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## Application of a smartphone based spectrophotometer for rapid in-field determination of nitrite and chlorine in environmental water samples

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### ABSTRACT

In this paper, a low cost and portable smartphone-based spectrophotometer with the purpose of measuring trace levels of two important anions, chlorine and nitrite ions in water samples, is introduced. This home-made spectrophotometer is made of Plexiglas, equipped with two LEDs as a light source, and a piece of DVD is acted as light dispersing element. Battery of smartphone was used as its power supply and spectral analysis was performed by a free software downloadable from Google Playstore. By using this lightweight spectrophotometer, various environmental samples were analyzed for their  $\text{NO}_2^-$  and  $\text{Cl}_2$  content in field. Good detection limits of  $5.00 \times 10^{-2} \text{ mg L}^{-1}$  and  $8.60 \times 10^{-3} \text{ mg L}^{-1}$  were obtained for chlorine and nitrite, respectively. The linear range for chlorine was  $1.00\text{--}4.00 \text{ mg L}^{-1}$  and this range for nitrite was  $0.05\text{--}1.20 \text{ mg L}^{-1}$ . Reproducibility as relative standard deviation for both chlorine and nitrite was better than 8.75%. In order to investigate validity of data, results were compared to standard methods of measuring chlorine and nitrite, using both spectrophotometry and commercial kits which showed no difference between results obtained. This very simple to use and inexpensive device can be used many times, so can be considered as a low-cost alternative to the detection device of commercial kits.

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### 1. Introduction

Nowadays there is an increasing need for low-cost technologies that can detect and monitor environmental contaminant concentrations quickly, easily and in-field to provide timely data regarding the extent and amount of pollution. The ultimate goal will be to enable each person to have a personal laboratory in his/her own pocket. The use of smartphone in the world grows in such a way that more than 2.6 billion people use this device. The accessibility, portability, high quality camera, operating systems and also improvement in their electronic, made them a useful measuring device in many fields of science such as medical science, food industry and analytical chemistry [1]. Application of smartphones for analytical purposes has been exploited in the last five years due to their high definition complementary metal oxide

semiconductor (CMOS) camera that can act as detectors [2]. Combining CMOS camera with a simple dispersion element, make the smartphone a portable and user-friendly smart spectrometer which could be replaced with traditional bulky and costly optical instrumentation [3]. Also the possibility of mobile phone to connect to internet through wired and wireless connectivity modes such as Wi-Fi and Bluetooth, caused to use mobile phone as a transmission device for health purposes such as sending biometric measurements to health specialists in real time [4]. Mobile phones with digital camera and inexpensive high-power light emitting diodes (LEDs), is recognized as a powerful tool for diagnosis [5]. This portable and achievable device with innovative digital technologies, easy wireless connectivity with other devices and easy operation, has changed several features of our life and cause to apply it as a biosensing and environmental monitoring device and point of care diagnosis. For this purpose, a verity of Apps have been designed which can be used with smartphones for health and environmental applications [6]. Furthermore, the importance of global healthcare and environmental monitoring; for example water quality monitoring or environmental pathogen screening, increased the demand of portable imaging system. So,

Abbreviations: CMOS, Complementary metal oxide semiconductor; LED, Light emitting diode; DPD, N,N-diethyl-p-phenylenediamine.

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smartphone could provide improved and simplified the way of analysis and tests in the field which can be used with everyone without training requirements [7,8]. Because of such powerful capabilities, it is possible to design accessory attachments on smartphones for analytical bio sensing and point-of-care diagnosis [9]. One of the widespread analytical devices in the field of trace analysis is spectrophotometer. It is a simple, reliable and low cost instrument with the ability of measuring organic compounds as well as anions and cations very precisely and quickly [10]. Colorimetric methods are used to determine various substrates in water which are benefited from the naked eye or other devices to measure spectral properties [11]. Smartphone based colorimetry which converts colorimetric data to analyte concentrations, was performed using built-in camera of smartphone with high resolution and the RGB color of smartphones to determine heavy metals and alkali ions in water samples [1,12–14]. However, not many reports can be found in the literature for determination of anions in water using this technique.

