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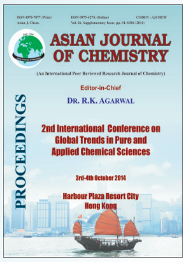

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Determination of Fe(II) in Drinking Water by Paper-Based Microfluidic Devices with Colorimetric Sensing

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A colorimetric method has been developed for determination of Fe(II) by paper-based microfluidic devices (µPADs). The analytical device is easily constructed using wax-printing on filter paper with was indicated that hydrophobic zone. Fe(II) was detected by the reaction of Fe(II) and 1,10-phenanthroline which the red/orange ferroin complex $[Fe(phen)_3]^{2+}$ was formed. Under the optimum conditions, the linear range between the color intensity and the concentration were found to be 0.1-3.5 and 3.5-15 mg L^{-1}, but with a different slope. The limits of detection were obtained at the concentrations as low as 0.07 mg L^{-1}. The proposed method can be successfully applied to the determination of Fe(II) in drinking water sample. The recoveries were in the range 86.60-109.80 %. The present procedure provides rapid, sensitive and selective for detection of Fe(II), minimal reagent consumption, low cost, thus it is suitable for on-site environmental monitoring.

Keywords: Paper-based microfluidic devices, Colorimetric method, Drinking water.

INTRODUCTION

The heavy metals contamination in the environment has still been a serious problem because of non-biodegradability. Drinking water and various food chains are polluted with toxic metals. These could affect humans *via* food, drinking water and air. For example, both deficiency and excess of iron can influence a variety of diseases. Ministry of Health in Thailand has set a limited value for iron in drinking water at 0.3 mg L^{-1}. Therefore, the highly sensitive method for the determination of heavy metals trace is required[1-3].

Several different techniques are available for determining heavy metals. The standard spectroscopic techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES)[4] and inductively coupled plasma-mass spectrometry (ICP-MS) have been used as typical methods. Although these methods provide highly sensitive, but they are sophisticated, time-consuming, high-cost operations that require complicated non-portable equipment and are, consequently, not suitable for field monitoring. Paper-based devices which have now received significant attention are a new alternative technology for point-of-care diagnostic devices. There are several advantages of using paper-based device as a platform for diagnosis. For instance, they are inexpensive analytical devices. They are easy to use, transportable, portable and disposable. Moreover, they can be applied for the quantitative analysis[5-10].

This kind of paper-based device, which can be used for colorimetric assays, uses a simple fabrication method that creates a hydrophobic wall containing and/or directing a fluid analyte into the detection zone. To create large-volume and moderate-resolution paper-based devices, the wax screen-printing is a kind of method which is specifically interesting procedure. In order to improve the accuracy and sensitivity of the method, a camera phone or scanner can be applied. The image is captured and transferred to a computer. Then the color is interpreted using imaging software where a pixel value is related to the concentration of the analyte[11-14].

The aim of this study was to develop a method for determination of Fe(II) using paper-based microfluidic devices with colorimetric sensing. It was successfully applied for determination of Fe(II) in drinking water.

EXPERIMENTAL

All chemical used in experiment were analytical reagent (AR) grade and solutions were prepared using deionized water (DI water). Sodium acetate trihydrate (Fluka Chemika, Switzerland), concentrated acetic acid (analytical grade, 100 %, Merck, Germany) and 3 M HCl solution were used to make the 0.1 M acetate buffers of the desired pH. Hydroxylamine and 1,10-phenanthroline were used as reagent solutions for colorimetric detection. $FeCl_3\cdot6H_2O$, $FeSO_4\cdot7H_2O$, $CoCl_2\cdot6H_2O$, $MnSO_4\cdot H_2O$, $Zn(NO_3)_2$, $CrCl_3\cdot6H_2O$ and $Pb(NO_3)$, were used for interference studies. In order to prevent metal contamination, laboratory glassware was kept overnight in a 10 % (v/v) nitric acid solution prepared by dilution of concentrated nitric acid (Merck, Germany) and rinsed with deionized water prior to use. Working standard of metal ions was prepared daily by appropriate dilution of stock solutions with acetate buffer pH 4.5.

