

Colorimetric Bisphenol-A Detection With a Portable Smartphone-Based Spectrometer

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Abstract—Water quality monitoring in resource-limited settings without access to a sophisticated laboratory requires the development of low cost and portable instrumentation. Herein, we propose a newly designed handheld reflection-based smartphone sensing platform to detect Bisphenol-A (BPA), a well-known endocrine disruptor agent abundantly used in plastic industry. An experimental investigation relying on color change due to the formation of quinone-type complex was conducted with samples from two different water sources: distilled and commercial drinking water. This colorimetric measurement device was used to determine BPA in distilled water in alkaline environments. The successful combination of colorimetric assay and spectrometer facilitates limit of detection in the low ppm levels, 0.29 ppm for smartphone and 0.23 ppm for commercial spectrometer, with a sensitivity of 0.1/ppm.

Index Terms—Bisphenol-A detection, image processing, optical sensing, smartphone spectrometer.

I. INTRODUCTION

THE detection of health-damaging chemicals and compounds in aqueous media has drawn a great interest to ensure public health protection. Bisphenol A (4, 4'-(propane-2, 2-diyl) diphenol, BPA) is one of the most well-known endocrine disrupting compounds [1]. Due to the presence of phenol groups on the structure, BPA has tendency to bind the estrogen receptors, and it changes or ceases endocrine functions within body [2], [3]. Even low exposure levels are identified with infertility, obesity, diabetes, thyroid malfunction, prostate cancer, breast cancer, attention deficit disorder [4]–[7]. Despite being a toxic organic compound, BPA is the most common synthetic compound utilized in plastic industry as a monomer [8], [9]. It indirectly affects public health as contaminated plastic utensils, water bottles or food containers [10], [11], since previous studies showed that BPA can

migrate from these plastic materials into food and beverages. Accordingly, BPA accumulation in human body is the main reason of increasing cancer rates and autoimmune diseases [12], [13]. Eventually, the development of field deployable, cost effective, and highly accurate detection methods are needed to monitor exposure levels of BPA in the environment, food and human body.

Up to now, numerous analytical methods for the analysis of BPA have been employed such as high performance liquid chromatography system with ultraviolet (HPLC-UV), HPLC-mass spectrometry (MS), gas chromatography (GC)-MS, fluorescence and electrochemical detection [14]–[17]. Although these methods can provide accurate and precise results, they mostly require complex instruments located in central laboratories with access to specialist labor. Recently, enzyme-linked immunosorbent assays (ELISA), chemiluminescence immunoassay, molecular imprinting-based detection approaches, nucleic acid-based aptamers, and electrochemical methods have been developed [18]–[22]. Among them, electrochemical sensing is a widely accepted technique with high sensitivity and simplicity for the detection of BPA. It is well known that BPA possesses electrochemical activity due to its electrochemical-active phenolic hydroxyl groups that can be oxidized. The electrochemical characteristics of BPA have been examined at different electrode materials such as carbon and metals [23], [24]. However, the relatively high potential requirement for the oxidation of phenolic compounds results in a decreased sensitivity due to the increase in background current. Various approaches including the use of enzymes and surface modification of the electrode have been proposed to reduce this disadvantage. Carbon nanotube [25]–[27], graphene [22], [24], [28]–[33], quantum-dot [33], [34], metal composite [23], [35], [36], and nanocomposite based [37]–[39] sensors have been developed to improve the electrochemical reactivity of electrodes. For example, Ma *et al.* [40] have fabricated an electrochemical impedance aptasensor performing in a range of femtomolar detection limit, in which gold nanoparticle coated boron doped-diamond was modified with aptamer. However, difficulties in efficient and repeatable sensing of BPA have been reported [41], [42] due to weak electroactivity and deposition of oxidation on the electrode surface.

