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A novel detection approach based on chromophore-decolorizing with free radical and application to photometric determination of copper with acid chrome dark blue

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Abstract

A novel detection approach named chromophore-decolorizing with free radicals is developed for determination of trace heavy metal. The hydroxyl radicals ($HO^{\bullet}$) generated from Fe(III) and hydrogen peroxide will oxidize the free chromophore into almost colorless products. The copper–acid chrome dark blue (ACDB) complexation was investigated at pH 5.07. In the presence of Fe(III) and hydrogen peroxide, the excess ACDB was decolorized in the Cu–ACDB reaction solution, and the final solution contained only one color compound, the Cu–ACDB complex. After oxidation of free hydroxyl radicals, the complexation becomes sensitive and selective and it has been used for the quantitation of trace amounts of Cu(II) dissolved in natural water. Beer's law is obeyed in the range from 0 to 0.500 $\mu g\,mL^{-1}$ Cu(II) and the limit of detection is only 6 $\mu g\,L^{-1}$ Cu(II). Besides, the Cu–ACDB complex formed was characterized.

Keywords: Chromophore-decolorizing; Hydroxyl radicals; Determination of copper; Acid chrome dark blue; Spectral correction technique; Spectrophotometry

1. Introduction

Copper is an essential trace element for the human body and contributes to important intracellular metabolic events [1,2]. Either an excess or a deficiency of copper can result in severe ailments to human [3]. Increases in copper concentration in waters and plants have resulted from industrial and domestic waste discharge, refineries, disposal of mining washing, and the use of copper as a base compound for antifouling paints [4]. In natural water, the majority of copper is bound to organic and inorganic ligands, leaving only around 1% of the total copper as dissolved state. Only the dissolved Cu(II) is essential as well as toxic [5]. Present concern about the level of copper in water is mainly related to its potential acute and chronic effect to human health [6]. Therefore, in order to understand the bioavailability or toxicity of copper in water, the sensitive and accurate detection methods are required [7].

Many analytical techniques have been developed for Cu(II) determination in water matrices, such as atomic absorption spectrometry [4], stripping potentiometry [8], stripping voltammetry [9], spectrofluorophotometry [10], electrochemiluminescence [11]. Except for the well-known advantages of these instrumental techniques, all of them cannot avoid the necessity of expensive instrumentation and sophisticated manipulation. For a long time, new photometric methods combined with derivative spectroscopy [12], flow injection [13], kinetic catalytic method [14] and light-absorption ratio variation [15] are reported increasingly and all of them have played important roles in improving the analytical sensitivity, selectivity and detection efficient [13,14]. In the present work, a new detection method named chromophore-decolorizing with free radicals (CDFR) was the first to be developed by using acid chrome dark blue (ACDB) chemically named 2-(2-hydroxyphenylazo)-1, 8-sdihydroxynaphthalene-3, 6-disulfonic acid as a chromogenic reagent to complex Cu(II) in the solution containing Fe ions and hydrogen peroxide. For analysis of natural water using the free radical reaction, Fe^{3+} was added because Fe(II) has a very short half-life in natural water, resulting from dissolved oxygen.

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Thus, Fe(III) in natural water can be utilized, too. Hydrogen peroxide is combined with Fe(III) as the Fenton reagent to generate the free radicals ($HO^{\bullet}$, $HOO^{\bullet}$) and to oxidize the excess azo chromophore from red to almost colorless [16] Thus, effect of the excess color reactant on the measurement of light-absorption of the Cu–ACDB complex was eliminated. Thus, the sensitivity and selectivity will be increased greatly. The mechanism of oxidization of ACDB is discussed and the Cu–ACDB complex characterized. Beer's law is obeyed between 0 and 0.500 μg mL^{-1} Cu(II) and the limit of detection (LOD) is only 6 ng mL^{-1} Cu(II). Most of the other metals hardly interfere the direct determination of Cu(II). The proposed method had been applied to determine Cu(II) dissolved in natural water with persuasion.

2. Principle and calculation

2.1. Chromophore-decolorizing with free radicals (CDFR)

Fenton and related reactions are potentially useful oxidation processes for destroying toxic organic compounds in water [17], where hydrogen peroxide is combined with Fe(II) or Fe(III) to generate hydroxyl radicals ($HO^{\bullet}$) as follows [18,19]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH$$

$$Fe^{3+} + {}^{\bullet}OOH \rightarrow Fe^{2+} + O_2 + H^{+}$$

$$Fe^{2+} + H_2O_2 + H^{+} \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O$$