Preparation of the paper devices: Paper-based devices were made from filter paper (Whatman No. 1, 125 cm diameter) having hydrophobic walls constructed in specific patterns. In the system used herein, the pattern was designed with Adobe Illustrator software (Adobe Systems, Inc.) and the block screen was fabricated by local shop (Nakhon Si Thammarat, Thailand). The paper devices were comprised of 14 pieces per one sheet of filter paper, each has a detection zone radius of 0.25 cm. To fabricate the hydrophobic walls, solid wax (purchased from a local stationery store) was rubbed through the finely perforated screen onto the filter paper, after which the printed wax was melted on a hot plate at 75 ºC for 30 s to allow the wax to be absorbed into the paper. When cooled to room temperature, this absorbed wax formed the hydrophobic barrier within the paper (Fig. 1)[15].

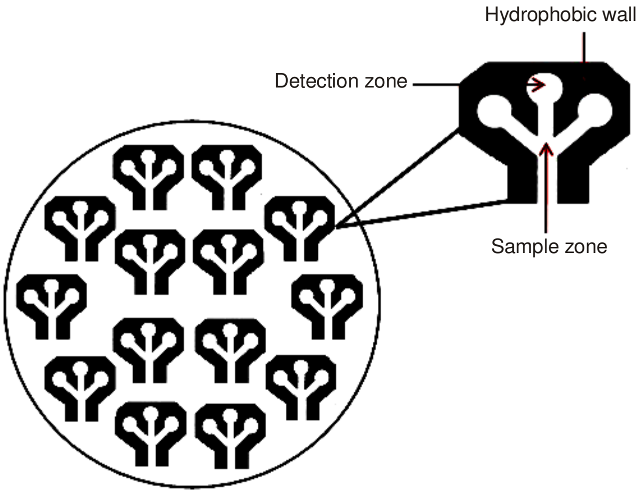

Fig. 1. A fabrication device by wax printing on Whatman No. 1 filter paper (125 cm diameter). The paper devices were comprised of 14 pieces per one sheet of filter paper

Detection of Fe(II) on the paper devices: An acetate buffer for Fe(II) assay was prepared with sodium acetate trihydrate and glacial acetic acid at pH 4.5. Both 1,10-phenanthroline (8 mg mL^{-1}) and hydroxylamine (0.1 g mL^{-1}) were prepared as separate solutions, each in the acetate buffer. Paper-based microfluidic devices (µPADs) were also prepared for Fe(II) detection. The detection zone of µPADs was spotted with two 0.5 µL aliquots of hydroxylamine and allowed dry. Aliquot (1 µL) of standard or sample was added in the detection zone in triplicate. After that, 10 µL of 1,10-phenanthroline was added to central of devices, the color was changed. The color of the test zones on µPADs was captured by a scanner and then, the color intensities were analyzed using ImageJ software in gray mode. The device was allowed to dry completely between each addition. The interference of this procedure was investigated by comparing the signal intensities obtained for six other metal ions, Cr(II), Co(II), Al(III), Zn(II), Pb(II) and Mn(II).

To evaluate the applicability of this proposed method, the Fe(II) in drinking water was quantified. Drinking water sample was obtained from drinking water dispenser in the region of Nakhon Si Thammarat Rajabhat University. 15 mL of sample was mixed with 10 mL of 0.1 M HNO_3 and then heated to evaporated excess water until 2.5 mL of samples remained. Finally, adjust volume and pH with acetate buffer. The proopsed paper-based method was validated by determinig Fe(II) with UV-visible absorption spectrometer at 510 nm.

RESULTS AND DISCUSSION

Characterization of $[Fe(phen)_3]^{2+}$: UV-visible spectrometer was used for the study as characterization of $[Fe(phen)_3]^{2+}$. After adding hydroxylamine and 1,10-phenanthroline in standard solution of iron, the wavelength of the $[Fe(phen)_3]^{2+}$ complex was shown at 510 nm.

Colorimetric detection of Fe(II): Colorimetric assays for detection of Fe(II) was determined through detection of the red/orange ferroin complex $[Fe(phen)_3]^{2+}$ formed by the reaction of Fe(II) and 1,10-phenanthroline[16,19]. The presence of hydroxylamine on the device helps the decrease of Fe(III) to Fe(II) and hydroxylamine also acts as a masking agent by complexing possible interfering metals Ni(II), Zn(II), Cd(II) and Co(II). The reagents volumes were optimized under the highest color intensity. In the previous research, Fe(II) was detected by the µPADs when add hydroxylamine to the detection zone, followed by 1,10-phenanthroline in the detection zone. Also, the standard or sample solution was added in sample reservoir. For this work, we found that reagent did not flow to the detection zone and the reaction did not occur on the detection zone. After changing the procedure as follow, the standard or sample was added in the detection zone while 1,10-phenanthroline was in sample reservoir[17]. The intense color was observed in the detection zone.

