Difluoroboron-Curcumin Doped Starch Film and Digital Image Colorimetry for Semi-Quantitative Analysis of Arsenic

Aree CHOODUM,*† Vanida JIRAPATTANASOPHON,* Chanita BOONKANON,* Tarawee TAWEEKARN,* and Worawit WONGNIRAMAIKUL**

* Integrated Science and Technology Research Center, Faculty of Technology and Environment, Prince of Songkla University, Phuket Campus, Kathu, Phuket 83120 Thailand

** Research Program: The Development of Management System for Reduction and Control of Water Contamination and Distribution in Songkhla Lake Basin and the Western Coastline of the South of Thailand, Center for Excellence on Hazardous Substance Management (HSM), Bangkok 10330, Thailand

† To whom correspondence should be addressed.

E-mail: aree.c@phuket.psu.ac.th
Abstract

This work presents a novel, simple, rapid, and cost effective method for semi-quantitative analysis of arsenic (III) in water sample. The method was based on the digital image colorimetry (DIC) of difluoroboron-curcumin doped starch film (BF$_2$-cur-film) and arsenic ion in water. A red BF$_2$-cur-film (9.4 μm) was fabricated by entrapped difluoroboron-curcumin (BF$_2$-curcumin, particle size of 60-113 nm) in tapioca starch film. When the standard solution of arsenic (1 mL) was added into small plastic tube containing BF$_2$-cur-film on its inner lid, blue solution ($\lambda_{\text{max}}$ at 610 nm) was observed instead of orange color in blank solution ($\lambda_{\text{max}}$ at 495 nm). When BF$_2$-cur-film was used in conjunction with DIC, a wide linear range of 0-10 mgL$^{-1}$ with good linearity ($R^2 > 0.99$) was obtained from green channel with low detection limit of 0.04 mgL$^{-1}$. Moreover, good precision (0.9-1.2%RSD, n = 4 days) and accuracy (0.03% relative error) were also achieved.

**Keywords:** Arsenic (III), difluoroboron-curcumin, starch film, digital image colorimetry.
Introduction

Arsenic is one of the most concern contaminants in potable water throughout the world\textsuperscript{1-2} that could be generated from both natural sources and/or anthropogenic sources. Although arsenic can appear in four oxidation states (-3, 0, +3, +5) in environment, it mainly exists as inorganic arsenite (As(III)) and arsenate (As(V)) in water which poses high toxicity to human.\textsuperscript{3} Arsenic toxicity affects millions of people worldwide, especially for Bangladeshi people that arsenic levels in water in some area are up to 2500 µgL\textsuperscript{-1}.\textsuperscript{2, 4} This contamination level far exceed from the World Health Organization (WHO) maximum contamination limit (MCL) at 10 µgL\textsuperscript{-1}.\textsuperscript{1, 5} Chronic exposure to high concentrations of arsenic can cause severe health effects, e.g. dermatitis, various cancers, nervous system disorder.\textsuperscript{6} Due to its high toxicity, the quantitative analysis of arsenic is thus very important.

Various instrumental analysis methods have been reported for determination of arsenic, e.g. atomic absorption spectroscopy for both hydride generation (HG-AAS)\textsuperscript{7-8} and graphite furnace (GF-AAS)\textsuperscript{9}, inductively coupled plasma method coupled with optical emission spectrometry (ICP-OES)\textsuperscript{10} or mass spectrometry (ICP-MS).\textsuperscript{11} Although these methods are accurate and sensitive for determination of trace arsenic, they are bulky, expensive, and require experts to operate and maintenance.\textsuperscript{2, 12} These sophisticated methods are also difficult to apply for on-site determination. Colorimetric method has also been reported for determination of arsenic because it is simple, easy to use, cost effective, and provides effective results without the need of sophisticated instruments. Various colorimetric tests have been applied for arsenic detection, e.g. the Gutzeit’s test,\textsuperscript{2, 13-14} leucomalachite green dye,\textsuperscript{15} molybdenum blue test,\textsuperscript{16-17} difluoroboron-curcumin (BF\textsubscript{2}-curcumin),\textsuperscript{12} gold nanoparticle and Rhodamine-B test.\textsuperscript{18} The Gutzeit’s test requires the formation of toxic arsine gas and also provided unreliable results at low concentrations\textsuperscript{2}, while molybdenum blue test suffers from interfering by phosphate ion.\textsuperscript{17}
Due to the toxicity of leucomalachite green dye which has been reported to have mutagenic and carcinogenic effects and also toxic to aquatic organism as well as Rhodamine B that induces lipid peroxidation and cervical epithelial cells proliferation, BF$_2$-curcumin synthesized from curcumin is thus an attractive choice for colorimetric test of arsenic. However, these colorimetric tests usually require spectrophotometer for quantitative measurement, which can limit to on-site determination of arsenic.