The hydroxyl free radical ($HO^{\bullet}$) thus generated attacks the unsaturated dye molecules and the azo bond (N=N) in the chromogen, thus decolorizing [20]. Hydroxyl is a reactive, nonselective radical underlying the chemistry of many advanced oxidation processes (AOPs) for degrading toxic organic compounds in water. Recently there has been a renewed interest in the use of Fenton-type AOPs, which generate $HO^{\bullet}$ from hydrogen peroxide and an iron compound [21,22]. In fact, the reaction in iron-catalyzed oxidation of organic compounds by hydrogen peroxide is very complicated where the free radicals such as $HO^{\bullet}$, ${}^{\bullet}OOH$ will result in a lot of the free radical chain reactions [23]. It is well known that the Fenton reactions are often used in treatment of organic wastewater for example, degradation of synthetic textile dyes and other industrial dyestuffs of environmental relevance [24]. Little is known, however, about its extensive application to detection of heavy metal trace. As shown in Fig. 1, ACDB (1) is one kind of phenolazo derivatives. It can coordinate Cu(II) at pH 5.07 to form a pink complex (4). The excess ACDB (3) always exists in the reaction solution (2) and it is mixed together with the Cu–ACDB complex. Without doubt, the excess chromogenic reactant affects seriously the accurate measurement of light-absorption of the complex [25]. Fortunately, it can be oxidized into colorless or light colored ring-opened products in the presence of Fe(III) and hydrogen peroxide as described above. Thus, only one color compound, Cu–ACDB complex exists in the final solution (5). By directly measuring the light-absorption of such a solution, Cu(II) can be determined accurately and selectively. This method is named CDFR detection and it might play an important role in increasing the analytical sensitivity and selectivity for trace analysis.

2.2. Spectral correction technique [25]

As shown in Fig. 1, the Cu–ACDB complexation solution (2) is consisted of the excess ACDB (3) and the Cu–ACDB complex (4) whereas neither 3 nor 4 can be measured directly. Thus, from ordinary spectrometry it is difficult to read the light-absorption of the Cu–ACDB complex solution only (4). Fortunately, the spectral correction technique can exclude the interference of excess ACDB existing in such a solution. Thus, the real absorbance (A_c) of solution 4 and the other parameters can be calculated by following equations:

$$A_c = \frac{A_{\lambda 2} - \beta A_{\lambda 1}}{1 - \alpha\beta} \quad (1)$$

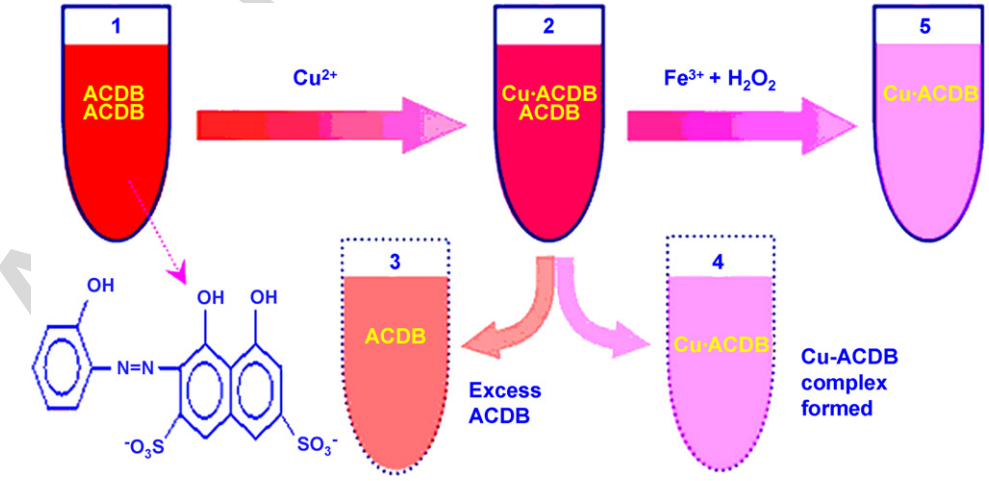

Fig. 1. Color change of the Cu–ACDB–Fe–H_2O_2 reaction solution: (1) ACDB solution; (2) Cu–ACDB complexation solution containing the excess ACDB (3) and Cu–ACDB complex (4), both (3) and (4) cannot be measured directly but their light-absorptions can be computed by the spectral correction technique. (5)-Only Cu–ACDB complex because Fe(III) and H_2O_2 oxidized the excess ACDB from red (3) into almost colorless.

