Difluoroboron Curcumin Complex: A Study on Determination of Acidity Constants and Quantitative Analysis of Arsenic(III)

Nguyen Quoc Thang[1], Tran Nguyen Minh An[1*], Le Thi Thanh Tran[2], Do Tam Nhan[3], Mai Ngoc Tan[4], and Le Van Tan[1]**

[1]*Faculty of Chemical Engineering, Industrial University of Ho Chi Minh City, Ho Chi Minh City, Vietnam*

[2]*Chemical and Environmental Science Department, Dalat University, Lam Dong Province, Vietnam*

[3]*Nuclear Research Institute, Lam Dong Province, Vietnam*

[4]*Faculty of Retraining and Continuing Education, Dak Nong Community College, Dak Nong Province, Vietnam*

Corresponding author:

email: trannguyenminhan@iuh.edu.vn[*]; levantan@iuh.edu.vn[**]

Received: June 24, 2021
Accepted: August 16, 2021

DOI: 10.22146/ijc.66990

Abstract: *In this study, the complex of difluoroboron curcumin (BF_2-Cur) has been synthesized and characterized via the combination of Boron trifluoride-diethyl etherate ($(C_2H_5)_2OBF_3$) and curcumin. However, the new dissociation constants, pK_{a1} and pK_{a2} of the BF_2-Cur complex, have been indicted by the values of 8.44 ± 0.16 and 9.76 ± 0.13, respectively. On the other hand, the reagent was also used to determine As(III) in aqueous solutions by UV–Vis spectrophotometry. As a result, the method was validated for accuracy, precision, linearity, and sensitivity, and the linear range was from 1.0 to 25.0 μmol/L, with the linear regression, A = 0.0027 C + 0.0106, correlation coefficient R^2 = 0.9969. Besides, the limit of detection (LoD) and limit of quantification (LoQ) were determined as 0.83 and 2.10 μmol/L, respectively. Thus, the developed method is successfully used for quantitative analysis of total arsenic in wastewater by reducing As(V) to As(III), then determining As(III) with high accuracy results.*

Keywords: *BF_2-Cur; total arsenic; UV-Vis spectrophotometry; the conformation of complex; UFF*

■ INTRODUCTION

Water is an essential component for maintaining life on earth. However, water quality declines seriously, and water contamination has become the most concerning global environmental issue. Polluted water includes many toxic components, such as organic and inorganic wastages [1-2], surfactants [3], synthetic dyes [4], and heavy metals [5]. Among various heavy metals found in this water, arsenic is determined as toxic metal, which has the most hazardous effects on living organisms. Once exposed to arsenic, various adverse health effects can be caused, including dermal changes and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic, and carcinogenic effects.

The mobility and toxicity of arsenic have been determined by its oxidation state [6]. The inorganic arsenic exists in four stable oxidation states of −3, 0, +3, and +5 [7]. Besides, the most prevalent forms found in aqueous solutions are the pentavalent arsenate ion, As(V), and the trivalent arsenite ion, As(III) [8]. The total arsenic analysis [As(III) + As(V)] is very crucial, and a reduction of As(V) to As(III) is required for correct analysis [9]. The analysis of arsenic is assessed to be essential because of its severe threats and risk to human health as arsenic-contaminated drinking water can be supplied through underground sources, especially in rural areas where another alternative water supply is not widely available. Various methods have been applied for determining the content of arsenic in water, such as ICP-OES [10], Electrothermal Atomic Absorption Spectrometry [11], VGA-AAS [10], AFS [12], ICP-AES [13], NAA [14], CA [15], and ASV [16].

On the other hand, curcumin is a natural polyphenol compound from the root of *Curcuma longa L.* (Zingiberaceae). It has many essential bioactivities reported in previous articles, including anti-inflammatory, anticancer, antioxidant, antivirus, and cytoprotective activities. Otherwise, it has been used to constitute complexes with metal ions, which have different properties than one free form of curcumin [17-18].

The synthetic strategies, structure identification, and medicinal applications of the metal complexes of curcumin have been studied [19-20]. Among these complexes, the difluoroboron curcumin (BF_2-Cur) complex has been widely used to analyze toxic environments. This complex is combined with digital image analysis for semi-quantitative analysis of arsenic [21]. Then, As(III) can be determined in water samples using UV-Visible spectrophotometry and naked-eye detection [22]. In fact, the BF_2-Cur has offered a remarkably promising ability of cyanide detection with 66-fold enhancement in aqueous media (CH_3CN/H_2O 4:1 v/v) [23], and it has been used as fluorophores to construct fluorescent probes, which were screened for their response to cyanide, hydrogen sulfide, hypochlorite, and bisulfite ion in aqueous solutions [24].

The difluoroboron-derivatized curcumins have been used as Near-Infrared Probes for *in vivo* detection of β-amyloid deposits [25]. Some of them have focused on the digital image colorimetry (DIC) of the difluoroboron-curcumin doped as starch film (BF_2-Cur-film) for the detection of As(III) in aqueous and resin beads. Its difluoroboron complex has been used as fluorophores to construct fluorescent probes with β-diketone or phenolic hydroxyl groups as recognition sites [26-28]. Because the variety of applications of the difluoroboron complex interested us, our research groups have been working on organic indicators. In this research, we not only conducted the novel dissociation constants, pK_{a1}, pK_{a2} of the BF_2-Cur, but also explored its feasibility in analyzing the total amount of As in water via the oxidizing As(V) to As(III).

