

Colorimetric determination of copper ions based on the catalytic leaching of silver from the shell of silver-coated gold nanorods

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Abstract We have developed a method for the colorimetric determination of copper ions (Cu^{2+}) that is based on the use of silver-coated gold nanorods (Au@Ag NRs). Its outstanding selectivity and sensitivity result from the catalytic leaching process that occurs between Cu^{2+} , thiosulfate ($\text{S}_2\text{O}_3^{2-}$), and the surface of the Au@Ag NRs. The intrinsic color of the Au@Ag NRs changes from bright red to bluish green with decreasing thickness of the silver coating. The addition of Cu^{2+} accelerates the leaching of silver from the shell caused in the presence of $\text{S}_2\text{O}_3^{2-}$. This result in a decrease in the thickness of the silver shell which is accompanied a change in color and absorption spectra of the colloidal solution. The shifts in the absorption maxima are linearly related to the concentrations of Cu^{2+} over the 3–1,000 nM concentration range ($R=0.996$). The method is cost effective and was applied to the determination of Cu^{2+} in real water samples.

Keywords Colorimetric assay · Copper ions · Silver-coated gold nanorods · Catalytic leaching

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Introduction

Copper ions (Cu^{2+}) play important roles in various biological systems and the environment, however, its high concentration in domestic water and groundwater become a serious threat to human health [1]. The U.S. Environmental protection Agency (EPA) issued the revised national water quality criteria for copper in 2007 and provided detailed recommendations on Cu^{2+} concentration limits for the protection of aquatic life in freshwater. For example, under $100 \text{ mg}\cdot\text{L}^{-1}$ hardness, the Cu^{2+} concentration limit is $20 \mu\text{M}$ [2]. Cu^{2+} can be absorbed through many ways, excess Cu^{2+} elicits toxicity to cells as they generate hydroxyl radicals, leading to apoptosis [3]. People who were exposed to excess uptake Cu^{2+} tend to experience some diseases such as kidney or liver damage, gastrointestinal disturbance, neurodegenerative diseases [4–6]. Therefore, the measurement and identification of Cu^{2+} in water has become increasingly important. In the last few years, various methods for detection of Cu^{2+} had been reported including inductively coupled plasma mass spectrometry [7], fluorescent probes [8, 9] and electrochemical methods [10]. Among these methods, some are available and suitable for the determination of Cu^{2+} due to their unique advantages such as high selectivity and availability. However, most of them had various limitations with respect to selectivity, sensitivity, cost, simplicity or toxicity. Hence, there is an alarming demand for developing a novel method that is not only selective, sensitive and available but also simple, cost-effective, and environmentally friendly.

Currently, noble metal nanomaterials have attracted much attention particularly due to their potential applications in chemical and biochemical sensing. Colorimetric methods based on nanomaterials are extremely attractive; in particular, for the sensing of ions and small organic molecules [11–16]. In comparison with other methods, they remained many advantages such as simplicity, reading out with the naked eyes,

requiring no sophisticated starting materials and complex instruments. Gold nanoparticles (Au NPs) and gold nanorods (Au NRs) were the most extensively used nanomaterials due to their strong surface plasmon resonance (SPR) absorptions in visible region; simple preparation, high stability, and color-tunable behaviour that depend on the interparticle distance or particle size [17, 18]. Recently, many colorimetric methods were developed based on labeled Au NPs. Typically, Mirkin's group reported the visual detection of Cu^{2+} with DNA-modified Au NPs, taking advantage of the click chemistry [19]. The limit of detection of the assay is 20 μM and its dynamic range is 20 μM to 100 μM . Zhu's group provided a new assay method for sensing Cu^{2+} based on the modulation of photoluminescent quenching efficiency between Au NPs and the perylene bisimide chromophore in the presence of Cu^{2+} [20].

