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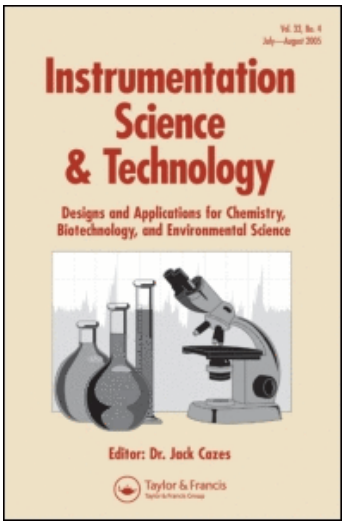

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Yi-Nan Tang [a]; Yuan Yuan [a]; Xing Chen [a]; Qing Zhu [a]; Hui Gong [a]; Hong-Wen Gao [a]
[a] State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, P. R. China

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Yi-Nan Tang, Yuan Yuan, Xing Chen, Qing Zhu, Hui Gong, and Hong-Wen Gao

State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, P. R. China

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Abstract: The complexation between Fe ions (II, III) and bromopyrogallol red (BPR) is sensitive at pH 6.23 with the composition ratio at 1:2 of Fe to BPR, and it is selective in the presence of F^- and thiocarbamide. Using this reaction, the light absorption ratio variation approach was applied to the direct determination of Fe ions. The limit of detection is only 4.5 μg/L Fe. The Fe ions content existing in the Yangtze River, Taihu Lake, tap water and Huangpu River in Shanghai was determined with the recovery rate between 95.5 and 106%.

Keywords: Bromopyrogallol red, Determination of Fe ions, Light-absorption ratio variation approach, Spectrophotometry

INTRODUCTION

Iron is one of the most abundant elements in nature, widely presenting in a variety of rock and soil minerals. Iron can exist in organic

Address correspondence to Hong-Wen Gao, State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, P. R. China. E-mail: emsl@mail.tongji.edu.cn

species[1] of Fe(III) or Fe(II), as complexes,[2] colloids of oxides,[3] oxyhydroxides, or mixed with organic material, and suspended as both biotic and abiotic particles.[4] Iron is important in the biosphere, serving as an active center of a wide range of proteins such as oxidases, reductases, and dehydrases. As the most abundant transition metal, it presents in higher mammals with 3–4 g of the element present in the normal human body. Oxygen transport proteins contain 70% iron; 0.7% is present in other intracellular protein and enzymes. The rest ~29% is stored. It plays an essential role in phytosynthesis.[5,6] Microbial processes result in the reduction of Fe(III).[7] Siderophores and some humic and fulvic acids are major ligands for iron(III) in surface and ground water.[8] The observed concentrations of the total dissolved iron in natural water systems vary from 0.2 nmol/L in mid ocean surface water,[9] up to 400 mmol/L in polluted urban clouds.[10]

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It is well known that iron is a necessary additive in foods and medicines, e.g., wine,[11] drinks, milk powder, health products, and multivitamins. Human activities have resulted in a series of environmental problems, e.g., water acidification, waste discharge, dissolution and digestion of solid substances by acidic rain, soil extract and surface run off and earth surface in filtration, so that a large amount of Fe has been released into natural water. Iron detection has been studied with many techniques[12] such as MS, ICP, stripping voltammetry, AAS, spectrophotometry, chromatography,[13] and flow injection chemiluminescence.[14] The MS, AAS, and ICP equipment are expensive, while spectrophotometry has advantages such as low cost, simple operation, easy spread, and wide applications. Up to now, it is still being studied and applied extensively, particularly in developing countries.

For example, more and more ways are still being developed to improve sensitivity and selectivity, such as H-point standard addition method,[15] synthesis of novel chromophores, and coupling flow injection analysis.[16] It is still very important to establish simple, sensitive, and selective ways for the determination of dissolved Fe. Therefore, the light-absorption ratio variation approach (LARVA)[17] can improve significantly the analytical sensitivity. In this work, it has been applied to the spectrophotometric determination of dissolved iron with bromopyrogallol red (BPR), which was synthesized and applied for the determination of rare earth metals. The applicability is in the linear range from 0 to 150 ng/mL Fe(II,III) and the detection limit only 4.5 ng/mL. In addition, the complexation between BPR and Fe (II, III) was characterized by the spectral correction technique.[18]

PRINCIPLE AND CALCULATION

Description of 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:

