# Heterodinuclear Replacement Complexation for Sensitive Determination of Iron Ion in Surface Water with Dibromocarboxyarsenazo

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Dibromocarboxyarsenazo (DBCA) was used to complex Fe and Cu ions at pH 6.22, and complexes Cu(DBCA) and Fe(DBCA) were formed. Fe ion replaced Cu competitively from its dinuclear complex Cu(DBCA)Cu to form the heterodinuclear complex, Cu(DBCA)Fe. The light-absorption ratio variation approach has been applied to the direct determination of Fe ions with a high selectivity and good sensitivity using heterodinuclear replacement complexation. The limit of detection of Fe is only 2.5 ng/mL. The results from the analyses of five Huangpu River (Shanghai) cross-section samples indicate that Fe ions are from 5.0 to 39.2 µg/L with the recovery rates between 85.5 and 111.5%.

**Keywords:** Determination of iron ions; Dibromocarboxyarsenazo; Light-absorption ratio variation approach; Heterodinuclear replacement complexation; Spectral correction technique.

## 1. INTRODUCTION

Nowadays, the research concerning iron has drawn particular attention because of its ubiquity in the natural environment.[1] As a vital element in life, iron is indispensable for almost all living organisms, participating in a wide variety of metabolic processes, including electron transport, DNA synthesis, and gene expression.[2] Iron deficiency is the most common nutritional deficiency, affecting as much as 66-80% of the population throughout the world and is the principal nutritional cause of anemia.[3] On the other hand, excess intake of iron is purported to be associated with the root of several chronic diseases, including cancer, diabetes, cardiovascular disease,[4] and sepsis.[5] Since the last century, human activities have given rise to a number of environmental problems, such as excessive mining of ores, arbitrary discharge of industrial wastewater, acid rain, etc. A large amount of iron has been transformed and released into water bodies around the world, especially the surface water. Under such circumstances, the analysis of iron at trace levels can be very helpful for the assessment of its environmental risk as well as its deleterious effect on humans. In general, iron concentration in surface water ranges for the most part from 0.061 to 2.68 mg/L,[6] and it usually exists as two valence states: Fe(II) and Fe(III). Ex-

cept for existing as dissolved phases, these valence states are also involved in the formation of soluble inorganic and organic complexes, colloids and particulate phases.[7]

During recent decades, many researchers involved in the analysis of trace amounts of iron faced the need to measure them sensitively and accurately. Hence, many appropriate analytical techniques have been developed, such as UV-visible spectrophotometry,[8] atomic absorption spectrophotometry,[9] catalytic spectrophotometry,[10] inductively coupled plasma-optical emission spectrometry,[11] voltammetry,[12,13] capillary electrophoresis,[14] and chemiluminescence.[15] Among the most widely applied methods are those based on spectrophotometry because they are remarkable for their simplicity, versatility, and precision.[16] However, the majority of such kinds of methods lack sufficient sensitivity or selectivity for iron speciation at a ng/mL level. Consequently, it is still very important to establish a simple but sensitive and selective way for the determination of iron. The appearance of the light-absorption ratio variation approach (LARVA) paves a new way for the advancement of spectrophotometry, because it can greatly improve analytical sensitivity.[17] Meanwhile, the competitive replacement[18] can effectively improve the selectivity of chromospheres.
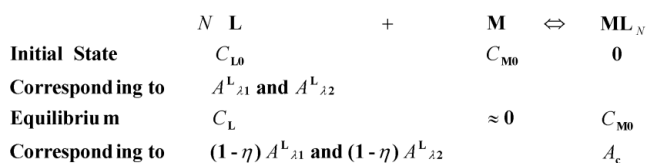
Various kinds of dinuclear complexes were continu-

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ously synthesized in recent years and their structural characteristics have been analyzed thoroughly.[19-20] However, few of them were used in trace analysis. Dibromocarboxy-arsenazo (DBCA) is a sensitive chromophore to complex a number of metal ions. It was applied to the determination of chromium[21] and ruthenium[22] several years ago. In the present work, DBCA is used to complex with Cu(II) to form a dinuclear complex Cu(DBCA)Cu in the presence of plenty of Cu(II) but Fe(II, III) can replace the Cu of this complex sensitively and selectively to form the heterodinuclear complex, Cu(DBCA)Fe. The dissolved Fe in five cross-sections of the Huangpu River in China was determined with recovery rates between 85.5% and 111.5%.