Digital image colorimetry (DIC) is an attractive choice for semi-quantitative analysis of arsenic in water. It has been reported as an effective method for the rapid quantitative analysis of various analytes that extends various advantages of colorimetric method. The use of digital image technology can eliminate human color subjectivity, allow greater precision, and reduce the frequency of false positive and false negative. DIC has been reported for arsenic determination by coupling with Hach EZ test and silver nitrate test.

In this work, the difluoroboron-curcumin doped starch film (BF$_2$-cur-film) was successfully developed and used in coupled with digital image analysis for a simple and rapid semi-quantitative analysis of arsenic. The BF$_2$-cur-film was fabricated on the inner lid of small plastic tube, thus an aqueous sample could be directly added into the plastic tube for in-tube detection. These can eliminate the need to carry reagents and negates any associated risks of spillage, thus increasing the convenience of the method application.

**Experimental**

**Reagents and chemicals**

Sodium (meta) arsenite (NaAsO$_2$, > 90%) was purchased from Fluka Chemie AG (Buchs, Switzerland). Boron trifluoride diethyl etherate and curcumin (≥65%) were obtained from Sigma-Aldrich (Darmstadt, Germany). Tapioca starch (Erawan Brand, Cho Heng, Nakhon
Pathom, Thailand) was purchased from local supermarket in Phuket. Ethanol, methanol, hydrochloric acid, and sodium hydroxide were supplied by Merck (Darmstadt, Germany). Stock solution of standard arsenic (As(III)) was prepared by dissolving of NaAsO$_2$ in ultrapure water purified by a Water Purification System (Merck, Darmstadt, Germany). All standard solutions were freshly prepared by diluting the stock solution with ultrapure water to appropriate concentrations.

**Preparation and characterization of BF$_2$-cur-film**

BF$_2$-cur-film was fabricated by the entrapment of BF$_2$-curcumin within tapioca starch matrix. Starch solution was prepared by dispersing tapioca starch (0.10, 0.25, 0.50 and 0.75 g) in ultrapure water (10 mL). It was stirred and heated at 100°C until a clear viscous solution was obtained. The solution was then cooled down to room temperature before adding BF$_2$-curcumin solution.

BF$_2$-curcumin was synthesized by modified previous report. Curcumin (0.1 g) was dissolved in methanol (100 µL) before additional of borontrifluoride diethyletherate (60 µL). The mixture was sonicated at 60°C for 2 hours (350 W, 40 KHz, Powersonic 405, Korea) and then cool down to room temperature. The BF$_2$-curcumin that obtained as a red solid was then dissolved in 60% ethanol to various concentrations (0.5, 1, 2, 3, 4, and 5 mM) for optimization.

The mixture of starch and BF$_2$-curcumin solution was then prepared for fabrication of BF$_2$-cur-film. BF$_2$-curcumin solution (0.5, 1, 2, 3, 4, and 10 mM) at appropriate volume (0.25, 0.50, 1.0, and 1.5 mL) was mixed with the starch solution (2, 3, 4, and 5 mL) under stirred condition at room temperature. The mixture (50, 100, 150 and 200 µL) was then dropped on the inner lid of 1.5 mL centrifuge tube and incubated at appropriate temperature (60, 80, 100 and 120°C) and time (15, 20, 30, and 60 minutes). The centrifuge tubes containing the thin film on their inner lids were cooled down to room temperature, before they were immediately closed.
and stored in zip locked plastic bag in a desiccator for further use.

The functional groups of BF$_2$-curcumin and BF$_2$-cur-film were investigated using Fourier transform infrared spectrometry (FTIR; Bruker, Germany) with KBr pellet and ATR technique, respectively. The morphology of the film was investigated using a field emission scanning electron microscope (FESEM; FEI, Czech Republic).

