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Copper Ion Detection Method Based on a Quantum Dot CdTe Fluorescent Probe

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This study aimed to establish a high-sensitivity and high-selectivity method for the rapid detection of heavy metals, such as Cu^{2+}, in water. The heavy metal ion Cu^{2+} was used as the research object, and the cadmium telluride quantum dot solution modified with cysteine and glutathione was used to detect Cu^{2+}. The compound of Cu^{2+} on the surface and the modified quantum dots caused fluorescence quenching of the quantum dots. A linear relationship was observed between the concentration and the changing intensity of fluorescence quenching. This linear relationship was used to achieve the quantitative detection of Cu^{2+} content in the solution by quantum dots. In a certain experimental environment, the preprocessing of the standard normal variables of the characteristic band and the partial least squares modeling and analysis produced good self-prediction and actual prediction capabilities. The correction factor was 0.9006; the root mean square prediction error of correction was 8.83084 µmol/L; the coefficient of determination for the validation set was 0.8686; and the root mean square error of prediction was 5.4320 µmol/L.

Keywords: copper ion detection, fluorescent probe, quantum dots, spectral analysis.

1. INTRODUCTION

Heavy metal pollution has received widespread attention in recent years. Heavy metal pollution refers to environmental pollution caused by heavy metals or their compounds [1]. Heavy metals that pollute water quality are mainly copper, cadmium, chromium, lead, vanadium, and mercury [2]. Among these, excess copper causes a series of diseases, such as liver cirrhosis, gastrointestinal disorders, and neurological disorders because it is potentially toxic to the human body. The research results showed that a daily intake of copper of about 12 mg and 10 mg in adult men and women, respectively, was safe and sufficient and did not cause harm to human health. Copper and its compounds also cause pollution in the ecological environment. For example, the exhaust of smelting gas from factories to the atmosphere causes copper pollution in the atmosphere [3, 4]. Therefore, the detection of copper ions (Cu^{2+}) in water is of great significance to prevent the damage caused by heavy metals.

Traditional heavy metal detection methods are mainly divided into spectroscopic methods and electrochemical analysis methods. Spectroscopy includes high-performance liquid chromatography [5], enzyme inhibition [6], atomic absorption spectrometry [7], inductively coupled plasma mass spectrometry [8], atomic emission spectrometry [9], ultraviolet–visible spectrometry [10], and so on. Traditional spectral analysis methods have the advantages of flexible sampling, fast speed, and nondestructive testing. However, defects, such as expensive instruments, inability to perform continuous real-time monitoring, high running costs, and inconvenience in handling, also exist. In general, the instrumental testing of heavy metals can only be accomplished in professional laboratories with national accreditation. Conducting timely and effective laboratory analysis of heavy metals in water samples is difficult due to various factors such as distance, sample collection, and storage difficulties [11, 12].

Quantum dots are semiconductor nanocrystals whose three-dimensional size is limited to the nanometer scale [13]. They show unique properties due to their small size, especially when the particle size is smaller than the exciton Bohr radius [14]. Also, quantum dots have surface and interface effects, macroscopic quantum tunneling effects, and special optical, photochemical, electrical, and nonlinear optical properties. Hence, they have received enormous attention from scholars in various fields at home and abroad. At present, the core/shell structure (such as CdS and HgS) composed of group II–VI [CdS, CdSe, and cadmium telluride (CdTe)] [15] and group III–V (GaAs, InGaAs, and InP) metals [16] has been reported. Quantum dots, such as CdS, CdSe, and CdTe, are currently the focus of research in this field. Quantum dots are mainly used for high-sensitivity detection of heavy metal ions through changes in fluorescence intensity (FI) [17].