where

$$\alpha = \frac{A_{\lambda 1}^{ML}}{A_{\lambda 2}^{ML}} \quad (2)$$

and

$$\beta = \frac{A_{\lambda 2}^{L}}{A_{\lambda 1}^{L}} \quad (3)$$

and

$$\gamma = \eta \times \frac{C_{L0}}{C_{M0}} \quad (4)$$

where

$$\eta = \frac{A_c - A_{\lambda 2}}{A_{\lambda 2}^{L}} + 1 \quad (5)$$

where both C_{M0} and C_{L0} are the initial concentrations of Cu and ACDB, η is the effective fraction of ACDB to complex Cu(II), and γ is the complexation number of ACDB with Cu(II). Both β and α are correction constants. $A_{\lambda 2}^{L}$ and $A_{\lambda 2}^{L}$ are the absorbances of the ACDB solution measured at λ_1 and λ_2 against water, $A_{\lambda 2}^{ML}$ and $A_{\lambda 2}^{ML}$ are the absorbances of only the Cu–ACDB complex solution measured at λ_1 and λ_2 against water, where the molarity of Cu(II) is much higher than that of ACDB. Both $A_{\lambda 2}$ and $A_{\lambda 1}$ are the read absorbances of the Cu–ACDB reaction solution, measured at λ_2 and λ_1 against water. From Eqs. (1), (4) and (5), A_c, γ and η can be calculated to characterize the Cu(II)–ACDB complex.

3. Experimental

3.1. Apparatus

The absorption spectra of the ACDB and its Cu(II) complex were recorded on a Model Lambda-25 spectrometer (Perkin-Elmer Instruments, Wellesley, USA) with UV WinLab software (Version 2.85.04). A Model Optima 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Instruments, USA) was used to determine Cu content in samples to examine the accuracy of the proposed method. A Model pHS-25 acidity meter (Shanghai Precise Science Instruments, Shanghai, China) was used to measure pH of the buffer solutions. A Model TS-030 thermostat water bath (Shanghai Yiheng S&T, China) was used to keep the reaction at a constant temperature.

3.2. Reagents and solutions

Two standard stock solutions containing 1000 mg L^{-1} Cu(II) (GSB07-1257-2000) and 1000 mg L^{-1} Fe(III) (GSB07-1264-2000), respectively, were purchased from the Institute for Reference Materials of SEPA, Beijing, China. Standard use solutions of 20.0 and 200 mg L^{-1} Cu(II) and 100 mg L^{-1} Fe(III) were prepared by diluting the above stock solutions. An ACDB solution, 0.100 mmol L^{-1} was prepared by dissolving 24.2 mg of ACDB (content: 80%, Shanghai Chemical Reagents) in 500 mL of deionized water and stored at less than 5 °C. Such a solution was used to complex Cu(II). Hydrogen peroxide (content: 30%, A. R. grade, Shanghai Chemical Reagents, Shanghai, China) was used to oxidize ACDB together with Fe(III). 0.100 mol L^{-1} ethylenediaminetetraacetic acid disodium (EDTA, A. R. grade, Shanghai Chemical Reagents) was prepared with deionized water and used to cease from the further oxidization. In addition, a series of acetate buffer solutions from pH 3.37 to 6.01 were prepared by mixing acetic acid (A. R. grade, Shanghai Chemical Reagents) and sodium acetate (A. R. grade, Shanghai Sihewei Chemicals) in deionized water. They were used to adjust pH of the solution, to optimize the complexation condition. Each of the solutions was measured accurately with the pH meter, and was kept in room temperature.

3.3. Procedures

3.3.1. Characterization of Cu(II)–ACDB complex

The characterization of Cu(II)–ACDB complex is mainly composed of two steps: measurement of α and β and calculation of A_c, η and γ. Firstly, into a series of 10 mL calibrated flasks were added Cu(II) from 0 to 100.0 μg. Afterwards, 1.00 mL of pH 5.07 buffer solution and 1.00 mL of 0.100 mmol L^{-1} ACDB were added, respectively. The solutions were then diluted to 10 mL with demonized water, and mixed well. The absorbances (A_{569nm} and A_{540nm}) of these solutions were measured at 569 and 540 nm against water. The absorbance ratio A_{569nm}/A_{540nm} of each solution was calculated. Thus, α can be worked out from Eq. (2). Secondly, into a series of 10 mL calibrated flasks were added 1.00 mL of pH 5.07 buffer solution and 0.100 mmol L^{-1} ACDB from 0.100 to 4.00 mL. The solutions were then diluted to 10 mL with deionized water, and mixed thoroughly. The absorbances (A_{569nm}^{0} and A_{540nm}^{0}) of these solutions were measured at 569 and 540 nm against water. Thus, β of each solution was calculated from Eq. (3). Then, 4.00 μg of Cu(II) was added into the solutions above. After mixing thoroughly, the absorbances (A_{569nm} and A_{540nm}) of these solutions were measured at 569 and 540 nm against water. The parameters, A_c, γ and η were calculated according to Eqs. (1), (4) and (5). Consequently, the Cu(II)–ACDB complex could be characterized.