Over the last decade, cameras are widely used in quantification of color images within the colorimetry and photometry methods in scientific domains. Sumriddetchkajorn *et al.* reported one of the pioneering works where a webcam 2D image sensor was used as spectrometer sensor and numerous

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fiber optic cables were used for signal translation to the sensor [43]. Advancements in 3D printing technology and camera marketing let smartphones become an infrastructure for scientific researches [44]. Zhu *et al.* [45] reported a smartphone based optofluidic fluorescent imaging cytometry and achieved to read a few micro range bead detection and Talukder *et al.* [46] reported smartphone integrated microfluidic impedance cytometer. Additionally, previous studies reported direct quantification of colors from test strips or solutions by using a smartphone device. This smartphone platform based colorimeters were used for monitoring chlorine concentration in water [47], [48], estimating nitrogen in rice leaf [49], quantifying peroxide content [50], the detection of saliva alcohol [51], biomarkers in sweat and saliva [52], urine [53], [54], pH and/or nitrite [55]. Recently, we have proposed smartphone spectrometer for investigation of methylene blue dye adsorption from water demonstrating the effect of fiber size on the spatial and spectral resolution [56]. Another smartphone-based sensing study has been reported by McCracken *et al.* [57] with the detection limit of BPA in micromolar range and LED flash has been used to stimulate the fluorescence molecules.

Camera and sensor advances together with the increasing capability in computer processing have led to emergence of more portable, cost-efficient and user-friendly platforms to quantify and analyze the particular content of the solutions. One method is to use color information which changes with the concentration (peroxide amount [50]) or time (methylene blue degradation [56]) depends on the application. After images are captured for each distinct condition, features are extracted to train the system (machine learning or neural network systems) which can then automatically perform colorimetric tests as new data arrives. This method can be used both solid samples like paper-based test and liquid samples like colored solutions. For liquids, besides this approach, spectral data can also be used as an alternative. Spectral data (derived by spectroscopic instruments like UV-Vis, FTIR, NIR and chromatographic instruments like HPLC, GC) specify variables with its properties and provide useful information about the molecules. With the use of spectral data, chemical composition of the materials can be identified. Therefore, spectrometers are used commonly in laboratories and scientific fields such as chemistry and biology as well as in many industries such as forensic, printing, and more. Our aim is to combine the aforementioned spectral data with the widely used spectrometer under the smartphone technology to reveal a portable and cost-effective design.

In the present study, we have developed an ultra-low cost, portable, plastic fiber based smartphone spectrometer with a custom designed immersion probe and a cradle for rapid and sensitive detection of BPA in distilled and commercial water samples. The colorimetric assay based on the formation of quinone-type complex in alkaline medium has been conducted. The smartphone system has been turned into a visible spectrometer system to accommodate absorbance measurements in BPA mediated solutions using the reflective probe. The proposed reflection based smartphone spectrometer is straightforward, robust and could facilitate remodeling the science of measurement for health disrupting agents.