The interaction between Cu^{2+} and quantum dots causes the quenching of fluorescence [18, 19]. Quantum dots, such as CdTe and CdSe, are often used to detect the Cu^{2+} content. Yan Yuxi et al. [20] prepared CdTe semiconductor quantum dots modified with glutathione and cysteine under certain conditions, thereby achieving qualitative and quantitative detection of Cu^{2+}. The detection limit of this method is 0.15 g L^{-1}. The detection mechanism is probably glutathione and cysteine modifications on the surface of CdTe quantum dots. The modifications involve rich amino and carboxyl groups. Cu^{2+} is bound to the surface of the quantum dots through coordination. The reduction of Cu^{2+} to Cu^{+} leads to the

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quenching of CdTe quantum dots. A new method for the detection of Cu^{2+} was developed based on the systematic analysis and verification of the effects of various factors on the luminous intensity of quantum dots. Compared with the traditional detection method, this method broadened the linear range of Cu^{2+} detection and, at the same time, relatively increased the detection sensitivity [21].

As early as 1997, Isarov et al. [22] proposed a method for measuring the Cu^{2+} content using CdS quantum dots and explained its mechanism of action. According to them, Cu^{2+} could be detected with CdS quantum dots because the presence of Cu^{+} was conducive to the recombination of excited electrons in the core conduction band of quantum dots and holes in the valence band when Cu^{2+} was rapidly reduced to Cu^{+} on the surface of CdS quantum dots. This led to the quenching of the fluorescence of quantum dots, causing the redshift of emission peak positions of quantum dots. Zhong et al. [23] synthesized a water-soluble CdSe/CdS quantum dot with unique optical properties using mercaptoethanol as a stabilizer. A new method for determining the Cu^{2+} content was established in a phosphate buffer solution at pH 7.4. Cu^{2+} was detected in hair and tea, and the detection limit was 8.5 g L^{-1}.

This study aimed to establish a high-sensitivity and high-selectivity method for the rapid detection of heavy metals, such as Cu^{2+}, in water. The rapid detection method for Cu^{2+} was explored based on an in-depth understanding of existing Cu^{2+} detection methods at home and abroad and the application of quantum dot probes, combined with chemometrics, fluorescence spectroscopy analysis, and quantum dot fluorescence technology. The detection and analysis included choosing economical, environmental friendly, and sensitive quantum dot fluorescence detection methods to chemically detect Cu^{2+} in water, collecting the fluorescence spectrum of the quantum dot solution that reacted with Cu^{2+} ions, and establishing a prediction model for Cu^{2+} in water.

2. MATERIALS AND METHODS

2.1. Experimental equipment

A SYNERGY™ 2 multifunctional microplate reader with a sensitive fluorescence detection system was used to collect the fluorescence spectrum data of the target solution. The wavelength range of this instrument was 230 – 1000 nm. The *p* wavelength was precisely selected to be 1 nm. The optical resolution was 0.0001 OD. It was measured at room temperature. The instrument could be arbitrarily switched between a high-performance filter system and a flexible four-grating system. The use of a four-grating system greatly improved the flexibility of detection and the broadness of the detection spectrum.

In this study, the FI detection mode was selected, and the data were collected at 27 °C. The FI of the samples was determined using the GENE5 software, and the data were processed using Matlab2011b (Mathworks, MA, USA) software. The image acquisition was performed in the dark to avoid the effect of external light.

2.2. Experimental materials and instruments

Cu^{2+} was used as the research object in this study. The experimental materials and instruments included cysteine- and glutathione-modified CdTe quantum dot solution (Beijing Beida Jubang Technology Co., Ltd., Beijing, China), $CuSO_4$ solution, pH 6.8 phosphate-buffered saline solution, deionized water, an electronic balance scale, a thermostatic shaker (SHZ-82 type), a beaker, a graduated cylinder, a constant-volume bottle, a medicine spoon, a constant-volume gun, an enzyme plate, and a pH meter.

2.3. Experimental steps

The experimental steps were as follows:

1. A total of 30 Cu^{2+} solutions, with concentrations ranging from 1×10^{-8} to 9×10^{-3} mol/L, were prepared by chemical methods.
2. Also, 10 µmol/L L-cysteine-modified CdTe quantum dots were diluted 20-fold as fluorescent probes.
3. A phosphate buffer solution with a pH of 6.8 was prepared.
4. Cu^{2+} solution was added to 100 µL of cysteine- and glutathione-modified CdTe quantum dot solution and 100 µL of phosphate buffer solution, in the volume ratio of 1:2:1, and allowed to stand for 10 min after shaking.
5. A SYNERGY™ 2 multifunctional microplate reader was used to collect the spectral data in the range of 476 – 800 nm, as shown in Fig. 1.