3.3.2. Determination of copper in water

Usually, a clear water sample can be directly analyzed without any pretreatment. Turbid samples must be filtered by a membrane filter paper with pore size 0.45 μm. Thus, the sample was colored and then measured according to following procedures. Five millilitres of a sample solution above was added into a 10 mL calibrated flask. One millilitre of pH 5.07 buffer solution and 2.00 mL of 0.100 mmol L^{-1} ACDB were added. After reacting for 5 min, 20.0 μg of Fe(III) and 0.500 mL of hydrogen peroxide were added. The solution was then diluted to 10 mL with deionized water. After 10 min, 50.0 μL of 0.10 mol L^{-1} EDTA was added to cease from the decolorization of solution. The absorbance of the solution was measured at 540 nm against a reagent blank, and the amounts of Cu(II) in the water sample could be calculated.

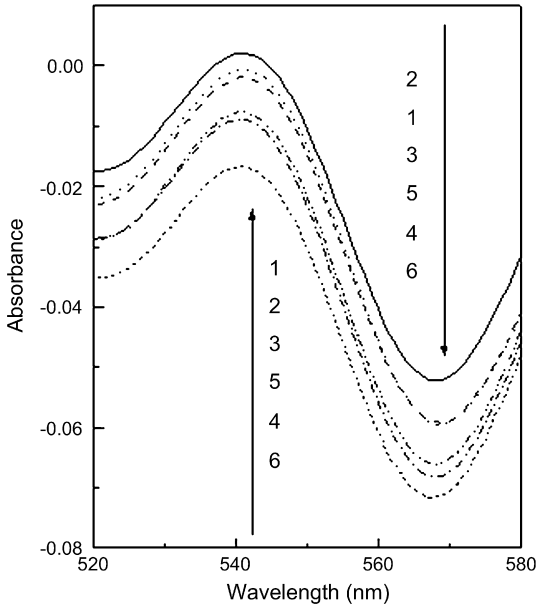

Fig. 2. Effect of pH on the absorption spectra of the Cu(II)–ACDB solutions containing 0.0200 mmol L^{-1} ACDB and 0.500 μg mL^{-1} Cu(II), measured against a reagent blank without Cu(II). From curve 1 to 6: pH 3.37, 3.95, 4.52, 5.07, 5.74 and 6.01.

4. Results and discussion

4.1. pH dependence of absorption spectra

The absorption spectra of the Cu(II)–ACDB solutions in various pH solutions are shown in Fig. 2. The reaction is sensitive between pH 3.37 and 6.01, but curve 4 shows a maximum peak-valley interval. This indicates that the complexation between Cu(II) and ACDB is the most sensitive at pH 5.07. Thus, pH 5.07 buffer solution was chosen in the present work. From curve 4, the peak is located at 540 nm and the valley at 569 nm. Therefore, these two wavelengths were used in the subsequent characterization of the Cu(II)–ACDB complex.

4.2. Oxidization of ACDB with hydroxyl radicals

Fig. 3 shows the variation of the absorption spectrum of the ACDB–Fe–H_2O_2 solution with the reaction time. The light-absorptions between 520 and 560 nm decrease as the reaction time was longer. After 6 min, the absorption peak disappears. In the reaction, H_2O_2 is combined with Fe(III) to generate hydroxyl radicals ($HO^{\bullet}$). The action of the $HO^{\bullet}$ radicals first attack azo group and open the azo (–N=N–) bond, destructing the long conjugated π systems, and consequently causing decolorization [20]. This is attributed to the fact that –N=N– bonds are easily destructed than aromatic ring structures. Then, the auxochrome, –OH will be oxidized by the hydroxyl radical chain reactions into quinone group, =O [23]. Thus, the long conjugated structure of ACDB was destroyed, and the products formed will be almost colorless, and the light-absorption of the Cu–ACDB complex may be measured accurately.

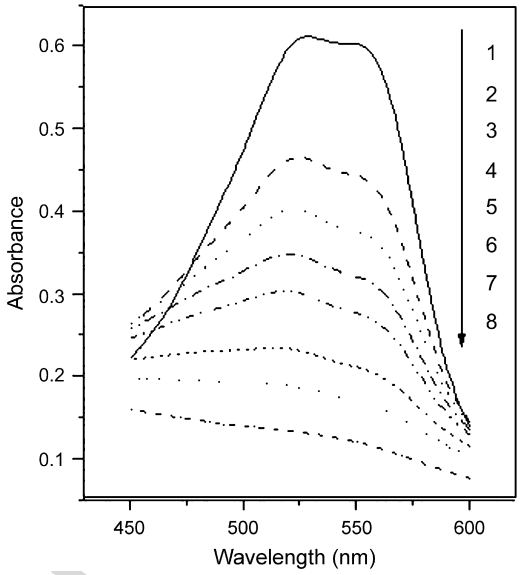

Fig. 3. Variation of the absorption spectra of the solution containing 0.050 μmol mL^{-1} ACDB, 0.50 μg mL Fe(III) and 0.6% H_2O_2 at pH 5.07: from 1 to 8: the reaction time is 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 10.0 min, respectively.

