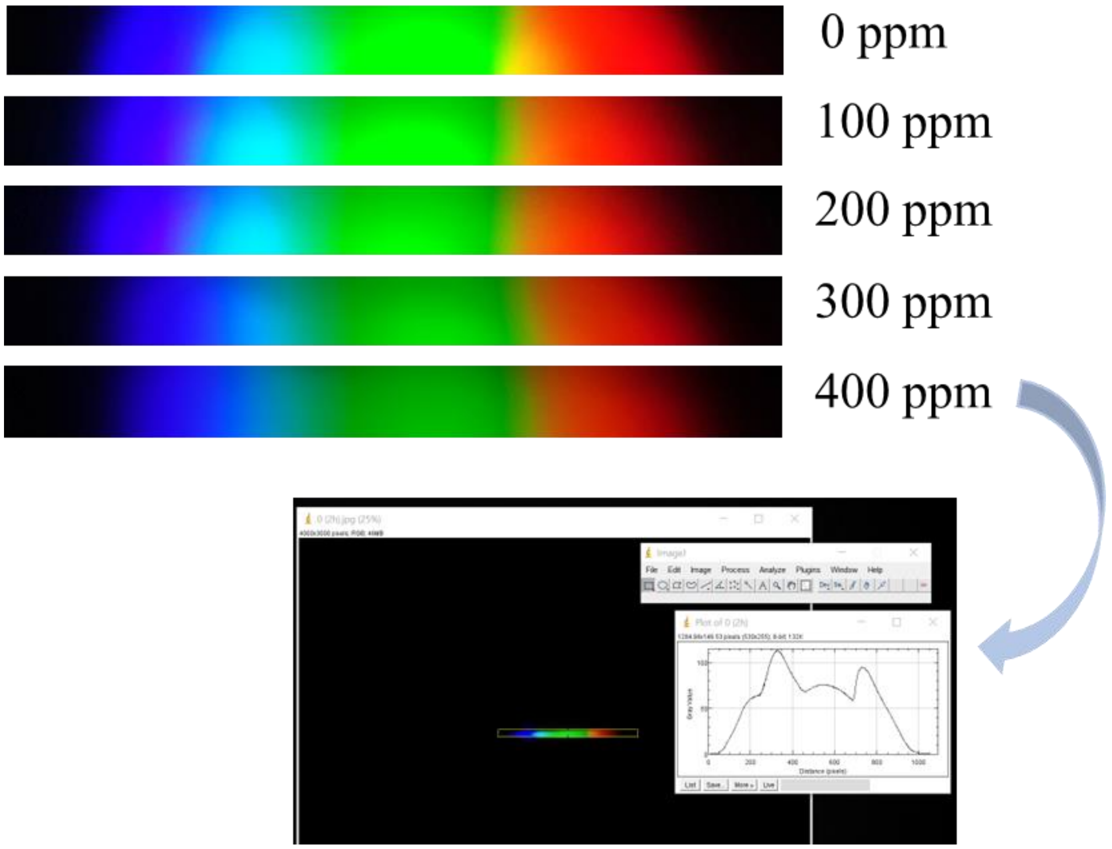


Figure 5.5. Spectral image of PANI label exposed to ammonia vapor obtained using the developed sensor and the spectral data extracted using ImageJ software.

5.2.4. *Performance evaluation of the developed sensor*

5.2.4.1. *Limit of detection, Limit of quantification, Accuracy, Precision, and % Recovery*

The limit of detection (LOD) and limit of quantification (LOQ) were evaluated by exposing the PANI label to the ammonia vapor of ammonia solution (0, 10, 100 ppm)) for 5min and the response of the label was examined by capturing five consecutive images for each standard solution by the sensor and the extracted data were evaluated. The LOD and LOQ were estimated using **Eq. 5.3** and **5.4** respectively (Irnawati et al., 2021; Hatiboruah et al., 2020):

$$\text{LOD} = \frac{3\ \sigma}{\text{S}} \tag{5.3}$$

$$\text{LOQ} = \frac{10\ \sigma}{\text{S}} \tag{5.4}$$

Where (σ) represents the standard deviation of the response of the blank sample and (S) represents the slope of the calibration curve.

Accuracy and precision are usually measured by calculating the % Bias (mean of individual difference) and % RSD (relative standard deviation). The accuracy and precision of the developed smartphone sensor were estimated by recording three consecutive intensity signals of each 0 ppm, 10 ppm, and 100 ppm of standard ammonia solution and were calculated using the following **Eq. 5.5** and **5.6** (Hatiboruah et al., 2020):

$$\%\ \text{Bias} = \frac{(\text{kc} - \text{mc})}{\text{kc}} \times 100 \tag{5.5}$$

Where, (kc) and (mc) represent the known concentration and mean concentration.

$$\%\ \text{RSD} = \frac{\text{SD}}{\text{Mean}} \times 100 \tag{5.6}$$

Where SD is the standard deviation.