As we all know, Au NRs possess distinctive optical properties, the absorption spectrum presented two peaks. One is the transverse surface plasmon resonance; the other is the longitudinal surface plasmon resonance (LSPR). The LSPR band is so sensitive that a tiny change in surface binding environment would lead to an obvious wavelength shift. Additionally, the extinction coefficient of Au NRs ($\sim 10^9 \text{ M}^{-1} \cdot \text{cm}^{-1}$) is larger than the value of Au NPs ($2.7 \times 10^8 \text{ M}^{-1} \cdot \text{cm}^{-1}$) [21, 22], thus, it was considered to be of great use in colorimetric detections. For example, Yan's group developed a new and selective method to detect Cu^{2+} based on the Cu^{2+} -induced longitudinal assembly of cysteine-modified Au NRs [23]; Uehara et al. reported a colorimetric assay of Glutathione based on the disassembly of aggregated Au NRs conjugated with water-soluble polymer [24]. They successfully utilized this material for colorimetric assay.

As a new composite material, silver coated gold nanorods (Au@Ag NRs) remain distinctive optical properties as well as Au NRs, which showed bright and distinctive colors with different shell thickness, changing from light gray to bluish green, purplish red, even bright red along with the increasing of thickness of the silver coatings, and the longitudinal plasmon mode of the nanorods shifted blue and was enhanced obviously [25–28]. It would be an excellent idea that using this dramatic color change caused by the different silver shell thickness to develop a colorimetric method. Herein, we designed a kind of Au@Ag NR-based platform for label-free colorimetric determination of Cu^{2+} . Our method took advantage of the special catalysis function of Cu^{2+} in the thiosulfate ($\text{S}_2\text{O}_3^{2-}$)-Ag leaching system, which had been applied for extraction of Ag from minerals for many years [29–32]. In the presence of Cu^{2+} , the catalytic leaching system induced obvious decreasing of thickness of the Ag shell and resulted in a red-shift concomitantly with a bright red-to-bluish green color change. Further tests proved that the unique method was suitable to detection of trace Cu^{2+} in real water samples.

Experimental

Reagents

Analytical-reagent grade chemicals were used in all experiments. Hydrogen tetrachloroaurate (III) dehydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), hexadecyltrimethyl ammonium bromide (CTAB), ascorbic acid (AA), sodium borohydride (NaBH_4), sodium hydroxide, sodium thiosulfate, Na_2HPO_4 , NaH_2PO_4 , AgNO_3 , KCl, LiCl, NaCl, ZnCl_2 , CaCl_2 , CrCl_3 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NiCl_2 , MgCl_2 , MnCl_2 , CoCl_2 , HgCl_2 and $\text{Pb}(\text{NO}_3)_2$ were received from Aladdin (Shanghai, China. <http://www.aladdin-reagent.com>), CuSO_4 was purchased from Sigma-Aldrich (Shanghai, China. <http://www.sigmaaldrich.com/china-mainland.html>). All of the reagents were used without further purification.

Instrumentation

UV–vis absorption spectra were performed on a Thermo Scientific NanoDrop 2000C spectrophotometer (Gene Company Ltd., USA). Transmission electron microscope (TEM) images were recorded on a JEM-1230 electron microscope (JEOL Ltd., Japan) operating at 100 kV. Solutions were prepared with deionized water (18.2 $\text{M}\Omega \text{ cm}$ specific resistance) purified by a Cascada LS Ultrapure water system (Pall Corp., USA). All glasswares used in the experiments were washed with freshly prepared aqua regia. Rinsed extensively in deionized water and dried in air.

Synthesis of Au NRs

Au NRs were prepared according to the seeded growth method with slight modifications [18]. Typically, the seeds were prepared firstly. Subsequently, Au NRs were produced by CTAB stabilized method. Then addition of the seed solution and stirred for another 2 min, kept at 28 °C water-bath for 24 h. The obtained Au NRs were purified by centrifugation (12,000 rpm for 10 min) before use.