**Colorimetric test of arsenic using BF$_2$-cur-film and quantification by DIC**

BF$_2$-cur-films fabricated under optimum conditions were used for colorimetric test of arsenic. One milliliter of arsenic standard solution (0 to 50 mgL$^{-1}$) was directly added into a centrifuge tube containing BF$_2$-cur-film on its inner lid and kept upside down for 3 minutes. The tube was then shaken and the color of the solution was observed. After that, the resultant color product was photographed for quantification of arsenic by DIC.

Influence of pH on colorimetric test was investigated by adjusting pH of arsenic standard solution from 1 to 14 using HCl or NaOH.$^{12}$ Tolerance limits of coexisting ions on determination of arsenic using BF$_2$-cur-film were investigated (<5% error, 10 mgL$^{-1}$).

For DIC, a custom-built photographic box (6.1×6.1×7.7 inch) modified from previous design$^{22}$ was used to eliminate any effects of environmental light. Three replicates were done for each arsenic concentration by placing the tubes at sample holders inside a custom-built photographic box. They were photographed for six times using the built-in digital camera of an iPhone 7 (12MP, backside illuminated CMOS, f/1.8 aperture, 1/17 s exposure time, ISO 50, no flash) with a fixed aperture setting. JPEG images (1.35 MB, 4032×3024 pixels) were saved to the iPhone’s memory before transfer to a computer for color analysis. The average intensities of red, green, and blue colors (RGB values) from 6 images of three replicates (18 values in total) at each arsenic concentration were investigated using a custom-built RGB analysis program.$^{21-23}$ Each average was used as a single data point to establish calibration curve.
Analytical performance and method validation

Analytical performance of BF$_2$-cur-film with DIC for quantification of arsenic was investigated including sensitivity, linearity, linear range. Accuracy is reported in terms of relative error (% RE) from quantifying control standard solution (3 mgL$^{-1}$), while precision is reported as % RSD. Intra-day precision was investigated by testing 12 films in one day (6 images each, n=72), and the experiments were repeated for four days (n=4) to determine the inter-day precision. The limit of detection (LOD) and limit of quantification (LOQ) were calculated, following the ICH harmonized tripartite guideline.\textsuperscript{26}

Analysis of real sample

BF$_2$-cur-film and DIC were applied for analysis of real sample. Six water samples were randomly collected by grab sampling from the abandoned tin mines (3 samples) and canal (3 samples) in Phuket, Thailand. All samples were adjusted to pH 9 before testing with BF$_2$-cur-film and quantified by DIC. The results from developed method were compared with those obtained from inductively coupled plasma-optical emission spectrophotometer (ICP-OES; PerkinElmer, USA).

Results and Discussion

Preparation and characterization of BF$_2$-cur-film

BF$_2$-cur-film was successfully fabricated by doping tapioca starch with BF$_2$-curcumin. Because the synthesized BF$_2$-curcumin was in the forms of a red solid, a red BF$_2$-cur-film was obtained (Fig.1a). When standard solution of As(III) was directly added into the plastic tube containing BF$_2$-cur-film, the blue product (Fig. 1b) was observed instead of orange solution with ultrapure water (Fig. 1c).
For optimization, the difference of RGB values from digital image of the blue product and blank ($|I_X-I_{X\text{Blank}}|$) was considered. When the amount of starch was increased from 0.10 to 0.25 g, the darker blue products were obtained by testing BF$_2$-cur-films with arsenic solution. The paler blue products were observed at 0.50 to 0.75 g due to increasing in the dense of the film and decreasing in a chance of BF$_2$-curcumin to be dissolved and reacted with arsenic ion in the solution. As the highest $|I_X-I_{X\text{Blank}}|$ was found at 0.25 g tapioca starch (S1), it was selected to prepare starch solution. The starch solution (1 mL) was then mixed with BF$_2$-curcumin solution (1 mL) to prepare BF$_2$-cur-film, but non-homogeneous mixture was obtained. Increasing in the volume of starch solution (2 to 5 mL) made BF$_2$-curcumin in the mixture dilute. This was resulted in paler blue product after testing the film with arsenic solution and decreased $|I_X-I_{X\text{Blank}}|$ (S2). Starch solution of 2.5% w/v for 2 mL was then chosen. When concentration of BF$_2$-curcumin solution was increased from 0.50 to 10 mM, darker orange film was obtained. The testing with arsenic solutions (10 mgL$^{-1}$) provided the blue products, if the concentration of BF$_2$-curcumin solution were in the range of 0.5 and 1 mM. No color change was observed at higher concentrations (3-5 mM) because of excess amount of BF$_2$-curcumin darken the blue product. BF$_2$-curcumin at 1 mM, which provided the highest $|I_X-I_{X\text{Blank}}|$ (S3), was therefore selected as optimum concentration. The volume of BF$_2$-curcumin solution was then varied (0.25 to 1.5 mL) and found that 1 mL provided the darkest blue products and the highest $|I_X-I_{X\text{Blank}}|$ (S4).

