Light-Absorption Ratio Variation Approach to Sensitive and Selective Determination of Iron with Trimethoxyphenylfluorone, Cetylpyridinium, and Thioglycollic Acid

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The complexation between trimethoxyphenylfluorone (TMPF) and Fe is highly sensitive at pH 11.80 in the presence of cetylpyridinium chloride (CPC) and thioglycolic acid (TGA), where TGA reduced TMPF into a reduced ligand (RTMPF) and Fe(III) into Fe(II). The complexations of RTMPF with CPC and Fe have been characterized by the break point approach and the spectral correction technique. The binuclear complex, Fe₂(RTMPF)₁₀(CPC)₂₀, was formed via coordination bond and ion-pair attraction. The Fe-TMPF-CPC complexation is selective in the presence of ethylenediamine tetraacetic acid (EDTA) and Al(III) so it was applied to the spectrophotometric determination of total Fe(II+III) by the light-absorption ratio variation approach (LARVA). Results indicated that ΔA of the Fe-RTMPF solution is linear at 568 and 641.5 nm at the range between 0 and 100 ng/mL Fe. The limit of detection (3σ) of Fe is only 2 ng/mL. This method was applied to analysis of several samples such as natural waters, cigarette ash, and urine with satisfactory results.

Keywords: Light-absorption ratio variation approach; Spectrophotometry; Trimethoxyphenylfluorone; Binuclear complex; Determination of iron; Thioglycolic acid.

INTRODUCTION

Iron is one of the most abundant elements in nature, widely presenting in a variety of rock and soil minerals. Iron can exist as inorganic species¹ of Fe(III) or Fe(II), as organic complexes,² exis as colloids³ of oxides, oxyhydroxides, or mixed with organic material, and be 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.⁵ Iron is the most abundant transition metal present 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 proteins and enzymes. The rest ~ 29% is stored. It plays an essential role in photosynthesis.⁶⁻⁷ Microbial processes result in the reductive formation of Fe(III).⁸ Siderophores and some humic and fulvic acids are major ligands for iron(III) in surface and groundwater.⁹ The observed concentrations of the total dissolved iron in natural water systems vary from 0.2 nmol/l in mid-ocean surface water to 400 μmol/l in polluted urban cloud.¹¹ It is well known that iron is a necessary additive in foods and medicines, e.g., wine,¹² drinks, milk powder, health products, and multi-vitamins. 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 erosion, and surface runoff and earth-surface filtration, so that a large amount of Fe has been released into natural water. Iron has been studied with many techniques¹³ such as MS, GF-AES, stripping voltammetry, flame AAS, flow injection analysis, spectrophotometry, chromatography,¹⁴ colorimetry, and chemiluminescence. The MS, GF-AAS, and ICP-AES equipment are more expensive. Spectrophotometry has advantages such as low cost, simple operating, easy spread, and wide applications. Up to now, it is still being studied extensively, particularly in developing countries.

It is well known that spectrophotometry has some obvious shortcoming of high complexity in aspects of on-line and real-time analysis, automaticity, micro miniaturization, and multi-components detection. Nevertheless, more and more ways are...
still being developed to improve sensitivity and selectivity such as H-point standard addition method, synchrosis of novel chromophores, and coupling flow injection analysis. It is still very important to establish a simple, sensitive, and selective way for the determination of dissolved Fe. The light-absorption ratio approach (LARVA) was established as a novel sensitive method.

**PRINCIPLE AND CALCULATION**

**Spectral Correction Technique**

A metal (M) - ligand (L) complexation is often used in analysis of trace M. The reaction equilibrium is expressed as follows:

\[
N\ L \quad + \quad M \quad \rightarrow \quad M\ L \quad \Delta G_{M\ L}^{o}
\]

where both \( C_{L}^{o} \) and \( C_{M}^{o} \) are the initial molarities of L and M, and \( \eta \) indicates the effective fraction of L. The symbol \( A_{\lambda} \) indicates the real absorbance of the ML complex at wave length \( \lambda_{2} \). Both \( A_{\lambda_{1}}^{M\ L} \) and \( A_{\lambda_{2}}^{M\ L} \) are the absorances of L so solution measured at wave lengths \( \lambda_{1} \) and \( \lambda_{2} \) against water reference. \( N \) refers to the coordination number of L with M.