	N L	+	M	⇔	ML_N
Initial State	C_{L0}		C_{M0}		0
Corresponding to	$A^{L}{}_{\lambda 1}$ and $A^{L}{}_{\lambda 2}$				
Equilibrium	C_L		≈ 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. η is the effective fraction of L to complex M, and A_c is the real absorbance of ML complex at wavelength λ_2. Both $A^{L}{}_{\lambda 1}$ and $A^{L}{}_{\lambda 2}$ are the absorbances of the L solution that are separately measured at wavelengths λ_1 and λ_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. The spectral correction technique has successfully eliminated the negative effect caused by excess L.[18,19]

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

where

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

and

$$\beta = \frac{A_{\lambda 2}^{L}}{A_{\lambda 1}^{L}} \tag{3}$$

and

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

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where

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

Both α and β are the correction constants, and γ is the complexation 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 enough M, respectively measured at λ_1 and λ_2 against water. From Equations (1–5), A_c, α, β, η, and γ can be calculated and used to characterize the Fe-BPR complex.

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Light Absorption Ratio Variation Approach

The primary principle of the light absorption ratio variation approach (LARVA) can be described as the following relations:[17]

$$\Delta A_r = pC_{M0} + q \tag{6}$$

where

$$\Delta A_r = A_r - A_{r0} = \frac{A_{\lambda 2}}{A_{\lambda 1}} - \frac{A^L_{\lambda 2}}{A^L_{\lambda 1}} \tag{7}$$

Where ΔA_r is the absorbance ratio variation of the M-L reaction solution measured at λ_1 and λ_2 against the water reference. Factors p and q are both constants. Equation (6) can be directly used to determine trace amounts (C_{M0}) of M. Because the sensitivity factor p is the inverse ratio of C_{L0},[17] the analytical sensitivity will go increasingly higher as the addition of L becomes less. Nevertheless, a too low L will cause an increase of the interference of instrumental noise. A proper light absorption of L is suggested to be between 0.01 and 0.1.

EXPERIMENTAL

Apparatus and Chemicals

The absorption spectra of the BPR 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 BPR. A Model SK3300H supersonic cleaner (Shanghai Kedao Supersonic Instruments Co. Ltd., Shanghai, China) was used to dissolve solutes completely.

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, Shanghai Chemical Reagents, Chinese Medical Group) in 50 mL of 50% sulfuric acid (A. R. grade, Shanghai Sihewei Chemicals). The solution was then diluted to 1000 mL with deionized water. A standard use solution containing 1.00 mg/L Fe(II) was prepared by diluting the standard stock solution. A standard solution containing 100 mg/L Fe(III) was prepared by dissolving 0.8640 g of $(NH_4)Fe(SO_4)_2 \cdot 12H_2O$ with the same method above. All the solutions were stored at less than 5°C. A solution containing 0.500 mmol/L BPR (CAS number 16574-43-9, A. R. grade, Shanghai Chemical Reagents) was prepared by dissolving 0.1395 g in 500 mL of ethanol. The solution used in subsequent experiments containing 0.100 mmol/L BPR was prepared by diluting 0.500 mmol/L BPR in deionized water. Both of them were stored at less than 5°C. In addition, a series of acetate buffer solutions from pH 3.86 to 7.16 was prepared with acetic acid (A. R. grade, Shanghai Chemical Reagents, Chinese Medical Group) and sodium acetate (A. R. grade, 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. A stock thiocarbamide solution (0.5 M) was prepared by dissolving thiocarbamide in 100 mL of deionized water, while a stock F^- solution (100 mg/L) was prepared by dissolving sodium fluoride in 100 mL of deionized water.

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General Procedures

Characterization of Complex

The characterization of the BPR complex mainly consists of two steps: determination of spectral correction constants α and β and calculation of parameters A_c, η, and γ. First, into a series of 10 mL calibrated flasks were added different amounts of Fe^{3+} from 0 to 100.0 μg. Then, 1.00 mL of pH 6.23 buffer solution and 1.00 mL of 0.100 mmol/L BPR were added, respectively. The solutions were diluted to 10 mL with deionized water and mixed well. The absorbances, $A_{558\,nm}$ and $A_{600\,nm}$ of these solutions were measured at 558 and 600 nm against water, and the ratio

