

Continuous Flow Analysis Combined with a Light-Absorption Ratio Variation Approach for Determination of Copper at ng/ml Level in Natural Water

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The complexation between Cu(II) and naphthochrome green (NG) is very sensitive at pH 4.09 with the formation of complex ion $[\text{Cu}(\text{NG})_2(\text{H}_2\text{O})_2]^{2-}$. It can thus be used for the determination of Cu(II) by the light-absorption ratio variation approach (LARVA) with a good selectivity. Both the ordinary detection procedure and continuous flow analysis (CFA) were carried out, where the latter is fit for continuous and rapid analysis of samples. The limit of detection (LOD) of Cu(II) is only 1 ng/ml, which is favorable for direct monitoring of natural water. About 30 samples could be analyzed per hour by CFA. Cu(II) contents in Yangtze River, West Lake, Taihu Lake of China and seawater near Shanghai were determined with satisfactory results. The CFA-LARVA spectrophotometry was the first to be coupled and it will play an important role in the *in-situ* analysis of natural water quality.

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Introduction

Copper is an essential element not only for life in mammals but also for plants, and plays an important role in carbohydrate and lipid metabolism.^{1,2} Increases in copper concentration in water systems and in 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.³ In natural water, the majority of copper is bound to organic and inorganic ligands, leaving only around 1% of the total copper in the dissolved state. As a result, the Cu(II) ion level is always low in natural water, and scientists require only such ions are considered to be bioavailable or toxic.⁴ In order to understand toxicity of copper in water, simple, sensitive and accurate detection methods.⁵ Actually, copper could be determined directly in water and food samples by inductively-coupled plasma optical emission spectrometry (ICP-OES)⁶ or electrothermal atomic absorption spectrometry (ETAAS),⁷ which usually have a sufficiently low detection limit. In spite of the well-known advantages of these instrumental techniques, they cannot avoid the necessity of expensive instrumentation and sophisticated manipulation. Atomic absorption spectrometry⁸ is available in most laboratories and is normally less subject to interferences than ICP-OES or ETAAS, but it requires the use of a preconcentration step in order to reach an appropriate level of sensitivity, such as coprecipitation with magnesium hydroxide as collector,⁹ liquid-liquid extraction,¹⁰ flotation¹¹ and solid phase extraction.¹² Besides, the stripping voltammetry,¹³ spectrophotometry,^{14,15}

spectrofluorophotometry,¹⁶ and chemiluminescence¹⁷ methods are used for determination of Cu(II) traces, too. New combination methods with derivative,¹⁸ flow injection,¹⁹ continuous flow analysis (CFA),^{20,21} kinetic catalytic,^{22,23} chemometric²⁴ and other methods are recently reported. All of them have played important roles in improving the analytical sensitivity, selectivity and detection efficiency.

Recently, the light-absorption ratio variation approach (LARVA) was developed²⁵ and applied. It has exhibited its most obvious advantage only in a quite diluted reaction solution by micro absorption of UV or visible light. The analytical sensitivity often increases to become 10 times better than that of ordinary spectrophotometry. It is well known that CFA is one of suitable techniques for water analysis since it has a high sampling rate together with excellent repeatability. In the present work, a new technique, the LARVA coupling CFA, was advanced to improve seriously the sensitivity as well as to increase greatly the analytical efficiency.

Experimental

Apparatus and materials

A Model S-4100 spectrometer (Scinco Instruments, South Korea) was used to measure the light absorption of NCG and its Cu(II) complex with Labpro Plus software. An LK2001 FIA System (Lanlike Chemical Electronic High Technology Co., Tianjin, China) with Ver. FIA2001 software was used. The FIA units were included the mixer, reactor, cell and soft plastic tubes. A Model Optima 2100 DV ICP-OES (PerkinElmer Instruments, USA) was used to determine Cu(II) content in samples to examine the results of the recommended methods. A Model pH-25 acidity meter (Shanghai Precise Science

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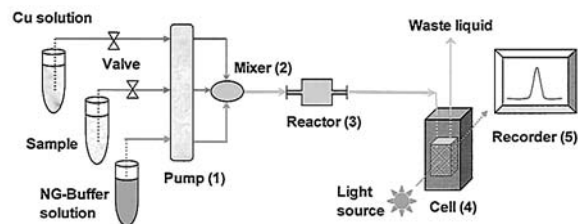


Fig. 1 CFA device sketch for continuous determination of Cu(II) trace with NG at pH 4.09.

