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Colorimetric determination of copper(II) ions by filtration on sol–gel membrane doped with diphenylcarbazide

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ABSTRACT

A simple and sensitive colorimetric method for the determination of trace copper(II) ions in aqueous solution has been developed using diphenylcarbazide (DPC) immobilized sol–gel matrices. To enhance the odds of chelating interactions between copper(II) ions and DPC, a peristaltic pump was utilized to drive copper(II) ions solution pass through the cellulose acetate/nitrate membrane, which was coated with DPC immobilized sol–gel matrices. The membrane was sandwiched in a home-made flow cell. The porous silica matrix serves as a preconcentrator, and enriches the trace copper(II) ions. Meanwhile, the filtration increases the chelating interaction probability between copper(II) ions and DPC, thereby improves the sensitivity significantly. After the formation of purple complex compound, the color changes of the DPC immobilized sol–gel membrane were recorded using a flatbed scanner. The images were digitized, and the red (*R*), green (*G*), and blue (*B*) values were investigated. The colorimetric method provides a rapid and reliable determination of trace copper(II) ions with a detection limit as low as 0.16 μM and a kinetic range up to 1.6 μM in neutral medium. Moreover, the method shows good selectivity, and the color changes of the DPC immobilized sol–gel membranes are remarkable for the copper(II) ions detection even in the presence of other metal ions.

1. Introduction

Copper, one of the most important heavy metals and additives, is widely utilized in industrial and agricultural processes. Due to its high thermal and electrical conductivity, copper has been used as a thermal conductor, an electrical conductor, and a constituent of various metal alloys [1]. From the agricultural point of view, copper has also been demonstrated to be effective in increasing growth performance and protecting plants, crops, livestock and poultry from diseases [2–4]. Because of various applications, copper can be released into the environment from many sources. Although copper is an important metal nutrient for metabolism of life, the excessive intake of copper could still result in kidney and liver damage, increased blood pressure and respiratory rates, and damage to central nervous system [5,6]. Menkes disease and Wilson disease are two kinds of human genetic maladies that have been found closely related to the disorder of copper metabolism [7–9].

Among the numerous analytical methods, high-performance analytical instruments (e.g., atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), etc.) are used extensively as standard methods for the detection of trace metals [10–13]. In addition to the costly running expenses, specific technical skills are usually required for the pre-treatment and instrument operation [8,14]. Other analytical methods include UV spectrophotometry, evanescent wave infrared absorption spectroscopic method, anodic or cathodic stripping voltammetry [15–17], etc. These methods are well used to determine trace copper ions, however, they are either inconvenient for on-site monitoring, lack of selectivity, or multi-step. Therefore, it is clear that the inexpensive, reliable, and portable detection of copper(II) ions remains an unsolved problem.

Recently, many laboratories have focused on sensor detection technique for the determination of copper(II) ions (e.g., infrared chemical sensor, chemiluminescence-based flow injection analysis, fluorescence resonance energy transfer (FRET) sensor, total reflection X-ray fluorescence (TXRF), diffusive gradient in thin films (DGT) sampling, chromophore-decolorizing, N,N′-bis (salycilidene)-1,2-phenylenediamine (salophen) based optical sensor [18–24], etc.). These methods show good sensitivity and selectivity, but usually require complicated synthesis processes and most of them are time-consuming.

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In this study, we report a simple, convenient and highly selective colorimetric method for the determination of trace copper(II) ions. The method is based on the filtration on the membrane created by the immobilization of diphenylcarbazide (DPC) in organically modified siloxanes (ormosils). The porous silica matrix serves as a preconcentrator [25–28] and enriches the trace copper(II) ions. The incorporation of indicator in porous silica matrices not only provides good stability and sensitivity, but also improves the solubility of the indicators. The matrices could favor the diffusion of analyte molecules to the sensing indicators [29–33]. Although DPC has been widely used for the detection of many metal ions, e.g., chromium(VI), lead, zinc, mercury, etc. [34–38], after immobilizing it in the sol–gel matrices and appropriately adjusting the microenvironment of sol–gel matrices, the DPC immobilized sol–gel membrane showed good selectivity for copper(II) ions determination in the presence of other metal ions.