The % Recovery was calculated by dividing the observed estimated concentration by the actual concentration.

5.3. Results and discussion

5.3.1. *Wavelength calibration for the developed smartphone sensor*

The wavelength value of the laser's light for the present smartphone sensor was found to be 391.84 nm indicating a wavelength resolution of 0.21 nm per pixel **(Fig. 5.6)**. The proposed sensor used about 1139 pixels for wavelengths between 391.84 and 633.54 nm **(Fig. 5.7)**. Though an external broad-band light (LED) source is utilized for the color spectrum, the in-built internal camera filter in the smartphone exhibits a wavelength range of 391.84-633.54 nm (Dutta et al., 2014; Kalinowska et al., 2021).

Pixel to wavelength conversion for the developed smartphone-based sensor was calculated using the following **Eq. 5.7** (de Oliveira et al., 2017):

$$Red - 1122pixel = 630nm$$

$$Blue - 62pixel = 405nm$$

Multiplying factor (MF),

$$(1122 - 62)pixel = (630 - 405)nm$$

$$1pixel = 0.2122nm$$

Then,

$$Wavelength = (MF) \times (Pixel\ value) + Constant$$

$$405nm = (0.2122) \times (62) + Constant$$

$$Constant = 391.8346$$

Therefore,

$$Wavelength = 0.2122 \times (Pixel\ value) + 391.8346 \tag{5.7}$$

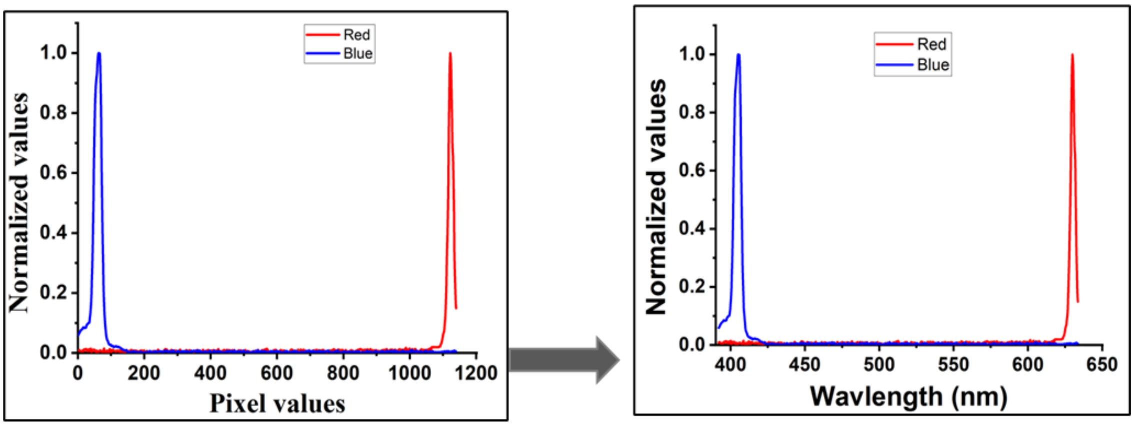


Figure 5.6. Pixels were converted to wavelength.

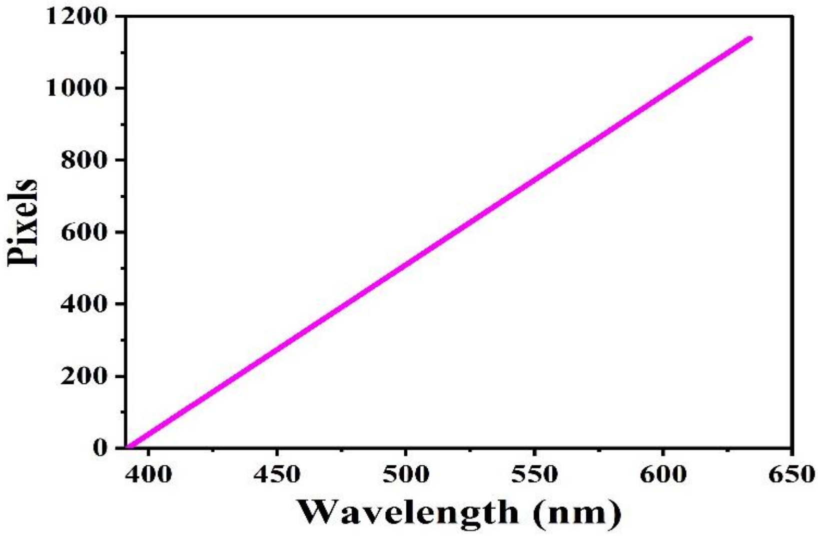


Figure 5.7. Linear relationship between pixel and calibrated wavelength.

