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Naked-eye and Colorimetric Detection of Arsenic(III) Using Difluoroboron-curcumin in Aqueous and Resin Bead Support Systems

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This work presents a new colorimetric method that is simple, rapid and cost effective for the determination of arsenic(III) in water samples. The method is based on changes in the absorbance of difluoroboron-curcumin (BF_2-curcumin), prepared by the reaction of borontrifluoride diethyletherate ($(C_2H_5)_2OBF_3$) and curcumin. The BF_2-curcumin was dissolved in 60% ethanol, which yielded an orange solution with the maximum absorbance at 509 nm. Upon the addition of arsenic(III), the color of the BF_2-curcumin solution changed from orange to blue and the absorbance was measured by UV-visible spectrometry at 632 nm. The BF_2-curcumin was applicable in both solution and coated resin. Under the optimal conditions, the detection limits achieved by means of UV-visible spectrometry, naked-eye detection with BF_2-curcumin solution and naked-eye detection with BF_2-curcumin-coated resin were found to be 0.26, 25 and 30 μM, respectively.

Keywords Arsenic(III), difluoroboron-curcumin, colorimetry, naked-eye detection

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Introduction

One of the most serious forms of environmental pollution encountered today is metal contamination in water, which has numerous adverse effects on humans and animals. Arsenic (As) is a well-known semi-metal element and toxic chemical that is found in natural water and waste water discarded from various industries, *e.g.* pesticide production, metal and alloy manufacturing, wood treatments, and petroleum refining.[1] Arsenic can exist in four oxidation states, –3, 0, +3 and +5, and these arsenic compounds can be found in rock, soil, water and even air. In water, arsenic mostly appears as oxyanions in both organic and inorganic forms.[2-4] The two inorganic forms of arsenic, arsenite or As(III) and arsenate or As(V), are very toxic and can result many adverse health effects such as dermatitis, skin cancer, lung, liver and renal cancers or may cause mutagenic effects.[4,5] Due to the extreme toxicity of arsenic, the quantitative monitoring and control of arsenic in waste water from industry is very important. The Pollution Control Department of Thailand has regulated the quantity of arsenic in waste water at the maximum allowed concentration of 0.25 mg/L.[6]

The most commonly used techniques for arsenic determination in water are based on spectroscopy, chromatography and electrochemistry, such as hydride generation atomic absorption spectrometry (HG-AAS),[7] graphite furnace atomic absorption spectrometry (GFAAS),[8] inductively coupled plasma optical emission spectrometry (ICP-OES),[9] inductively coupled plasma mass spectrometry (ICP-MS),[10] cathodic stripping voltammetry (CSV)[11] and anodic stripping voltammetry (ASV).[12] Although these methods are sensitive and accurate for the determination of trace amounts of arsenic, they require costly instruments and extensive skills to operate.[13-15]

Colorimetric detection is an alternative and attractive method. This method has been recently proposed for the determination of arsenic in aqueous solutions because the technique is relatively simple and economical, yet effective without the need of sophisticated instruments.

Most of the colorimetric methods for the determination of arsenic require the formation of volatile arsine gas (AsH_3) prior to the measurement. These methods include the Gutzeit's test,[16,17] the Marsh's test,[18] and the formation of silver diethyldithiocarbamate complex.[19,20] However, the major drawbacks of these methods are the toxicity of arsine gas and its complicated preparation. Therefore, much research has been conducted on the colorimetric detection of arsenic by using a solution system that does not involve the formation of arsine gas, such as those employing molybdenum blue,[21] Rhodamine-B,[22] and modified gold nanoparticles.[23-25] In addition, some researchers have developed this method into a solid system, for example, molybdenum loaded resin.[26] The main advantage of the solid system is easier handling, which makes it much more convenient than using a liquid system.

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Moreover, a simple detection for As(III) can be useful for on-site analysis and arsenic monitoring.