## 2. PRINCIPLES AND CALCULATIONS

### 2.1 Spectral correction technique

A metal (M) - ligand (L) complexation is routinely applied to the analysis of trace amounts of metal. The reaction equilibrium can be expressed as below:[23]

|  | $N$ **L** | + | **M** | $\Leftrightarrow$ | **ML**$_N$ |
|---|---|---|---|---|---|
| **Initial State** | $C_{L0}$ | | $C_{M0}$ | | 0 |
| **Corresponding to** | $A^L_{\lambda 1}$ and $A^L_{\lambda 2}$ | | | | |
| **Equilibrium** | $C_L$ | | $\approx 0$ | | $C_{M0}$ |
| **Corresponding to** | $(1 - \eta) A^L_{\lambda 1}$ and $(1 - \eta) A^L_{\lambda 2}$ | | | | $A_c$ |

Both $C_{L0}$ and $C_{M0}$ represent the initial molarities of L and M. $N$ is the maximal coordination number of L to M. $\eta$ is the effective fraction of L to complex M, and $A_c$ is the real absorbance of ML complex at wavelength $\lambda_2$. Both $A^L_{\lambda 1}$ and $A^L_{\lambda 2}$ are the absorbances of L solution that are separately measured at wavelengths $\lambda_1$ and $\lambda_2$ against water. In the M-L reaction, excess L always coexists with ML, which would inevitably affect the measurement of the absorbance of ML complex. Fortunately, the spectral correction technique (SCT) can successfully eliminate the negative effect caused by excess L. $A_c$ of ML complex can be calculated and the complex reaction can be characterized according to the following relations:

$$A_c = \frac{A_{\lambda 2} - \beta A_{\lambda 1}}{1 - \alpha\beta} \tag{1}$$

where

$$\alpha = \frac{A^{ML}_{\lambda 1}}{A^{ML}_{\lambda 2}} \tag{2}$$

and

$$\beta = \frac{A^L_{\lambda 2}}{A^L_{\lambda 1}} \tag{3}$$

and

$$\gamma = \eta \times \frac{C_{L0}}{C_{M0}} \tag{4}$$

where

$$\eta = \frac{A_c - A_{\lambda 2}}{A^L_{\lambda 2}} + 1 \tag{5}$$

Both $\alpha$ and $\beta$ are the correction constants, and $\gamma$ is the coordination number of L to M. $A_{\lambda 1}$ and $A_{\lambda 2}$ are the absorbances of the M-L solution and $A^{ML}_{\lambda 1}$ and $A^{ML}_{\lambda 2}$ are those of the ML complex formed in an M-L solution containing excess M, respectively measured at $\lambda_1$ and $\lambda_2$ against water. From Equations (1) to (5), $A_c$, $\alpha$, $\beta$, $\eta$ and $\gamma$ can be calculated and used to characterize the Fe-DBCA and Cu-DBCA complexes.

### 2.2 Development of heterodinuclear replacement complexation (HRC)

In order to improve analytical selectivity, the model of competitive replacement was proposed,[24] and it has been applied to some complexations with satisfactory results. However, a multi-dentate L may often coordinate two or more M (M$^1$) when excess M$^1$ is added into L. Thus, a dinuclear complex M$^1$LM$^1$ may be formed. One M$^1$ in the dinuclear complex will be replaced by another M (M$^2$) to form another dinuclear complex M$^1$LM$^2$ because of the different connection stabilities of the coordination groups. The HRC is expressed as follows:

M$^1$ (excess) + L $\rightarrow$ M$^1$LM$^1$
M$^2$ + M$^1$LM$^1$ $\rightarrow$ M$^1$LM$^2$ + M$^1$
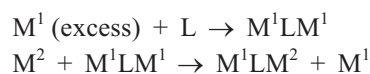
The HRC is the first to be proposed and applied to the detection of M$^2$ where the M$^1$L M$^1$ complex is regarded as a new chromophore of M$^2$. Since M$^1$ is present in an adequate amount, it will prevent the interference from other co-existing foreign ions in the solution except for M$^2$. Therefore, the HRC improves the analytical selectivity remarkably.

### 2.3 Light-absorption ratio variation approach

The primary principle of the light-absorption ratio variation approach (LARVA) can be described as the fol-

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lowing relations:[17]

$$\Delta A_r^{-1} = p' C_{M0}^{-1} + q' \qquad (6)$$

or

$$\Delta A_r = p C'_{M0} + q \quad (\text{only when } C'_{M0} << C_{M0}) \qquad (7)$$

where

$$\Delta A_r = A_r - A_{r0} = \frac{A_{\lambda 2}}{A_{\lambda 1}} - \frac{A^L_{\lambda 2}}{A^L_{\lambda 1}} \qquad (8)$$

where $\Delta A_r$ is the absorbance ratio variation of the $M^2$-$M^1 L M^1$ reaction solution measured at wavelengths $\lambda_1$ and $\lambda_2$ against water reference. Both $C_{M0}$ and $C'_{M0}$ represent the initial concentration of $M^2$. Plots $\Delta A_r$ vs. $C_{M0}$ are linear as in Equation (7) only when $C_{M0}$ is in a lower concentration of $M^2$ e.g. less than $C'_{M0}$. Factors $p'$, $q'$, $p$ and $q$ are all constants. Equations (6) or (7) can be directly used to determine trace amounts of $M^2$. Because the sensitivity factor $p$ is the inverse ratio of $C_{L0}$, the analytical sensitivity will go increasingly higher as the addition of L becomes less. Nevertheless, too low L will cause an increase of the measurement error because of the interference of instrumental noise.