5.3.2. *Calibration of the developed sensor*

The PANI label was placed between the optical setup, a light source (LED) is allowed to pass through the label and a calibration curve was plotted between grayscale intensity and ammonia concentration **(Fig. 5.8)**. A linear relationship between grayscale intensity and ammonia concentration was observed with a mean correlation coefficient of 0.97. The linearity and uncertainty of the calibration curve were calculated and presented in **Table 5.1.**

The LOD and LOQ of PANI labels using a developed smartphone sensing device were estimated to be 3.83 ppm and 12.96 ppm respectively. The % bias and % RSD value obtained from the developed sensing device were found to be 0.14 %, and 1.87 %

respectively. Based on the low % bias and low % RSD, it appears that the developed smartphone-based sensor is dependable and produces almost accurate readings when detecting the ammonia content in fish samples. The % recovery of standard ammonia solution using the developed smartphone sensor was within 94-108 % **(Table 5.2)** which is within the common target of 80-120 % (Irnawati et al., 2021) and confirmed that the PANI label-based smartphone sensor is effective to detect the fish spoilage. The table summarizing the above parameters for the developed smartphone sensing system is shown in **Table 5.3**.

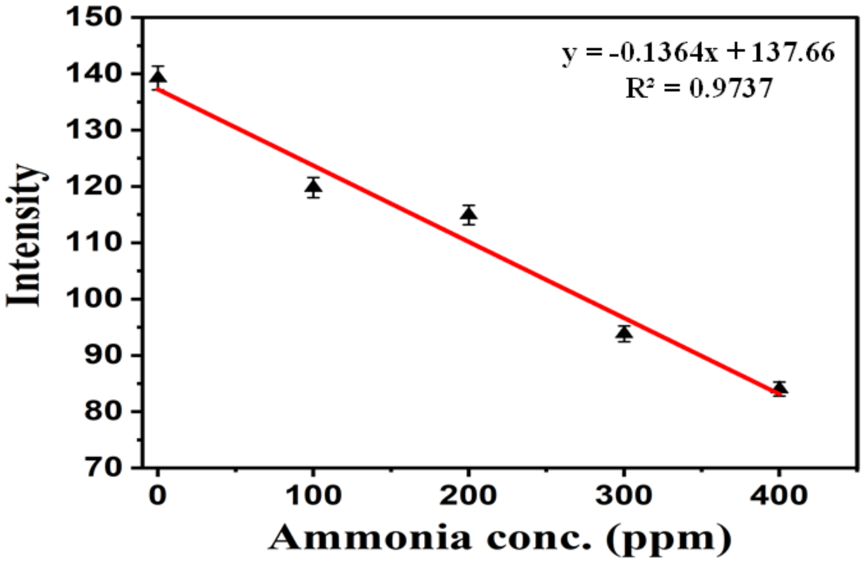


Figure 5.8 Calibration curve of PANI label response using smartphone-based sensor.

Table 5.1. The linearity and the uncertainty of the calibration curve

Parameters	Smartphone
Coefficient of Determination (R^2)	0.9795
Slope (s)	-0.12915
Intercept (i)	136.7524
Standard deviation of Slope (SDs)	0.000615
Standard deviation of Intercept (SDi)	0.486165
Standard deviation of Regression (SDr)	0.00153

Table 5.2. Percent (%) Recovery for ammonia solution using the developed smartphone sensor

Ammonia solution (ppm)	Smartphone (% Recovery)
100	107.73
200	82.47
300	102.83
400	94.94

Table 5.3. Limit of detection (LOD), Limit of quantification (LOQ), Accuracy, Precision, and % Recovery of the developed smartphone sensor

Parameters	Values
LOD (ppm)	3.83
LOQ (ppm)	12.96
% Bias	0.14
% RSD	1.87
% Recovery	94-108

5.4. Conclusion

An optical cradle as an accessory for a smartphone using engineering drawing software and a 3D printer was successfully produced. The wavelength value of the laser light for the present smartphone sensor was found to be 391.84 nm indicating a wavelength resolution of 0.21 nm per pixel. The developed sensor used about 1139 pixels for wavelengths between 391.84 and 633.54 nm. The PANI label showed a response peak at 549 nm using the developed smartphone-based sensor and the sensor was calibrated using a standard ammonia solution (0- 400 ppm). The sensor exhibited a LOD of 3.83 ppm with minimal bias (0.14 % Bias) and variation (1.87 % RSD). It achieved a recovery percentage of 94-108 % for standard ammonia solution. The developed smartphone sensing system was calibrated effectively for further analysis with fish samples.