2. Experimental

2.1. Chemicals and materials

Analytical grade chemicals were used as received without further purification unless otherwise specified. Deionized water was utilized throughout this work and the pH was adjusted to around 7 using diluted hydrochloric acid or sodium hydroxide. Diphenylcarbazide and all the heavy metal salts were purchased from Shanghai Jingchun Reagent Co., PR China. Tetraethoxysilane (TEOS) and phenyltriethoxysilane (PTES) were obtained from Alfa Aesar. Isopropanol and hydrochloric acid were purchased from Tianjin Bodi Chemical Co., PR China. The cellulose acetate/nitrate membrane with 3 μm pore diameter was used as the substrate for sol–gel coating.

The copper(II) ions stock solution was prepared by dissolving 27.3 mg of $CuCl_2{\cdot}2H_2O$ in 100 mL of deionized water to obtain a final concentration of 1.6 mM. The testing solutions of copper(II) ions at different concentrations were diluted from above-mentioned stock solutions using deionized water. No buffer was used to avoid the cross-contaminations. Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} were in the form of their chloride salts in deionized water; solutions of $CrO_4{}^{2-}$ were prepared from sodium chromate.

2.2. Preparation of sol–gel membrane

The organically modified sol–gel (ormosil) formulation was prepared by mixing 1.2 mL of TEOS, 0.015 mL of PTES, 1.0 mL of deionized water, and 2.56 mL of isopropanol. The pH was adjusted to pH 2 using 0.1 M hydrochloric acid to catalyze the hydrolysis of the silica precursors. After stirring for 1 h, DPC was added to the resulting solutions. The mixture was stirred for another 3 h. The cellulose acetate/nitrate membrane was withdrawn vertically from the coating bath consisting with the sol–gel colloid solution at a constant speed (0.7 cm s^{-1}). Once coated, the membrane was allowed to set in the air for 30 min, and then stored in a nitrogen-filled desiccator at 33% relative humidity for at least two days before any experiment performed.

2.3. Procedures and data analysis

The cellulose acetate/nitrate membrane coated with DPC immobilized sol–gel matrices was sandwiched in a home-made poly (methyl methacrylate) flow cell, as shown in Fig. 1. The copper(II) ions solutions at desirable concentrations were pumped into the flow cell using a peristaltic pump (Baoding Longer Precision Pump Co., PR China) at a steady flow rate (4 mL min^{-1}). The solutions were pumped through the membrane from bottom to top. After 1 min of exposure to deionized water, the sample solutions were then introduced for 10 min. For all sensing experiments, imaging of the membrane colors was performed using a flatbed scanner. The images were intercepted from the centre part using Adobe Photoshop™ software. The before image was obtained after 1 min of exposure to deionized water. The after image was acquired after every minute of exposure to copper(II) ions solutions at desirable concentrations. Difference maps were obtained by taking the differences of the red, green and blue (RGB) values from the centre of the membrane from the 'before' and 'after' images. The colorimetric response of the membrane was expressed using the Euclidean distance (ED), which could be defined by the following formula:

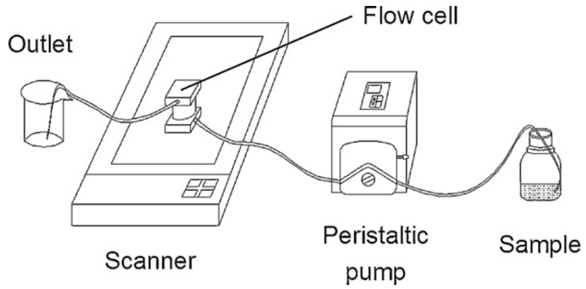


Fig. 1. The experimental set-up for copper(II) ion testing.

$$ED = \sqrt{(\Delta R)^2 + (\Delta G)^2 + (\Delta B)^2}$$

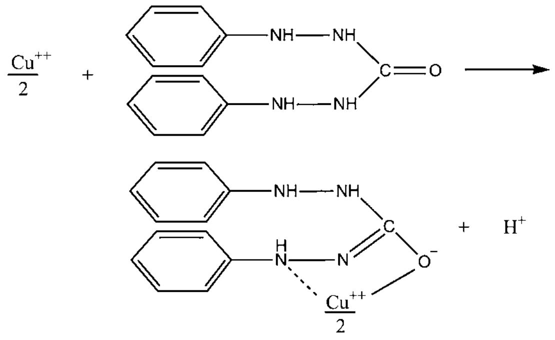
The pH measurement was conducted using a FE20 pH meter with LE438 pH electrode (Mettler-Toledo Instruments Co., PR China).

3. Results and discussion

3.1. Colorimetric response of copper(II) ions

The sample solutions containing copper(II) ions at a concentration range from 0.16 to 32 μM at pH 7 were pumped into the flow cell using a peristaltic pump. The copper(II) ions were filtered by sandwiched DPC immobilized sol–gel membrane due to the chelating reaction between DPC and copper(II) ions, as shown in Scheme 1 [39].