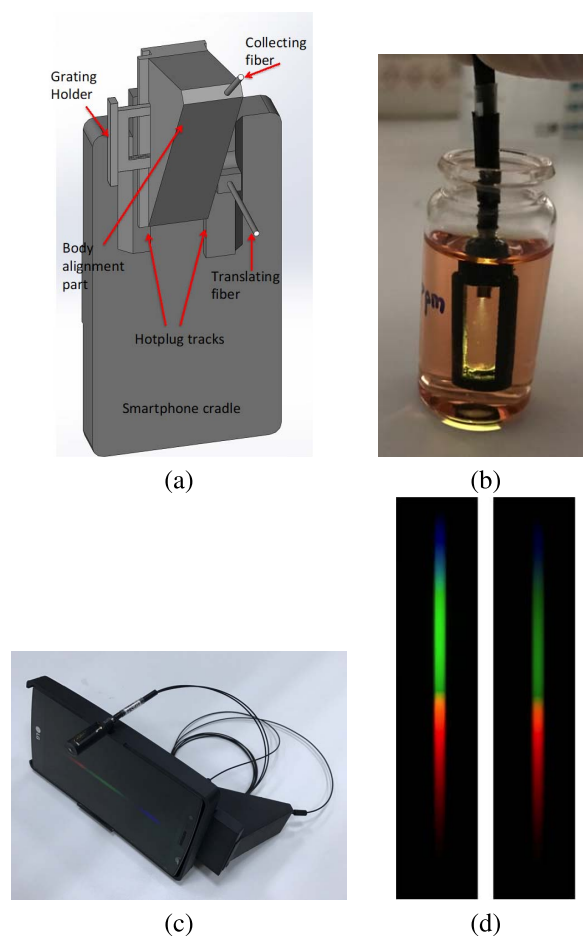


Fig. 1. (a) The schematic design of the 3D printed components for smartphone based spectrometer. (b) The photographic image of the probe immersed into an analyte solution during the absorbance measurement. (c) A photograph of the smartphone spectrometer with a plastic immersion probe. (d) Representative spectral images obtained from smartphone spectrometer.

II. MATERIALS AND METHODS

A. Portable Smartphone-Based Design

The custom design of the 3D printed components smartphone based spectrometer is shown in Fig 1a. LG G4 (South Korea) smartphone rear-facing camera was used as detector with the specifications of 1/2.6 inch sensor size, 5312×2988 pixel resolution, and $1.12 \mu\text{m}$ pixel size. Smartphone cradle, body alignment part, diffraction grating holder and the immersion probe were all custom designed and fabricated using a 3D printer (Zortrax M200) by consuming of $\sim 100\text{g}$ Acrylonitrile Butadiene Styrene polymer. Smartphone cradle and body alignment part include hot-plug tracks for easy alignments. Also, grating holder is designed as pluggable and carries grooves for the grating to firmly position. Body alignment part maintains the alignment of collecting fiber and transmission diffraction grating (1000 lines per mm, Rainbow Symphony). Collecting fiber that collects reflected radiations from probe is positioned with the degree of 42° to the normal of the grating in order to drop first order-diffracted light spectrum ($m=1$) on the camera. Therefore, the distance is arranged as 11.7 mm between grating and camera. Fiber-coupled smartphone flashlight is connected to the immersion

probe and then the reflected radiation is coupled to the camera through the grating. Here the probe is developed using a plastic (PMMA) based bifurcated fiber bundle with the diameter of 0.5 mm (also known as Y-cable) and it includes fine polished stainless steel (UNS S31600, AK Steel Corporation). The distance between the bifurcated optical fibers and the steel surface is 16.5 mm. The immersion probe is shown in Fig. 1b. Total cost of reflection based the smartphone spectrometer system is less than \$5 except smartphone. Designed spectrometer system does not include any additional optical components. The smartphone based spectrometer system is shown in Fig. 1c. Fig. 1d shows the spectral images obtained from blank solution (the left image) and 5 ppm BPA solution (the right image) demonstrating the color intensity variation in different concentrations of solutions.

B. Image Processing

A digital camera captures an image using an array of millions of tiny pixels that are sensitive to light. Pixel intensity value is directly related to the number of photons received by each pixel. Since pixels are incapable of distinguishing the photons with respect to color, only grayscale images can be created in this way. Color images are created by covering neighboring pixels with the color filter array that permits only one of three primary colors such as red (R), green (G) or blue (B). This means each pixel has only one color information, which leads to a generation of RAW image. Demosaicing method, interpolation of two known color from the neighbors, is used to estimate the other two color values of the pixel. After this step, the RAW image becomes viewable on the screen. To obtain more appealing images, post-processing methods such as white-balance, gamma correction, color space correction, and compression are performed, which eventually leads to a commonly used format like JPEG.

JPEG images have certain advantages over RAW images such as small memory to store and being instantly displayable. However, some issues arise from this conversion such as non-linear RGB color space [58], data loss due to the compression and having only an eight-bit color depth. On the other hand, RAW images are free from post-processing which means they include original image data with 10 – 14 bits color depth. The post-processing methods cause corruption in linearity of the image. In RAW images, the relation between the intensity value and the number of photons in the pixel is linear which is necessary for quantitative scientific data acquisition.