5.5 References

Cheng, J. H., Dai, Q., Sun, D. W., Zeng, X. A., Liu, D., & Pu, H. B. (2013). Applications of non-destructive spectroscopic techniques for fish quality and safety evaluation and inspection. *Trends in Food Science & Technology*, *34*(1), 18-31.

Cheng, J. H., Sun, D. W., Han, Z., & Zeng, X. A. (2014). Texture and structure measurements and analyses for evaluation of fish and fillet freshness quality: a review. *Comprehensive Reviews in Food Science and Food Safety*, *13*(1), 52-61.

de Oliveira, H. J. S., de Almeida Jr, P. L., Sampaio, B. A., Fernandes, J. P. A., Pessoa-Neto, O. D., de Lima, E. A., & de Almeida, L. F. (2017). A handheld smartphone-controlled spectrophotometer based on hue to wavelength conversion for molecular absorption and emission measurements. *Sensors and Actuators B: Chemical*, *238*, 1084-1091.

Ding, H., Chen, C., Qi, S., Han, C., & Yue, C. (2018). Smartphone-based spectrometer with high spectral accuracy for mHealth application. *Sensors and Actuators A: Physical*, *274*, 94-100.

Dutta, S., Choudhury, A., & Nath, P. (2014). Evanescent wave coupled spectroscopic sensing using smartphone. *IEEE Photonics Technology Letters*, *26*(6), 568-570.

Franceschelli, L., Berardinelli, A., Dabbou, S., Ragni, L., & Tartagni, M. (2021). Sensing Technology for Fish Freshness and Safety: A Review. *Sensors*, *21*(4), 1373.

Hatiboruah, D., Das, T., Chamuah, N., Rabha, D., Talukdar, B., Bora, U., Ahamad K. U. & Nath, P. (2020). Estimation of trace-mercury concentration in water using a smartphone. *Measurement*, *154*, 107507.

Irnawati, I., Idroes, R., Zulfiani, U., Akmal, M., Suhartono, E., Idroes, G. M., Muslem, M., Lala, A., Yusuf, M., Saiful, S. & Jalil, Z. (2021). Assessment of arsenic levels in water, sediment, and human hair around Ie Seu'um geothermal manifestation area, Aceh, Indonesia. *Water*, *13*(17), 2343.

Kalinowska, K., Wojnowski, W., & Tobiszewski, M. (2021). Smartphones as tools for equitable food quality assessment. *Trends in Food Science & Technology*, *111*, 271- 279.

Khan, A., Munir, M. T., Yu, W., & Young, B. R. (2020). A review towards hyperspectral imaging for real-time quality control of food products with an illustrative case study of milk powder production. *Food and Bioprocess Technology*, *13*(5), 739-752.

McGonigle, A. J., Wilkes, T. C., Pering, T. D., Willmott, J. R., Cook, J. M., Mims, F. M., & Parisi, A. V. (2018). Smartphone spectrometers. *Sensors*, *18* (1), 223.

Morsy, M. K., Zór, K., Kostesha, N., Alstrøm, T. S., Heiskanen, A., El-Tanahi, H., Sharoba, A., Papkovsky., Larsen., J., Khalaf, H., Jakobsen, M. H. & Emnéus, J. (2016). Development and validation of a colorimetric sensor array for fish spoilage monitoring. *Food Control*, *60*, 346-352.

Pérez-Santaescolástica, C., Fraeye, I., Barba, F. J., Gómez, B., Tomasevic, I., Romero, A., Moreno, A., Toldrá, F., & Lorenzo, J. M. (2019). Application of non-invasive technologies in dry-cured ham: an overview. *Trends in Food Science & Technology*, 86, 360– 374.

Rezaei, F., & Shahbazi, Y. (2018). Shelf-life extension and quality attributes of sauced silver carp fillet: A comparison among direct addition, edible coating, and biodegradable film. *LWT*, *87*, 122-133.

Wu, D., Zhang, M., Chen, H., & Bhandari, B. (2021). Freshness monitoring technology of fish products in intelligent packaging. *Critical Reviews in Food Science and Nutrition*, *61*(8), 1279-1292.

Zhao, Z., Wei, L., Cao, M., & Lu, M. (2019). A smartphone-based system for fluorescence polarization assays. *Biosensors and Bioelectronics*, *128*, 91-96.

Zhu, F., Zhang, D., He, Y., Liu, F., & Sun, D. W. (2013). Application of visible and near-infrared hyperspectral imaging to differentiate between fresh and frozen-thawed fish fillets. *Food and Bioprocess Technology*, *6*(10), 2931-2937.