The silica matrix serves as a preconcentrator and enriches the trace copper(II) ions. The colored complex compound formed in the DPC immobilized sol–gel matrices, and the images of the cellulose acetate/nitrate membranes were captured using a conventional flatbed scanner. Compared to regular soaking colorimetric methods, the filtration increased the odds of chelating interactions between copper(II) ions and DPC, thus significantly improved the sensitivity. The *R* (red), *G* (green), and *B* (blue) values of the membrane images were measured before and after exposure to



Scheme 1. The chelating reaction between diphenylcarbazide and copper(II) ion.

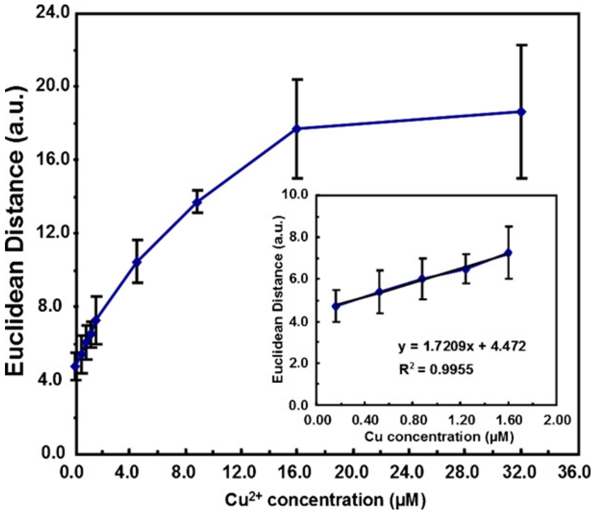


Fig. 2. The relationship between colorimetric response of DPC immobilized sol–gel membrane and copper(II) ions concentrations. The inset is the linear relationship between colorimetric response of DPC immobilized sol–gel membrane and copper(II) ions at the concentration range from 0.16 to 1.6 μM.

copper(II) ions. All experiments were run in triplicate trials. The relationship between the colorimetric response of the DPC immobilized sol–gel membrane and the concentrations of copper(II) ions is shown in Fig. 2.

The Euclidean distance value initially enhances with the increase of copper(II) ions concentrations at a range from 0.16 to 1.6 μM, and reached the saturation point at around 32 μM. The inset in Fig. 2 reveals the good linear relationship between the colorimetric response of the DPC immobilized sol–gel membrane and the copper(II) ions concentrations at the range of 0.16–1.6 μM with the correlation coefficient of 0.9955. Apparently, the colorimetric sensor designed in this work is sensitive enough to detect trace copper(II) ions in environmental water samples, even in drinking water. The quantitative analysis of copper(II) ions at a concentration range from 0.16 to 1.6 μM is also feasible.

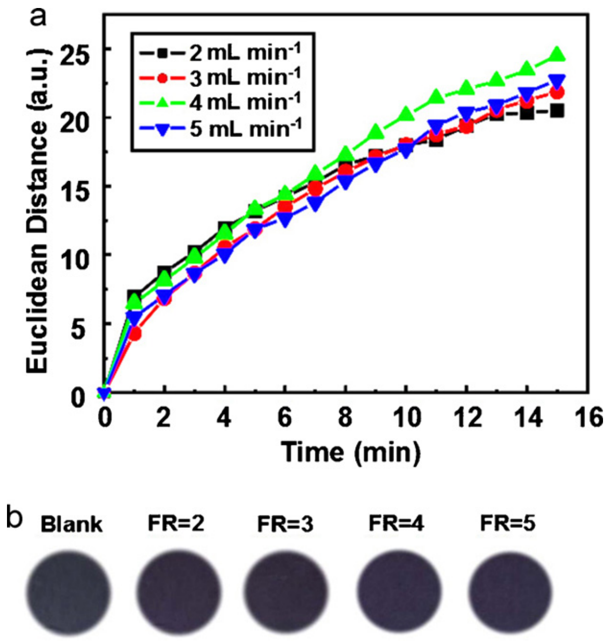


Fig. 3. (a) Effect of flow rates on the colorimetric response of the DPC–copper(II) complex compound. The concentration of copper(II) ion was 16 μM. (b) The membrane colors after 10 min exposure at 2, 3, 4, and 5 mL/min flow rates, separately.