## 3. EXPERIMENTAL SECTION

### 3.1 Apparatus

The absorption spectra of the DBCA and its metal complexes were recorded on a Model Lambda-25 spectrometer (Perkin-Elmer Instruments, USA) with UV WinLab software (Version 2.85.04). A Model pHS-25 acidity meter (Shanghai Precise Science Instruments, China) was used to measure the pH of the solutions. A Model BS110S electronic balance (Sartorius Instruments, Beijing, China) was used to precisely weight the standard substances and DBCA. A Model SK3300H supersonic cleaner (Shanghai Kedao Supersonic Instruments Co. Ltd., Shanghai, China) was used to dissolve solutes completely. A Model BCD-196 refrigerator freezer (Meiling Production, Hefei, China) was used to store experimental solutions. A Model HSS-11-2 water-bath (Shanghai Jingheng Instruments, China) was used to maintain the temperature of reacting solutions.

### 3.2 Reagents and solutions

Two standard stock solutions, respectively containing 1000 mg/L Fe(III) (GSB07-1264-2000) and 1000 mg/L Cu(II) (GSB07-1257-2000), were purchased from the Institute for Reference Materials of SEPA, Beijing, China. Standard use solutions of 200, 1.00 mg/L Fe(III) and 200 mg/L Cu(II) were prepared by diluting the above stock solutions. A standard solution containing 100 mg/L Fe(II) was prepared by dissolving 0.7020 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (A. R. grade, purchased from Shanghai Chemical Reagents, Chinese Medical Group) in 50 mL of 50% sulfuric acid (A. R. grade, purchased from Shanghai Sihewei Chemicals). The solution was then diluted to 1000 mL with deionized water. Standard use solution containing 1.00 mg/L Fe(II) was prepared by diluting the standard stock solution. All the above solutions were stored at less than 5 °C.

DBCA was purchased from Shanghai Changke Reagents Institute. A solution containing 0.500 mmol/L DBCA was prepared by dissolving 106.8 mg of DBCA in 250 mL of deionized water. The solution used in subsequent experiments containing 0.0500 mmol/L DBCA was prepared by 0.0500 mmol/L DBCA was prepared by diluting 0.500 mmol/L DBCA in deionized water. Both of them were stored at less than 5 °C. A Cu(II)-DBCA complex solution containing 0.0500 mmol/L DBCA was prepared by mixing 25 mL of 0.500 mmol/L DBCA with 25 mL of pH 6.22 acetate buffer solution and 40 mL of 200 mg/L Cu(II) and then diluting to 250 mL with deionized water. It was used as the chromophore in the determination of Fe ions and stored at less than 5 °C.

In addition, a series of acetate buffer solutions from pH 2.79 to 7.67 was prepared with acetic acid (A. R. grade, purchased from Shanghai Chemical Reagents, Chinese Medical Group) and sodium acetate (A. R. grade, purchased from Shanghai Sihewei Chemicals). They were used to adjust the pH of the solution so as to optimize the complexation conditions. Each of the solutions was measured accurately with the pH meter.

### 3.3 Recommended procedures
#### 3.3.1 Characterization of complexes

The characterization of DBCA complex mainly consists of two steps: determination of spectral correction constants $\alpha$ and $\beta$ and calculation of parameters $A_c$, $\eta$ and $\gamma$. At first, into a series of 10 mL calibrated flasks were added different amounts of Fe(III) from 0 to 50.0 μg. Afterwards, 1.00 mL of pH 6.22 buffer solution and 1.00 mL of 0.0500 mmol/L DBCA were added, respectively. The solutions

were diluted to 10 mL with deionized water and mixed well. The absorbances, $A_{535nm}$ and $A_{625nm}$ of these solutions were measured at 535 and 625 nm against water, and the ratio $A_{535nm}/A_{625nm}$ in each solution was calculated. The ratio value will remain at a minimal constant when Fe(III) is more than a certain concentration. Thus, such a solution will not contain free DBCA. From its spectrum, α may be worked out from Equation (2). Secondly, into a series of 10 mL calibrated flasks were added 1.00 mL of pH 6.22 buffer solution and 0.0500 mmol/L DBCA from 0.050 to 5.00 mL. The solutions were then diluted to 10 mL with deionized water and mixed thoroughly. The absorbances, $A^0_{535nm}$ and $A^0_{625nm}$, of these solutions were measured at 535 and 625 nm against water and each β was calculated from Equation (3). Then, 2.0 μg of Fe(III) was added into the solutions above. After mixing thoroughly, the absorbances ($A_{535nm}$ and $A_{625nm}$) of these solutions were measured at 535 and 625 nm against water. The parameters $A_c$, η, and γ were calculated according to Equations (1), (5) and (4). Thus, the Fe(III)-DBCA complex could be characterized.

According to similar procedures as detailed above, the absorbances of the Cu(II)-DBCA solutions were measured at 513 and 614 nm. Thus, the Cu(II)-DBCA complex was also successfully characterized.