In fact, a great deal of L is added in order to complex M completely. The excess of L thus oc crisis a high color fraction in the reaction solution. However, the reaction sensitivity is usually positively correlated to the high light-absorption of L. Recently, a large number of chromophores with big conjugate planes have been synthesized in creating and applied to the detection of trace M. However, a negative appearance was found to restrict the practical application because the exess of L of ten influences the mean surement of light-absorption of the ML complex. Thus, an alytical error increases. With out doubt, this problem must be solved. The spectral correlation technique has a specific advantage because it may eliminate the effect of the light-absorption of excess of L in the ML reaction solution. Absorbance of each color component in cluding the reagent and product may be measured and calculated. Thus, not only the light-absorption of ML complex is obtained, but also the complex is characterized clearly. The principal equations are given below:

\[
A_{\lambda} = \frac{A_{\lambda_{2}} - \beta A_{\lambda_{1}}}{1 - \alpha \beta}
\]

where

\[
\beta = \frac{A_{\lambda_{2}}^{M\ L}}{A_{\lambda_{1}}^{M\ L}}
\]

and

\[
\alpha = \frac{A_{\lambda_{1}}^{M\ L}}{A_{\lambda_{2}}^{M\ L}}
\]

\[
\gamma = \eta \times \frac{C_{L}^{o}}{C_{M}^{o}}
\]

where

\[
\eta = \frac{A_{\lambda_{1}} - A_{\lambda_{2}}}{A_{\lambda_{2}}^{M\ L}} + 1
\]

Both \( \beta \) and \( \alpha \) are the correlation constants, \( \gamma \) the complexation number of L on M. \( A_{\lambda_{1}} \) and \( A_{\lambda_{2}} \), \( A_{\lambda_{1}}^{M\ L} \), and \( A_{\lambda_{2}}^{M\ L} \) are the absorbances of the M-L reaction solution and a ML complex solution with out free L, respectively, measured at \( \lambda_{1} \) and \( \lambda_{2} \) against a water reference. From Equation 4, \( \gamma \) increases up to a maximal coordination constant \( N \) with increase in the molar ratio of L to M. In this study, it was applied to identify the composition of Fe-TMPF complex.

**LARVA**

The main equations of the LARVA are described as follows:
\[ \Delta A = pC^{'}_M + q \]  

\[ \Delta A = \frac{A_2 - A_0}{A_{12} - A_{11}} \]  

The symbols \( A_{11}, A_{12}, A_{21}, \) and \( A_{22} \) have the same meanings as the equations above. \( \Delta A \) in dedicates the absorbance ratio variation of the reaction solution. \( C_{M0} \) is the initial concentration of M but is much lower than \( C_{M0} \). All \( p', q' \), \( p \) and \( q \) are constants when both \( \lambda_1 \) and \( \lambda_2 \) and the reaction conditions are selected.

Thus, the sensitivity factor \( p \) is the inverse ratio of absorbance change with \( \text{pH} \) change. The ammonium buffer solution was used as the chromophore to react with Fe. The ammonium buffer solution, \( \text{pH} \) 9.43, 10.0, 10.48, 10.98, 11.53, 11.80 and 12.23 were prepared with ammonium and ammonium chloride, and they were used as the solvent for Fe.

The LARVA is different from two earlier absorbance ratio ways: the first utilizes the variation of absorbance ratio with \( \text{pH} \) change, and the other utilizes the absorbance ratio at two wave lengths to examine purity of an organic compound, e.g. protein, or to identify a molecular structure.