Effect of sample pH: The pH of solution has effect on the ability of the reaction between 1,10-phenanthroline and sample solution. Therefore, the influence of the sample pH was evaluated from pH 3.5 to 5.5 by adjusting the pH of metal ion solutions with 0.1 M acetate buffer, which was in the pH range of acetate buffer (pH 3.7-5.6). The intensity of Fe(II) was maximal in the range of pH 3.5-4.5 and reached a minimal level at pH 5.5. Thus, we used the sample solution at pH 4.5 as the highest intensity.

Interferences study: Cr(III), Co(II), Al(III), Zn(II), Pb(II) and Mn(II) are likely to be present in the studied samples. The presently selected method was evaluated by investigating as the concentration ratio of the desired analyte [Fe(II) ions] to the potential interference one. The analytical responses of a solution containing only Fe(II) were compared with the addition of the potential interfering ions at various concentration ratios. Compared to the response recovery of the analyte alone[18], the defined interference was shown when 10 % or more of a negative or positive change was seen. Each of 10-fold or higher excess of Cr(III), Co(II), Al(III), Zn(II), Pb(II) and Mn(II) ions had no significant affect on the color intensity signals of Fe(II) and did not interfere (Fig. 2). Moreover, the other metal ions did not alter color when added the complexing agent (1,10-phenanthroline). Only Fe(II) was complexed with 1,10-phenanthroline while the other metal ions did not. Hence, the developed method was selected for detection of Fe(II).

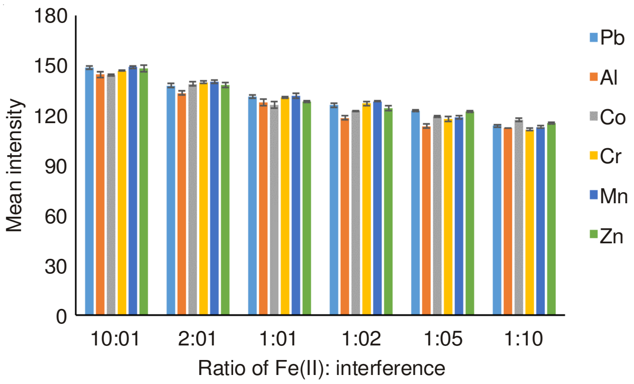

Fig. 2. Study of selectivity of Fe(II) with interfering ions, Cr(III), Co(II), Al(III), Zn(II), Pb(II) and Mn(II)

Analytical characteristics: Under the optimized conditions, the calibration curve for the determination of Fe(II) was shown in Fig. 3a and b. The linear range between the colour intensity and the concentration were found to be 0.1-3.5 mg L^{-1} ($R^2 = 0.9968$) and 3.5-15 mg L^{-1} ($R^2 = 0.9954$), but with a different slope, which suggests the high sensitivity of the proposed method. The calibration cuves of low concentration have higher sensitivity than high concentation. The limits of detection were obtained at the concentrations as low as 0.07 mg L^{-1} by naked eyes. The limits of quantitative were obtained at 0.1 mg L^{-1}. The relative standard deviations (% RSD) of three concentrations which were 0.3, 5.5 and 15 mg L^{-1}, (n = 10), were 1.06, 1.04 and 0.62 %, respectively. The low % RSD indicated that the developed method high precision. 0.3 mg/L is the maximum allowable levels of Fe(II) in drinking water which has been defined by the Pollution Control Department, Thailand. These results clearly show the ability to visually discriminate and the device should therefore be useful for determining in drinking water. Hence, our paper devices are an interesting, low cost and portable point-of-measurement (POM).