In this study, all the images were taken and processed in RAW format to avoid the limitations of JPEG format. Also, raw data allow making more precise image analysis. There are three RAW file formats to work. Nikon cameras produce RAW image with “.NEF” extension while Canon creates image with “.CR2” extension. Here, “.DNG” raw file format, developed by Adobe Company, was studied because it is released as an open format and widely employed compared to “.NEF” and “.CR2”. The images were transferred to a computer to process in MATLAB after capturing with smartphone since processing raw images require high computational power which cannot be provided by the current smartphones. In that sense, there is no mobile application released for the processing of raw

images. Initially, reliability of the camera was tested using five consecutive images captured in JPEG format. After the intensity values were normalized, the deviation was found $\pm 2.73\%$ which could be considered negligible. Thus, it was found to be adequate to use average of five consecutive images in order to enhance the reliability of the results. Also, all parameters like shutter speed and ISO were kept same to capture the images under same conditions, and the manual mode was employed to avoid possible post-processing operations than could be performed by the smartphone. The images in “.DNG” format were then converted to tagged image file format (TIFF) for easier extraction of the red (R), green (G) and blue (B) values with DCRAW software [59] which maintains the linear relationship between RAW images and the radiance scene. After that, RGB values of the images were converted to HSV (Hue-Saturation-Value) to reduce the effect of illumination change. The V (Value) was used in further processing steps of the images to quantify the amount of the transmitted light through the solution for this study. The image processing pipeline is depicted in Fig. 2a which summarizes the overall process in four steps. To calculate corresponding wavelength value of each pixel, a calibrated fiber-optic spectrometer (HR2000; Ocean Optics, FL, USA) was used. The calibration method [60] assumes that the wavelength value and pixel index have a linear relationship and the peak locations in the visible wavelength range for a fluorescent light source and distances between them were used to extract the linear equation to convert from pixel index to nanometers. As illustrated in Fig. 2b, after the smartphone spectrometer was calibrated successfully with a dispersion value of 0.248 nm/pixel, these peaks overlap completely.

C. Detection of Bisphenol A in Aqueous Media

BPA (Sigma-Aldrich, $\geq 99\%$), 4-Aminoantipyrine (4-AAP) (Sigma-Aldrich, $> 98\%$), potassium ferricyanide (Carlo Erba), sodium bicarbonate (Sigma-Aldrich, $\leq 99.7\%$) were analytical grade and used as received without further purification. The concentration of the phenolic compound was determined by a colorimetric reaction with 4-AAP and potassium ferricyanide [61]. A stock solution of BPA (200 ppm) was prepared in ethanol; subsequently diluted to the concentrations ranging from 0.1 to 10.0 ppm. The pH of BPA solutions was adjusted to 8.0 using 0.25 M NaHCO_3 and distilled water. 1.5 mL of 20.8 mM 4-AAP and 1.5 mL of 83.4 mM potassium ferricyanide solutions were consecutively added to 12 mL of BPA solutions. After 10 min incubation, the solution absorbance was measured using a smartphone based spectrometer system and a calibrated spectrometer. The absorbance value was read at 506 nm and the BPA concentration was determined from a standard curve. The limit of detection (LOD) was calculated based on the standard deviation and the slope of the calibration curve [62]. The effect of pH on the detection of BPA (10 ppm) was conducted after adjusting the initial pH levels of the solutions to 7.0, 8.0, and 10.0 using 0.25 M NaHCO_3 , NaOH and HCl solutions. To evaluate the accuracy of the proposed method, an accurate determination of BPA in commercial drinking water was obtained by the standard addition method