■ EXPERIMENTAL SECTION

Materials

The BF_2 and curcumin were purchased from Sigma Aldrich, Singapore, while other chemicals and solvents were purchased from Merck, Darmstadt, Germany. In this study, the chemicals were used in analytical grade; thus, they could be used without further purification.

Instrumentation

UV-Vis absorption spectra were recorded on UV-Vis Evolution 60, THERMO (USA), and the pH of solutions was detected using pH S220 Seven Compact, Ion-Mettler Toledo (USA). FT-IR spectrum was performed on Jasco 4700 (Japan). Besides, the NMR spectra were recorded on one Bruker Avance-500 MHz, external TMS, and the HR-MS was performed on a 6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1). In addition, Titration Equipment was tested on Metrohm, Model 888-Switzerland, and analysis balance (Minimum Display 0.1 mg-USA). Finally, the most stable conformation complex, BF_2-Cur, was calculated using the Avogadro package via UFF (Universal Force Field) method.

Procedure

Synthetic of BF_2-Cur complex

The BF_2-Cur was synthesized by following [22-23] and tested by TLC when the reaction was completed. The structures of the BF_2-Cur complex and the base forms of Cur-BF_2 with AsO_3^{3-} ion were analyzed by ^{1}H-NMR and HR-MS spectra. The base forms of complex Cur-BF_2 or Cur-BF_2 with Cur-BF_2 with AsO_3^{3-} ion were investigated by adding one mmol of Cur-BF_2 and two mmol of AsO_3^{3-} ion to 0.5 mL of the $(CD_3)_2C{=}O$, d_6 commercial deter solvent.

Determination of acidity constants for BF2-Cur complexes

First, 6.087×10^{-3} M of BF_2-Cur solution in ethanol and 10^{-3} M of NaOH solution were prepared. Then, the V_o volume of 2.5 mL of $6.087.10^{-3}$ M BF_2-Cur solution was titrated with 10^{-3} M of NaOH solution using a 798 MPT Titrino using a syringe pump. The titration (NaOH) was added to titrate (BF_2-Cur) in increments of 0.01 mL, with a pause of 7 sec. The pK_a values were calculated from the experimental based on data points [(V_i, pH_i) according to the Kostrowicki and Liwo algorithm [29-30]. The equation was as follows.

$$pK_a = pH - \log \frac{[Na^+] + [H^+] - [OH^-]}{C_{Curcumin-BF_2} - [Na^+] - [H^+] + [OH^-]}$$

whereas $[Na^+]$ = the amount of the NaOH solution added, $[H^+] = 10^{-pH}$, and $[OH^-] = 10^{14-pH}$. All measurements were conducted at T = 25 ± 1 °C.

Determination of the total content of arsenic in the water samples [28]

To analyze the total content in the sample, As(V) needed to be reduced to As(III), then the same analytical procedure was proceeded for As(III). The whole method to analyze the total As can be presented as follows.

(i) A sample of 50 mL wastewater was accurately pipetted into a flask of Soxhlet. Then, 5 mL purity H_2SO_4 and 5 mL of H_2O_2 were added to the wastewater. It was heated until a large quantity of white smoke (H_2SO_4) was released. The solutions were cooled to room temperature, and NaOH was used to adjust pH 7.5.

(ii) To reduce As(V) to As(III): About 50 mL of the sample was poured into a round-bottomed flask, and then it was added with 20 mL of hydrochloric acid and 4 mL of the potassium iodide (KI) in an ascorbic acid solution to the sample flask. The mixture was heated gently at 50 °C for 15 min. The solution was let cool down, transferred entirely to a 100 mL volumetric flask, and makeup to 100 mL with water. The final solution was used directly for the determination of total As.

(iii) 5 mL of the final solution was pipetted into a 25 mL flask, and then it was added with 10 mL of ethanol, 5 mL of BF_2-Cur, and diluted to 25 mL using ethanol. Blank and calibration solutions were prepared in a similar way to achieve the same final concentrations. After 30 min, these solutions were used directly for the determination of total As.

(iv) The determination of As(III) in the water samples. 20 mL of filtered water was placed into a volumetric flask of 25 mL, and then the indicator paper was used to adjust pH = 8, and the solution was filled up to 25 mL with distilled water to create the sample at pH = 8. Then, 5 mL of reagent BF_2-Cur 10 ppm was aspirated into 5 mL of the sample at pH = 8 in another 25 mL volumetric flask. Then ethanol was filled up to 25 mL and measured by UV-Vis spectrometry at 632 nm.

(v) On the other hand, a wastewater sample containing As(III) and As total were analyzed concurrently with the HPLC-ICP-MS method to compare the results.

■ RESULTS AND DISCUSSION

The Acidity Constants for BF_2-Cur Complexes

The pK_a values were calculated from the reaction of NaOH, which titrated the complex. The pK_a was calculated from the experimental data of points according to the Kostrowicki and Liwo algorithm, corresponding to ΔpH/ΔV–V curve. The ΔpH/ΔV–V curve has indicated that it has had two pH transitions at volume NaOH 3.20 mL and 6.15 mL and proved that the BF_2-Cur complex had a diprotic acid form. Based on the titration curve of the BF_2-Cur complex (presented in the form of weak acids), the values of pK_a were calculated.