$A_{558\,nm}/A_{600\,nm}$ in each solution was calculated. The ratio value will remain at a minimal constant when Fe^{3+} is more than a certain free BPR. From its spectrum, α may be worked out from Equation (2). Second, into a series of 10 mL calibrated flasks were added 1.00 mL of pH 6.23 buffer solution and 0.100 mmol/L BPR from 0.05 to 5.00 mL. The solutions were then diluted to 10 mL with deionized water and mixed thoroughly. The absorbances, $A^0_{558\,nm}$ and $A^0_{600\,nm}$ of these solutions were measured at 558 and 600 nm against water, and each β was calculated from Equation (3). Then, 1.0 μg of Fe^{3+} was added into the solutions above. After mixing thoroughly, the absorbances ($A^0_{558\,nm}$ and $A^0_{600\,nm}$) of these solutions were measured at 558 and 600 nm against water. The parameters A_c, η, and γ were calculated according to Equations (1), (5), and (4). Thus, the Fe^{3+} –BPR complex was characterized. The same procedures were used in the characterization of Fe^{2+}–BPR complex.

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Determination of Iron Ions in Natural Water

Water samples were collected from Yangtze River, Taihu Lake, tap water, and two cross sections of 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. Of each water sample, 100 mL was filtered by an acetate membrane with a 0.45 μm aperture and the filtrate was collected. These five samples were then measured according to the following procedures. A known volume of a sample solution was added into a 10 mL calibrated flask. Of the pH 6.23 buffer solution of 1.00 mL, 0.40 mL of 0.100 BPR, 0.5 mL of 100 mg/L F^-, and 0.5 mL of 0.5 mol/L thiocarbamide were added. After diluting to 10 mL with deionized water and mixing thoroughly, the absorbances, $A_{558\,nm}$ and $A_{600\,nm}$ of the solution were measured at 558 and 600 nm against a water reference. Meanwhile, a corresponding reagent blank without Fe ions was prepared and its absorbances, $A^0_{558\,nm}$ and $A^0_{600\,nm}$, were measured. Thus, Equation (7) was changed into:

$$\Delta A_r = \frac{A_{600\,nm}}{A_{558\,nm}} - \frac{A^0_{600\,nm}}{A^0_{558\,nm}} \tag{8}$$

Then, from Equation (6), $C_{Fe(II,III)}$ (C_{M0}) is calculated from the calibration graph of Fe series.

RESULTS AND DISCUSSION

pH Dependence of Absorption Spectra

The absorption spectra of the Fe(III) – BPR solutions in various pH solutions are shown in Figure 1A. The Fe(III) – BPR complexation is the most sensitive at pH more than 5.14 from spectra 5–9. In the present work, pH 6.23 buffer solution was added. Curve 8 indicates that the peak is located at 600 nm and the valley at 558 nm. Therefore, these two wavelengths were used in characterization of the Fe(III) – BPR complex and the detection of Fe(III) by LARVA.

Effects of the reaction time on the absorption spectra of the Fe(III) – BPR complexation were performed. The absorbance difference between peak and valley indicated that the reaction is complete in 5 min. Moreover, the light absorption of the complex solution is stable for at least 120 min.

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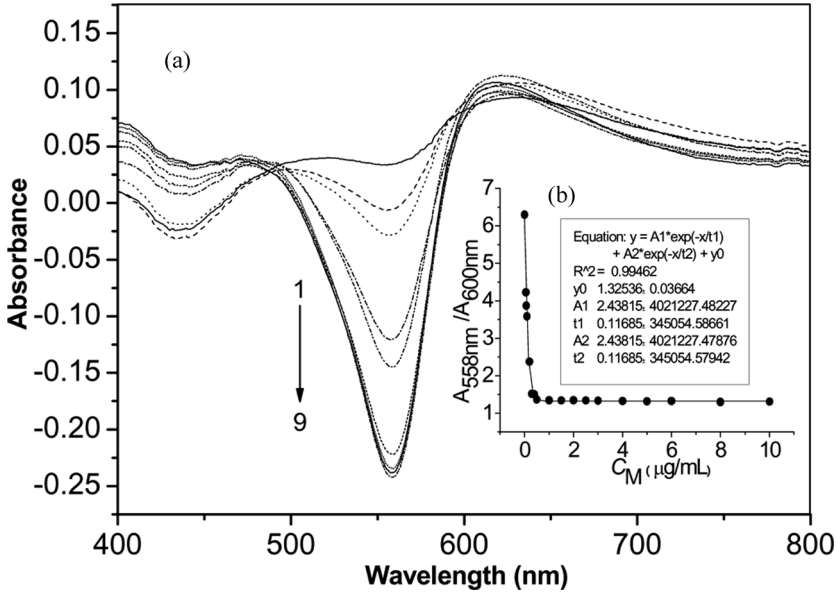