Therefore, the polymer mixture for preparation of BF$_2$-cur-film was prepared by mixing the starch solution (2.5% w/v) for 1 mL with 2 mL of 1 mM BF$_2$-curcumin solution. The mixture was then dropped on the inner lid of centrifuge tube to fabricate the BF$_2$-cur-film. Increasing volume of the mixture (50 to 100 µL) resulted in thicker film, and darker blue products were obtained from testing with arsenic solution. However, paler blue products were observed from the films of 150 and 200 µL. This was contributed to less ability of
BF$_2$-curcumin entrapped within thicker film to be reacted with arsenic ion in the solution. The mixture of 100 µL was then chosen to fabricate the BF$_2$-cur-film due to the highest |I$_X$-I$_{X\text{Blank}}$| (S5). This mixture can be casted as a film under optimum temperature of 80°C for 30 minutes. The fabrication of the optimized BF$_2$-cur-film for four lots in one day provided good precision of RGB values of the blue product (0.5 to 1.6%RSD), while 1.2 to 2.1%RSD were obtained from four lots of four days (n= 4 days). The films could be kept in zip locked plastic bag and stored at ambient conditions inside and outside desiccator for at least one month with 0.24 and 0.53% change compared to the day of preparation. When they were stored in refrigerator (4°C) and freezer (-18°C) for a month, 12.8% and 13.2% change were obtained.

Using these optimum conditions, BF$_2$-cur-film with the thickness ~9.4 µm was fabricated (Fig. 2a), while BF$_2$-curcumin particles with the size of 60-113 nm were homogeneously entrapped within tapioca starch film (Fig. 2b). FTIR spectrum of BF$_2$-cur-film (Fig. 3b) showed similar pattern as tapioca starch (Fig. 3a) rather than BF$_2$-curcumin (Fig. 3c) due to only 1 mM BF$_2$-curcumin was used to fabricate the film. All remarkable absorption peaks observed from the BF$_2$-cur-film spectrum were contributed to the vibration in tapioca starch, while only small absorption peaks from 1500 to 1600 nm were assigned to the vibration in BF$_2$-curcumin. These results were similar to previous report that BF$_2$-curcumin were loaded in zein. The large peaks at 3284 and 2925 cm$^{-1}$ were assigned to O-H and CH$_2$ symmetrical stretching, while the peaks from 1149 to 933 cm$^{-1}$ were contributed to the C-O vibrations in amylopectin.

**Colorimetric reaction of BF$_2$-cur-film**

Colorimetric reaction of BF$_2$-cur-film and As(III) was based on the change of BF$_2$-curcumin structure due to the deprotonation of an oxyaion of As(III), H$_2$AsO$_3^-$, on the hydroxyl group of BF$_2$-curcumin molecule. These made the color of the solution changed from orange to blue in the presence of As(III), and the higher concentrations caused the darker
blue products (Fig. 4). It was found that the maximum absorption of the blue product shifted to a longer wavelength from 495 nm (blank solution) to 610 nm (S6), which was corresponded to the report (509 to 632 nm\(^{12}\)).

The pH of the solution showed the influence on the formation of the blue complex (S7). When the pH of As(III) solution and blank were adjusted to 1 to 8, no color change were observed. The color of the blank solution remained orange when the pH was adjusted to 9, while the color of solution in the presence of As(III) was turned to blue. At the pH higher than 9, the color of both solutions were changed. The results from adjusting the pH using glycine/NaOH buffer in the range of pH 8 to 10 (S7-b) provided the same results with HCl/NaOH (S7-a) with %different in green intensity of the blue complex for 2.7%. The standard solution of arsenic and sample were thus adjusted to pH 9 before testing with BF\(_2\)-cur-film to eliminate the effect from pH.