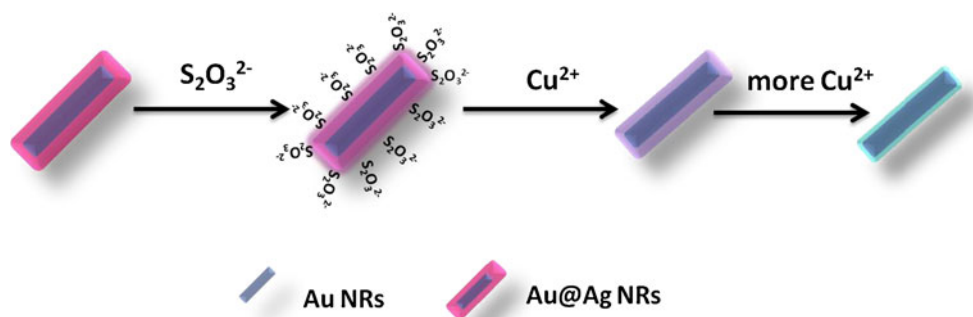
Synthesis of Au@Ag NRs

Au@Ag NRs were prepared according to a published seeded growth approach with necessary modifications [27]. Briefly, purified Au NRs diluted by CTAB and using NaOH to initiate the coating reaction in the presence of AA and AgNO_3 . All of these steps were carried out at 30 °C water-bath. The Au@Ag NRs solution was stored without disturbance for at least 20 h before use.

Sample preparation

Rational designed tests were carried out to optimize the detecting conditions. For Cu^{2+} sensing, a stock solution

Scheme 1 Schematic mechanism of sensing Cu^{2+} based on catalytic leaching of $\text{S}_2\text{O}_3^{2-}$ -Au@Ag NRs



containing 300 μL phosphate buffer solution (pH 7.2), 200 μL Au@Ag NRs and 10 μL of 60 mM $\text{S}_2\text{O}_3^{2-}$ were prepared. And then the different concentrations of Cu^{2+} were added to each of the stock solutions, which were equilibrated at 45 $^\circ\text{C}$ for 5 min. Finally, UV-vis absorption spectra were recorded. In the experiments of selectivity procedure, all samples were prepared in the same way.

Analysis of real water samples

A tap water sample obtained from our institute and a pond water sample collected from a pond on the campus of Yantai University (Yantai, China). The real water samples were filtered through a 0.2 μm membrane before use, and then were spiked with standard Cu^{2+} solutions at certain concentrations. The spiked solutions mixed with the stock solutions containing 300 μL phosphate buffer solution (30 mM, pH 7.2), 200 μL Au@Ag NRs and 10 μL of 60 mM $\text{S}_2\text{O}_3^{2-}$.

Safety considerations

As Cu^{2+} , Pb^{2+} , Hg^{2+} and most of tested metal ions are highly toxic and have adverse effects on human healthy, all experiments should be performed with protective gloves. The waste solutions containing heavy metal ions should be collectively reclaimed to avoid polluting the environment.

Results and discussion

Sensing mechanism

In this approach, we took advantage of the special catalysis function of Cu^{2+} in the $\text{S}_2\text{O}_3^{2-}$ -Ag leaching system to develop a colorimetric sensing system for sensing Cu^{2+} in aqueous solution. As seen from Scheme 1. The addition of Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ to Au@Ag NRs colloidal resulted in the decreasing of thickness of the Ag shell and an obvious change of color and UV-vis absorption spectra. However, in the absence of Cu^{2+} , there was a slight red shift at maximal absorption. Because $\text{S}_2\text{O}_3^{2-}$ could strongly adsorbed to the surface of Au@Ag NRs to form the

$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ complexes in the presence of dissolved oxygen, and the complexes immediately generated a passive layer on the surface of Au@Ag NRs [33]. For this reason, the leaching reaction could be blocked by the passive layer. Fortunately, subsequent addition of trace Cu^{2+} could accelerate the leaching rate of $\text{S}_2\text{O}_3^{2-}$ -Au@Ag NRs due to the formation of $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ complexes [34, 35]. And then the complexes could also be oxidized to Cu^{2+} by dissolved oxygen (Eq. 2). Herein, Cu^{2+} was employed as a catalytic agent to accelerate this reaction, thus, we utilized this special function to develop a simple colorimetric approach for Cu^{2+} sensing based on the $\text{S}_2\text{O}_3^{2-}$ -Au@Ag NRs.