The pK_{a1} and pK_{a2} of the standardized BF_2-curcumin complex in the ethanol and water mixed solvent system were 8.44 ± 0.16 and 9.76 ± 0.13, respectively. The complex acid was found to be dissociated to K_{a1} and K_{a2} in solutions. As shown in Fig. 4, the value of pK_{a1} was determined based on our calculation via titration and explained the resonance effects, the positive resonance, and +R of hydroxyphenyl of an aromatic ring. The resonance ring system made one hydrogen atom (left side) of the phenolic hydroxy group of A ring more flexible, as indicated in Fig. 4. Due to this reason, the deprotonation of the A ring occurred more quickly than the B ring. This positive resonance, +R, only appeared for the phenolic of A and without B ring.

These results are pretty consistent with the previous results of Margarita Bernabé-Pineda on curcumin [26]. This article reported the acetylacetone group and two groups of hydroxyl phenolic of curcumin structure, which corresponded to the values of pK_{a1} = 8.38 ± 0.04 pK_{a2} = 9.88 ± 0.02, and pK_{a3} = 10.51 ± 0.01, respectively, and they were performed in the Fortran program. The value of pK_{a1} in the article [26] was relative to an enol equivalent in base media, and our research did not explain based on this site. For the BF_2-Cur complex,

we determined the pK_{a1} and pKa_2 to be 8.44 ± 0.16 and 9.76 ± 0.13, respectively. The pK_{a1} and pK_{a2} values of the BF_2-Cur complex were compared to pK_{a2} and pK_{a3} of Cur in the article.

The results indicated that the Cur-BF_2 complex had more acidic than curcumin. It was explained that the solvate was formed from the hydrogen atoms of the solvent molecules such as ethanol and water and one negative B atom of Cur-BF_2, as seen in Fig. 4 [23]. That the protonations of positive hydrogens of the solvent molecules and EtOH formed around a negative boron atom led to the decrease of the negative electron density on it, supported the +R effect of phenolic hydroxy groups (EDG) at A ring in Fig. 4, and increased the acidic property of Cur-BF_2 complex.

BF_2-Cur: (^{1}H-NMR-acetone, d_6, 25 °C, TMS), δ (ppm): 8.67 (s, 2H, Ar-O<u>H</u>), 7.87 (d, *J* = 15.5 Hz, 2H, alkene proton, H-9, H-10), 7.46 (d, *J* = 1.9 Hz, 2H, Ar-H, H-6, H-6'), 7.34 (dd, *J* = 8.3, *J* = 1.9 Hz, 2H, H-2, H-2'), 6.93 (d, *J* = 15.6 Hz, 2H, alkene proton, H-7, H-8), 6.92 (d, *J* = 8.2 Hz, 2H, H-3, H-3'), 6.36 (s, 1H, H-11), 3.93 (s, 6H, $2OCH_3$). The 19 resonance proton signals were conformed via ^{1}H-NMR spectrum.

BF_2-Cur-AsO_3: (^{1}H-NMR-acetone, d_6, 25 °C, TMS), δ (ppm): 7.94 (d, *J* = 15.6 Hz, 2H, alkene proton, H-9, H-10), 7.46 (d, *J* = 1.8 Hz, 2H, Ar-H, H-6, H-6'), 7.34 (dd, *J* = 8.2, *J* = 1.8 Hz, 2H, H-2, H-2'), 6.93 (d, *J* = 8.2 Hz, 2H, H-3, H-3'), 6.92 (d, *J* = 15.6 Hz, 2H, alkene proton, H-7, H-8), 6.36 (s, 1H, H-11), 3.93 (s, 6H, $2OCH_3$). The 17 resonance proton signals were assigned via ^{1}H-NMR spectrum.

The NMR spectrum of complex BF_2-Cur indicated the resonances of 19 protons. As compared to the NMR spectra results in Fig. 1 and Fig. 2, the BF_2-Cur-AsO_3 complex had 2 protons of hydroxy phenolic reduced when two equivalent mols of base AsO_3^{3-} was added to the number of mol of Cur-BF_2. It was proved by two disappeared protons at 8.67 ppm in two NMR spectra, as shown in Fig. 2. The values of coupling constants of alkene protons (*J*, coupling constant of vinyl protons from 12–18 Hz, trans-isomer and 6-12 Hz, cis isomer) were calculated in the range of 15.5–15.6 Hz, which demonstrated the configuration of the complexes of Cur-BF_2, Cur-BF_2-AsO_3 with the conformation of trans and trans in 2 alkenyl groups [23,31].