Instruments, Shanghai, China) was used to measure the pH of the buffer solutions.

A standard stock solution containing 1000 mg/l Cu(II) (GSB07-1257-2000) was purchased from the Institute for Reference Materials of SEPA, Beijing, China. A standard Cu(II) solution (1.00 $\mu\text{g}/\text{ml}$) was prepared by diluting the above solution. Stock NG solutions (0.500 mM) were prepared by dissolving naphthochrome green (Koch-Light Laboratories, Colnbrock Berks, England) in 250 ml of deionized water. A series of buffer solutions from pH 2.64 and 6.07 were prepared with acetic acid-sodium acetate and they were used to adjust the acidity of the solution. The NG-buffer solution was prepared by mixing 30% pH 4.09 buffer solution with 10 μM NG, and this mixture was used in the CFA.

Characterization of the Cu-NG complexation

Into a series of 10 ml calibrated flasks were added 1.0 ml of pH 4.09 buffer solution and a known volume (from 0.050 to 1.0 ml) of 0.500 mmol/L NG. The solutions were then diluted to 10 ml with deionized water and mixed thoroughly. The absorbances ($A_{506\text{nm}}^0$ and $A_{586\text{nm}}^0$) of these solutions were measured at 506 and 586 nm against water. The correction constant β of each solution was calculated by $\beta = A_{586\text{nm}}^0/A_{506\text{nm}}^0$. Then, 5.00 μg of Cu(II) was added into the above solutions. After thorough mixing, the absorbances ($A_{506\text{nm}}$ and $A_{586\text{nm}}$) of these solutions were measured against water. Thus, the real absorbance of the Cu-NG complex (A_c), the effective fraction (η) of NG to complex Cu(II) and the complexation number (γ) of NG with Cu(II) were calculated according to the relations:²⁶

$$A_c = \frac{A_{586\text{nm}} - \beta A_{506\text{nm}}}{1 - \alpha\beta} \quad (1)$$

and

$$\gamma = \eta \times \frac{C_{\text{NG}0}}{C_{\text{Cu}0}} \quad (2)$$

where

$$\eta = \frac{A_c - A_{586\text{nm}}}{A_{586\text{nm}}^0 + 1} \quad (3)$$

where $C_{\text{Cu}0}$ and $C_{\text{NG}0}$ are the initial molar concentrations of Cu(II) and NG. The correction constant α is calculated by $\alpha = A_{506\text{nm}}^{\text{complex}}/A_{586\text{nm}}^{\text{complex}}$ where $A_{506\text{nm}}^{\text{complex}}$ and $A_{586\text{nm}}^{\text{complex}}$ are the absorbances of a solution containing only the Cu-NG complex and no free NG, measured at 506 and 586 nm against water. As a result, the Cu(II)-NG complex could be characterized.

Analysis of samples

If the sample number or sample volume is little, an ordinary

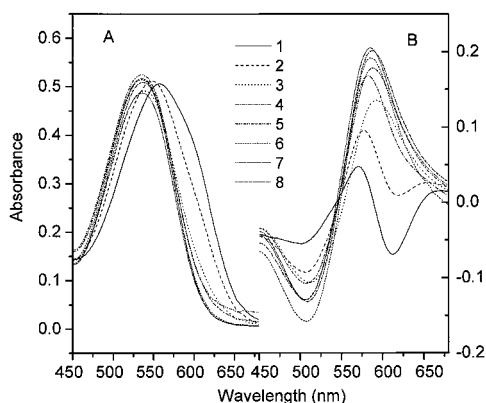


Fig. 2 Effect of pH on the absorption spectra of NG (A) and the Cu-NG (B) complex solutions. Solutions from A-1 to A-8 contained 0.0040 mM NG at pH 2.63, 3.20, 3.75, 4.09, 4.57, 5.08, 5.69 and 6.07 against water reference. Solutions from B-1 to B-8 contained 0.0040 mM NG and 1.00 mg/l Cu(II) at pH 2.63, 3.20, 3.75, 4.09, 4.57, 5.08, 5.69 and 6.07 against the reagent blank.