Determination of chlorine in water is important because water disinfection is normally performed by chlorination [15]. Due to the hazards of high levels of chlorine for human health, the amount of free chlorine should be determined very carefully. According to the World Health Organization, the amount of free chlorine in drinking water should be  $0.2 \text{ mg L}^{-1}$  up to  $5.0 \text{ mg L}^{-1}$  [16]. Chemical species of chlorine which can be employed in this process are “free available chlorine” (including HOCl,  $\text{OCl}^-$ ,  $\text{Cl}_2$ ) (which was measured in this paper) and combined chlorine (mono-, di- and trichloramines) in which the latter is produced due to the reaction of free chlorine with ammonia. Various standard methods such as spectrophotometric, chromatographic, potentiometric, iodometric, amperometric and colorimetric are used to determine chlorine in aqueous samples [17,18]. One of the most commonly used methods is colorimetric method with the N,N-diethyl-p-phenylenediamine (DPD) reagent. The reaction of DPD with chlorine at pHs near neutral, produces a relatively stable free radical of semi-quinoid cationic compound known as a Würster dye. Further oxidation of DPD cause to make an unstable colorless imine compound [19,20].

Nitrite ( $\text{NO}_2^-$ ) is another environmental pollutant that is identified as a harmful compound to human health, atmosphere and natural water [21]. Nitrite is often used as an additive to meat products in order to preserve food against the food poisoning microorganism. Presence of nitrite in blood leads to interfere with oxygen transport and produce toxic compounds such as carcinogenic nitrosamines. It is also an intermediate ion of the nitrogen cycle so it appears in soils and surface waters [22,23]. Because of its high toxicity, it is important to determine nitrite in water samples. European Union rules allow  $0.1 \text{ mg L}^{-1}$  of nitrite in drinking water as maximum amount [24]. Of the most methods which have been developed to measure nitrite are electrometric, chromatographic, spectrophotometric, spectrofluorimetric and kinetic-based [25,26] methods which most of them, need expensive instrumentation and are also time-consuming. Among them, colorimetric analysis is known as a simple, low-cost and fast method to measure nitrite [27]. Colorimetric determination of nitrite was made in the presence of diazotization of sulfanilamide (4-aminobenzenesulphonamide) to produce an azo dye which was additionally reacted with N-(1-naphthyl) ethylenediamine dihydrochloride to make a bluish violet azo dye [28].

In this paper, we designed and constructed a new portable smartphone-based spectrophotometer for in field analysis of nitrite and chlorine in water samples. The results of measuring chlorine and nitrite were compared with the standard method of their measurements. We believe that the use of this device may be a good alternative to the detection device of commercial kits.