**EXPERIMENTAL**

**Apparatus and Reagents**

The absorbion spectrum of the TMPF and its complex solutions were recorded with a Perkin-Elmer Model Lambda-25 spectrometer. The spectrometer was computer controlled using a UV WinLab software (Version 2.85.04). A Model KQ318T super sonic wave cleaner (Kunshan Analytical Instruments, China) was used for rapid dissolution of TMPF and EDTA in solution. The \( \text{pH} \) of the solution was measured with a Model pH-25 acidity meter (Shanghai Precise Scientific Instruments, China). A Model BCD-196 refrigerated freezer (Meiling Produc tion of Anhui Province, China) was used to store the dilute \( \text{Fe(II)} \) and TMPF solutions.

1000 mg/l iron standard solution (National Certified, GSB 07-1264-2000) was pur chased from the Institute for Determination of Iron by LARVA. Refer ence Ma terials of SEPA of China. Both 1.00 and 10.0 \( \mu \text{g} \)/mL Fe solutions were prepared by diluting the above solution. 0.250 mmol/l TMPF was prepared by dissolving 51.7 mg of purified trimethoxyphenylfluorone (provid ed by Chang Ke Reagents Institute for the study of Shanghai) in 250 mL of ethyl alcohol ab soleute (AR, Zhenxing Chem i cal Reagents Co.) in deionized wa ter, and then it was diluted to 500 mL with deionized water. It was used as the chromophore to react with Fe. The ammonium buffer solutions, \( \text{pH} \) 9.43, 10.0, 10.48, 10.98, 11.53, 11.80 and 12.23 were prepared with ammonium and ammonium chloride, and they were used as the solvent for Fe.

**General Procedures**

**Characterization of Fe-TMPF complexation:** Into a series of 10-mL calibrated flasks, 1 mL of \( \text{pH} \) 11.80 buffer solution, 0.5 mL of 2 mmol/l CPC, 0.5 mL of 5% TGA and 0.500 mg of Fe were added. 0.250 mmol/l TMPF was added from 0.100 to 0.800 mL and they were diluted to 10 mL and mixed well. After 10 min, the absorbances were measured at 521.5 and 641.5 nm against the reagent blank with out Fe. The symbols, \( \beta, \alpha, \eta \), and \( \gamma \) were calculated by the equations above.

**Determination of Fe:** Less than 5.00 mL of a sample solution was added into a 10-mL flask. 0.5 mL of 2 mmol/l CPC, 1 mL of \( \text{pH} \) 11.80 buffer solution, 1 mL of 0.1 mmol/l EDTA, 0.50 mL of 5% TGA and 0.400 mL of 0.250 mmol/l TMPF were added. It was diluted to 10 mL and mixed well. After 10 min, 50 \( \mu \text{g} \) of 100 mg/l Al(III) were added and mixed well immediately. After 10 min, the absorbances were measured at 568 nm (\( \lambda_1 \)) and 641.5 nm (\( \lambda_2 \)) against the water. If the measurement error is not too large, a reagent blank with out Fe was prepared and then measured at \( A_{568nm}^{\prime} \) and \( A_{641.5nm}^{\prime} \). Thus, \( \Delta A \), is calculated by the relation:
From Equation (6) or (7), $C_{Fe}$ in the sample was calculated.

**RESULTS AND DISCUSSION**

**Dependence of pH**

The absorption spectra of the Fe-TMPF solutions in various pH mediums are shown in Fig. 1. From curves 1-7 in A, the peaks are located at about 540 nm and the valleys at about 520 nm. From change of the interval between the peak and valley shown in B, the TMPF-Fe complexation is more sensitive at pH between 10 and 12. From experiments, we observed that the complexation goes in sensitive in the presence of EDTA at pH less than 10. It is attributed to the fact that EDTA coordinates Fe strongly. If pH is more than 11, the coordination ability of TMPF will go much stronger to react with Fe than that of EDTA. The reason is that the dehydrogenation of TMPF will happen to form negative bicovalent ions. Thus, it is favorable for complexation with CPC. In this work, pH 11.80 ammonia buffer solution was specified and added. The absorption peak of such a solution is located at 641.5 nm and the valley at 521.5 nm, and two such wavelengths were selected in characterization of the Fe-TMPF complexation.