detection of Cu(II) was recommended according to the following procedure. Usually, a clear water sample can be directly analyzed without any pretreatment. For a turbidity sample, it should be filtered through a piece of filter paper with pore size 0.45 μm . After such a pretreatment, the sample was colored and then measured according to the following procedures. The sample solution above (5.0 ml) was added into a 10 ml calibrated flask. One milliliter of pH 4.07 buffer solution and 0.050 ml of 0.040 mM NG were added. The solution was then diluted to 10 ml with deionized water. After 5 min, the absorbances ($A_{508\text{nm}}$ and $A_{586\text{nm}}$) of the solution were measured at 508 and 586 nm against water reference. In the same way, a reagent blank without Cu(II) was prepared according to the procedure above. Thus, its absorbances ($A_{508\text{nm}}^0$ and $A_{586\text{nm}}^0$) were measured. The light-absorption ratio variation (ΔA_r) of such a sample solution was calculated by the relation:

$$\Delta A_r = \frac{A_{586\text{nm}}}{A_{508\text{nm}}} - \frac{A_{586\text{nm}}^0}{A_{508\text{nm}}^0} \quad (4)$$

According to the LARVA,²⁵ ΔA_r is the direct ratio to the Cu(II) concentration (C_{Cu} , ng/ml) in the sample. Thus, C_{Cu} is calculated from the calibration graph of Cu(II) series.

If the number of samples is great or the sample volume is enough, the following CFA procedure was recommended. The continuous flow device for determination of Cu(II) was equipped according to Fig. 1. Pump (1) at 1000 r/h of speed pushed a sample or Cu(II) solution and the NG-buffer solution into mixer (2) and the mixed solution flowed into reactor (3) where the Cu-NG complexation occurred at pH 4.09. Then, the solution flowed into cell (4) for the automatic absorbance measurement at 506 and 586 nm at 2 min intervals. According to Eq. (4), ΔA_r was calculated. Thus, about 30 samples can be analyzed in 1 h.

Results and Discussion

pH dependence of absorption spectra

The absorption spectra of the Cu(II)-NG solutions in various pH solutions are shown in Fig. 2. The Cu-NG complexation is the most sensitive at pH between 3.20 and 4.57 as seen from

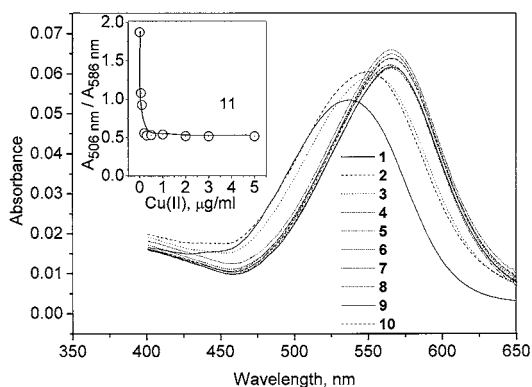


Fig. 3 Spectral change of the Cu-NG complexes at pH 4.09 containing 0.0050 mM NG and a Cu(II) concentration from 1 to 10: 0, 0.050, 0.100, 0.200, 0.300, 0.500, 1.00, 2.00, 3.00 and 5.00 mg/l. Eleven-variations of $A_{506\text{nm}}/A_{586\text{nm}}$ with Cu(II) concentration, measured at 506 and 586 nm against water.

spectra 2–5 in Fig. 2(B). The absorption peak shift of the NG solution is little at pH between 2.64 and 5.08, as seen from curves 1–6 in Fig. 2(A). In the present work, pH 4.09 buffer solution was added. Curve 4 shows that the peak is located at 586 nm and the valley at 506 nm. Therefore, these two wavelengths were used in characterization of the Cu(II)-NG complex and the direct detection of Cu(II) by LARVA.

Effects of the reaction time on the absorption spectra of the Cu-NG complexation were studied. The absorbance difference between peak and valley indicated that the reaction is complete in 2 min. Moreover, the light-absorption of complex solution is stable for at least 60 min. As a result, the CFS is feasible for continuous detection of Cu(II).