**Digital image colorimetry of BF\(_2\)-cur-film**

Colorimetric products obtained from testing of As(III) solution with BF\(_2\)-cur-film were photographed and their digital images were analyzed using custom-built color analysis program in order to get RGB data. The relationships between RGB intensities (I\(_X\)) and concentration of arsenic were shown in Fig. 5a. The intensity of blue channel remained constant with increasing concentration of arsenic, while the intensities of green and red channels was decreased. When the concentration of As(III) was higher than 20 mgL\(^{-1}\), the RGB intensities of colorimetric products were constant. At low concentration (< 5mgL\(^{-1}\)), the intensity of red color was higher than green and blue, since the background red color from BF\(_2\)-cur-film darkened the blue color from arsenic product. The intensity of blue became the highest intensity at concentration higher than 5 mgL\(^{-1}\) due to the dominant color from blue complex.

Because orange color of the solution without the presence of arsenic and the color from
sample may affect to accuracy of quantitative analysis, relationships between RGB intensities with blank subtracted (|I_X - I_{XBlank}|) and concentration of arsenic were investigated (Fig. 5b). The higher concentrations of arsenic, the higher subtracted RGB values. The red channel showed higher subtracted intensity than green and blue, respectively.

It could be noticed that the relationships either I_X or |I_X - I_{XBlank}| had linear portions which can be used for quantitative analysis.

**Analytical performance and method validation**

Analytical performance of the BF_2-cur-film and DIC for quantitative analysis of As(III) were summarized in Table 1. The LOD from |I_G - I_{GBlank}| (0.04 mg L\(^{-1}\)) was lower than I_G (0.39 mg L\(^{-1}\)), however both of them were higher than the WHO maximum contamination limit (MCL) of arsenic in drinking water (10 µg L\(^{-1}\)).\(^5\) The LOD from |I_G - I_{GBlank}| and its LOQ (0.14 mg L\(^{-1}\)) were lower than the maximum allowance concentration of arsenic in waste water regulated by the Pollution Control Department of Thailand (0.25 mg L\(^{-1}\)).\(^3\) The accuracy in term of %RE on analyzing control sample (3 mg L\(^{-1}\)) and quantified by I_G and |I_G - I_{GBlank}| equations were 0.04% and 0.03%, respectively. The intra-day precision of 12 films was in the range from 0.8 to 2.1%RSD, while the inter-day precision from 12 films over four days was obtained in the range of 0.9 to 1.2%RSD.

**Influence of coexisting ions**

The influence of coexisting ions on detection of arsenic was investigated by addition of various ions in As(III) solution (10 mg L\(^{-1}\)) before testing by BF_2-cur-film. Tolerable concentration of coexisting ions that changes the response of arsenic <5% are shown in Table 2. It showed that the presence of most coexisting ions could affect to the determination of arsenic at concentration ratio higher than 100, while Pb^{2+} and Zn^{2+} would affect at the ratio of 50.
**Real sample analysis**

The developed method, *i.e.* BF$_2$-cur-film and DIC, was applied for analysis of real sample in comparison with standard method (ICP-OES). No arsenic contamination was found in all samples for both developed method and the ICP-OES (LOD=0.012 mgL$^{-1}$, LOQ=0.039 mgL$^{-1}$). The recoveries from spiked real samples (5 mgL$^{-1}$) in the range of 88.5 to 101.2% were obtained (S8).

**Conclusions**

BF$_2$-cur-film based on the entrapped of difluoroboron-curcumin within tapioca starch film showed good selectivity for arsenic at pH 9 with high tolerance limit on various coexisting ions. It can be precisely prepared under optimum conditions even different lot and can be kept at ambient condition for at least a month with the change <0.53%. The developed film could be used in conjunction with digital image colorimetry for quantitative analysis of arsenic in water sample with good recovery (88.5 to 101.2%). Both $I_G$ and $|I_G-I_{GBlank}|$ relationships can be used for quantification of arsenic, but $|I_G-I_{GBlank}|$ provided lower LOD and LOQ. The developed method can be applied for quantification of arsenic in waste water and potable water in highly contaminated area. The method facilitates a simple and rapid on-site quantitative analysis of arsenic.