**Reaction of CPC and TGA with TMPF**

From spectra A-1, A-2 and A-3 shown in Fig. 2, both CPC and TGA can react with TMPF at pH 11.80. From curve A-1, the TMPF-H$_2$O complex peak is at 507 nm. From curve A-2, the CPC-TMPF complex peak is at 577 nm. The spectral red shift (SRS) of the CPC-TMPF complex is 77 nm so the ion-pair complexation is strong. Also, the light-absorption of spectra A-2 be comes greater than that of spectrum A-1. There fore, TMPF was reduced into the re duced TMPF (RTMPF) as shown in Fig. 3. RTMPF is one of the quadridentate ligands. In basic medium, its two sides will form quadrivalent anions which can all complex metal ions (see Fig. 3). It is favorable for the use of LARVA because it has a stronger light-absorption than TMPF. From curve A-4, the main peak at 577 nm and the shoulder peak at 515 nm indicate the complexation of CPC with RTMPF. Curve A-5 presents spectrum of only the Fe-RTMPF complex without free RTMPF in the presence of CPC because Fe is over RTMPF molarity. The reason is that the dehydrogenation of TMPF will happen to form negative bicovalent ions. Thus, it is favorable for complexation with CPC. In this work, pH 11.80 ammonia buffer solution was specified and added. The absorption peak of such a solution is located at 641.5 nm and the valley at 521.5 nm, and two such wavelengths were selected in characterization of the Fe-TMPF complexation.

**Characterization of Fe-TMPF complexation by spectral correction technique**

From curve A in Fig. 5, the correction constant, $\beta$ of
RTMPF decreases with increase of RTMPF molarity at pH 11.80 in the presence of CPC. It indicates that the self-aggregation of RTMPF will happen to form a dimer or polymer in such a medium. From curve B, the effective fraction $\eta$ of RTMPF increases rapidly and then decreases rapidly when RTMPF is more than 0.010 mmol/l in the presence of 0.050 mg/l Fe(III). This is attributed to the effect of the complexation equilibrium between Fe and RTMPF. At the peak, $\eta$ of 0.010 mmol/l RTMPF is only 41.6%. Therefore, 58.4% RTMPF has not reacted with Fe(III). With out doubt, so high an excess of RTMPF free in the Fe-RTMPF solution will influence the measurement of light-absorption of the Fe-RTMPF complex. Thus, ordinary spectrometry is limited for characterization of the Fe-RTMPF complex and accurate determination of Fe trace. From curve C, $\gamma$ of TMPF to coordinate Fe(III) increases with increase of RTMPF molarity and then approaches a maximal constant at 5.0. Therefore, the formation of Fe(RTMPF)$_5$ was confirmed at pH 11.80.

![Absorption spectra of TMPF in the presence of the assistants and Fe(III) at pH 11.80](image)

**Fig. 2.** Absorption spectra of TMPF in the presence of the assistants and Fe(III) at pH 11.80: A-1 - 0.010 mmol/l TMPF; A-2 - 0.010 mmol/l TMPF and 0.10 mmol/l CPC; A-3 - 0.010 mmol/l TMPF in 0.25% TGA medium; A-4 - 0.010 mmol/l TMPF and 0.10 mmol/l CPC in 0.25% TGA medium; A-5 - 0.0050 mmol/l TMPF, 0.10 mmol/l CPC and 0.50 mg/l Fe(II); B-1 - 0.010 mmol/l TMPF and 0.050 mg/l Fe(III) in the absence of CPC and TGA; B-2 - 0.050 mg/l Fe(III), 0.010 mmol/l TMPF and 0.10 mmol/l CPC in the absence of TGA; B-3 - 0.010 mmol/l TMPF, 0.050 mg/l Fe(II) and 0.10 mmol/l CPC; B-4 - 0.010 mmol/l TMPF and 0.050 mg/l Fe(III) in 0.25% TGA medium and B-5 same as B-4 but in the presence of 0.10 mmol/l CPC. From A-1 to A-5 against water reference and the others against the corresponding blank.