### 3.3.2 Determination of Fe ions

Water samples were collected from five cross-sections of the Huangpu River in Shanghai, China. After sample collection, the samples were sealed and then stored at 5 °C before analysis. Usually, a clear water sample can be directly analyzed without any pretreatment. However, in order to investigate the dissolved iron in water, the pretreatment of a sample is often necessary. 100 mL of each water sample was filtered by filter paper with a 0.45 μm aperture and the filtrate was collected. These five samples were colored and then measured according to the following procedures.

A known volume of a sample solution was added into a 10 mL calibrated flask. 1.00 mL of pH 6.22 buffer solution and 0.50 mL of 0.0500 mmol/L Cu(II)-DBCA complex solution were added. After diluting to 10 mL with deionized water and mixing thoroughly, the flask was kept in a constant-temperature water bath at 40 °C for 30 min to perform the replacement of Cu by Fe(II, III). Then, it was cooled at room temperature for 20 min. The absorbances, $A_{500nm}$ and $A_{600nm}$, of the solution were measured at 500 and 600 nm against a water reference. Meanwhile, a corresponding reagent blank without Fe ions was prepared and

its absorbances, $A^0_{500nm}$ and $A^0_{600nm}$, were measured. Thus, $\Delta A_r$ of each could be calculated by the following equation:

$$\Delta A_r = \frac{A_{500nm}}{A_{600nm}} - \frac{A^0_{500nm}}{A^0_{600nm}} \qquad (9)$$

## 4. RESULTS AND DISCUSSION

### 4.1 pH dependence of absorption spectra

The absorption spectra of Fe(III)-DBCA and Cu(II)-DBCA solutions in various acetate buffer solutions are shown in Fig. 1. From Fig. 1(A), curve 8 shows the maximum peak-valley interval among all of the 11 curves, which indicates that the complexation between Fe(III) and DBCA is most sensitive at pH 6.22. But when the pH of the solution approached or surpassed 7.0, the above complexation becomes less sensitive. As shown in Fig. 1(B), the complextion between Cu(II) and DBCA becomes increasingly sensitive as the pH rises. However, by comparison of curves 8-11, the sensitivity of the reaction at pH 6.22 is slightly less than those at pHs 7.11 and 7.67. By considering both the reactions together, pH 6.22 was chosen in this present work. From curve 8 in Fig. 1(A), the peak is located at 625 nm and the valley at 535 nm. From curve 8 in Fig. 1(B), the peak is located at 614 nm and the valley at 513 nm. These four wavelengths were selected for the characterization of the Fe(III)-DBCA and Cu(II)-DBCA complexes.

### 4.2 Composition of complexes

Shown as curve 1 in Fig. 2, the absorbance ratio, $A_{535\ nm}/A_{625\ nm}$ of the Fe(III)-DBCA solution, decreases rapidly when the molarity of Fe(III) is less than that of DBCA. However, such a ratio approaches a constant minimum at 1.27 from curve 1 when the molar ratio of Fe(III) to DBCA is more than 3. This indicates that DBCA is almost complete to complex with Fe(III) and only one color compound, the Fe(III)-DBCA complex exists in the solution. Similarly, from curve 2, the ratio, $A_{513\ nm}/A_{614\ nm}$ remains constant when the molarity of Cu(II) is more than double that of DBCA. The absorption spectra of these solutions are shown in Fig. 1C. From these curves, the spectral red shift caused by the formation of Cu(II)-DBCA complex is about 54 nm from at 536 nm of DBCA peak to 590 nm of the Cu(II)-DBCA peak. Similarly, from curve 3, the spectral red shift of the Fe(III)-DBCA complex is about 25 nm. From curve 1, β = 0.113 for $A_{625\ nm}/A_{535\ nm}$ and 0.194 for
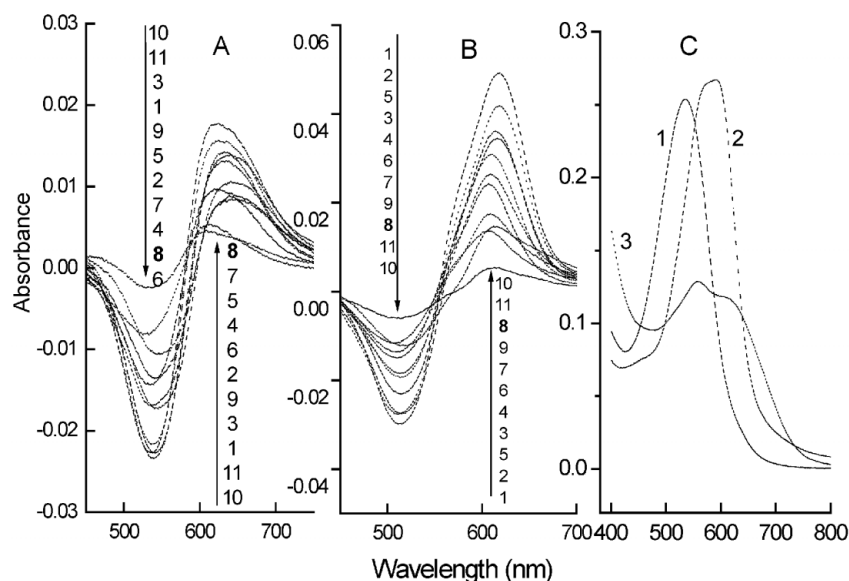
Fig. 1. Effect of pH on absorption spectra of Fe(III)-DBCA (A) and Cu(II)-DBCA (B) complex solutions that contained 5.00 μmol/L DBCA and 0.100 μg/mL Fe(III) (A) or 0.100 μg/mL Cu(II) (B) against a reference without Fe(III) or Cu(II). From curves 1 to 11: pH 2.79, 3.36, 3.88, 4.37, 4.88, 5.43, 5.88, 6.22, 6.67, 7.11, and 7.67. C: Absorption spectra of DBCA and its Cu(II) and Fe(III) complexes at pH 6.22: 1 - 5.00 μmol/L DBCA; 2 - 5.00 μmol/L DBCA plus 4.00 μg/mL Cu(II); 3 - 5.00 μmol/L DBCA plus 4.00 μg/mL Fe(III).