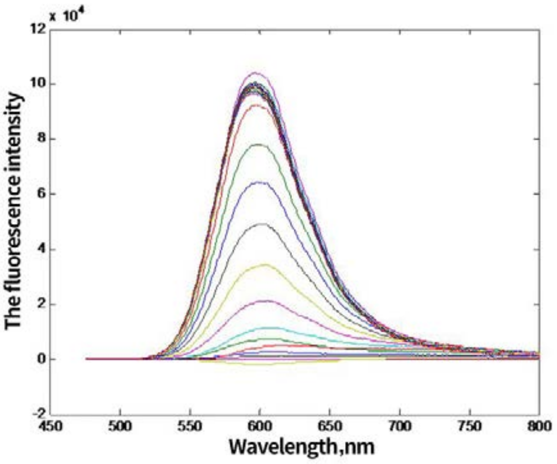

Fig. 1. Raw data of sample fluorescence spectrum

3. RESULTS

3.1. Optimization of experimental conditions

The experimental factors affecting the detection of Cu^{2+} included system pH, reaction time, buffer volume, CdTe quantum dot concentration, and other metal ions. The optimal experimental conditions were obtained by optimizing the aforementioned factors.

3.1.1. Impact of pH on detection

The emission of quantum dots is very sensitive to the pH of the reaction solution system. Buffers with pH 5.5, 5.9, 6.7, 6.8, 7.0, 7.5, 8.0, and 8.5 were prepared; the buffers were disodium hydrogen phosphate–sodium dihydrogen phosphate solution prepared by mixing in different proportions. The results are shown in Fig. 2. When the pH was less than 6.8, the quenching intensity of the fluorescence emission of the quantum dot solution increased with the increase in pH. When the pH was greater than 6.8, the quantum dot fluorescence quenching degree decreased, and finally it was stable. The fluorescence emission of the solution system was quenched the most when the pH was 6.8. Therefore, the pH of the system was selected as 6.8 in this experiment of Cu^{2+} detection.

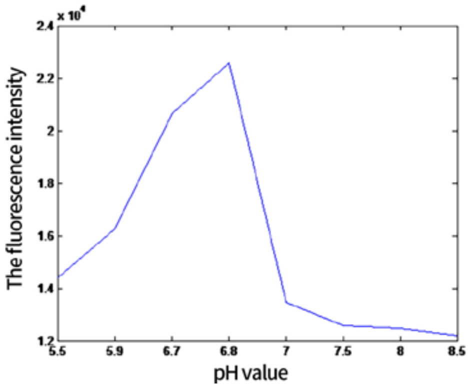

Fig. 2. Effect of pH value on the fluorescence intensity of quantum dot solution.

3.1.2. Effect of reaction time on detection

The reaction time of the entire experimental process was determined, and the FI of seven experimental samples with different reaction times was measured at room temperature. The diluted quantum dot solution was divided into seven identical samples, and the same volume of phosphate buffer solution of the same pH was mixed. The same concentration of equal volume of Cu^{2+} solution was added, mixed well, and allowed to react at room temperature. The fluorescence was measured in batches. The results are shown in Fig. 3. The optimization of the reaction time between cysteine and glutathione/CdTe quantum dots and the Cu^{2+} solution showed that the intensity of the strong light reached the maximum at the beginning of the reaction. As the reaction progressed, the FI of the quantum dots gradually decreased. When the reaction proceeded to about 25 min, the FI of the system tended to be stable. This indicated that the quantum dot solution reacted completely with Cu^{2+}. Hence, 25 min was considered as the reaction time for this experiment.