**Fig. 3.** TMPF and its structural change in the presence of TGA and complexation between metal ion (M) and RTMPF.
From the complexation numbers of CPC and Fe with RTMPF, the binuclear complex \( \text{Fe}^{2+}(\text{RTMPF})_{10}(\text{CPC})_{20} \) was formed by coordination bond and ion-pair attraction.

**Effect of Reaction Time and Addition of Al(III)**

From the variation of the absorption spectra of the Fe-TMPF solution at pH 11.80 in the presence of CPC, TGA and EDTA, the reaction is complete after 10 min. However, from the experimental phenomena, the light-absorption of the reagent blank is unstable and variable with time. It is possible for RTMPF to be oxidized by dissolved oxygen in the basic medium. Thus, it will affect seriously the following application of LARVA. If enough Al(III) was added in the solution to completely coordinate the excessive RTMPF in the Fe-RTMPF solution, such an effect can be eliminated and the selectivity of the method will improve obviously for the determination of Fe trace. The absorption spectrum of such a solution is shown in Fig. 6(A). By comparing this spectrum with spectrum 6 in Fig. 1, the peak at 641.5 nm has no change, but the valley shifts from 521.5 to 568 nm. This is attributed to the complete complexation of RTMPF free in the Fe-RTMPF reaction with Al. In the following experiments, both the wavelengths 641.5 and 568 nm are used in the determination of Fe trace. From curve B-1, \( \Delta \alpha_0 \) of the RTMPF-CPC solution always in creases with time. This confirms the experimental phenomena observed above. After 10 min, the addition of Al(III) plays an obvious role in the stabilization of \( \Delta \alpha_0 \) from curve B-2 but also \( \Delta \alpha_0 \) is much less than that in curve B-1. This is very important in application of the LARVA. Therefore, Al(III) must be added while the Fe-RTMPF reaction is at 10 min and then both \( \alpha \) and \( \Delta \alpha_0 \) were measured after 10 min.

**Variation of \( \Delta \alpha \) and Option of RTMPF Molarity**

Change of \( \Delta \alpha \) of the Fe-RTMPF solutions is shown in Fig. 7 with a constant molar ratio of Fe to TMPF at 0.0716:1.
µmol/µmol in the presence of EDTA, CPC, TGA and Al(III).

ΔAr reaches a peak at 0.020 mg/l Fe(III) and then decreases. Similarly, the less TMPF molarity is, the lower the detectable Fe will go. Of course, the fraction of the instrumental noise will increase seriously if the light-absorption is too low. In the following calibration series, three additional volumes, 0.200, 0.300 and 0.400 mL of 0.250 mmol/l TMPF were tried so as to find an optimal addition.

Calibration Graphs and Limit of Detection

Three series of standard Fe(III) between 0 and 0.050, 0 and 0.070 and 0 and 0.100 µg/mL were prepared and 0.200, 0.300 and 0.400 mL of 0.250 mmol/l TMPF were added, respectively. The reactions were carried out according to the recommended procedures. The absorbances of each solution were measured at 568 and 641.5 nm and then ΔAr was calculated by Equation (9). The linear scope of Fe and the regression equations are given in Table 1. The limit of detection of Fe, defined as the blank values plus 3 times the standard deviation of 10 replicated blanks, was calculated and is given in Table 1, too. Among them, Line 3 is the best because of the good blank precision to result in the lowest limit of detection (LOD) at only 2 ng/mL Fe. Therefore, 0.400 mL of 0.250 mmol/l TMPF is added in analysis of samples. The rec-
The recommended method is one of the most sensitive detections of Fe at present, but also it is simple in operation. It is suitable for natural water, body liquids, food, medicine, materials, and biological and many other samples.