4.3. Composition of the Cu(II)–ACDB complex

As shown by curve 1 in Fig. 4, the ratio A_{569nm}/A_{540nm} of the Cu(II)–ACDB solution decreases rapidly when the molarity of Cu(II) is less than that of ACDB. However, such a ratio approaches a minimum and remains constant when the molar ratio of Cu(II) to ACDB is more than 2. This indicates that ACDB has coordinated with Cu(II) completely in such a solution and only one color compound, the Cu(II)–ACDB complex, exists. The absorption spectrum of such a solution has been shown as curve 3 in Fig. 4. By comparing it with curve 4, the two curves coincide almost completely. This indicates that the free ACDB approaches zero when Cu(II) concentration is

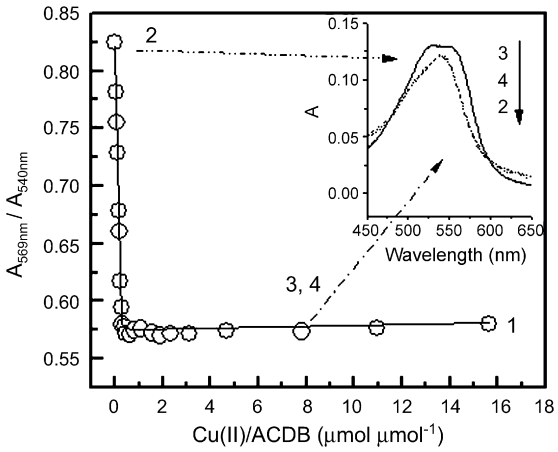

Fig. 4. Variation of the absorbance ratio and the absorption spectra of the solutions at pH 5.07: (1) A_{569nm}/A_{540nm} of the solutions containing 10.0 μmol L^{-1} ACDB and Cu(II) from 0 to 10.0 μg mL^{-1}; (2) the absorption spectrum of 10.0 μmol L^{-1} ACDB; (3) the absorption spectrum of the solution containing 10.0 μmol L^{-1} ACDB and 5.00 μg mL^{-1} Cu(II); (4) the same solution as 3 but 2.00 μg mL^{-1} Fe(III), and 0.15% H_2O_2 added.

much higher than ACDB. Moreover, the Cu–ACDB complex has not been destroyed by Fe(III) and H_2O_2. From curves 3 and 4, the peak of the Cu–ACDB complex is located at 540 nm. By comparing these curves with spectrum 2 of the ACDB solution with the peak wavelengths between 520 and 560 nm, the peak wavelengths of the complex were rather similar. Therefore, the coordination of Cu has not caused the Cu–ACDB complex an obvious spectral shift. Thus, an ordinary spectrophotometry except for ACDB is not fit to the detection of trace Cu(II) using the Cu–ACDB complexation. From curves 3 and 4, α of the Cu(II)–ACDB complex can be calculated to be 0.570 according to Eq. (2). From curve 2, β of the ACDB solution can be estimated to 1.20.

A series of solutions containing various molarities of ACDB and a constant molarity of Cu(II) were prepared and measured at 569 and 540 nm. A_c, γ and η of each solution were worked out by Eqs. (1), (4) and (5). In order to examine the accuracy of A_c, both Fe(III) and hydrogen peroxide were added into all the solutions to oxidize the excess ACDB in colorless products. Thus, the light-absorption of the solutions at 540 nm will be made of only the Cu–ACDB complex. The relationship between A_c calculated by the spectral correction technique and the measurement absorbance (A) of the solutions above at 540 nm after the oxidization of excess ACDB are shown in Fig. 5. Plots A_c versus A in highly linear but also the line scope is close to 1. Therefore, A_c of the Cu(II)–ACDB complex calculated by the spectral correction technique is accurate and trustworthy. From A_c, the molar absorptivity (ε^{540nm}) of the complex was computed to be 3.33×10^4 L mol^{-1} cm^{-1}. This indicates that the complexation between Cu(II) and ACDB is highly sensitive. The variations of η and γ are shown in Fig. 6. From curve 1, η increases initially from about 52% to 100% and then decreases rapidly with increase of ACDB. η decreases to about 47% when ACDB is more than 35.0 μmol L^{-1}. Thus, over half of the ACDB has not reacted with Cu(II). Undoubtedly, so excess ACDB will affect the accurate measurement of the light-absorption of the Cu(II)–ACDB complex. From curve 2, γ increases with the increase of ACDB molarity and then approaches a maximal constant at about 2.0.