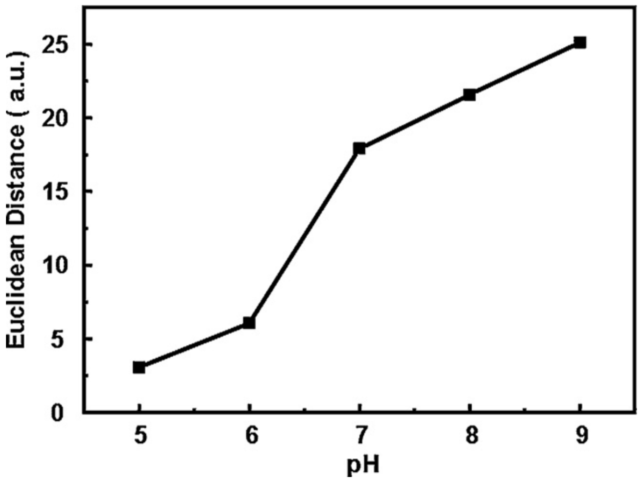


Fig. 4. Effect of pH on the colorimetric response of the DPC–copper(II) complex compound. The concentration of copper(II) ion was 16 μM.

3.2. Effect of flow rate

The flow rate of the solution passing through the cellulose acetate/nitrate membrane was considered as the mass transport process of the reaction between copper(II) ions and DPC. Hence, the kinetic curve of this reaction was studied under different flow rates (Flow Rate (FR) = 2–5 mL min^{-1}). Apparently, if the flow rate is too fast, the copper(II) ions will be flushed away before they react with DPC. On the contrary, it will take a long time to load enough copper(II) ions to react with DPC if the flow rate is too slow. Theoretically, at relatively slow flow rates, the sensor is supposed to show linear relationship between colorimetric response and flow rates.

Fig. 3a, however, shows that the flow rate has no obvious influence on kinetics of this reaction at the relatively slow flow rate range of 2–5 mL min^{-1}. Fig. 3b proves that the color changes of the cellulose acetate/nitrate membrane coated with DPC immobilized sol–gel matrices are almost same after exposure to copper(II) ions under these different flow rates. This could be due to the slow reaction rate between copper(II) ions and DPC in the sol–gel matrices. Bigger flow rates provided relatively larger copper(II) loading capacity in the silica matrices, but did not influence the reaction rate at all. This was further confirmed by the kinetic curves shown

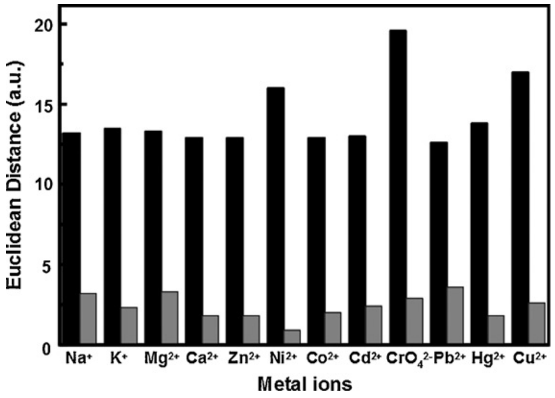


Fig. 5. Colorimetric response of DPC immobilized sol–gel membrane in the (■) presence and (▨) absence of 16 μM copper(II) solution containing a specific interference metal ion.

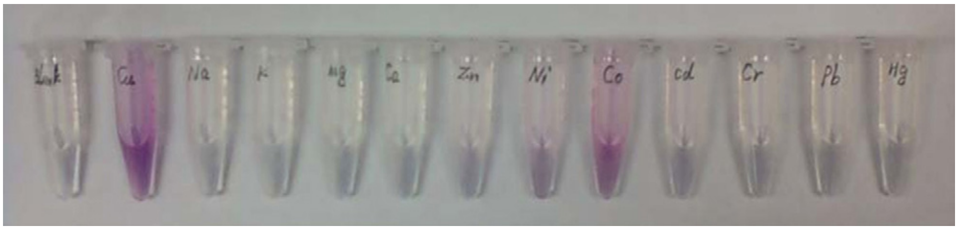


Fig. 6. The colors of DPC solutions (0.5 mg in 1 mL 1:2.5 water/isopropanol) after reacting with copper(II) ion and other metal ions at pH 7.

in Fig. 3a. The reaction rates did not change that much at the different flow rates. The colorimetric response of the DPC immobilized sol–gel membrane kept increasing as the time went by. 10 min data and 4 mL min^{-1} flow rate were chosen in this experiment to get relatively clearer color changes.