Recently, Chaicham *et al.*[27] reported the synthesis and properties of difluoroboron-curcumin (BF_2-curcumin) (Fig. S1, Supporting Information) by the addition of borondifluoride on the carbonyl group of curcumin from the extracts of turmeric. In the presence of cyanide, the color of this BF_2-curcumin solution changed from red to blue, which can be described by the basicity of the anions that can abstract protons from the hydroxyl groups in the BF_2-curcumin molecule.

Based on this approach, As(III) is also a conjugated base of arsenous acid with a low acid dissociation constant (K_a) and so is believed to potentially behave like the hydrocyanic acid under similar conditions. Therefore, this work aims to develop a new colorimetric method that is simple, rapid, low cost and applicable for field analysis for the determination of As(III) in water samples by BF_2-curcumin solution and BF_2-curcumin-coated resin.

Experimental

Instruments

UV-visible absorption spectra were recorded by an HP Hewlett Packard 8435 UV-visible spectrophotometer (Agilent Technologies, UK). Reflectance spectra of BF_2-curcumin-coated resin were obtained by a diffuse reflectance ultraviolet visible spectrophotometer (DR-UV-Vis), Model UV-2500PC (Shimadzu, Japan). The pH of all solutions was measured using a pH/mv meter, Model UltraBASIC-10 (Denver Instrument, USA). Photographs were taken with a Lumix FZ 150 digital camera (Japan).

Materials and reagents

The stock solution of As(III) was prepared by dissolution of $NaAsO_2$ (BDH Chemicals, UK) in deionized water. The Amberlite XAD-2 resin beads (Supelco Analytical, USA) were stirred with deionized water for 24 h, and then filtered and washed with deionized water. The resin was dried at 100°C for 2 – 3 days in an oven. All other chemicals used in this work were analytical grade. All glassware were cleaned by soaking in 10% (v/v) HNO_3 overnight and followed by rinsing with deionized water before use.

Synthesis of the BF_2-curcumin and preparation of BF_2-curcumin-coated resin

BF_2-curcumin was synthesized by following the procedures of Chaicham *et al.*[27] Briefly, borontrifluoride diethyletherate ($(C_2H_5)_2OBF_3$) was added into a curcumin solution previously dissolved in methanol. The reaction was refluxed at 60°C for 2 h under a nitrogen atmosphere and then cooled down to room temperature. The BF_2-curcumin was obtained as a red solid that can be dissolved in 60% ethanol.

For the preparation of the BF_2-curcumin-coated resin, 2 grams of Amberlite XAD-2 resin bead was stirred with 25 mL of 50 μM BF_2-curcumin solution for 24 h. The BF_2-curcumin coated resin was filtered and washed with deionized water. The color of the coated resin clearly changed from white to orange, indicating the incorporation of BF_2-curcumin onto the beads. The coating of this resin was later confirmed by a diffuse reflectance ultraviolet visible spectrometer (DR-UV-Vis).

Naked-eye and colorimetric determination of As(III)

In the solution system, 30 μL of BF_2-curcumin in 60% ethanol was added into cuvettes followed by different volumes of 1000 mg/L As(III) stock solution. The solution was made up to 3 mL with 60% ethanol. After the addition of As(III), the color of the solution was visually observed and subsequently detected by a UV-visible spectrophotometer in the wavelength range of 350 – 800 nm.

In the solid system, 1 mL of As(III) standard solution in the concentration range of $0 - 5 \times 10^{-3}$ M, previously adjusted to pH 10 with 1 M NaOH, was brought into a microcentrifuge tube containing 20 mg of BF_2-curcumin-coated resin. The mixture was shaken for approximately 1 min and allowed to settle before visual inspection. The presence of As(III) in these solutions was visually determined by the color of the coated resin changing from orange to blue. The degree of color change on resin by As(III) standard solutions in the concentration range of 0, 3×10^{-5}, 1×10^{-4}, 5×10^{-4}, 1×10^{-3} and 5×10^{-3} M were used as a color calibration chart for the naked-eye detection of As(III). The residual concentration of As(III) in the solution was measured using an ICP-OES, Model iCAP 6500 Duo (Thermo Scientific, UK), in order to evaluate the reaction mechanism of BF_2-curcumin and As(III).