Characterization of complex

Variation of the absorption spectra of the Cu-NG solutions with increase of Cu(II) is shown in Fig. 3. Curve 1 shows that the absorption peak of NG is located at 540 nm. However, an obvious spectral red shift appears with increase of Cu(II) by comparison of curve 1 with the others. The peak wavelength hardly changes at all in curves 4–10 when Cu(II) is more than 0.200 mg/l. Variation of the absorbance ratio, $A_{506\text{nm}}/A_{586\text{nm}}$ of the solutions is shown as curve 11. The ratio value drops down rapidly with increase of Cu(II) when Cu(II) is less than 0.200 mg/l. This drop is attributed to the formation of Cu-NG complexes. However, the ratio value approaches a minimal constant at 0.51 when Cu(II) is more than 0.200 mg/l. This limit is attributed to the fact that Cu(II) has reacted with almost all the NG to form the Cu-NG complex, *i.e.* less and less free NG exists in the solution. Thus, the visible absorption of such a solution was caused by only the Cu-NG complex, *i.e.*, α is 0.51. Curves 4–10 show that the peak of the Cu-NG complex is located at 564 nm. Thus, the spectral red shift of the complex is about 24 nm, as seen by comparison of curve 1 with curves 4–10.

By varying NG concentration in the Cu(II) solution, one can calculate η of NG and γ of NG to Cu(II) by Eqs. (2) and (3); and their variations are shown in Fig. 4. Curve 2 shows that η increases with increase of NG and then remains almost constant at about 2 when NG is over 0.0175 mM. Therefore, the complexation ratio of Cu(II) to NG is 1:2, *i.e.*, complex ion $[\text{Cu}(\text{NG})_2(\text{H}_2\text{O})_2]^{2-}$ was formed at pH 4.09. Its possible structure is illustrated as Scheme 1. η decreases with increase

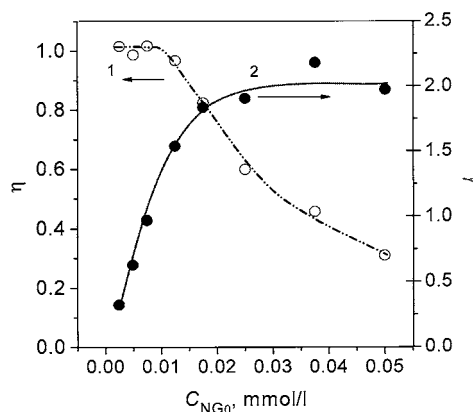
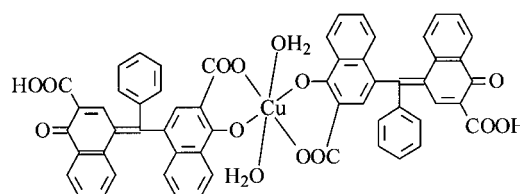


Fig. 4 Variations of η (1) and γ (2) of the solutions at pH 4.09 containing 0.500 $\mu\text{g/ml}$ Cu(II) and an NG concentration from 0.0025 to 0.050 mM.



Scheme 1 The chemical structure of $[\text{Cu}(\text{NG})_2(\text{H}_2\text{O})_2]^{2-}$.

of NG from curve 1. For example, η is only 60% at 0.0250 mM NG, *i.e.*, 40% of NG is still free not to react with Cu(II). Without doubt, such excess NG would exert a serious influence on the direct measurement of light absorption of the NG-Cu complex. Thus, the single wavelength photometric method is unfit for the determination of Cu(II) trace using such a complexation.

Effect of NG on ΔA_r

From variation (Fig. 5) of ΔA_r of the solutions with the initial constant molar ratio of Cu(II) to NG at 25 $\mu\text{g}/\mu\text{mol}$, ΔA_r approaches a maximal constant from curve 1 only when NG is more than 0.010 $\mu\text{mol/ml}$. Curve 2 shows the variation with copper concentration of the sensitivity factor, $\Delta A_r/C_{\text{Cu}}$. The measurement sensitivity goes higher and higher with decrease of NG concentration but it reaches a maximum between 1.2 and 2.0 μM NG. However, the noise of spectrometer will become serious when the NG concentration is too low. In order to select a suitable addition of NG solution, one must carry out a blank test.