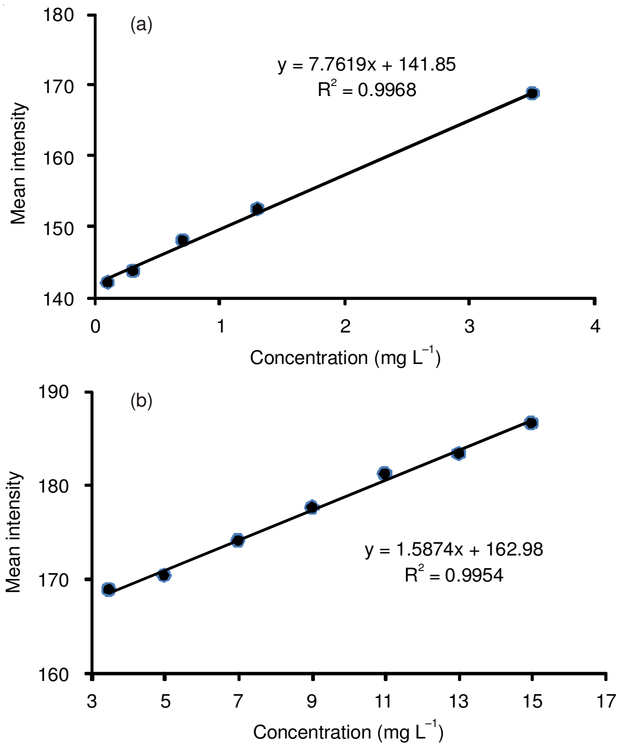

Fig. 3. Linear concentration ranges of Fe(II) in solution containing 0.1-15 mg L^{-1} under the optimized, (a) The calibration cuves of low concentration and (b) the calibration cuves of low concentration

Analytical application: The developed method was applied to the determination of Fe(II) in drinking water by standard addition method, spiked with 0.5 and 3 mg L^{-1}. The recoveries were in a range of 86.6 to 109.8 %, which are acceptable under all conditions. We compared the developed method with the standard UV-visible spectrometry method on the same samples. No significant difference between the two methods was found at the 95 % confidence interval (*t-critical* = 3.182). This suggests that this proposed method is more sensitive, reliable and acceptable under all conditions. Experimental results show that the proposed method can be successfully applied to the determination of Fe(II) in drinking water sample as shown in Table-1.

TABLE-1
DETERMINATION OF Fe(II) IN DRINKING WATER SAMPLES

Samples	Spiked level (mg L^{-1})	Fe(II) found (mg L^{-1})		Recovery of Fe(II) (%)	
		Propose method	UV-visible	Propose method	UV-visible
Drinking water	0.00	ND	ND	ND	ND
	0.50	0.50 ± 0.38	0.43 ± 0.06	100.0	86.6
	3.00	3.07 ± 0.46	3.20 ± 0.28	102.3	109.8

ND = not detected

Lifetime of the devices: For practical use in developing countries, it is necessary for devices to remain stable for weeks. Hence, we studied the stability of devices after storing the prepared paper devices for 4 weeks. The reagent solutions were coated on paper devices and allowed dry before storage at a room temperature. The results were measured by the naked eyes and using a scanner and calculated the intensity that there is no significant difference from freshly prepared paper devices. The results were as shown in Fig. 4. Thus, the devices can be kept for 28 days (4 weeks) and the results have been corresponding with the previous research[17].

Conclusion

A colorimetric sensing method by paper-based microfluidic device was developed for determination of Fe(II). The paper-based microfluidic device is easily constructed using wax-printing and Fe(II) can easily detected with the naked eyes *via* the color change results after application of the test solution. Analytical signal was calculated with ImageJ software in gray mode. The proposed method provides a cost-efficient, environmental-friendly, convenient and highly sensitive quantification of Fe(II) ion concentrations. The persent work herein has been successfully used to determine Fe(II) in drinking water.

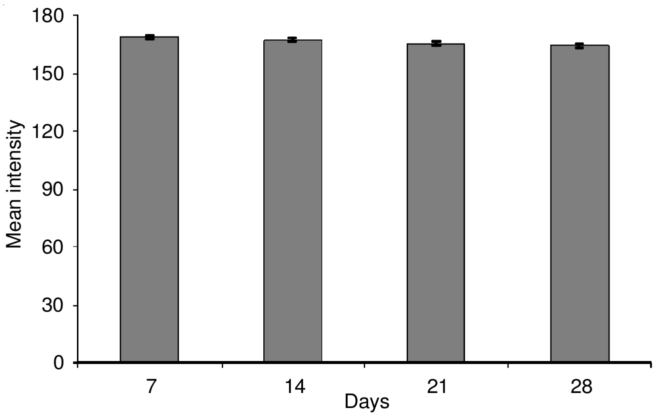

Fig. 4. Lifetime of the paper devices for 28 days (4 weeks). Data are shown as the mean ± SD and are derived from three replicates (n = 3)

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