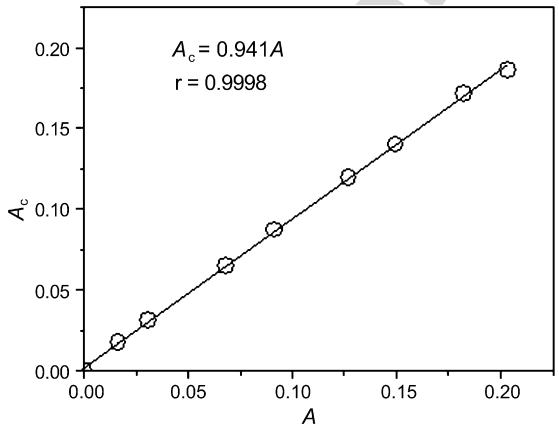

Fig. 5. Correlation between A_c and A of the Cu–ACDB complex at pH 5.07. A_c was calculated from the solutions containing 0.400 μg mL^{-1} Cu(II) and 1.0, 2.0, 5.0, 7.0, 10.0, 12.0, 15.0 and 17.0 nmol mL^{-1} ACDB and A measured from the above solutions which 2 μg mL^{-1} Fe(III) and 1.5% H_2O_2 were added.

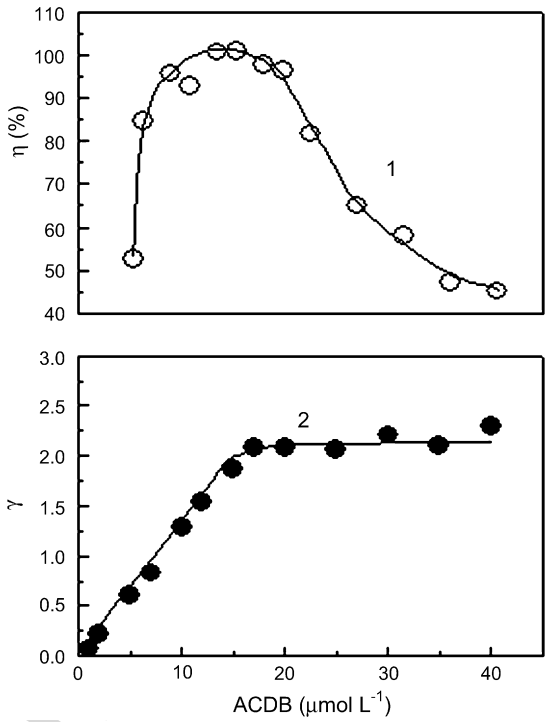

Fig. 6. Variation of η and γ at pH 5.07: (1) η of ACDB in the solutions containing 0.400 μg mL^{-1} Cu(II) and ACDB from 0 to 40.0 μmol L^{-1}; (2) γ of ACDB to Cu.

Therefore, the maximum coordination number of ACDB with Cu(II) is 2 and the possible chemical structure of the Cu(ACDB)$_2$ complex is sketched in Fig. 7. From Fig. 7, Cu(II) will coordinate with the chromophore, azo (–N=N–) group and auxochrome, –OH group. Thus, they were protected from split caused by hydroxyl radicals (HO•).

4.4. Effect of Fe(III) and hydrogen peroxide

Into a series of 10 mL calibrated flasks were added 1.00 mL of pH 5.07 buffer solution, 1.00 μg of Cu(II) and 1.00 mL of 0.100 mmol L^{-1} ACDB. After reacting for 5 min, various amounts of Fe(III) from 0 to 30.0 μg and 0.200 mL of 30% hydrogen peroxide were added. These solutions were then diluted to 10 mL with deionized water and mixed thoroughly. The absorbances of these solutions were measured at 540 nm against water every 30 s for 30 min. The measurement results are shown in Fig. 8A. From curve 1, the light-absorption of

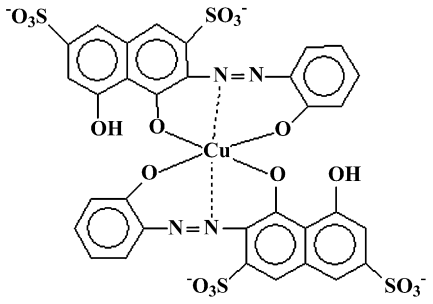

Fig. 7. The possible chemical structure of complex Cu(ACDB)$_2$ formed.