Optimization of parameters

The parameters including concentration of BF_2-curcuminin, pH of the As(III) solution, and sampling time were optimized. The concentration of the BF_2-curcumin solution was varied in a range of 10 – 70 μM. The pH of the As(III) solution was investigated in a range of pH 3 – 10. The pH of these solutions was adjusted by the addition of either 1 M HCl and/or 1 M NaOH. In addition, the sampling time was varied from 0 – 45 min.

Application in real samples

In the solution system, 200 μL of a bottled drinking water sample, spiked with As(III) in the concentration range of 10 – 75 μM (pH 8), was added into a cuvette containing 30 μL of 2 mM BF_2-curcumin in 60% ethanol and made up with 2.77 mL of 60% ethanol. Then this solution was shaken for 30 s and its absorbance was measured at 632 nm within 3 min. The recovery of As(III) in these spiked samples was determined.

In the solid system, 1 mL of a pond water sample spiked with As(III) in the concentration range of 0 to 1×10^{-3} M (pH 10) was loaded into a microcentrifuge tube containing 20 mg of BF_2-curcumin-coated resin. The mixture was shaken approximately 1 min and visually observed for the color change of the coated resin. The concentration of As(III) in this sample was evaluated by comparing with the color calibration chart of As(III) standard solutions.

Results and Discussion

As(III) detection in the solution system

Colorimetric method with BF_2-curcumin solution. The BF_2-curcumin solution in 60% ethanol displayed an orange solution with the maximum absorbance at 509 nm. In the presence of As(III), the color of this solution changed to blue, and the maximum absorbance shifted to a longer wavelength that can be measured by a UV-visible spectrometer at a wavelength of 632 nm (Fig. 1). This change of color can be ascribed to the change of the BF_2-curcumin molecular structure. The BF_2-curcumin consists of two methoxy phenol groups as electron donor parts conjugated to the difluoroboron enolate as the electron acceptor part (Fig. 1). As(III) in water is normally present as oxyanion, $H_2AsO_3^-$, with a relatively low acid dissociation constant ($pK_a = 9.2$);[2,28] therefore, it can presumably