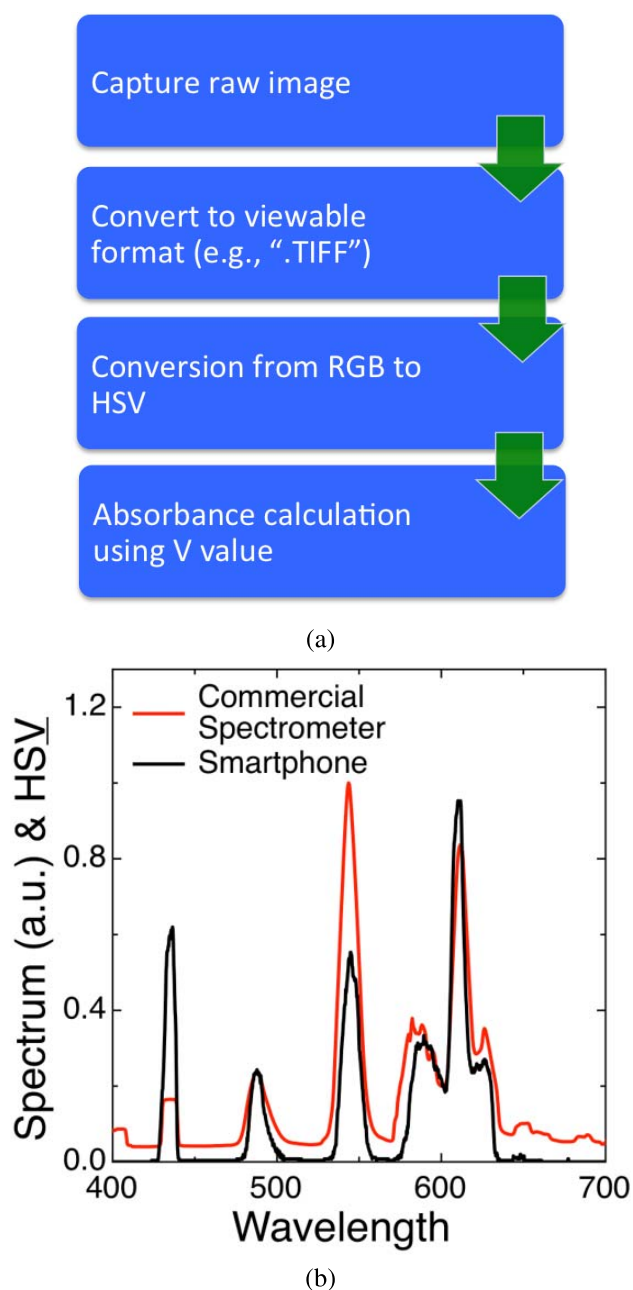


Fig. 2. (a) Image processing steps for the conversion of raw image into absorbance data. (b) The output spectra from commercial and smartphone spectrometers for calibration process.

at pH 8.0 both with a smartphone based spectrometer system and a calibrated spectrometer.

III. RESULTS AND DISCUSSION

BPA concentrations were measured using a colorimetric assay described by Emerson [63]. The use of Emersons reaction offers many advantages such as speedy results, ease of manipulation, the use of relatively stable reagents, and applicability over a wide range of concentrations of phenolic material [64]. Under alkaline environment when a phenolic solution is reacted with 4-AAP in a presence of potassium ferricyanide as an oxidant, the colored complex is formed. The primary amine of 4-AAP exerts an electrophilic attack on