$A_{614\ nm}/A_{513\ nm}$ by Equation (3). Similarly, $\alpha = 0.525$ for the Cu(II)-DBCA complex from curve 2 and 1.27 for the Fe(III)-DBCA complex from curve 3. Such $\alpha$ values can
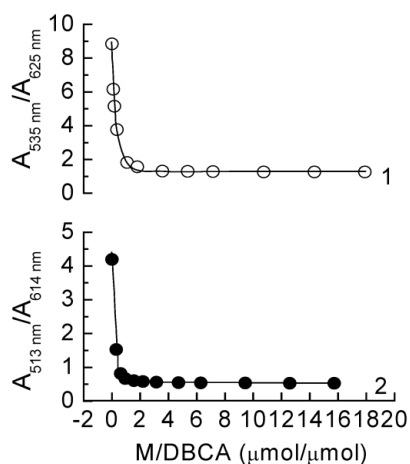


Fig. 2. Variation of the absorbance ratio with increasing molarity of metal ions (M) in corresponding solutions containing constant molarity of DBCA at pH 6.22: 1 - the variation of $A_{535\ nm}/A_{625\ nm}$ of the solution containing 5.00 μmol/L DBCA solution and Fe(III) from 0 to 5.00 μg/mL. 2 - the variation of $A_{513\ nm}/A_{614\ nm}$ of the solution containing 5.00 μmol/L DBCA solution and Cu(II) from 0 to 5.00 μg/mL.

still be observed and confirmed from the minimum constants of curves 1-2 in Fig. 2.

Also, all of the absorption spectra of the complexes have shoulders in the presence of plenty of metal ions. This means that the dinuclear complex of DBCA with Cu(II) and Fe(III) may be formed. In fact, DBCA is a both sides multidentate ligand as shown in Fig. 3(1). Both sides may coordinate with M e.g. Cu, Fe to form a dinuclear chelate if enough M is present in the solution. Therefore, complexes $Cu_2(DBCA)$ and $Fe_2(DBCA)$ might be formed only when Cu(II) and Fe(III) is high enough. Their possible chemical structures are shown in Fig. 3(2, 3).

The absorbances of three series of solutions containing different concentrations of DBCA, but a constant molarity of metal ions, were measured. All the parameters, $A_c$, $\eta$ and $\gamma$, were calculated by Equations (1), (5) and (4), and their curves are shown in Fig. 4. From curves 1 and 2, $\eta$ decreases rapidly with the increase of DBCA. $\eta$ is less than 20% when the concentration of DBCA is more than 0.0200 mmol/L. It indicates that over 80% DBCA has not reacted with Fe(III) or Cu(II). Undoubtedly, the excess DBCA mixed in the solution would affect the measurement of absorbance of the complex product, i.e. it is difficult for traditional spectrophotometry to measure accurately the light-adsorption of the complex. The spectral correction

technique is applied to solve this problem because it can eliminate the inference of the excess DBCA. From curves 3 and 4, $\gamma$ increases with an increase of DBCA and remains almost constant at 1 while DBCA is more than 0.0100 mmol/L. Therefore, complexes Cu(DBCA) and Fe(DBCA) are formed at pH 6.22.

### 4.3 HRC

Fig. 5A gives the absorption spectra of the DBCA complexes with Cu(II), Fe(III), Pb(II), Al(III), Zn(II), Ni(II), Ca(II), Mn(II), and Mg(II). By comparison of 9 curves, only Fe(III) caused an obvious change of the absorption spectrum of the Cu(II)-DBCA complex. Other metals will barely affect the shape of the absorption spectrum of the Cu(II)-DBCA complex. Such a phenomenon indicates that only Fe(III) may replace Cu(II) competitively from the Cu(II)-DBCA complex. Therefore, the Cu(II)-DBCA complex can be used as a new chromophore to determine Fe ion with good selectivity.