The novel mechanism forming of pK_{a1} and pK_{a2} of

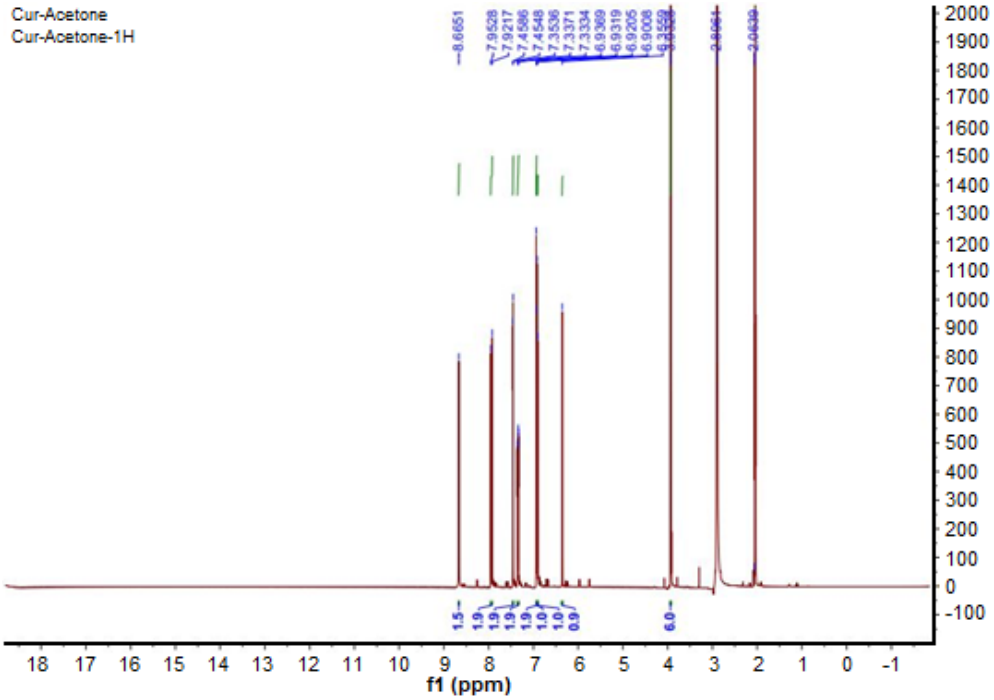

Fig 1. The ^{1}H-NMR, 500 MHz in acetone-d_6 of complexes the BF_2-Cur

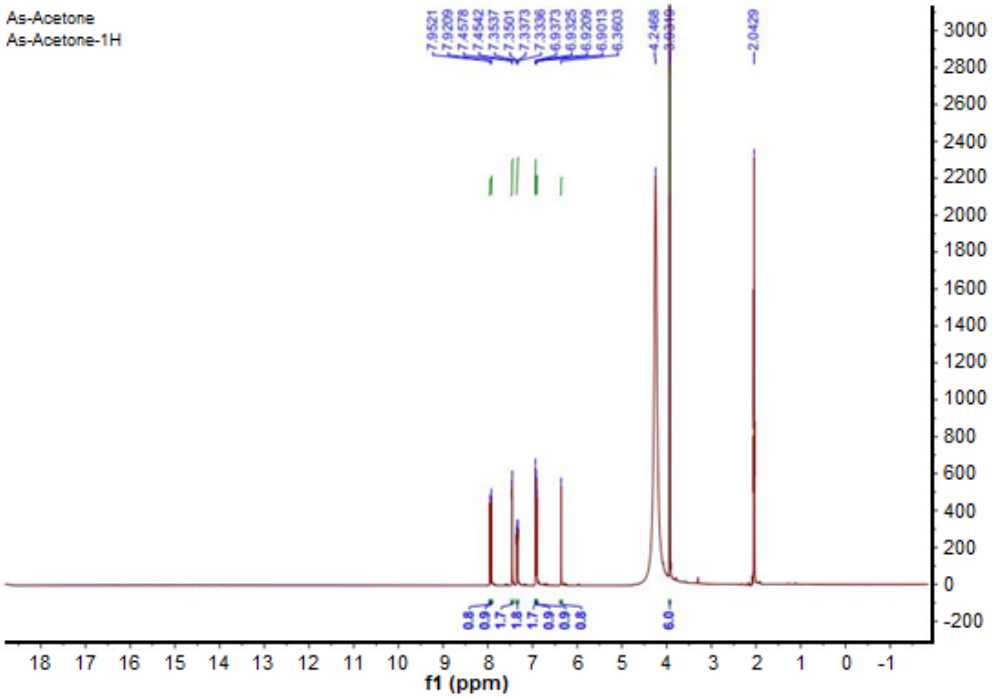

Fig 2. The ^{1}H-NMR, 500 MHz in acetone-d_6 of complexes the BF_2-Cur-AsO_3

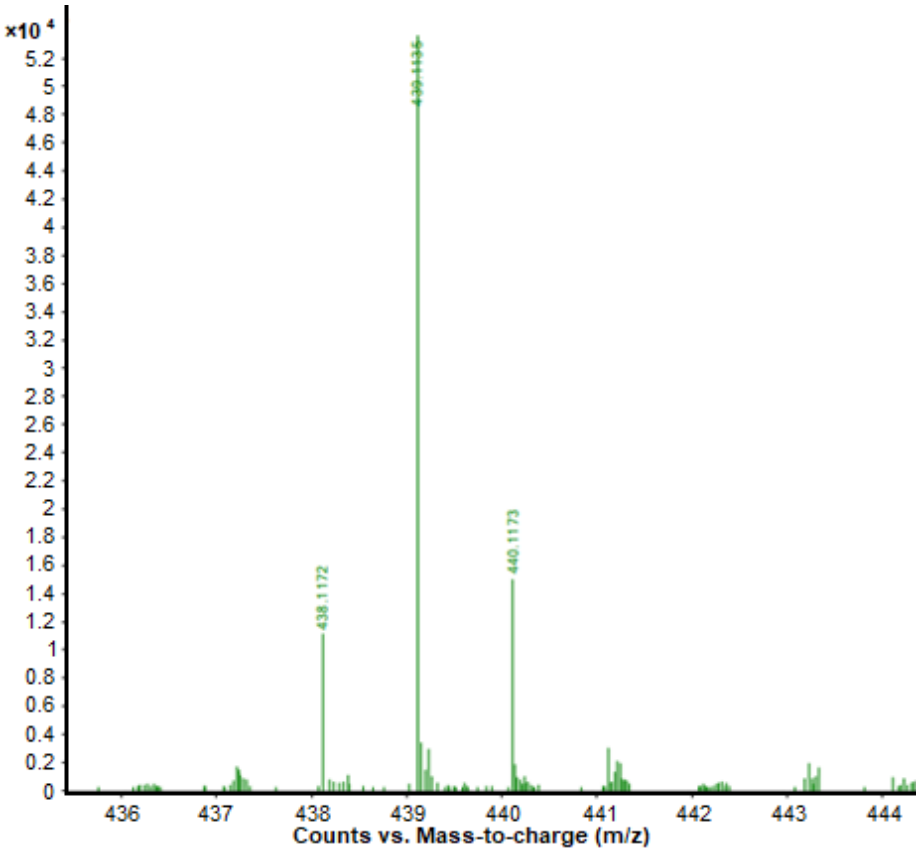

Fig 3. The HR-MS of BF_2-Cur-AsO_3

BF_2-Cur proposed by our research was based on the +R effect of one phenolic hydroxy bonding to A ring in Fig. 4. In Fig. 3, the HR-MS spectra (ESI) of BF_2-Cur-AsO_3 showed the experiment value of the positive molecule ion, m/z, which was 439.1135. This value corresponds to molecular ion, $[M+2H+Na]^+$. The calculation value was 439.1157 and confirmed that the molecular ion was $C_{21}H_{17}BF_2O_6^{3-}$ when two mols of AsO_3^{3-} added to the 1 mol BF_2-Cur complex solution.

As seen in Fig. 4, the phenolic hydroxy groups on the structure of the BF_2-Cur complex and resonance effects on this structure determined what hydroxyl groups were corresponding to K_{a1} and K_{a2}. The acid-base reactions between the complex BF_2-Cur with AsO_3^{3-} ion were proved by ^{1}H-NMR and HR-MS spectra and conformed the most stable conformation of BF_2-Cur BF_2-Cur-AsO_3 was confirmed via ^{1}H-NMR as seen in Fig. 1–3.

The configuration of the BF_2-Cur complex was calculated based on the UFF method via the Avogadro package in Fig. 5, and the optimal energy value of the most stable conformation of BF_2-Cur was 31.23 kJ mol^{-1} [32]. Fig. 5 shows the significant properties of the complex in calculation via Avogadro package exposed such angles as F_2BO_6, O_6BF_1, and F_1BO_5 of 109.56°, 109.52°, 109.25°, and 108.27°, respectively, formed a tetrahedral structure, $F_1F_2BO_5O_6$ (B atom in central tetrahedron). It was an irregular tetrahedral structure due to its different angles. Other angles were F_1BF_2 and O_5BO_6 in the values of 108.24° and 111.34°, respectively.