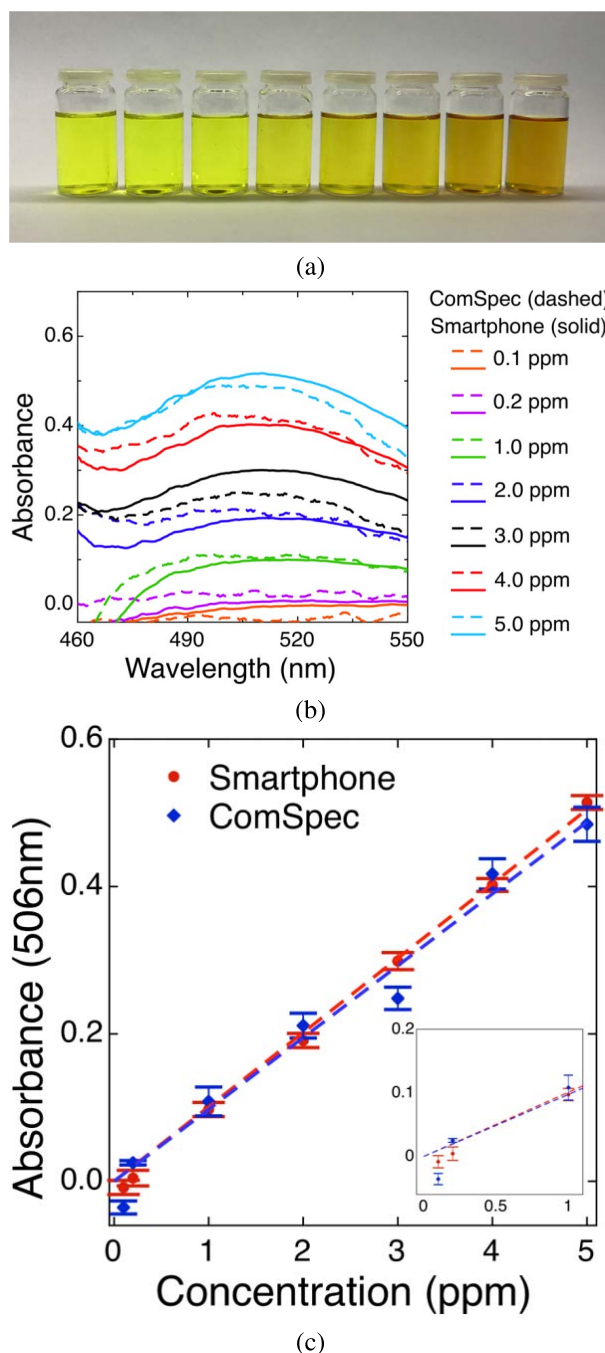


Fig. 3. (a) The photograph of BPA solutions from 0 to 5.0 ppm. (b) Absorbance spectra obtained from smartphone and commercial spectrometers for the serial dilutions. (c) The absorbance at 506 nm was measured by smartphone and commercial spectrometers. (The inset shows the enlargement of curve at low concentrations ranging from 0 to 1.0 ppm.)

the para-position of an oxidized phenol forming a quinone-type complex. Maximum wavelength for BPA after completion of the reaction was reported as 506 nm [61]. The absorbance of BPA solutions at different concentrations was measured by both smartphone and commercial spectrometers. BPA solutions were prepared as 0.1, 0.2, 1.0, 2.0, 3.0, 4.0 and 5.0 ppm and the final pH values were adjusted to 8.0. Fig. 3a shows the color change of the solutions, which turns gradually from yellow to orange with respect to the increase in BPA concentration. To obtain the absorbance spectrum,

the multicolored images from smartphone were processed and the absorbance value was calculated using Beer-Lambert Law. Proportionality in the absorbance with the initial concentration of BPA in the solution was observed. Fig. 3b shows a comparison of the spectra, performed with distilled water, obtained by the smartphone and commercial spectrometer. The related calibration curves for the BPA solutions are shown in Fig. 3c, with coefficient of determination values (R^2) of 0.996 and 0.977, respectively. The possible reason for the small shift in absorptivity may be due to internal filters of smartphone camera and non-linear responsivity of the sensor [56]. The calibration curves indicate an LOD of 0.29 ppm and 0.23 ppm for the smartphone and commercial spectrometer, respectively. The sensitivity of the smartphone spectrometer system was found to be 0.1/ppm. The dynamic range of the sensing system varies between 0.29 - 5.0 ppm. The inset graph magnifies the concentration range between 0 - 1.0 ppm. Here, the negative absorbance was observed in low concentration values (smaller than 0.2 ppm) as the negative absorbance values arise from measurements higher than the blank measurement. These measurements are below the LOD and are more likely to noise due to CMOS imager on smartphone. The number of blank measurements could bring the absorbance values close to 0, leads to signal to noise ratio improvement. Having similar results with commercial spectrometer also proves that low analyte levels are prone to measurement errors.