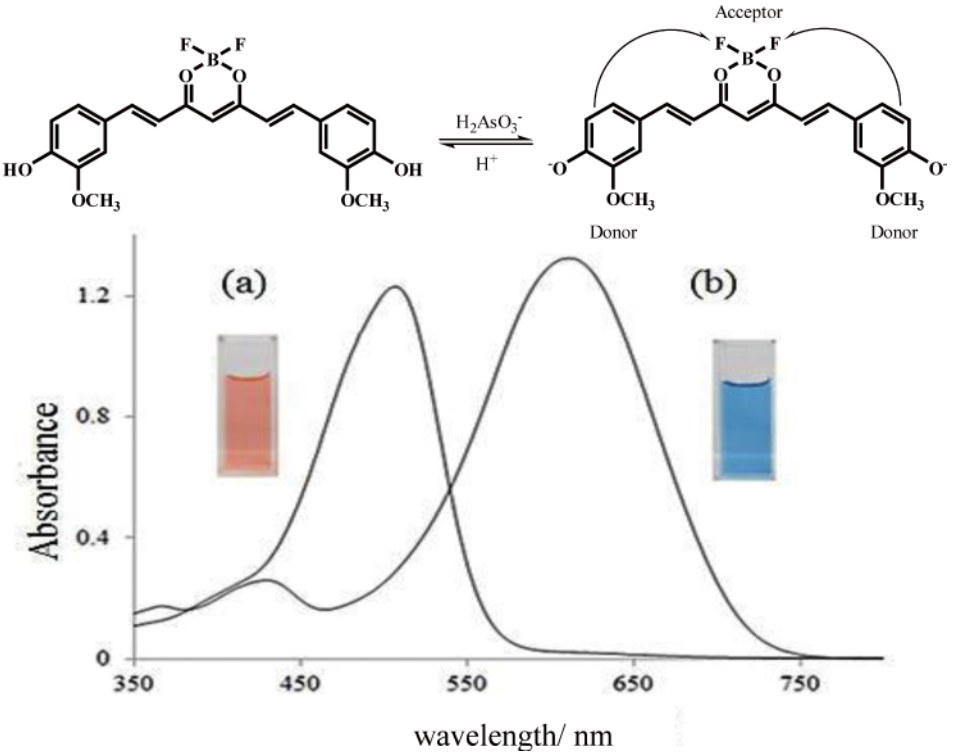

Fig. 1 The color change mechanism of BF_2-curcumin upon addition of As(III) and the UV-visible spectra of (a) BF_2-curcumin solution and (b) in the presence of 100 μM of As(III).

deprotonate the hydroxyl moiety of BF_2-curcumin molecule. The negative charges produced could then delocalize to the acceptor part resulting in the change of BF_2-curcumin color.

Effect of concentration of BF_2-curcumin. The concentration of BF_2-curcumin solution was varied in the range of 5 – 30 μM in the presence of different As(III) concentrations from 0 - 200 μM. When the concentration of BF_2-curcumin was lower than 20 μM, the absorbance at 632 nm increased with increasing concentration of As(III); however, the sensitivity was significantly low. On the other hand, the experiment using the concentration of BF_2-curcumin above 20 μM showed higher sensitivity yet the linear range was narrower. As the toxicity of As(III) can occur at relatively low levels, the sensitivity of the method was given priority over its quantitative range and thus a BF_2-curcumin concentration of 20 μM was chosen for all further experiments.

Effect of pH. The pH value of the As(III) solution was varied in the range of 3 – 10. At pH 3 – 7, the resulting color of the BF_2-curcumin solution with As(III) was still orange, while the color of this solution turned to purple or blue at pH 8 – 10 with the absorption maxima at around 632 nm. The BF_2-curcumin solutions without the addition of As(III) in the same pH range were also investigated for comparative purposes. It was found that the color of these solutions did not change at pH 3 – 8 but turned to red at pH 9 – 10. Hence, to avoid any color interference, pH 8 was deemed the most appropriate pH of the test solution for As(III) determination and was used throughout the following experiments.

Sampling time. After the addition of As(III) into the BF_2-curcumin solution, the color of the solution rapidly turned to blue and its absorbance was then measured at 632 nm. Nonetheless, after approximately 3 min the solution color gradually blanched and the absorbance slightly decreased. Based on this observation, the change of the solution color and its absorbance for the determination of As(III) by this method should be detected well within a reasonable time frame of roughly 3 min after adding As(III) to the BF_2-curcumin solution.

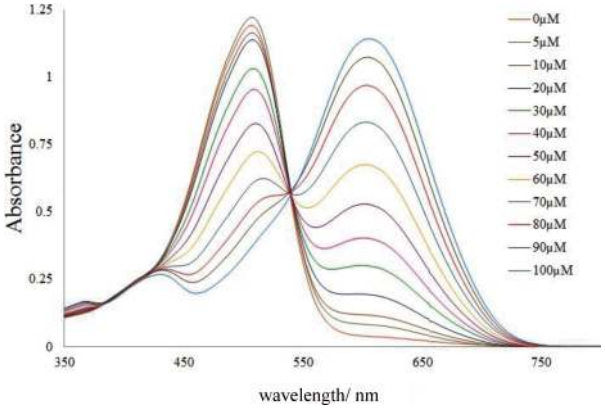

Fig. 2 The UV-visible spectra of BF_2-curcumin solution with varying concentrations of As(III) from 0 – 100 μM.

Linear range and detection limit of the method. Under the optimal condition, the UV-visible absorption spectra of BF_2-curcumin with varying concentrations of As(III) from 0 – 100 μM were obtained as shown in Fig. 2. The maximum absorbance of BF_2-curcumin at 509 nm decreased while the absorbance at 632 nm continually increased as the concentration of As(III) increased. The color of the solution remained unchanged as blue at concentrations of As(III) above 100 μM. It was presumed that the complete deprotonation of the BF_2-curcumin molecules in the solution was established and no significant change was attained afterward. Thus, the

Fig. 3 The color of BF_2-curcumin solution in various concentrations of As(III) solution between 0 and 100 μM As(III).