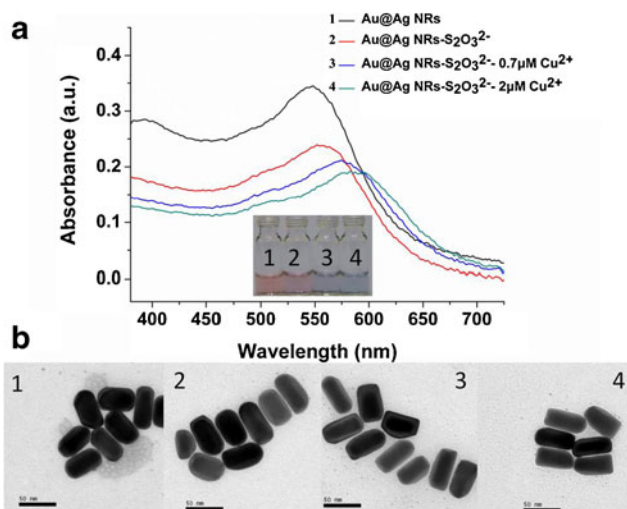
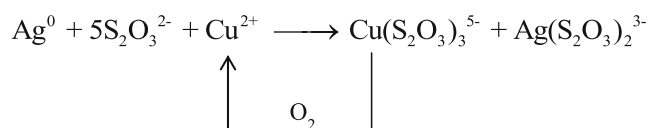
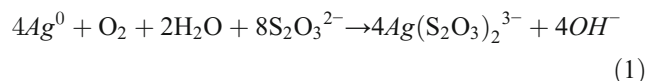


Fig. 1 a UV-vis spectra (inset image is colorimetric response) (b) TEM images of silver coating of (1) Au@Ag NRs (2) $\text{S}_2\text{O}_3^{2-}$ -Au@Ag NRs (3) $\text{S}_2\text{O}_3^{2-}$ -Au@Ag NRs with 0.7 μM Cu^{2+} (4) $\text{S}_2\text{O}_3^{2-}$ -Au@Ag NRs with 2 μM Cu^{2+}

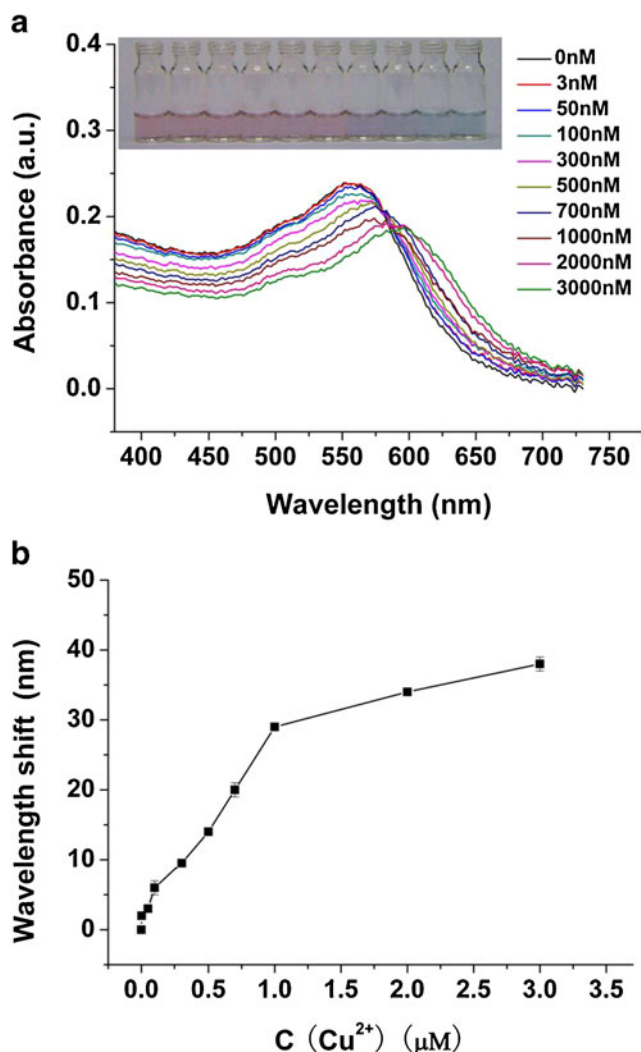


Fig. 2 **a** UV-vis absorption spectra of $S_2O_3^{2-}$ -Au@Ag NRs solutions with different concentrations of Cu^{2+} (3–3,000 nM) (inset image is colorimetric response to different concentrations of Cu^{2+}). **b** Shifts in maximal absorption wavelength of the $S_2O_3^{2-}$ -Au@Ag NRs with different concentrations of Cu^{2+} (3–3,000 nM)