By comparison of curve 1 in Fig. 5B with curve 2 in Fig. 1C, in the presence of plenty of Fe(III), the spectrum of complex $Cu_2$(DBCA) generates a blue shift of 20 nm from 590 nm of the complex peak to 570 nm. This demonstrates that Fe(III) replaced Cu in complex $Cu_2$(DBCA). However, curve 1 in Fig. 5B is not coincident with curve 3 in Fig. 1C.
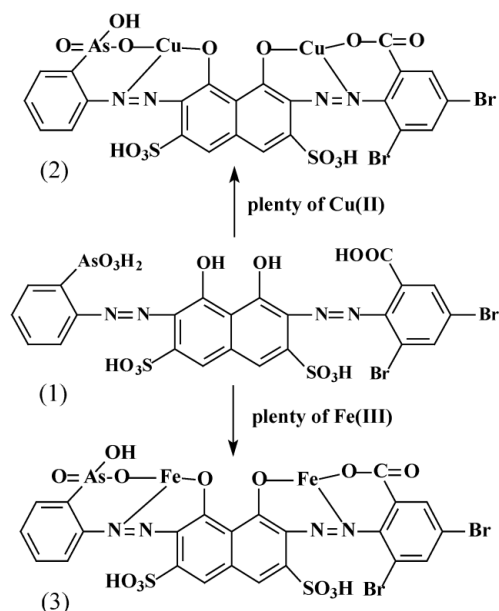
Therefore, Fe(III) might replace only one Cu of complex $Cu_2$(DBCA) to form a heteronuclear chelate. Simultaneously, small amounts of both Cu-DBCA-Cu and Fe-DBCA-Fe complexes still existed in the solution for controlling the equilibrium. Because the left multi-dentate groups of DBCA may chelate Cu more strongly than the right groups, it is possible for the right Cu of complex $Cu_2$(DBCA) to be replaced by Fe ion. This is named as the HRC. Curve 2 in Fig. 5B shows the absorption spectrum of the Cu(II)-DBCA-Fe(III) reaction solution against the reagent blank without Fe(III). The absorption peak is located at 500 nm and the valley at 600 nm. Two such wavelengths were chosen for the determination of trace amounts of Fe ion.

### 4.4 Effect of time and temperature

The effects of the replacement time and the reaction temperature on $\Delta A_r$ of the Cu-DBCA-Fe solution are shown in Fig. 6. From curves 3 and 4, both $\Delta A_r$ of the Cu(II)-DBCA-Fe(III) and Cu(II)-DBCA-Fe(II) solutions always increase at room temperature, and they cannot reach a final equilibrium within 60 min. Moreover, both the Cu(II)-DBCA-Fe(II) and Cu(II)-DBCA-Fe(III) reactions are not non-synchronous. On the contrary, both $\Delta A_r$ of Cu(II)-DBCA-Fe(II) and Cu(II)-DBCA-Fe(III) solutions approach an equilibrium after 30 min at 40 °C from curves 1 and 2. Besides, $\Delta A_r$ of Cu(II)-DBCA-Fe(II) solution re-
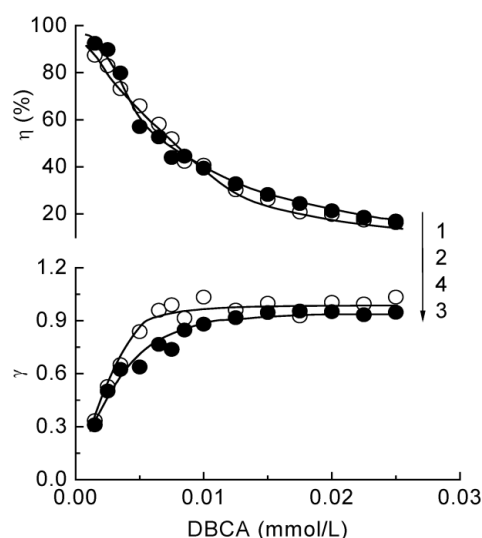
Fig. 3.  Structures of DBCA and its Cu(II) and Fe(III) complexes in the presence of plenty of metal ions: (1) - DBCA; (2) - $Cu_2$(DBCA); (3) - $Fe_2$(DBCA).

Fig. 4.  Variations of $\eta$ and $\gamma$: 1 and 2 - $\eta$ of DBCA in solutions containing 0.200 µg/mL Fe(III) and 0.200 µg/mL Cu(II), respectively. 3 and 4 - $\gamma$ of the same solutions as curves 1 and 2.