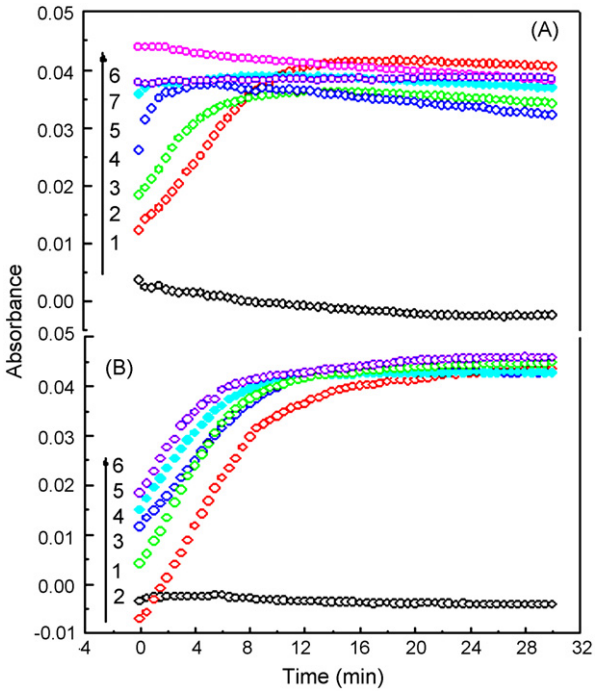

Fig. 8. Variation of absorbances of the solutions with the reaction time at 540 nm at pH 5.07: (A) containing 0.0100 mmol L^{-1} ACDB, 0.100 μg mL^{-1} Cu(II), 0.6% H_2O_2 and Fe(III) from 1 to 6: 0, 0.05, 0.10, 0.15, 0.20 and 0.30 μg mL^{-1}; 7 – the same as 5, but 5 μmol L^{-1} EDTA was added after reacting for 10 min. (B) Containing 0.0100 mmol L^{-1} ACDB, 0.100 μg mL^{-1} Fe(III), 0.100 μg mL^{-1} Cu(II), and H_2O_2 from 1 to 6: 0, 0.6, 0.9, 1.5, 2.1 and 3.0%.

the Cu(II)–ACDB reaction solution is so low that it cannot be applied to analysis of trace Cu. However, The absorbance of the Cu(II)–ACDB reaction solution at 540 nm increases with increase of Fe(III) molarity. The absorbance maximum appears at shorter and shorter time with increase of Fe(III). From curve 5, it approaches a maximum at 2 min when Fe(III) is over 0.15 μg mL^{-1} but increases slowly with extension of time. From curve 7, the addition of EDTA at 5 min makes the absorbance maximum changes after 5 min. This is attributed to the fact that EDTA complexes Fe(III) to cease from the oxidization of ACDB. Similarly, from curves 1–6 in Fig. 8B, variation of the light-absorption of the Cu(II)–ACDB reaction solution can be observed with increase of hydrogen peroxide. From curve 1, in absorbance of hydrogen peroxide, the light-absorption of the Cu(II)–ACDB reaction solution is so insensitive. However, the absorbance maximum appears at shorter and shorter time with increase of hydrogen peroxide. From curve 5, the absorbance approaches a maximum at 8 min and then remains almost constant when 0.10 μg mL^{-1} Fe(III) was added. Therefore, both Fe(III) and hydrogen peroxide must be added simultaneously into the Cu–ACDB solution. Thus, the hydroxyl radicals ($HO^{\bullet}$) can be formed to oxidize strongly the free ACDB. From all curves above, the ACDB coordinated with Cu(II) has hardly been oxidized by hydroxyl radicals ($HO^{\bullet}$). It indicates that the complexation between Cu and ACDB protected the chromophore, –N=N– group and auxochrome, –OH group from split.

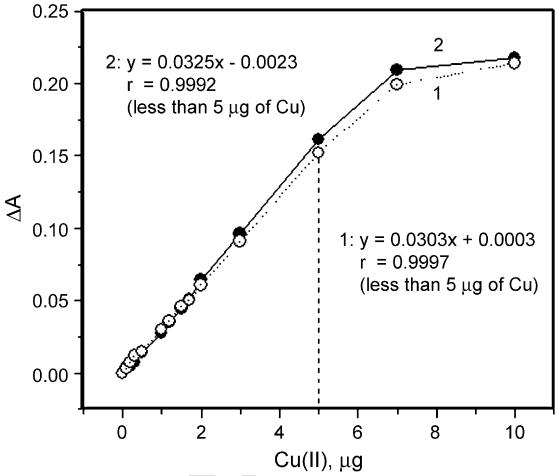

Fig. 9. Calibration graph and the regression equations for the determination of Cu(II) at 540 nm. (1) Fe(II) added and (2) Fe(III) added.