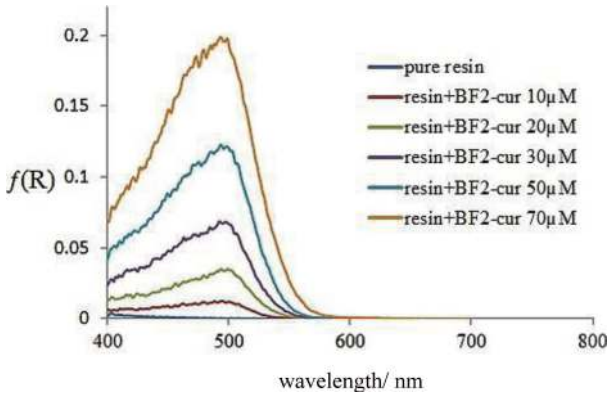

Fig. 4 DR-UV-Vis spectra of BF_2-curcumin-coated resin with various concentrations of BF_2-curcumin for the preparation of the coated resin.

concentrations of As(III) in the range of 2 – 100 μM were plotted as the calibration curve in Fig. S2 (Supporting Information). The linear response was clearly observed at two different concentration levels: the lower concentration level of 2 – 30 μM with the linear equation of $y = 0.0065x - 0.0002$ and $R^2 = 0.9954$, and the higher concentration level of 30 – 100 μM with the linear equation of $y = 0.0115x - 0.1638$ and $R^2 = 0.9972$, respectively. The limit of detection (LOD), based on 3 times the standard deviation of the blank signal, was estimated to be 0.26 μM (19.8 μg/L), with a relative standard deviation (RSD) of 2.0% ($n = 10$).

In terms of naked-eye detection with BF_2-curcumin, the 10 μM BF_2-curcumin solution was selected because its color can be clearly observed. The changes of solution color from orange to blue are correlated with different concentrations of As(III). The photographs of the solutions spiked with As(III) in various concentrations of 25 – 100 μM are shown in Fig. 3. The LOD, estimated by the lowest concentration that produce a minimum change of color that can be visually differentiated from that of the blank solution, was found to be 25 μM (1.87 mg/L).

As(III) detection in the solid system

C*olorimetric method with BF_2-curcumin coated resin.* Amberlite XAD-2 resin was selected as a support for the naked-eye detection in the solid phase because of its excellent physical and chemical properties.[29-32] The coating of this resin was confirmed by DR-UV-Vis spectrophotometer, and the result shows that the maximum absorbance of BF_2-curcumin on Amberlite XAD-2 resin at 498 nm constantly increased with the concentration of BF_2-curcumin (Fig. 4).

Fig. 5 The color of BF_2-curcumin-coated resin in the standard solutions containing different concentrations of As(III) of 0, 3×10^{-5}, 1×10^{-4}, 5×10^{-4}, 1×10^{-3} and 5×10^{-3} M, from left to right.

Effect of concentration of BF_2-curcumin for coating resin. The concentration of BF_2-curcumin solution was varied in the range of 10 – 70 μM in preparation of the coated resin. When the concentration of BF_2-curcumin increased, the color of resin changed from light orange to dark orange, which inevitably obscured the color for the naked-eye detection of As(III) on the coated resin. However, it was found that the BF_2-curcumin solution in the concentration of 50 μM exhibited a clear and distinct change of the resin color from orange to blue by the increase of As(III) concentration. Therefore, this concentration was chosen as optimal for the preparation of BF_2-curcumin-coated resin for the following experiments.