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Supporting Information

Results for optimization step and recovery obtained from spiked real samples. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

S1: Amount of starch (0.1 to 0.75 g) in 10 mL ultrapure water (3 mL starch solution: 1 mL 1mM BF$_2$-curcumin; casting at 80°C for 30 min).

S2: Volume of starch solution (2 to 5 mL): 1 mL 1mM BF$_2$-curcumin (0.25% w/v starch solution; casting at 80°C for 30 min).

S3: Concentration of BF$_2$-curcumin solution (0.5 to 10 mM; 3mL 2.5% w/v starch solution: 1 mL BF$_2$-curcumin; casting at 80°C for 30 min).

S4: Volume of 1 mM BF$_2$-curcumin solution (0.25 to 1.5 mL; 3mL 2.5% w/v starch solution; casting at 80°C for 30 min).

S5: Volume of the mixture (50 to 200 µL) (3mL 2.5% w/v starch solution: 1 mL 1mM BF$_2$-curcumin; casting at 80°C for 30 min).

S6: Absorption spectrums and chemical structures of orange solution (1 mM BF$_2$-curcumin) and blue product (As(III) 20 mgL$^{-1}$).

S7: Influence of pH on testing BF$_2$-cur-film with blank and As(III) solution (10 mgL$^{-1}$) adjusting pH using (a) HCl/NaOH (b) glycine/NaOH.

S8: Recovery obtained from spiked real samples (200 mL sample pH 9).

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Table 1  Analytical performance of BF2-cur-film and DIC for quantitative analysis of arsenic.

| Parameter      | \( I_G \) and concentration | \( \Delta I_G - \Delta I_G\text{Blank} \) and concentration |
|----------------|-------------------------------|----------------------------------------------------------|
| Equation       | \( y = -(2.75 \pm 0.08)x + (147 \pm 0.5) \) | \( y = (2.75 \pm 0.09)x + (35 \pm 0.6) \) |
| \( R^2 \)      | 0.9937                        | 0.9937                                                   |
| Linear range (mgL\(^{-1}\)) | 0-10                          | 0-10                                                     |
| LOD (mgL\(^{-1}\))      | 0.39                          | 0.04                                                     |
| LOQ (mgL\(^{-1}\))       | 1.43                          | 0.14                                                     |
Table 2  Tolerable concentration level of coexisting ions for arsenic detection (5 mgL<sup>-1</sup>).

| Ions             | Concentration (mgL<sup>-1</sup>) | % Change (I<sub>g</sub>) |
|------------------|-----------------------------------|--------------------------|
| Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> | 5000 | -1.7 to +3.4 |
| Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> | 1000 | -3.4 to +2.4 |
| Co<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, F<sup>-</sup> | 500 | +0.6 to +3.0 |
| Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> |                          |                          |
Figure Captions

Fig. 1  a, optimized BF$_2$-cur-film; b, color product of As(III) (1 mL, 20 mgL$^{-1}$ pH 9, reaction time 3 minutes); c, color product of blank.

Fig. 2  SEM images of optimized BF$_2$-cur-film.
   a, showing thickness of the films; b, showing particle sizes of BF$_2$-curcumin.

Fig. 3  FTIR spectrums using KBr pellet and ATR method.
   a, starch film; b, optimized BF$_2$-cur-film; c, BF$_2$-curcumin.

Fig. 4  Color products from testing optimized BF$_2$-cur-film with various As(III) concentrations (1 mL standard solution pH 9, reaction time 3 minutes).

Fig. 5  Relationships between concentration of arsenic and RGB values.
   a, RGB intensity (I$_X$); b, RGB intensities with blank subtracted (|I$_X$-I$_{XBlank}$|).
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a, starch film; b, optimized BF$_2$-cur-film; c, BF$_2$-curcumin.
Fig. 4  Color products from testing optimized BF₂-cur-film with various As(III) concentrations (1 mL standard solution pH 9, reaction time 3 minutes).
Fig. 5  Relationships between concentration of arsenic and RGB values.

a, RGB intensity ($I_X$); b, RGB intensities with blank subtracted ($|I_X - I_{X\text{Blank}}|$).
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