The angle O_5BO_6 was 111.84°, which was the biggest value because the oxygen atoms have lone pairs, which increased its angle. The angles of $C_{12}O_6B$ and $C_{10}O_6B$ were 123.11° and 124.57°, respectively, which indicated the $O_5C_{10}C_{11}C_{12}O$-B ring of complex BF_2-Cur has nearly a plane structure. This structure of the planned ring affects the acidic ability of complex BF_2-Cur via the +R effect of one phenolic hydroxy, which bounds to A ring. The bond length of O_1-H_1, one phenolic hydroxy bond, was longer than that of O_3-H_2, so that the hydro atom, H_1, was more flexible than H_2. The deprotonation on O_1-H_1 was easier than that of O_3-H_2. The bond lengths of B–O and B–F were equal. The bond lengths of C–O, single bond, and C=O, a double bond was different because the orders' values were also different. The photophysical and photochemical phenomena of BF_2-Cur in the presence of AsO_3^{3-} were assumed to undergo the deprotonation of phenolic hydroxyl groups by nitrile ion, AsO_3^{3-}.

The ^{1}H-NMR spectra showed strong evidence to support this assumption, as shown in Fig. 1–2. According to the ^{1}H-NMR spectra of BF_2-Cur and AsO_3^{3-}, the phenolic hydroxyl protons at 8.66 ppm, completely

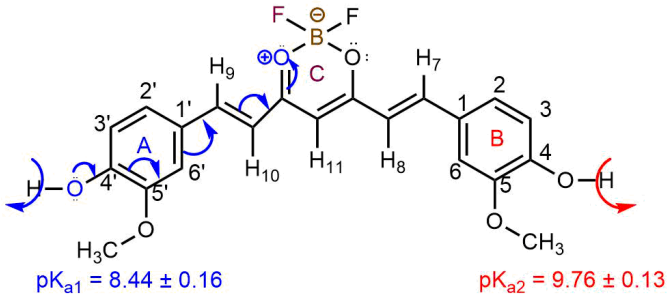

Fig 4. The resonance structure proposed of BF_2-Cur-AsO_3 complex

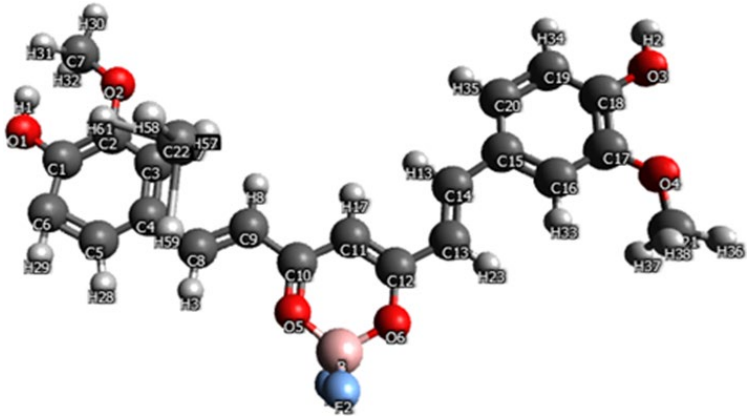

Fig 5. The configuration of Cur-BF_2 showed after completing the optimal calculation based on the UFF method