## 2. Material and methods

### 2.1. Chemicals, reagents and solutions

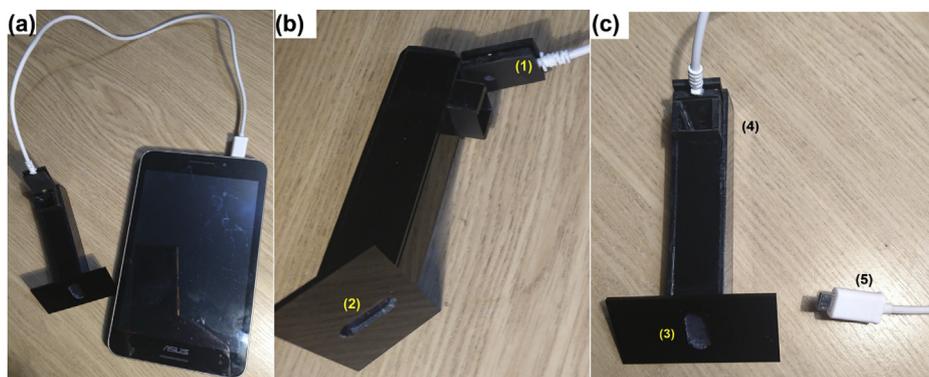
All reagents were of analytical reagent grade and were purchased from Merck KGaA (Darmstadt, Germany). Chlorine (Cat. No.114434) and nitrite (Cat. No.116973) kits were obtained from the same company. Milli-Q® (Merck-Millipore, MA, USA) water ( $18.3 \text{ M}\Omega \text{ cm}^{-1}$ ) was used throughout the experiment after filtering through  $0.22 \text{ nm}$  Nylon membrane. Certified reference materials of chlorine (Cat. No. QC1450, Sigma-Aldrich, USA,  $1.10 \text{ mg L}^{-1}$ ) and nitrite (Cat. No.125041, Merck-Millipore, MA, USA,  $0.20 \text{ mg L}^{-1}$ ) were used to control accuracy of the suggested method. A stock standard permanganate solution was prepared by dissolving  $891 \text{ mg}$  permanganate in  $1000 \text{ mL}$  water.  $10 \text{ mL}$  of this solution diluted to  $100 \text{ mL}$  with distilled water in a volumetric flask. By 100 times more dilution, a chlorine equivalent of  $1.00 \text{ mg L}^{-1}$  would be produced in reaction with N, N-diethyl-p-phenylenediamine (DPD). DPD indicator solution was prepared by dissolving  $1.1 \text{ g}$  anhydrous DPD sulfate in chlorine-free distilled water containing  $8 \text{ mL}$  1:3  $\text{H}_2\text{SO}_4$  and  $200 \text{ mg}$  disodium ethylenediamine tetraacetate dihydrate (EDTA) and making to  $1 \text{ L}$ . This solution was stored in a brown glass-stoppered bottle in the dark, and discard when discolored. Phosphate buffer solutions was prepared by dissolving  $24 \text{ g}$  of anhydrous  $\text{Na}_2\text{HPO}_4$  and  $46 \text{ g}$  of anhydrous  $\text{KH}_2\text{PO}_4$  in distilled water and combined with  $100 \text{ mL}$  distilled water in which  $800 \text{ mg}$  EDTA have been dissolved and diluted to  $1000 \text{ mL}$ . Standard ferrous ammonium sulfate (FAS) titrant was prepared by dissolving  $1.106 \text{ g}$   $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in distilled water containing  $1 \text{ mL}$  1:3  $\text{H}_2\text{SO}_4$  and make up to  $1 \text{ L}$  with freshly boiled and cooled ultrapure water. A stock standard solution of nitrite was prepared by dissolving  $25 \text{ mg}$  of sodium nitrite in  $250 \text{ mL}$  distilled water. The solution of sulfanilamide (4-aminobenzenesulphonamide) was prepared by dissolving  $0.5 \text{ g}$  sulfanilamide in  $100 \text{ mL}$  of 20% v/v hydrochloric acid. N-(1-naphthyl)-ethylenediamine dihydrochloride solution was prepared by dissolving  $0.3 \text{ g}$  of the solid reagent in  $100 \text{ mL}$  of 1% v/v hydrochloric acid.

### 2.2. Instruments

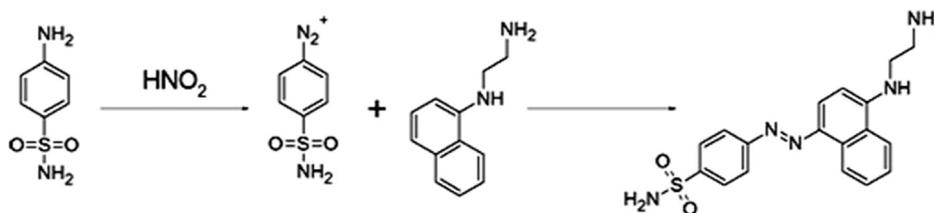
A double beam UV/Vis spectrophotometer (LABNICS equipment, model LUV-100A UV–Vis spectrophotometer, CA, USA) was used to measure absorption of the solutions. Images of smartphone spectrophotometer were taken by a Samsung smartphone model SM-G925F. Ordinary 1-cm polymeric cells were used as cuvettes. ImageJ software was used to analyze the images. An android application, “Light Analyser”, was used to analyze the intensity of lights which was downloaded as a free App from Google Playstore.