Effect of pH. The pH of the As(III) solution was investigated in the range of pH 3 – 10. The resulting color of coated resin in the As(III) solution was still orange at pH 3 – 9, while the color of the coated resin turned to blue at pH 10 and this could be clearly observed by the naked-eye. Under this condition, it was found that the color of these coated resins in a blank solution (deionized water) did not change. Therefore, pH 10 of the As(III) solution was chosen for further experiments.

Naked-eye detection and detection limit of the method. Under the optimal condition, *i.e.* 50 μM of BF_2-curcumin-coated resin and pH 10 of As(III) solution, the color of the resin changed progressively from orange to blue in correlation with the concentration of standard As(III) solution from 0 to 5×10^{-3} M (Fig. 5). After being evaluated by ICP-OES (data not shown), it was found that the residual As(III) concentration was similar to the initial As(III) concentration. Thus, the proposed reaction mechanism that the As(III) oxyanions only abstract protons from hydroxyl moiety in the BF_2-curcumin molecule on the coated resin was confirmed. It was also found that the LOD of As(III) was 3×10^{-5} M or 2.25 mg/L by the observation of the change of the resin color that can be differentiated with the naked-eye.

Regeneration of the BF_2-curcumin-coated resin. The used resin can be regenerated by the protonation of the BF_2-curcumin with 1 M HCl solution as indicated by the color of the resin that rapidly turns from blue to orange. After that, the resin was washed with deionized water before the next use. The regenerated resin can be used again for the determination of As(III) to show a normal color change from orange to blue. This suggested that the used resin can be regenerated and repeatedly used for naked-eye detection of As(III).

Application in real samples

In the solution system, commercial bottled drinking water was sampled for the determination of As(III) using this method. Because no As(III) was essentially contaminated in this sample,

Fig. 6 The color of the BF_2-curcumin-coated resin in the pond water sample spiked with As(III) in concentrations of 0, 3×10^{-5}, 5×10^{-4} and 1×10^{-3} M, from left to right.

the recovery of the spiked sample was employed to validate the accuracy of this method instead. The changes in color of the solutions were observed together with the absorbance monitored by a UV-visible spectrophotometer at 632 nm. The recoveries of the spiked samples containing 10, 25, 50 and 75 μM of As(III) were found to be 109.4 ± 0.1%, 101.8 ± 0.5%, 93.6 ± 1.3% and 89.4 ± 2.1% (n = 3), respectively.

In the solid system, this proposed method was applied to detect As(III) in Chulalongkorn University's pond water. The color of the BF_2-curcumin-coated resin did not change when it was initially attempted to analyze the pond water sample. This indicated that the As(III) concentration was lower than the LOD of this method. Therefore, the procedures were re-applied to the pond water samples spiked with As(III) in the concentration of 3×10^{-5}, 5×10^{-4} and 1×10^{-3} M, respectively. The photographs of BF_2-curcumin-coated resin applied with the spiked samples are shown in Fig. 6. The results demonstrated that the color of the coated resins obtained in this application were similar and in good agreement with those of the color calibration chart of As(III) standard solutions (Fig. 5). These results implied that this method can be applied for the determination As(III) in water samples by naked-eye detection.

Conclusions

This work presents a new colorimetric method for the determination of As(III) in water samples by using BF_2-curcumin in both the solution and solid phase. In the presence of As(III), the BF_2-curcumin was deprotonated leading to the shift of maximum wavelength of BF_2-curcumin from 509 to 632 nm, at which the UV-visible spectrophotometry can be carried out to determine the As(III) concentration. Furthermore, the color of the solution changing from orange to blue can be simply detected by visual observation. The detection limits of this method were 0.26, 25 and 30 μM for UV-visible spectrometry, naked-eye detection with BF_2-curcumin solution and naked-eye detection with BF_2-curcumin-coated resin, respectively. The advantages of this new colorimetric method are simple, rapid, low cost and applicable for naked-eye detection for the determination of As(III) in water samples.

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Supporting Information

Figure S1 illustrating the preparation of BF_2-curcumin and Fig. S2 showing the calibration curve of BF_2-curcumin solution with 2 – 100 μM As(III) obtained under optimal conditions are available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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