**Effect of Foreign Ions**

The coordination position of RTMPF ligand is $\text{O}^-$ but that of EDTA ligand is $\text{N}^-$. The former binds more strongly to Fe(II) than the latter. Therefore, the addition of EDTA will not replace RTMPF in the RTMPF-Fe complex. On the contrary, EDTA can coordinate most heavy metals, so it was used to mask foreign metal ions. In addition, a great deal of Al(III) was added to complex the excessive RTMPF in the Fe-RTMPF solution because of optical instability of RTMPF in basic medium. Thus, the mixed reaction will change to be more favorable to spectrophotometry. Fourteen foreign metal ions were added in the Fe(III)-RTMPF complexation and their effect errors are shown in Table 2. We observed that most metals will not influence the direct determination of dissolved Fe(Fe$^{II}$ + Fe$^{III}$) in samples. Therefore, this method is highly selective.

**Preparation and Analysis of Sample Solution**

Water and liquid samples can be analyzed directly without deep pre-treatment. Necessary filtration or elimination of the back ground color is of ten possible. Solid samples, e.g. soil, plants, and food, must be dis solved in strong acidic me dium and the whole Fe extracted from the sample. The cleaning solution was neutralized to pH of about 4 with 2 mol/l NaOH and then an analyzed. Here, nine samples: five natural waters, a tap water sample, a cigarette ash sample and a human urine sample were prepared into the solutions, and total iron was determined according to the recommended procedures. The results are listed in Table 3. The recovery rates of Fe are between 88.0 and 111%. It was seen that the results obtained by the recommended method are in good agreement with those obtained by an ISO standard method using 1,10-phenanthroline. The method is simple, inexpensive, accurate, and reproducible and so is suitable for the monitoring of various samples.

**CONCLUSIONS**

As a result, it can be concluded that the proposed method enhances sensitivity and improves the detection limit in terms of Fe(III). Also, in the proposed method, none of the metal ions have been found to interfere with the direct determination of Fe(III). Two significant advantages are identified: (i) more sensitive direct spectrophotometric detection of Fe can be performed; and (ii) the presence of EDTA and addition of Al(III) improves greatly the detection sensitivity. The per force of the method described here allows the detection of iron species. The LARVA as a novel spectrophotometric way makes the detection sensitivity over 10 times as high as the ordinary method. Micro-volume of a sample, e.g. 0.100 mL of biological or food sample may be

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**Table 1. Regression equations and limit of detection of Fe**

<table>
<thead>
<tr>
<th>Line</th>
<th>Fe(III), µg/10 mL</th>
<th>TMPF, mM</th>
<th>$p$</th>
<th>$\Delta A_r$ vs. C$_{Fe}$</th>
<th>R$^a$</th>
<th>$\sigma^b$</th>
<th>LOD$^c$, ng/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-0.40</td>
<td>0.0050</td>
<td>1.205</td>
<td>$\Delta A_r = 1.205C_{Fe} + 0.0391$</td>
<td>0.9904</td>
<td>0.0238</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>0-0.70</td>
<td>0.0075</td>
<td>0.9095</td>
<td>$\Delta A_r = 0.9095C_{Fe} + 0.0190$</td>
<td>0.9962</td>
<td>0.0129</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>0-1.00</td>
<td>0.0100</td>
<td>0.6428</td>
<td>$\Delta A_r = 0.6428C_{Fe} + 0.0004$</td>
<td>0.9991</td>
<td>0.0046</td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$ Linear correlation coefficient. $^b$ Standard deviation of 10 repetitive blanks. $^c$ Limit of detection of Fe(III) was calculated by LOD = $3\sigma/p$.