disappeared as shown in Fig. 1–2. As seen in Fig. 4, the protons of two phenolic hydroxy groups in the BF_2-Cur complex were shielded by the negative charge on the boron atom, which effectively removed hydrogen atoms from those hydroxyl groups. This deprotonation caused a high charge separation between acceptor and donor units in BF_2-Cur, excellent electron delocalization to BF_2 unit on the structure of the complex, BF_2-Cur. The excited states in the complexes were stabilized upon the binding of AsO_3^{3-}. The result is a bathochromic shift in the absorption band with Dl¼ 142 and 92.9 nm for BF_2-Cur and curcumin, respectively. Moreover, a new emission band at 750 nm for BF_2-Cur and AsO_3^{3-} was observed. A schematic illustration is shown in Fig. 2.

Qualitative Results of Total Arsenic

Method validation

The standard curve equation was obtained at the best conditions such as 632 nm, BF_2-Cur 60% in ethanol, and pH = 8 for As(III) analysis. According to the absorbance at 1–25 µM, the equation was y = 0.0027x + 0.0106, with R^2 = 0.9969.

Evaluation of As(III) analytical procedure

For As(III) analysis method applying the above-proposed procedure, it is necessary to define the limit of detection (LoD) and limit of quantitative (LoQ) and evaluate the accuracy through the evaluation of precision and trueness of this method. The LoD of As(III) by the analytical method was determined using a linear equation to calculate the theoretical concentration of As(III). Then,

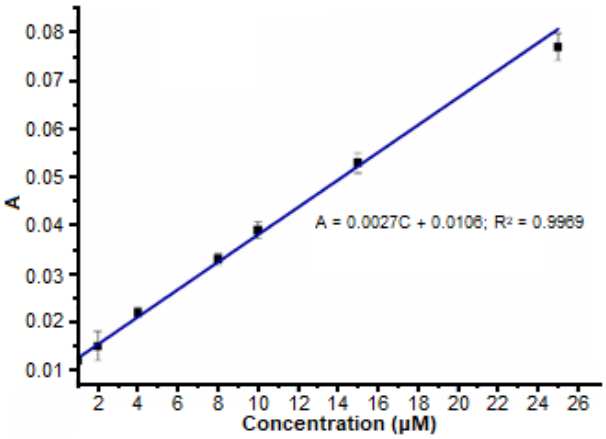

Fig 6. The linear range of As(III)

the mean, $\bar{x}_0$ and the standard deviation, SD_0, were calculated in the values of $\bar{x}_0$ = 0.2815, SD_0 = 0.1816, respectively. The values of LoD and LoQ were calculated by the expressions of $\bar{x}_0 + 3\ SD_0 = 0.83$ µM and LOQ = $\bar{x}_0 + 10\ SD_0 = 2.10$ µM for the blank sample, respectively.

Precision

The precision of the method was expressed quantitatively by the standard deviation. It was carried out through many analytical procedures with standard samples at the As(III) concentration of 30 µM, corresponding to 4.8 µM after dilution. The mean concentration of As(III), $\bar{x}$ = 29.7454 and SD = 0.2642 were determined. The relative standard deviation, RSD %, followed the expression of RSD% = $\frac{SD}{\bar{x}} \times 100\%$ = 0.89%. The relative standard deviation is within the allowable range when comparing the calculated value with the maximum acceptable repeatability table at different concentrations according to AOAC (Annex 11), so the method precision is satisfactory.

Trueness

The t standard can be used to evaluate the trueness of the method. The analytical results from 20 repeated experiments are used as the standard sample As(III) concentration of 30 µM above. The mean concentration of As(III) was $\bar{x}$ = 29.7454 and SD = 0.2642. From those results, the experimental t value, t_{tn} was calculated according to the expression, $t_{tn} = \frac{|\mu - \bar{x}|}{SD} = 0.967$, with k = 19, α = 0.95 and t_c = 2.093. Due to $t_{tn} < t_c$, there was no difference in the average value and the reference at the significant level α, so the method was satisfactorily true. The various proportions of the conditions to analyze the total As such as pH, equability time, the volume of BF_2-Cur solution, linear range, the limit of detection, the limit of quantification, reduced reagent, and precision (%RSD) were tested to establish the optimal conditions as shown in Table 1.