Figure 1. (a) Effect of pH on the absorption spectra of the Fe(III) – BPR complex Solutions. solutions from 1 to 9 contained 0.010 mM BPR and FE(III) at pH 3.86, 4.03, 4.38, 4.71, 5.14, 5.54, 6.05, 6.23, and 7.16 against the reagent blank. (b) Variation of $A_{558\,nm}/A_{600\,nm}$ value of the solutions containing 0.01 mM BPR and Fe(III) from 0 to 10 mg/L, measured at 558 and 600 nm against water.

Characterization of Complex

Variation of the absorbance ratio, $A_{558\,nm}/A_{600\,nm}$ of the solutions with the increase of Fe(III) is shown in Figure 1B. The ratio value drops down rapidly with an increase of Fe(III) when Fe(III) is less than 0.50 mg/L. This is attributed to the formation of Fe(III) – BPR complex. However, the ratio value approaches a minimal constant at 1.33 ± 0.04 by fitting with the exponential decay – second order method. It is attributed to the fact that Fe(III) has reacted with almost all the BPR to form the Fe(III) - BPR complex, i.e., less and less free BPR existed in the solution. Thus, the visible absorption of such a solution was caused by only the Fe(III) - BPR complex. Thus, $\alpha = 1.33$.

By varying BPR concentration in the Fe(III) solution, η and γ of BPR were calculated by Equations (3) and (2); and their variations are shown in Figure 2. From curve 2, γ increases with the increase of BPR and then remains almost constant at 2.1 ± 0.1 when BPR is over 0.005 mM. Therefore, the complexation ratio of Fe(III) to BPR is 1:2, i.e., complex ion $[Fe(BPR)_2]^-$ was formed at pH 6.23. η decreases with the increase of BPR from curve 1. For example, η is only 40% at 0.008 mM BPR, i.e., 60% of BPR is still free not to react with Fe(III). Without doubt, such excess BPR would cause a serious influence on the direct measurement of light absorption of the Fe(III) – BPR complex.

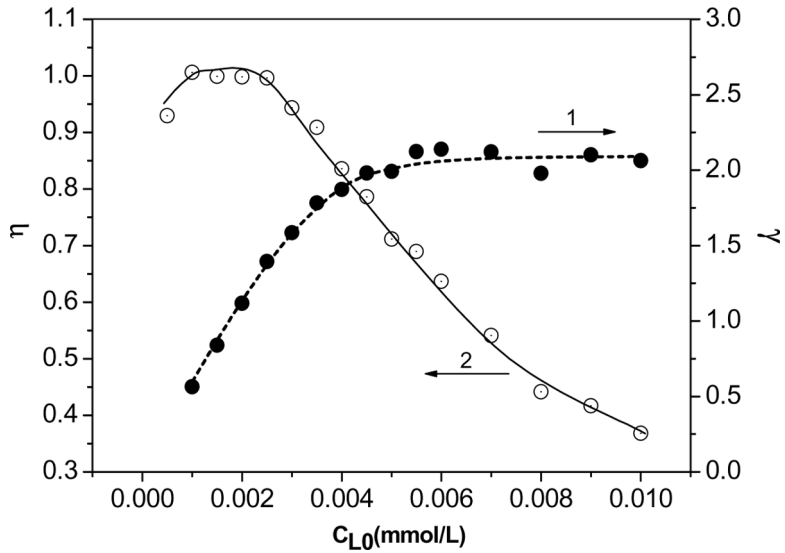

Figure 2. Variations of η (1) and complexation ratio γ (2) of the solutions at pH 6.23 containing 0.100 μg/ml Fe(III) and an BPR concentration from 0.0005 to 0.050 mM.

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Thus, the single wavelength photometric method is unfit to the determination of Fe(III) trace using such a complexation.

Effect of BPR on ΔA_r

From variation (Figure 3) of ΔA_r of the solutions with the initial constant molar ratio of Fe(III) to BPR at 10 μg/μmol, ΔA_r approaches a maximal constant only when BPR is more than 0.010 μmol/mL. The curve indicates the variation of the sensitivity $\Delta A_r/C_{Fe(III)}$ with Fe(III) concentration. The sensitivity becomes higher and higher with a decrease of BPR concentration. However, the noise of the spectrometer will become serious when the BPR concentration is too low. In order to optimize the addition of BPR, some blank tests were carried out.