**Table 2. Effect of foreign ions on $\Delta A_r$ of the solutions containing 0.50 µg of Fe(III) and error showing**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ion</th>
<th>Added, µg/10 mL</th>
<th>Error$^a$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(III)</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ca(II)$^b$</td>
<td>50.0</td>
<td>7.1</td>
</tr>
<tr>
<td>3</td>
<td>Mg(II)</td>
<td>20.0</td>
<td>4.7</td>
</tr>
<tr>
<td>4</td>
<td>Co(II)</td>
<td>5.00</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>As(III)</td>
<td>1.00</td>
<td>9.2</td>
</tr>
<tr>
<td>6</td>
<td>Zn(II)</td>
<td>5.00</td>
<td>-3.1</td>
</tr>
<tr>
<td>7</td>
<td>Cr(III)</td>
<td>1.00</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>Pb(II)</td>
<td>2.00</td>
<td>-4.0</td>
</tr>
<tr>
<td>9</td>
<td>Cd(II)</td>
<td>1.00</td>
<td>0.9</td>
</tr>
<tr>
<td>10</td>
<td>Cu(II)</td>
<td>2.00</td>
<td>-0.8</td>
</tr>
<tr>
<td>11</td>
<td>Al(III)</td>
<td>5.00</td>
<td>2.1</td>
</tr>
<tr>
<td>12</td>
<td>V(V)</td>
<td>2.00</td>
<td>-7.7</td>
</tr>
<tr>
<td>13</td>
<td>Ni(II)</td>
<td>1.00</td>
<td>-5.1</td>
</tr>
<tr>
<td>14</td>
<td>Mn(II)</td>
<td>2.00</td>
<td>-6.0</td>
</tr>
<tr>
<td>15</td>
<td>Ge(IV)</td>
<td>1.00</td>
<td>-8.9</td>
</tr>
</tbody>
</table>

$^a$ Error = ($\Delta A_r^\text{No.x} - \Delta A_r^\text{No.1}$)/$\Delta A_r^\text{No.1} \times 100$ (x is from 2 to 15). $^b$ Added 0.500 µg of Fe(III) into all the solutions from No. 2 to 15.
Table 3. Determination of Fe in samples

<table>
<thead>
<tr>
<th>Sample from</th>
<th>Fe added, µg/l</th>
<th>Fe found, µg/l</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Lake</td>
<td>0</td>
<td>9.8 ± 2.5a</td>
<td>88.0 - 111c</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>18.6-20.9b</td>
<td></td>
</tr>
<tr>
<td>Taihu Lake</td>
<td>0</td>
<td>12.7 ± 1.6c</td>
<td>94.0 - 111c</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>22.1-23.8d</td>
<td></td>
</tr>
<tr>
<td>Underground water</td>
<td>0</td>
<td>36.7 ± 4.1e</td>
<td>91.2 - 106f</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>73.2-78.9g</td>
<td></td>
</tr>
<tr>
<td>Offshore water</td>
<td>0</td>
<td>69.2 ± 2.8h</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>67.1i</td>
<td></td>
</tr>
<tr>
<td>Yangtze River</td>
<td>0</td>
<td>37.9 ± 2.3j</td>
<td>91.0 - 108.7c</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>65.2-70.5k</td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>0</td>
<td>143.2 ± 3.7l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>151m</td>
<td></td>
</tr>
<tr>
<td>Urine</td>
<td>0</td>
<td>164 ± 17n</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>259.1-272.4o</td>
<td></td>
</tr>
<tr>
<td>Smoking ash (mg/g)</td>
<td>0</td>
<td>1.26 ± 0.03p</td>
<td>95.1 - 108.4c</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>1.19q</td>
<td></td>
</tr>
</tbody>
</table>

a Average of four determinations. b Average of three determinations. c e.g. 88% = (18.6 - 9.8)/10.0 × 100%. d Average of two determinations with 1,10-phenanthroline by spectrophotometry.

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