Calibration graphs and LOD of Cu(II)

Four series of standard Cu(II) between 0 and 0.020, 0 and 0.050, 0 and 0.100 and 0 and 0.200 $\mu\text{g/ml}$ were prepared and 0.020, 0.050, 0.200 and 0.300 ml of 0.040 mM NG were added. The absorbances of each solution were measured at 506 and 586 nm and ΔA_r was calculated by Eq. (4). Their regression equations and these values are given in Table 1. The LOD of Cu(II), defined as 3 times the standard deviation (σ) of 10 replicated blanks, was calculated and given in Table 1, too. By comparison, series 2 has the lowest LOD of Cu(II). Therefore, it was selected in analysis of water quality. The CFA of series 2 was still carried out according to Fig. 1. Its standard curve is

Table 1 Calibration graphs for determination of Cu(II) with NG at pH 4.09

| Series | NG/mM | Cu(II) ^a , C _{Cu} /μg | Standard equation | R ^b | σ ^c | LOD of Cu(II)/μg l ⁻¹ |
|--------|--------|---|-------------------------------------|----------------|----------------|----------------------------------|
| 1 | 0.0012 | 0 - 0.20 | $\Delta A_r = 2.33C_{Cu} + 0.0131$ | 0.9972 | 0.0115 | 1.5 |
| 2 | 0.0020 | 0 - 0.50 | $\Delta A_r = 1.66C_{Cu} - 0.0289$ | 0.9976 | 0.0054 | 1.0 |
| 3 | 0.0080 | 0 - 1.00 | $\Delta A_r = 0.747C_{Cu} - 0.0056$ | 0.9982 | 0.0040 | 1.6 |
| 4 | 0.0120 | 0 - 2.00 | $\Delta A_r = 0.390C_{Cu} + 0.0272$ | 0.9984 | 0.0018 | 1.4 |

a. Every series contains 7 concentrations. b. Linear correlation coefficient. c. Standard deviation from 10 replicated blanks.

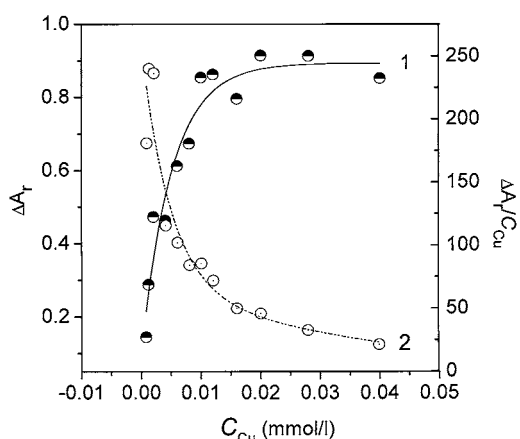


Fig. 5 Variation of ΔA_r and $\Delta A_r/C_{Cu}$ of the solutions with the same molar ratio of Cu(II) to NG at 25 $\mu\text{g}/\mu\text{mol}$.

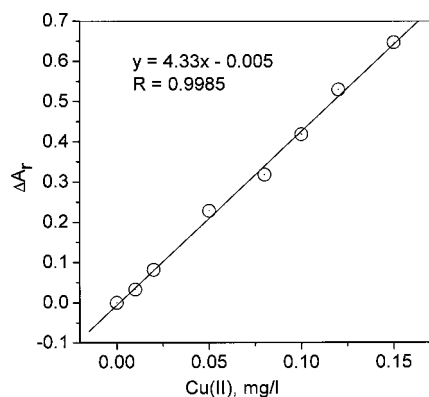


Fig. 6 CFA standard curve for continuous determination of Cu(II) from 0 to 0.150 $\mu\text{g}/\text{ml}$.

shown in Fig. 6 to have a good linearity. Ten replicated blanks were measured by CFA, the σ is 0.0061. Thus, LOD from CFA was calculated to be 4 ng/ml Cu(II). However, the CFA can make the direct analysis of samples continuously and rapidly. About 30 samples were analyzed in 1 h.

Effect of foreign ions

Fourteen foreign ions including 12 metal ions and anionic detergent sodium dodecyl sulfate (SDS) and phosphate (PO_4^{3-}) were tested without any masking agent. Their effects on ΔA_r of 0.050 $\mu\text{g}/\text{ml}$ Cu(II) are shown in Fig. 7. From bar charts A and B, one can see that most of them have not affected the direct assay of 0.050 $\mu\text{g}/\text{ml}$ Cu(II) (error < 5%). From bar chart B, only 0.500 $\mu\text{g}/\text{ml}$ Fe^{3+} and 0.500 $\mu\text{g}/\text{ml}$ PO_4^{3-} brought errors of ΔA_r over 6% but less than 10%. Therefore, the recommended method is highly selective and suitable for the direct monitoring