McCracken *et al.* reported smartphone-based fluorescence detection of BPA via 8-hydroxypyrene-1, 3, 6-trisulfonic acid (HPTS) as a fluorescent probe. They determined BPA with a detection limit of 1.0 ppm in waste leachate and industrial samples using fluorescence spectroscopy and iPhone 5S or Nexus 5X standalone sensor platforms [57]. Our proposed method differs from McCracken's with respect to limit of detection range which allows to work with lower concentrations of BPA.

Ettinger *et al.* [64] suggested that pH is an important variable in the quantitative application of Emersons reaction [64]. It is well established that this colorimetric reaction should be carried out in a controlled pH conditions. Under acidic pH values, the reaction between the phenolic material and 4-AAP leads to the formation of antipyrine red [64]. On the other hand, under alkaline conditions, the complex between phenolic material and 4-AAP, which form the basis of this method, is stronger. Similar observation has been reported by Gottlieb and Marsh [65]. They noted that the most suitable pH was 10.4-10.6 for 2, 2'-methylenebis[4-chlorophenol] and 4-AAP. Therefore, the effect of pH was studied in solutions containing 10 ppm BPA. Photographs of BPA solutions with pH values of 7.0, 8.0 and 10.0 were demonstrated in Fig. 4a. The images on the left show blank solutions (containing no BPA) and on the right show colored complexes with BPA. As expected, 4-AAP forms a stable orange-colored complex with BPA and exhibits a yellow color in the absence of the analyte under alkaline conditions. However, at pH 7.0, blank solution has completely different color, and a nonstable colored complex forms which is also observed below pH 7.0. Fig. 4b shows the corresponding absorbance values of BPA

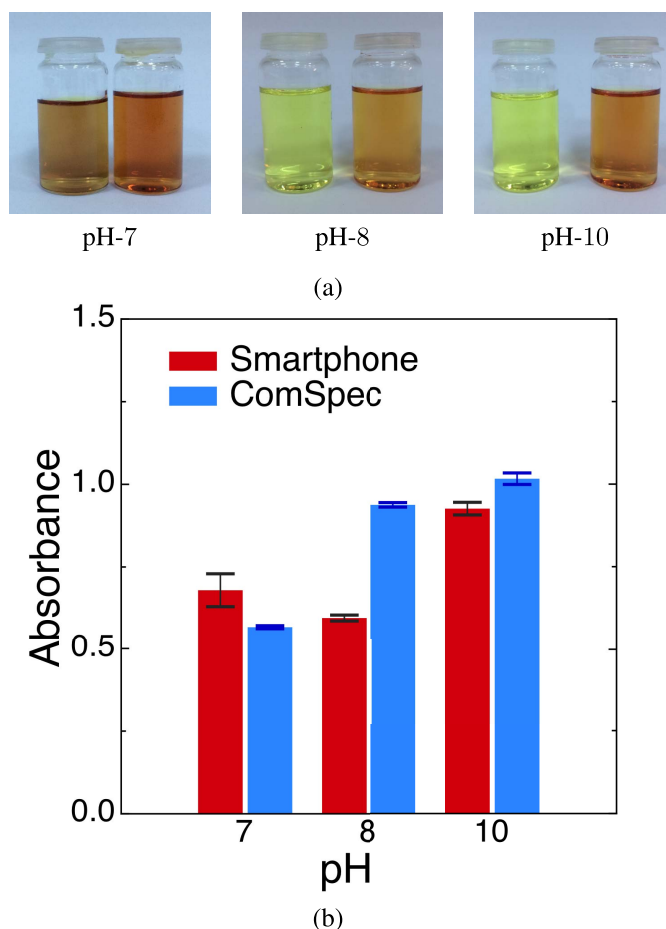


Fig. 4. (a) The photographs showing the color of BPA solutions at different pH values. The images on the left show blank solutions and on the right show analyte solutions at 10 ppm. (b) Effect of pH on the absorbance of BPA solutions measured using smartphone and commercial spectrometers.