To prove that Cu^{2+} acted as the catalytic agent in the $S_2O_3^{2-}$ -Au@Ag NRs leaching system, UV-vis absorption spectra and TEM images were also monitored. As shown in Fig. 1a, the prepared Au@Ag NRs showed a LSPR peaked at 548 nm (curve 1). After the addition of $S_2O_3^{2-}$, the LSPR peak was changed to 557 nm and the intensity decreased (curve 2). This absorption change was associated with the fact that $S_2O_3^{2-}$ can react with Au@Ag NRs and further form Ag (S_2O_3) $_2^{3-}$ complexes which could induce decrease of the SPR absorption of the solution and partly dissolving of Ag shell. These dramatic changes of silver coatings on Au NRs were observed in Fig. 1b and their thickness changes were counted as shown in Fig. S1 (in [Electronic Supplementary Material, ESM](#)). Subsequently, after adding Cu^{2+} to the system, the UV-vis absorption spectra showed an obvious red-shift and the intensity further decreased due to the reduction of Ag shell (curve 3 and 4), as evidenced

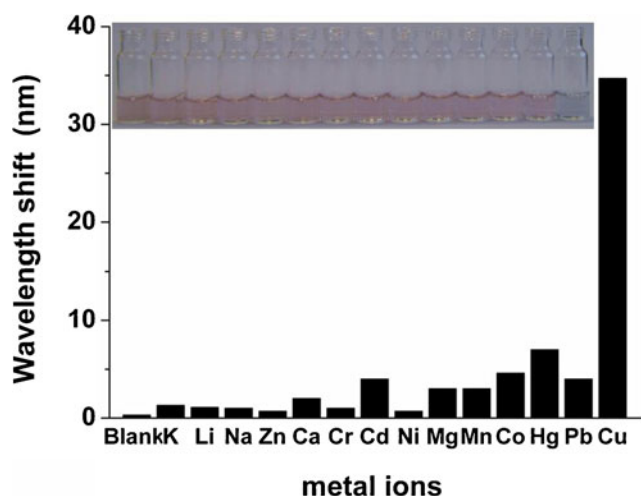


Fig. 3 Wavelength shift of the $S_2O_3^{2-}$ -Au@Ag NRs solutions in the presence of various metal ions, respectively (inset image is the corresponding colorimetric response to different metal ions)

by TEM image (Figs. 1b3, b4). With increasing of Cu^{2+} , the thickness of Ag shell decreased gradually. Meanwhile, the color of colloidal solutions changed significantly from red to purplish red, even bluish green as shown in the inset of Fig. 1a. It was proved that the presented facile colorimetric system was suitable for Cu^{2+} sensing.

Optimization of experimental conditions

In order to obtain the best performance of our colorimetric method, additional assay parameters were evaluated. The optimum conditions were tested in the presence of 2 μM Cu^{2+} . Error bars represent the standard deviations based on three independent measurements. A wavelength shift of the longitudinal surface plasmon band of Au@Ag NRs was employed to determine the optimum detection conditions.

The effect of pH value in the range from 5.8 to 8.0 on the $S_2O_3^{2-}$ -Au@Ag NRs leaching system was tested. As seen from Fig. S2A (in ESM), at pH 7.2, wavelength shift in absorption spectra of the sensing system changed most obviously. If pH toward lower values, the $S_2O_3^{2-}$ could not be stable, broke down to form sulfate, sulfide, sulfite, tetrathionate, trithionate, polythionates and polysulfides [30]. However, pH towards higher value was not benefit to the catalytic leaching of the $S_2O_3^{2-}$ -Au@Ag NRs (Eq. 1). In

Table 1 The comparison of proposed method and ICP-MS detection of Cu^{2+}

Samples	Detected (μM)	ICP-MS (μM)	RSD (%)
Tap water	0.0283	0.0267	0.810
Pond water	0.0236	0.0213	0.790

addition, as shown in Fig. S2B (in ESM), the effect of the phosphate buffer solution concentration ranging from 10 to 80 mM on the leaching system was also investigated. Therefore, 30 mM phosphate buffer solution at pH 7.2 was chosen as the optimum buffer system for the further detection. The concentration of $S_2O_3^{2-}$ had a great influence on the leaching rate of Au@Ag NRs. As shown in Fig. S2C (in ESM), the effect of $S_2O_3^{2-}$ concentration under the optimum pH was presented, ranging from 10 to 80 mM. It was noticed that at a concentration of 60 mM, the wavelength shift in absorption spectra was the biggest. Thus, 60 mM $S_2O_3^{2-}$ was selected in the following test.