Determination the total content of arsenic in water samples

In this work, the experiments were measured three times, calculating the As(III) concentration in the samples from the calibration curve, y = 0.0027x + 0.0106,

Table 1. The optimum conditions to analyze total As

STT	Parameters	Optimal conditions
1	Absorbance wavelength	632 nm
2	pH	7.5–8.0
3	Solvent	Ethanol: H_2O (60:40, v/v)
4	Equabilities time	Until 70 min
5	Volume of BF_2-curcumin (12 mg/L)	4 mL
6	Linear range	1–25 µmol/L
7	Linear regression	A = 0.0027 C + 0.0106
8	Correlation coefficient (r^2)	0.9969
9	Limit of detection (LoD)	0.83 µmol/L
10	Limit of quantification (LoQ)	2.10 µmol/L
11	Reduce reagent	KI-ascorbic acid mixer
12	Precision (%RSD)	0.89%

Table 2. The content of As(III) and total As in water samples

As(III) (our research)	As(III) by HPLC-ICP-MS	Total As (our research)	Total As by HPLC-ICP-MS
37.96 µM	38.83 µM	45.06 µM	45.86 µM

and the As(III) concentration in the original sample from the formula $C_{As(III)\ original} = 6.25 \times C_{As(III)}$ measured. The average concentration of As(III) in the original sample was 37.96 µM, and the result of the HPLC-ICP-MS method for As(III) concentration was 38.93 µM. Total arsenic in wastewater by reducing As(V) to As(III) was 45.06 µM, and the result measured by the HPLC-ICP-MS method was 45.86 µM. These results are quite relevant and can be studied for practical applications (Table 2).

■ CONCLUSION

In this study, BF_2-Cur reagent was synthesized, the structure was featured, then the pK_{a1} and pK_{a2} values were determined. The results demonstrated the effectiveness of BF_2-Cur reagent in analysis. In addition, BF_2-Cur reagent can also be used as a specific and selective reagent to determine the concentration of As(III) and total arsenic content in a water sample by UV-Vis spectrophotometry. The BF_2-Cur complex can be synthesized easily in the lab and be studied for practical applications.

■ REFERENCES

[1] Saxena, G., and Bharagava, R.N., 2017, "Organic and Inorganic Pollutants in Industrial Wastes, Their Ecotoxicological Effects" in *Environmental Pollutants and Their Bioremediation Approaches*, 1st Ed., Eds. Bharagave, R.N., CRC Press, Boca Raton, Florida, US, 23–56.

[2] Li, H., Zhang, Q., Jiang, W., Collier, S., Sun, Y., and Zhang, Q., 2021, Characteristics and sources of water-soluble organic aerosol in a heavily polluted environment in Northern China, *Sci. Total Environ.*, 758, 143970.

[3] Hanif, N.M., Adnan, S.N.N., Latif, M.T., Zakaria, Z., Abdullahand, M.P., and Othman, M.R., 2012, The composition of surfactants in river water and its influence to the amount of surfactants in drinking water, *World Appl. Sci. J.*, 17 (8), 970–975.

[4] Lellis, B., Fávaro-Polonio, C.Z., Pamphile, J.A., and Polonio, J.C., 2019, Effects of textile dyes on health and the environment and bioremediation potential of living organisms, *Biotechnol. Res. Innovation*, 3 (2), 275–290.

[5] Ali, M.M., Ali, M.L., Islam, M.S., and Rahman, M.Z., 2016, Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh, *Environ. Nanotechnol. Monit. Manage.*, 5, 27–35.

[6] Shankar, S., Shanker, U., and Shikha, 2014, Arsenic contamination of groundwater: A review of

sources, prevalence, health risks, and strategies for mitigation, *Sci. World J.*, 2014, 304524.

[7] Flora, S.J.S., 2015, *Handbook of Arsenic Toxicology*, Academic Press, Oxford, UK.

[8] Mähler, J., Persson, I., and Herbert, R.B., 2013, Hydration of arsenic oxyacid species, *Dalton Trans.*, 42 (5), 1364–1377.

[9] Uddin, A.H., Khalid, R.S., Khan, U.A., and Abbas, S.A., 2013, Determination of arsenic content of available traditional medicines in Malaysia using hydride generation atomic absorption spectrometry, *Trop. J. Pharm. Res.*, 12 (6), 1053–1056.

[10] Paula, J.F.R., Froes-Silva, R.E.S., and Ciminelli, V.S.T., 2012, Arsenic determination in complex mining residues by ICP OES after ultrasonic extraction, *Microchem. J.*, 104, 12–16.

[11] Shahlaei, M., and Pourhossein, A., 2014, Determination of arsenic in drinking water samples by electrothermal atomic absorption spectrometry after preconcentration using the biomass of *Aspergillus niger* loaded on activated charcoal, *J. Chem.*, 2014, 912619.

[12] Musil, S., Matoušek, T., Currier, J.M., Stýblo, M., and Dědina, J., 2014, Speciation analysis of arsenic by selective hydride generation-cryotrapping-atomic fluorescence spectrometry with flame-in-gas-shield atomizer: Achieving extremely low detection limits with inexpensive instrumentation, *Anal. Chem.*, 86 (20), 10422–10428.

[13] Mutic, J.J., Manojlovic, D.D., Stankovic, D., and Lolic, A.D., 2011, Development of inductively coupled plasma atomic emission spectrometry for arsenic determination in wine, *Pol. J. Environ. Stud.*, 20 (1), 133–139.

[14] Paul, R.L., 2011, Evaluation of radiochemical neutron activation analysis methods for determination of arsenic in biological materials, *Anal. Chem.*, 83 (1), 152–156.

[15] Babar, N.U.A., Joya, K.S., Tayyab, M.A., Ashiq, M.N., and Sohail, M., 2019, Highly sensitive and selective detection of arsenic using electrogenerated nanotextured gold assemblage, *ACS Omega*, 4, 13645−13657.