### 2.3. Fabrication of smartphone-based spectrophotometer and its assessment

The shape of our smartphone spectrophotometer was based on what being sold by Publiclab Company under the name Papercraft Spectrometer Kit, but other features are new. It was constructed by black Plexiglas for being waterproofed and anti shock (Fig. 1). A cuvette holder compartment grants tightly encompassment a standard 1-cm cell. In this way, position of the cell to the source, and other parts of the device can keep constant, which results better precision. Size of entrance light slit is also adjustable; it was found that a  $3 \times 1 \text{ mm}^2$  slit has the best performance for our application. As radiation source, two white LEDs with powers of  $3 \text{ W}$  were mounted. Instead of using external power supply, the battery of smartphone is used to feed the light source. This source can be easily removed in case ambient light is desired to be used. A piece of a DVD disk was employed as its light dispersing element.



**Fig. 1.** Fabricated smartphone spectrometer and its compartments (a); rear view (b); front view (c). 1: light source, 2: detecting window, 3: dispersing element, 4: cuvette compartment, 5: connection port to smartphone.



**Fig. 2.** Diazotization of nitrite in acidic medium.

For this purpose, a  $2 \times 2.5 \text{ cm}^2$  slice of DVD was cut and the opaque layer of it was carefully peeled off from the purplish transparent layer and discarded. This slice was glued onto the back of detecting window as showed in part (3) of Fig. 1. The exposed area to mobile camera was about  $1 \times 2 \text{ cm}^2$  with an elliptical shape. This made the spectrophotometer, a robust portable device which could be used everywhere.

#### 2.4. Determination of chlorine

Since standard solutions of chlorine are not stable, in order to have accurate measurements, potassium permanganate was used instead of chlorine dioxide for test experiments. A series of aqueous standard samples of  $\text{KMnO}_4$  containing the chlorine equivalent range of  $0.05\text{--}4.00 \text{ mg L}^{-1}$  were prepared. A mixture of 5 mL phosphate buffer and 5 mL indicator reagent (DPD) was added to each flask of 100 mL of standard solution. Changing the color of solution into pink showed that the reaction is completed. Further oxidizing of DPD causes an unstable, colorless imine compound. A 1 mL portion of the flask's solution was transferred into the polymeric photometer cell to measure absorption. In this medium, the reaction of DPD with trace amounts of chlorine in neutral pH, generates a semi-quinoid cationic compound known as Würster dye. This free radical makes the solution coloured with a maximum absorbance at wavelength of 550 nm. Blank solution was prepared in the same way that standard solutions were made, but without presence of any chlorine. For this purpose, a mixture of 5 mL of phosphate buffer and 5 mL of indicator reagent (DPD) were added to a flask containing 100 mL of distilled water and mixed. Then 1 mL portion of the flask's solution was transferred into the polymeric photometer cell to correct the baseline.

#### 2.5. Determination of nitrite

Determination of nitrite was made under acidic conditions based on diazotization reaction (Fig. 2). An aliquot of 100 mL sample solution was placed in a flask and 2 mL of sulphanilamide

(4-aminobenzenesulphonamide) was added to form a diazo compound. After 5 min, 2 mL of N-(1-naphthyl)-ethylenediamine dihydrochloride solution was added ( $\text{pH} = 1.5$ ). After 10 min, the absorbance was measured at 543 nm against the blank solution which was prepared in the same manner [28].

### 3. Results and discussion

In this study, determination of chlorine and nitrite in environmental and tap water samples was performed by smartphone based spectrophotometer and results were compared to commercial kits. In order to validate the method, results were compared to those obtained by a standard method, using a bench top commercial spectrophotometer. Standard methods were SM 4500-Cl G and 4500-NO<sub>2</sub> B For chlorine and nitrite, respectively [29]. To obtain quantitative information, calibration curves for both fabricated and commercial spectrophotometers were constructed and values of their analytical figures of merit are presented in Table 1. As can be

**Table 1**  
Analytical figures of merit for determination of  $\text{NO}_2^-$  and  $\text{Cl}_2$  by smartphone-based and commercial spectrophotometers.

Analytical feature	Smartphone-based SP <sup>a</sup>	Commercial SP
<b>Chlorine</b>		
Dynamic range of calibration curve ( $\text{mg.L}^{-1}$ )	1.00–4.00	1.00–4.00
LOD <sup>b</sup> ( $\text{mg.L}^{-1}$ )		$4.00 \times 10^{-2}$
RSD <sup>c</sup> , %	$5.00 \times 10^{-2}$ 8.75	6.54
<b>Nitrite</b>		
Dynamic range of calibration curve ( $\text{mg.L}^{-1}$ )	0.05–1.20	0.05–1.20
LOD ( $\text{mg.L}^{-1}$ )	$8.60 \times 10^{-3}$	$4.00 \times 10^{-3}$
RSD, %	8.75	1.95

<sup>a</sup> SP, spectrophotometer.