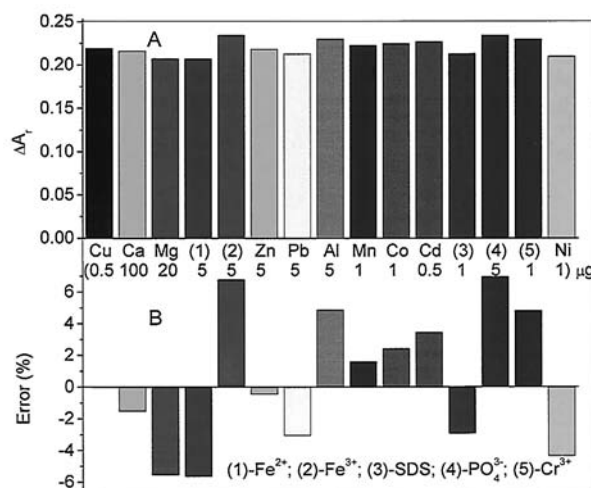


Fig. 7 Effect of foreign ions on the direct determination of 0.050 $\mu\text{g}/\text{ml}$ Cu(II).

of natural water.

Analysis of natural water

In the current work, four types of surface water were analyzed. They were sampled from Yangtze River in China, world-famous West Lake located in Hangzhou of China, the important drinking water source Taihu Lake for the eastern region of China and the seawater near Shanghai. Each of the samples was colored and measured according to the direct procedure and CFA and all the results are listed in Table 2. The recovery rates of Cu(II) are between 92.1 and 111.8%. Moreover, the analytical results of fresh water and seawater accord well to those determined by ICP-OES. The proposed method is accurate and credible for practical analysis.

Conclusion

In fact, there are a lot of spectrophotometric methods for determination of trace Cu(II), but most of them have high LOD. It is well known that more and more highly sensitive chromogenic agents have been synthesized and applied recently. Though they increase greatly the sensitivity in detection of heavy metals,²⁷ the excess free reactant will interfere seriously with the measurement of the light-absorption of the complex product formed. NG as a sensitive chemosensor was used to determine Cu(II) in the presence of polyvinylpyrrolidone at pH 11.5 but the LOD at 20 $\mu\text{g}/\text{l}$ Cu(II)²⁶ was too high to analyze natural water. Moreover, the CFA was not performed. The present work provides a very useful experimental strategy for direct online continuous analysis of Cu(II) at trace level, and both the sensitivity and analytical efficiency have great

Table 2 Determination of Cu(II) in natural water with NG at pH 4.09

| Sample ^a | Cu(II) added/ μg | Cu(II) found/ μg | Rec., ^{b,c} % | Cu(II) in sample/ mg l ⁻¹ |
|---------------------|---------------------|------------------------------|---------------------------|---|
| Yangtze River | 0 | 0.0515 ± 0.0009 ^b | | 0.0103 ± 0.0002 ^b |
| | 0.050 | 0.0975 | 92.1 | 0.0113 ± 0.0013 ^d |
| Seawater | 0.050 | 0.1020 | 100.2 | 0.010 ^e |
| | 0 | 0.116 ± 0.0043 ^b | | 0.0233 ± 0.0009 ^b |
| | 0.100 | 0.2188 | 102.4 | 0.0355 ± 0.0013 ^d |
| West Lake | 0.100 | 0.2282 | 111.8 | 0.028 ^e |
| | 0 | 0.0617 ± 0.0027 ^b | | 0.0123 ± 0.0005 ^b |
| | 0.050 | 0.1139 | 104.4 | 0.0125 ± 0.0004 ^d |
| Taihu Lake | 0.050 | 0.1100 | 96.6 | 0.019 ^e |
| | 0 | 0.0637 ± 0.0056 ^b | | 0.0127 ± 0.0011 ^b |
| | 0.100 | 0.1643 | 100.6 | 0.0107 ± 0.0014 ^d |
| | 0.100 | 0.1622 | 98.5 | 0.015 ^e |

a. A 5.0-ml volume of a sample was added for complexation.

b. Three replicated determinations by the direct procedure.

c. e.g., 92.1 = (0.0975 - 0.0515)/0.050 × 100.

d. Three replicated determinations by CFA.

e. One determination by ICP-OES.

improvements. Surely, such an approach will bring an extensive application to monitoring of natural water quality in the near future.

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