In addition, the effect of incubation temperature and reaction time were investigated. As shown in Fig. S3A (in ESM), the different incubation temperature was tested. It was noteworthy that there was a maximum wavelength shift at 45 °C. So, 45 °C was selected as optimum reaction temperature. Fig. S3B (in ESM) displayed the effect of incubation time on the wavelength shift of the $S_2O_3^{2-}$ -Au@Ag NRs sensing system. With the increase of reaction time, the wavelength shift, depending on the thickness of silver coating, increased gradually. However, considering the thickness of silver coating and the slight color change of the Au@Ag NRs induced by $S_2O_3^{2-}$, 5 min was selected as the optimum reaction time to obtain an obvious color difference in our colorimetric sensing system.

Sensitivity and selectivity for Cu^{2+}

To evaluate the sensitivity of the $S_2O_3^{2-}$ -Au@Ag NRs probe toward Cu^{2+} under the optimum conditions, the UV–vis spectra of the $S_2O_3^{2-}$ -Au@Ag NRs probe in the presence of different concentrations of Cu^{2+} were recorded. As shown in Fig. 2a, with the increase of the concentration of Cu^{2+} , shifts in maximal absorption wavelength gradually increased. And, as seen from Fig. 2b, over the concentration of 1,000 nM, the reaction tends to be saturated, a good linear relationship, $y = 26.2x + 1.99$ ($R^2 = 0.993$), was obtained over the range of 3 nM to 1,000 nM. It indicated that our probe can be used to detect Cu^{2+} with a low minimum detection concentration of 3 nM. It's not only far below the concentration (20 μ M) in freshwater issued by the EPA, but also has an obvious advantage over some representative reports [19, 20].

To investigate the selectivity of $S_2O_3^{2-}$ -Au@Ag NRs toward Cu^{2+} , the different competitive metal ions, including 200 μ M of K^+ , Li^+ , Na^+ , Zn^{2+} , Ca^{2+} , Cr^{3+} , Cd^{2+} , Ni^{2+} , Mg^{2+} , Mn^{2+} and Co^{2+} , and 20 μ M of Hg^{2+} and Pb^{2+} (200 μ M of Hg^{2+} and Pb^{2+} have slight influence on the $S_2O_3^{2-}$ -Au@Ag NRs probe) were examined under the optimum conditions, respectively. As shown in Fig. 3, only Cu^{2+} (2 μ M) could cause obvious increase of the wavelength shift and the distinctive color change, which suggested that this detection system exhibited a high selectivity for Cu^{2+} .

Sensing of Cu^{2+} in real water samples

We have also validated the applicability of this assay by determination Cu^{2+} in real water samples. Table 1 provided the analytical results obtained with our proposed colorimetric method and the inductively coupled plasma-mass spectrometry (ICP-MS) method. The results obtained by both methods were in good agreement, indicating the accuracy and reliability of our proposed colorimetric method. The comparison of analytical performances between our developed colorimetric method and some reported colorimetric, fluorescent and electrochemical methods for Cu^{2+} detection was shown in Table S1.

Conclusions

A novel colorimetric method for sensing of Cu^{2+} was developed by exploiting the decrease of the silver shell thickness on the Au@Ag NRs composite nanomaterial based on the fact that Cu^{2+} could accelerate the leaching rate of Au@Ag NRs by $S_2O_3^{2-}$. The color of the sensing solution changed from bright red to bluish green dramatically in accordance with an increase of Cu^{2+} concentration in 5 min. This colorimetric change could be easily observed by the naked eyes and used for quantification of Cu^{2+} . Furthermore, this method exhibited a satisfactory selectivity over other interfering metal ions and was applied to determining the concentration of Cu^{2+} in real water samples.

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