Calibration Graphs and LOD of Fe

Three series of standard Fe(III) between 0 and 0.050, 0 and 0.150, and 0 and 0.150 μg/mL were prepared and 3.00, 4.00, and 5.00 μM BPR were added, respectively. The absorbances of each solution were measured at

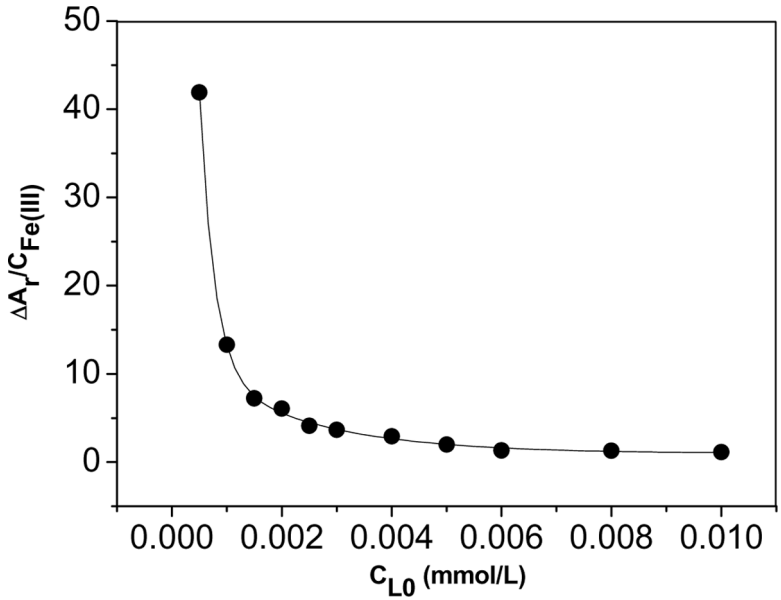

Figure 3. Variation of $\Delta A_r/C_{Fe(III)}$ of the solutions with the same ratio of Fe(III) to BPR at 10 μg/μmol.

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Table 1. Calibration graphs for determination of FE(III) with BPR at pH 6.23

Series	BPR μM	$C_{Fe(III)}$ μg/ml[a]	Standard equation	R^b	σ^c	LOD (μg/L)
1	3.0	0 – 0.050	$\Delta A_r = 2.62\ C_{Fe} + 0.0033$	0.9912	0.0065	7.5
2	4.0	0 – 0.150	$\Delta A_r = 2.29 C_{Fe} - 0.0067$	0.9953	0.0034	4.5
3	5.0	0 – 0.150	$\Delta A_r = 2.02 C_{Fe} - 0.0236$	0.9931	0.0035	5.2

[a]Every series contains nine concentrations.
[b]Linear correlation coefficient.
[c]Standard deviation from 12 replicated blanks.

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600 and 558 nm and ΔA_r was calculated by Equation (4). Their regression equations are given in Table 1. The LOD of Fe, defined as 3 times the standard deviation (σ) of 12 replicated blanks, was calculated and given in Table 1, too. By comparison, series 2 has the lowest LOD at 4.5 ng/mL Fe. Therefore, it was selected in the analysis of water quality.

The calibration range of Fe(II) was prepared, colored, and measured according to the same method as that of Fe(III), where 4.0 μM BPR was added. The comparison of the standard curves (Figure 4) indicated that both the slope values are very near. In fact, Fe^{2+} is often oxidized into