<sup>b</sup> LOD, was based on 3Sb/m criterion for 10 blank measurements.

<sup>c</sup> RSD, relative standard deviation, for 3 replicate measurements.

**Table 2**  
Analysis of chlorine in water samples using smartphone-based spectrophotometer (all concentrations are in mg.L<sup>-1</sup>).

Water sample	Spiked amount	Chlorine found	RSD (%), n = 3
Tap	0.00	0.15	2.35
	1.50	1.69	8.69
	2.00	2.21	3.42
	3.00	3.06	5.55
Spring	0.00	0.00	8.27
	1.50	1.52	8.75
	2.00	1.89	6.31
	3.00	2.94	4.54
River	0.00	0.00	4.39
	1.50	1.56	8.75
	2.00	2.11	7.95
	3.00	3.06	6.43
Well	0.00	0.00	3.61
	1.50	1.44	7.28
	2.00	1.94	6.18
	3.00	2.93	5.03
CRM <sup>a</sup>	0.00	1.06	7.44

<sup>a</sup> Original concentration 1.10 mg L<sup>-1</sup>.

seen, LODs attained for both spectrophotometers are within the same order; though, lower reproducibility was obtained for smartphone-based spectrophotometer. This is mainly due to low resolution power of dispersing element and hence formation of fade optical images on the phone's camera.

### 3.1. Analysis of real water samples

In order to evaluate performance of the developed method while real samples need to be analyzed in the environment, spectrophotometer was taken to the field and analyses were performed. All samples were also analyzed using standard methods applying commercial spectrophotometer. *F*-test and paired *t*-test at confidence level of 95% showed no difference between the two instruments. The trueness of the methods was evaluated by analyzing

**Table 3**  
Analysis of nitrite in water samples using smartphone-based spectrophotometer (all concentrations are in mg.L<sup>-1</sup>).

Water sample	Spiked amount	Nitrite found	RSD (%), n = 3
Tap	0.00	0.00	5.98
	0.10	0.09	8.75
	0.40	0.42	5.81
	0.80	0.84	3.10
Spring	0.00	0.00	5.23
	0.10	0.17	8.52
	0.40	0.44	5.90
	0.80	0.86	3.68
River	0.00	0.02	3.02
	0.10	0.16	8.43
	0.40	0.31	6.97
	0.80	0.85	3.36
Well	0.00	0.30	4.37
	0.10	0.49	4.86
	0.40	0.81	5.21
	0.80	0.92	8.49
CRM <sup>a</sup>	0.00	0.23	6.57

<sup>a</sup> Original concentration 0.20 mg L<sup>-1</sup>.

standard environmental spike mix with certified chlorine and nitrite concentrations. Results are summarized in Tables 2 and 3. It is evident that the measured values are in good agreement with the certified reference material.

## 4. Conclusions

In this study, a simple, handheld, lens-free and portable smartphone-based spectrophotometer was designed and used to determine chlorine and nitrite ions in water samples directly in the field. No power supply is needed for measurements and the body is water/shock proof. Detection limits achieved for chlorine and nitrite were  $5.00 \times 10^{-2}$  mg L<sup>-1</sup> and  $8.60 \times 10^{-3}$  mg L<sup>-1</sup> respectively, which are quite below recommended values. This light-weight spectrometer can be fabricated in minutes and can be used for many times with high precision. In comparison to a commercial instrument, readouts of this device showed the same or better analytical features. Ease of operation and portability of this promising analytical tool, capable everyone to use it in a wide field of applications. The superiority of smartphone-based spectrophotometer to detection devices of commercial kits (often colorimeters) is obviously its lower price and possibility of applying it many times. While nitrite and chlorine kits are not fully quantitative, our method can give more quantitative data. Besides, this portable device, coupled with smartphone, can be considered as an alternative detection system for commercial kits.

## Declaration of competing interest

The authors have declared no conflict of interest.

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