3.3. *Effect of pH on colorimetric response*

To examine the effect of pH, copper(II) ions solutions at pH 5, 6, 7, 8 and 9 were prepared, respectively. The pH of these solutions was adjusted using 0.1 M HCl or 0.1 M NaOH. No buffer was used to avoid cross-contaminations. The colorimetric responses of DPC immobilized sol–gel membrane ($[(\Delta R)^2 + (\Delta G)^2 + (\Delta B)^2]^{1/2}$) at various pH are shown in Fig. 4.

The Euclidean distance reduced with the decrease of pH, and leveled off to zero in acidic conditions. The chelating reaction mechanism showing in Scheme 1 explained this phenomenon reasonably. As Tracy and Turkington reported [39], in this chelating reaction, the mole ratio of DPC to copper(II) is 2 to 1. The copper(II) ion is bonded to the oxygen of the enol form of the reagent, and the resulting chelate complex compound is neutral. From the chelating reaction mechanism, apparently, due to the generation of the proton, the reaction shifts rightward in alkaline solutions and is restrained largely in acidic conditions. In this experiment, pH 7 was chosen to simulate the natural circumstance pH.

3.4. *Interferences*

As we all know, various metal ions are ubiquitous in real samples. Hence, it is essential to carry out an interference study to evaluate the performance of sol–gel membrane doped with DPC as a selective colorimetric sensor. The experiments were carried out in deionized water at pH 7, and the concentrations of copper(II) ions and other metal ions were selected according to Chinese wastewater discharge standard [28]. In real samples, the concentrations of some metal ions, such as Zn^{2+} and Ni^{2+}, are significantly higher than that of copper(II); while the concentrations of Pb^{2+} and Hg^{2+} are much lower than that of copper(II). Hence, the concentrations of interfering ions in this study were chosen as the same magnitude as Chinese wastewater discharge standard (See Table 1).

Table 1
Concentrations of copper(II) ions and interference metal ions.

Ions	Concentration (μM)	Ratio
Cu^{2+}	16	1
Na^{+}	1600	100
K^{+}	1600	100
Mg^{2+}	160	10
Ca^{2+}	160	10
Zn^{2+}	160	10
Ni^{2+}	160	10
Co^{2+}	160	10
Cd^{2+}	160	10
$CrO_4{}^{2-}$	16	1
Pb^{2+}	1.6	0.1
Hg^{2+}	0.16	0.01

The results are shown in Fig. 5. The gray bar portions illustrate that no significant response was observed in the case of interfering ions alone. The black bar portions reveal that this colorimetric method exhibits good selectivity for copper(II) ions in the presence of other metal ions, including Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, $CrO_4{}^{2-}$, Pb^{2+} and Hg^{2+}. The Euclidean distance for DPC–copper(II) chelating complex compound showing in Fig. 5 does not change much in the presence of interference metal ions.

Fig. 6 shows the color changes of DPC solutions (0.5 mg in 1 mL 1:2.5 water/isopropanol) after reacting with copper(II) ions and other interference ions at the same concentrations as previous membrane testing. Some metal ions show interfering response to DPC in solution, e.g., Zn^{2+}, Ni^{2+}, Co^{2+}, etc. However, after immobilizing DPC in the sol–gel matrices and appropriately adjusting the microenvironment of silica matrices, DPC shows good selectivity for copper(II) ions even at the presence of strongly interfering ions, such as Co^{2+}, in solution.

4. Conclusions

In summary, we have developed a convenient, sensitive and selective colorimetric method for the determination of copper(II) ions in aqueous solution. A metal ion indicator (diphenylcarbazide, DPC) was immobilized in the silica matrices, and the cellulose acetate/nitrate membrane was used as substrate to provide silica matrices a support skeleton with large pore size. The silica matrix in this case serves as a preconcentrator, and enriches the copper(II) ions. The filtration increased the odds of chelating interactions between copper(II) ions and DPC, thus significantly improved the sensitivity. The imaging of the membrane color changes was accomplished using a conventional inexpensive flatbed scanner, and the RGB values of the membrane images were digitized using Photoshop^{TM} software package. The colorimetric method exhibits a kinetic response for copper(II) ions in the range of 0.16–1.6 μM and shows good sensitivity with low limit of detection. Linear relationship between the colorimetric response of membrane and copper(II) ions concentrations indicates a quantitative determmination. Moreover, other metal ions had no significant interference on this copper(II) ions detection. Further development, we expect, will lead to a convenient and inexpensive miniaturized unit for the real sample determination.

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