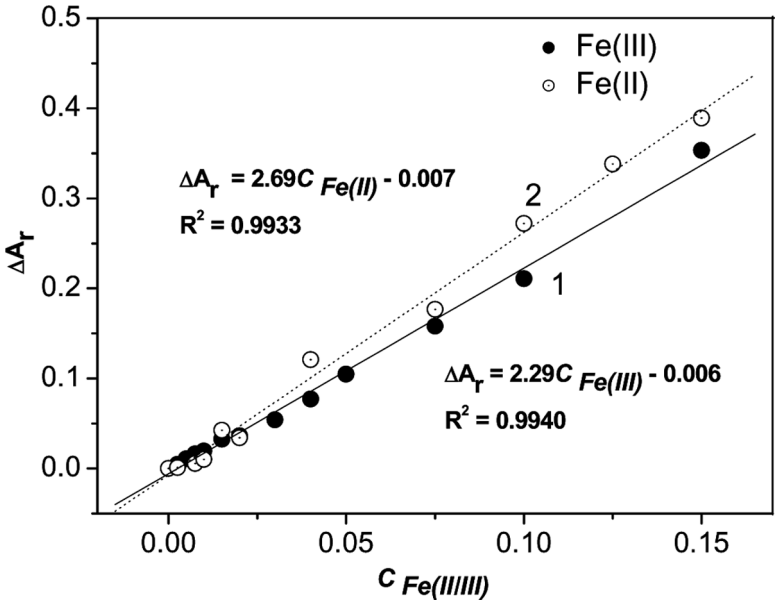

Figure 4. Standard curves for determination of Fe(III) (1) and Fe(II) (2) with BPR in the presence of F^- and thiocarbamide at pH 6.23.

Fe(III), e.g., $Fe(OH)_3$ colloid in neutral natural water. Therefore, line 1 may be used to calculate total Fe^{2+} and Fe^{3+} concentration.

Effect of Foreign Ions

Fifteen foreign ions including 14 kinds of metal ions and 2 anions were added in order to investigate the selectivity of this method in the presence of thiocarbamide and F^-. Their effects on ΔA_r are shown in Table 2. All of them have not affected the direct assay of 0.050 μg/mL Fe(III) (error $< 10\%$). Therefore, the recommended method is highly selective and suitable for the direct monitoring of natural water.

Analysis of Water Samples

In the current work, five types of surface water were analyzed. They were sampled from Yangtze River, Taihu Lake, tap water, and two cross sections of Huangpu River in Shanghai, China. Each of the samples was treated according to the procedures and was colored. The results are listed in Table 3. The recovery rates of Fe(III) are between 95.5 and 106%, and the results corresponded to those detected by ICP.

Table 2. Effect of foreign ions on ΔA_r of the solutions containing 0.050 μg/mL Fe(III)

No.	Foreign ion[a]	Added, μg/ml	Error, %[b]
1	Fe(III)	0.050	
2	Ca(II)	10.00	2.7
3	Mg(II)	10.00	1.4
4	Zn(II)	0.050	−2.6
5	Co(II)	0.050	−5.6
6	Mn(II)	0.250	7.3
7	Ni(II)	0.250	0.6
8	Pb(II)	0.050	−6.5
9	Cd(II)	0.050	4.4
10	Cr(III)	0.050	−7.7
11	Al(III)	0.050	3.6
12	Cu(II)	0.050	−2.7
13	As(III)	0.050	−0.1
14	Mo(□)	0.050	−5.3
15	NO_2^-	0.250	1.6
16	PO_4^{3-}	0.250	7.0

[a]added 0.050 μg/ml Fe(III) into all the solutions from No. 2 to 16;
[b]Error $= (\Delta A_r^{\text{No.x}} - \Delta A_r^{\text{No. 1}})/\Delta A_r^{\text{No.1}} \times 100$ (x : from 2 to 16).

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Table 3. Determination of Fe(II, III) in natural water with BPR at pH 6.23

Sample[a]	Fe^{3+}added (μg)	Fe ions found (μg)	Recovery (%)	Average Fe ions in sample (mg/L)	Fe detected by ICP (mg/L)
Yangtze River	0	0.260 ± 0.062[b]		0.130	0.148
	0.300	0.546 ± 0.556	95.5 98.7		
Taihu Lake	0	0.163 ± 0.080[b]		0.073	
	0.300	0.471 ± 0.455	102.6 97.4		
Tap Water	0	0.322 ± 0.034[b]		0.161	
	0.300	0.620 ± 0.640	99.3 106.0		
Yangshupugang Road Bridge	0	1.00 ± 0.07[b]		0.500	0.524
	0.300	1.31 ± 1.31	102.7 103.0		
Rendelu Road Bridge	0	1.67 ± 0.08[b]		0.835	0.909
	0.300	1.98 ± 1.99	104.6 105.6		

[a]A 2.0 ml volume of a sample was added for complexation.
[b]Four replicate determinations.

CONCLUSIONS

Two significant advantages are identified: (i) more sensitive spectrophotometric detection of iron was performed; and (ii) the presence of F^- and addition of thiocarbamide improve greatly the detection selectivity. Besides, this method is easy operated in ordinary conditions, the reagent is stable enough to be stored long term. The detection results are accurate by comparison with those detected by the classical method. As a result, there is the potential for this method to provide a field detection of Fe ions in natural water.

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