Table 1. Regression equations for determination of Fe ions and their LOD

| Series | 0.0500 mmol/L $Cu_2$(DBCA) (mL) | Linear range of Fe(III) (μg/ mL) | Calibration graph | R [a)] | σ [b)] | LOD [c)] (ng/mL) |
|---|---|---|---|---|---|---|
| 1 | 0.30 | ≤ 0.030 | $\Delta A_r = 0.9245 C_{Fe} - 0.0098$ | 0.9954 | 0.00811 | 2.6 |
| 2 | 0.50 | ≤ 0.050 | $\Delta A_r = 0.6659 C_{Fe} + 0.0056$ | 0.9966 | 0.00564 | 2.5 |
| 3 | 1.00 | ≤ 0.100 | $\Delta A_r = 0.2487 C_{Fe} - 0.0061$ | 0.9983 | 0.00409 | 4.9 |

[a)] Linear correlation coefficient.
[b)] SD for 10 repetitive reagent blanks.
[c)] LOD = $3\sigma/p$.

mains almost equal to that of the Cu(II)-DBCA-Fe(III) solution. Thus, the determination of total Fe ions involving $Fe^{2+}$ and $Fe^{3+}$ can be carried out without any measurement correction or pretreatment of sample.

### 4.5 Calibration graphs and LOD of Fe

Three series of standard Fe(III) between 0 and 0.300, 0 and 0.500, and 0 and 1.000 μg were prepared. 0.300, 0.500 and 1.00 mL of 0.0500 mmol/L Cu(II)-DBCA complex solution were added, respectively. The reactions were
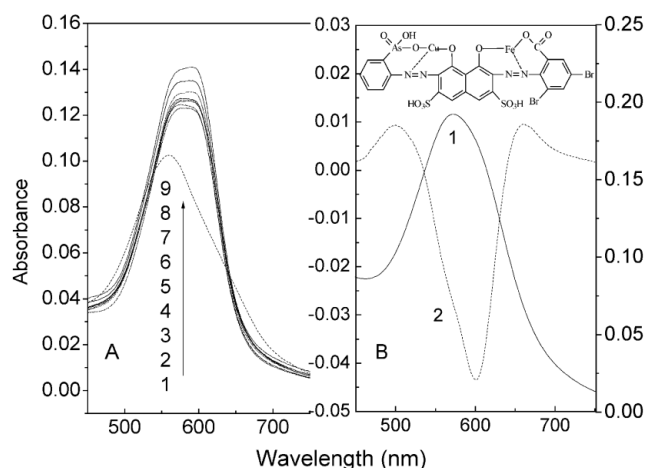


Fig. 5. A: Absorption spectra of the Cu(II)-DBCA complex solutions at pH 6.22 in the presence of various metal ions with the same molarity, containing (from 1 to 8) 5.00 μmol/L Cu(II), 5.00 μmol/L DBCA and additional 0.050 mmol/L Fe(III), Pb(II), Al(III), Zn(II), Ni(II), Ca(II), Mn(II), and Mg(II), respectively; 9 - 0.050 mmol/L Cu(II) and 5.00 μmol/L DBCA. B: Absorption spectra of the Cu(II)-DBCA-Fe solutions containing: 1 - 5.00 μmol/L Cu(II)-DBCA complex and 17.2 μmol/L Fe(III), measured against water and 2 - 5.00 μmol/L Cu(II)-DBCA complex and 0.050 μg/mL of Fe(III), measured against the corresponding blank without Fe(III).

carried out according to the recommended procedures. $\Delta A_r$ was calculated by Equation (9). The regression equations, plots $\Delta A_r$ vs $C_{Fe}$, are given in Table 1. The LOD of Fe, defined as 3 times of the standard deviation ($\sigma$), was calculated and is shown in Table 1. Series 2 is optimal due to the lowest LOD and good linearity. Therefore, it was selected in the analysis of water samples.

### 4.6 Effect of foreign ions

Fe ion was able to replace Cu(II) of the Cu-DBCA complex but whether the other metals co-existing in natural water would replace the Cu(II), such as Ca(II), Mg(II), Zn(II), Mn(II) and so on was unknown. In order to investigate the effect of the foreign ions on the determination of Fe ions, fourteen kinds of foreign ions were added separately into the solutions containing 0.0200 μg/mL of Fe(III),
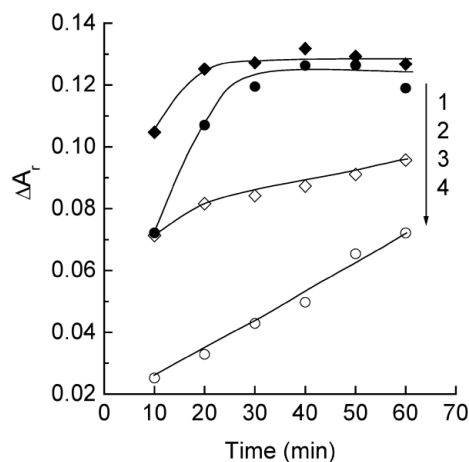