4.5. Calibration graphs and LOD

According to the recommended procedures, a series of standard Cu(II) solutions (10 mL) containing 0 to 10.0 μg of Cu(II) were prepared, colored and measured at 540 nm. The regression equation is shown as curve 2 in Fig. 9. Beer's law was obeyed in the range of 0 to 5. 00 μg of Cu(II) and plots ΔA versus $C_{Cu(II)}$ is linear. In addition, Fe(II) was added in replace of Fe(III) to examine its effect on decolorization of excess ACDB and the results showed as line 1. The addition of Fe(II) results in the almost same ΔA as that of Fe(III) when Cu(II) is less than 2.0 μg. Therefore, used of Fe(III) is reasonable. The LOD of Cu(II), defined as the blank values plus 3 times of the standard deviation (S.D.) of twenty replicated blanks. The S.D. is equal to 0.00075 in the presence of EDTA but 0.0016 in the absence of EDTA. Therefore, the addition of EDTA improved obviously the precision of the reagent blanks. Thus, LOD of Cu(II) was calculated to be only 6 μg L^{-1}. Therefore, the proposed method is sensitive and it can be used for the direct determination of trace Cu in surface water.

4.6. Effect of foreign ions

The effects of potential interference ions were examined by respectively added into the solutions containing 0.200 μg mL^{-1} of Cu(II) and the results are shown in Fig. 10. The tolerable concentration of each ion was taken as a highest concentration. All of them cause error of less than 10%. Therefore, the Cu–ACDB reaction is highly selective in the presences of Fe(III) and hydrogen peroxide. Thus, it can be applied to analysis of natural water.

4.7. Analysis of natural water

In the current work, four natural waters were analyzed. They were sampled from Yangtze River in China, Huangpu River located in Shanghai of China, Taihu Lake as the important drinking water source of Jiangsu Province of China and the

Table 1
Determination of Cu(II) in natural water

Sample from	Cu added[a] (μg)	Cu found[b], (μg)	Recovery%[c]	Cu in sample (mg L^{-1})
Yangtze River	0	0.056	/	0.011
	0.200	0.264	104	0.014[d]
Huangpu River	0	0.144	/	0.029
	0.200	0.327	91.5	0.026[d]
Taihu Lake	0	0.051	/	0.010
	0.200	0.218	83.5	0.015[d]
West Lake	0	0.053	/	0.011
	0.200	0.255	101	0.019[d]

[a] 5.00 mL of a sample was added for complexation.
[b] Average of two replicated determinations.
[c] e.g. $104 = (0.264 - 0.056)/0.200 \times 100$.
[d] One determination by ICP-OES.

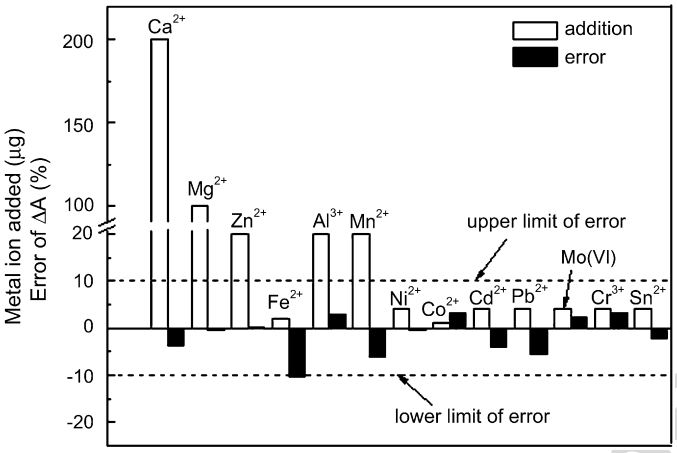

Fig. 10. Effect of thirteen types of foreign ions on ΔA of the solutions containing 0.200 μg mL^{-1} Cu(II) and 0.0200 mmol L^{-1} ACDB.

world-famous scenic spot, West Lake, located in Hangzhou of China. Each of the samples was colored directly without any pretreatment and measured. The results are given in Table 1. The recovery rates of Cu(II) are between 83.5% and 104%. Moreover, the analytical results of the four water samples are well accordance to those determined by ICP-OES. As a result, the proposed method is accurate and credible for practical analysis.

5. Conclusions

In fact, there are a lot of spectrophotometric methods for determination of Cu trace but most of them have high LOD. The present work is the first to establish CDFR detection method, which provides a very helpful experimental strategy for trace analysis of heavy metal. As an example, the Cu–ACDB complexation was used for the quantitative detection of Cu trace in the presences of both Fe(III) and hydrogen peroxide. It has confirmed that such a method is very simple in operation not as the other methods such as catalytic spectrophotometry with the complicated procedure and the strict experimental condition. It is well known that more and more highly sensitive chromogenic reagents have been synthesized and applied recently. Though they increase greatly the sensitivity in detection of heavy metals [26,27], the excess free reactant will interfere seriously the measurement of light-absorption of the complex product formed. It is possible for CDFR detection method to solve this problem by oxidizing the excess chromophore with both Fe(III) and hydrogen peroxide. Thus, the accuracy and sensitivity for trace analysis will improve highly. Surely, such an approach might bring an extensive application to the quantitative detection of heavy metals in the future.

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