[16] Gamboa, J.C.M., Cornejo, L., Acarapi, J., and Squella, J.A., 2013, Determination of arsenic (III) by differential pulse polarography in the waters of Camarones area, Chile, *J. Chil. Chem. Soc.*, 58 (4), 2031−2034.

[17] Ferrari, E., Asti, M., Benassi, R., Pignedoli, F., and Saladini, M., 2013, Metal binding ability of curcumin derivatives: a theoretical vs. experimental approach, *Dalton Trans.*, 42 (15), 5304–5313.

[18] Jiang, T., Zhi, X.L., Zhang, Y.H., Pan, L.F., and Zhou, P., 2012, Inhibitory effect of curcumin on the Al(III)-induced $A\beta_{42}$ aggregation and neurotoxicity in vitro, *Biochim. Biophys. Acta, Mol. Basis Dis.*, 1822 (8), 1207–1215.

[19] Pucci, D., Bellini, T., Crispini, A., D'Agnano, I., Liguori, P.F., Garcia-Orduña, P., Pirillo, S., Valentini, A., and Zanchetta, G., 2012, DNA binding and cytotoxicity of fluorescent curcumin-based Zn(II) complexes, *Med. Chem. Commun.*, 3 (4), 462–468.

[20] Meza-Morales, W., Estévez-Carmona, M.M., Alvarez-Ricardo, Y., Obregón-Mendoza, M.A., Cassani, J., Ramírez-Apan, M.T., Escobedo-Martínez, C., Soriano-García, M., Reynolds, W.F., and Enríquez, R.G., 2019, Full structural characterization of homoleptic complexes of diacetylcurcumin with Mg, Zn, Cu, and Mn: Cisplatin-level cytotoxicity in vitro with minimal acute toxicity in vivo, *Molecules*, 24 (8), 1598.

[21] Choodum, A., Jirapattanasophon, V., Boonkanon, C., Taweekarn, T., and Wongniramalkul, W., 2020, Difluoroboron-curcumin doped starch film and digital image colorimetry for semi-quantitative analysis of arsenic, *Anal. Sci.*, 36 (5), 577–582.

[22] Sirawatcharin, S., Saithongdee, A., Chaicham, A., Tomapatanaget, B., Imyim, A., and Praphairaksit, N., 2014, Naked-eye and colorimetric detection of arsenic(III) using difluoroboron-curcumin in aqueous and resin bead support systems, *Anal. Sci.*, 30 (12), 1129–1134.

[23] Chaicham, A., Kulchat, S., Tumcharern, G., Tuntulani, T., and Tomapatanaget, B., 2010, Synthesis, photophysical properties, and cyanide

detection in aqueous solution of BF_2-curcumin dyes, *Tetrahedron*, 66 (32), 6217–6223.

[24] Zhang, Y., Tu, L., Lu, L., Li, Y., Song, L., Qi, Q., Song, H., Li, Z., and Huang, W., 2020, Screening and application of boron difluoride complexes of curcumin as colorimetric and ratiometric fluorescent probes for bisulfite, *Anal. Methods*, 12 (11), 1514–1521.

[25] Ran, C., Xu, X., Raymond, S.B., Ferrara, B.J., Neal, K., Bacskai, B.J., Medarova, Z., and Moore, A., 2009, Design, synthesis, and testing of difluoroboron-derivatized curcumins as near-infrared probes for in vivo detection of Amyloid-β deposits, *J. Am. Chem. Soc.*, 131 (42), 15257–15261.

[26] Bernabé-Pineda, M., Ramírez-Silva, M.T., Romero-Romo, M., González-Vergara, E., and Rojas-Hernández, A., 2004, Determination of acidity constants of curcumin in aqueous solution and apparent rate constant of its decomposition, *Spectrochim. Acta, Part A*, 60 (5), 1091–1097.

[27] Baum, L., and Ng, A., 2004, Curcumin interaction with copper and iron suggests one possible mechanism of action in Alzheimer's disease animal models, *J. Alzheimer's Dis.*, 6 (4), 367–377.

[28] Behari, J.R., and Prakas, R., 2006, Determination of total arsenic content in water by atomic absorption spectroscopy (AAS) using vapour generation assembly (VGA), *Chemosphere*, 63 (1), 17–21.

[29] Klotz, E., Doyle, R., Gross, E., and Mattson, B., 2011, The equilibrium constant for bromothymol blue: A general chemistry laboratory experiment using spectroscopy, *J. Chem. Educ.*, 88 (5), 637–639.

[30] Zabihi, F., Kiani, F., Yaghobi, M., Shahidi, S.A., and Koohyar, F., 2020, The theoretical calculations and experimental measurements of acid dissociation constant and thermodynamic properties of glycyl-aspartic acid in aqueous solution at different temperatures, *J. Chil. Chem. Soc.*, 65 (2), 4759–4768.

[31] Laali, K.K., Greves, W.J., Correa-Smits, S.J., Zwarycz, A.T., Bunge, S.D., Borosky, G.L., Manna, A., Paulus, A., and Chanan-Khan, A., 2018, Novel fluorinated curcuminoids and their pyrazole and isoxazole derivatives: Synthesis, structural studies, computational/docking and *in-vitro* bioassay, *J. Fluorine Chem.*, 206, 82–98.

[32] Dubbeldam, D., Vreede, J., Vlugt, T.J.H., and Calero, S., 2019, Highlights of (bio-)chemical tools and visualization software for computational science, *Curr. Opin. Chem. Eng.*, 23, 1–13.