Fig. 6. Effects of time and temperature on $\Delta A_r$ of the dinuclear complexation solutions: 1 and 3 - containing 0.020 μg/mL Fe(II) and 2.50 μmol/L Cu(II)-DBCA complex and 2 and 4 - solution containing 0.020 μg/mL Fe(III) and 2.50 μmol/L Cu(II)-DBCA complex. Both 1 and 2 at 40 °C, both 3 and 4 - at room temperature (20 °C).
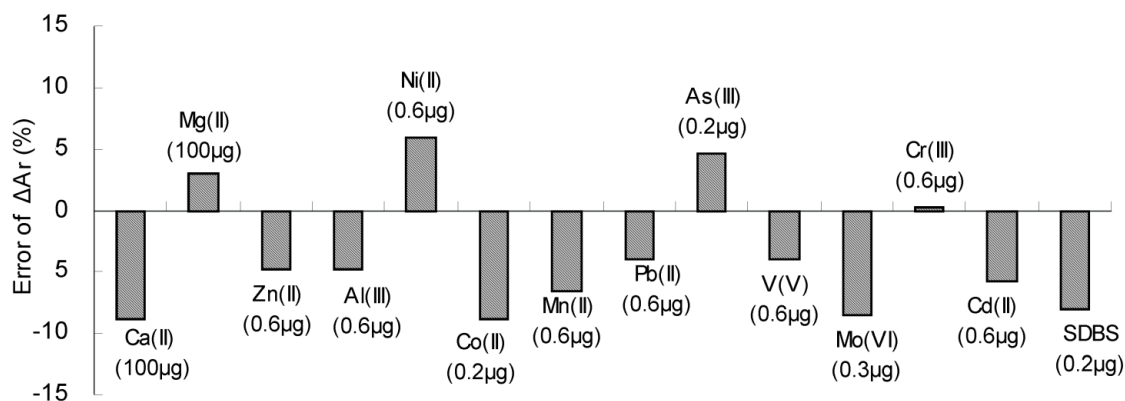
Fig. 7.  Effect of foreign ions on $\Delta A_r$ of the solutions containing 0.0200 μg/mL Fe(III) and 2.50 μmol/L Cu(II)-DBCA complex solution.

where no masking reagent was added. Their effect on $\Delta A_r$ of the solutions is shown in Fig. 7. All of them caused less than 10% of error. Thus, none of the foreign ions had a serious effect on the direct determination of Fe ions even when their amounts were much more than that of Fe ion. This is attributed to the fact that the excess Cu(II) existing in the solution plays an important role in excluding the interference from the foreign ions. Therefore, this method is selective for the analysis of Fe ion in water samples.

**4.7 Analysis of samples**

In this work, totally five surface water samples were analyzed. They were sampled from five cross-sections of the Huangpu River located in Shanghai, named Qingshui bridge, Yangshupu bridge, Jungong bridge, Rende bridge

and Sanmen bridge. Each of the samples was analyzed according to the recommended procedures, and the results are listed in Table 2. The recovery rates of Fe added are between 85.8 and 111.5% and the RSD less than 8.0%. Therefore, the LARVA is accurate and credible for practical analysis.

**5. CONCLUSION**

As a common heavy metal, iron can react with many chromophores such as 5-sulfosalicylic acid,[25] curcumin,[26] ferrozine,[27] which can show satisfactory results in iron determination. Nevertheless, $Cu_2$(DBCA) complex as a new style chromophore to react with Fe(II, III) to determine dissolved Fe in the Huangpu River of China exhibited a high

Table 2.  Determination of Fe ions in the Huangpu River in Shanghai

| Sampled from across section: | Fe ions added (μg/L) | Fe ions found (μg/L) | Recovery [c] (%) | RSD [d] (%) |
|---|---|---|---|---|
| Qingshui bridge | 0 | 5.0 ± 0.3 [a] | | 6.0 |
| | 20.0 [b] | 26.0 ± 0.6 [a] | 105.0 | 2.3 |
| Yangshupu bridge | 0 | 15.0 ± 1.2 [a] | | 8.0 |
| | 20.0 [c] | 36.2 ± 0.8 [a] | 106.0 | 2.2 |
| Jungong bridge | 0 | 11.0 ± 0.7 [a] | | 6.4 |
| | 20.0 [c] | 33.3 ± 1.2 [a] | 111.5 | 3.6 |
| Rende bridge | 0 | 39.2 ± 1.0 [a] | | 2.6 |
| | 20.0 [c] | 60.8 ± 1.6 [a] | 108.0 | 2.6 |
| Sanmen bridge | 0 | 37.7 ± 1.0 [a] | | 2.7 |
| | 20.0 [c] | 54.8 ± 2.0 [a] | 85.5 | 3.6 |

[a] Average of three replicated determinations.
[b] with 10.0 μg of Fe(III) and 10.0 μg of Fe(II) mixed together.
[c] *e.g.* 105.0% = (26.0-5.0)/20.0 × 100%.
[d] *e.g.* 2.3% = 0.6/26.0 × 100%.

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selectivity in determination of trace amounts of Fe. The development of the HRC has brought a good beginning for the selective detection of a metal at the ng/mL level. Furthermore, the application of LARVA as a novel colorimetric method plays an important role in increasing analytical sensitivity. Thus, the combination of both HRC and LARVA will improve significantly the application of spectrophotometry in environmental trace analysis.

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