solutions at different pH values obtained from smartphone and commercial spectrometers. We can draw two conclusions from the results described here. The first is that it can conveniently be studied above pH 7.0. The second is, with the exception of pH 7.0, higher absorbance values were obtained by commercial spectrometer compared to the smartphone spectrometer. This can also be attributed to different absorptivity values obtained from calibration curves, which concludes that same smartphone should be used to study the absorptivity of the analyte.

To demonstrate the potential application of this technique in an analysis of real sample, the smartphone spectrometer was tested on the commercial drinking water by the standard addition method at pH 8.0. Fig. 5 shows a comparison of absorbance intensities of spiked BPA in commercial drinking water using smartphone and commercial spectrometers. Here, two lines are separated from each other by the concentration level while they are almost overlapping in Fig. 3c. The common ion effect is most encountered reason for the noticeable separation observed in commercial water which contains several types of interfering ions compared to the distilled water. Therefore, the stability of complex formation is negatively affected by the increased number ions, resulting in deviation between the two curves. Moreover, a detection

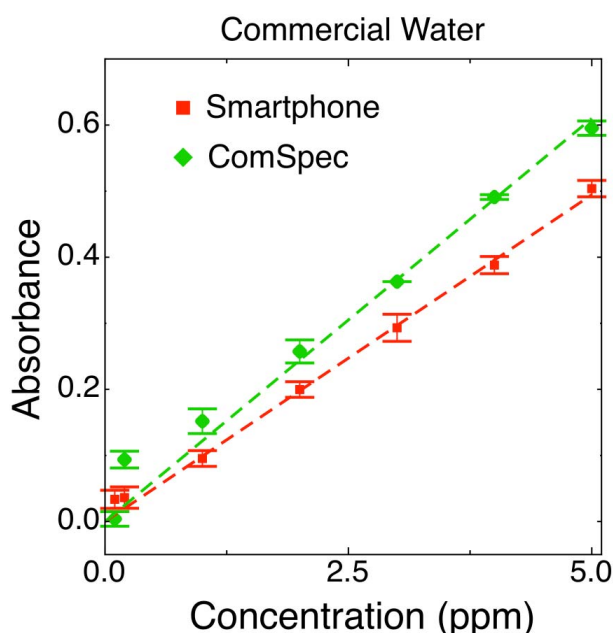


Fig. 5. Comparison of absorbance intensities of spiked BPA in commercial water samples using smartphone and commercial spectrometers.

limit of 0.64 ± 0.014 ppm was obtained in commercial water using the smartphone spectrometer while it was found as 0.55 ± 0.011 ppm using the commercial spectrometer. The BPA concentrations show relatively similar characteristics, indicating that the performance of the smartphone spectrometer is comparable to the commercial spectrometer. Our results prove that the proposed smartphone spectrometer can readily be used for rapid detection of BPA in water samples under controlled pH conditions.

IV. CONCLUSION

A rapid quantification of BPA was reliably performed by colorimetric analysis in water samples with the help of a reflection based smartphone sensing platform with plastic immersion probe. This colorimetric system provides detection of BPA in the dynamic range of 0.29–5.0 ppm under alkaline pH conditions. The detection limit of the system was found as 0.29 ppm with the sensitivity of 0.1/ppm. The findings of this study suggest that the smartphone spectrometer, successfully recognizing chemicals with a low limit of detection, is capable of subrogating benchtop spectrometers. As a consequence, our approach opens the door toward the portable micropollutant monitoring which can be extended to smartphone-based point-of-care diagnostics and environmental analysis.

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