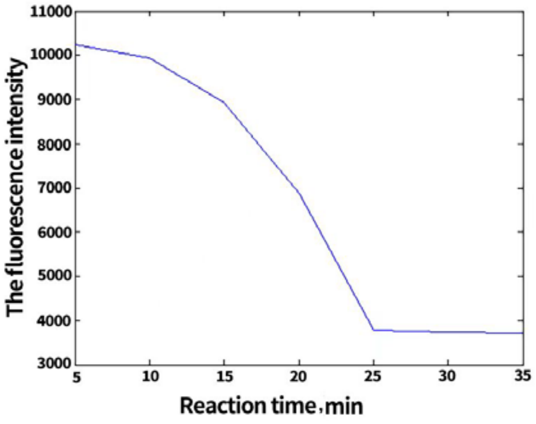

Fig. 3. Effect of reaction time on the fluorescence intensity of quantum dot solution

3.1.3. Effect of quantum dot concentration on detection

The concentration of the quantum dot solution had a certain influence on the analysis of detection results. In this study, five quantum dot solutions (10, 1, 0.5, 0.2, and 0.1 µmol/L) were investigated as fluorescent probes for detection. That is, the quantum dot solution was diluted 1 time, 10 times, 20 times, 50 times, and 100 times respectively. Studies showed that when the quantum dot solutions were diluted two and three times, the FI was too large to exceed the microplate reader range. When the quantum dot solution was diluted 10 times, the FI and the variable range were large. When the quantum dot solution was diluted 50 and 100 times, the FI of the quantum dot solution was low and the variable range was narrow. Therefore, in this experiment, the concentration of the quantum dot solution was selected as 0.5 µmol/L to detect Cu^{2+}.

3.1.4. Effect of the order of reagent addition on detection

The reagents in this experiment were added in the following order: (1) quantum dot solution-Cu^{2+} solution-buffer solution; (2) quantum dot solution-buffer solution-Cu^{2+} solution; (3) Cu^{2+} solution-buffer solution-quantum dot solution. The results showed that the first order of reagent addition, that is, the quantum dot solution-Cu^{2+} solution-buffer solution, had a significant effect on the fluorescence of quantum dots. The second order of reagent addition, that is, the quantum dot solution-buffer solution-Cu^{2+} solution, had no obvious effect on the quenching effect of quantum dots. Therefore, in this experiment, the second order of reagent addition was used to detect Cu^{2+}.

3.1.5. Other metal ion interference

This experiment investigated the effects of common interference ions on the detection results of Cu^{2+}. The effects of cadmium, iron, lead, chromium, potassium, silver, manganese, zinc, magnesium, and copper on the detection of Cu^{2+} using quantum dots were studied. As shown in Fig. 4, Cu^{2+} increased cysteine and glutathione/CdTe.

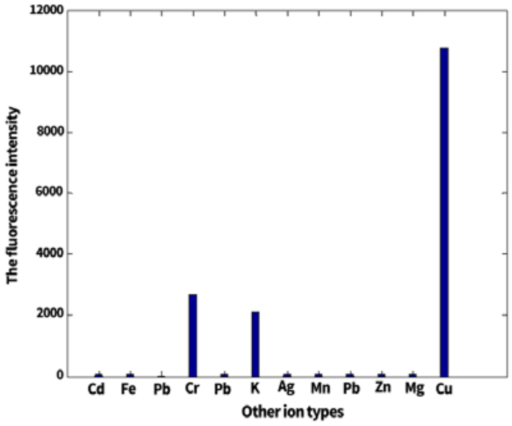

Fig. 4. Interference effect of other ions on Cu^{2+}detection

The quantum dot solution had a strong quenching effect, while chromium and potassium ions had a slight quenching effect. Other metal ions had almost no effect on the FI of quantum dots. The specificity of Cu^{2+} ions indicated that this method was suitable for detecting Cu^{2+} ions in water.

3.2. Univariate linear regression model

The detection curve was drawn, and the linear equation and the determination coefficient were as follows: $y = 0.7395x + 16.305$ (μmol/L), where x is the Cu^{2+} concentration and y is the fluorescence quenching intensity; $R^2 = 0.8389$. The linear range was 3×10^{-5} to 8×10^{-3} mol/L, calculated using the following formula: LOD = 3 sb/m (where LOD is the limit of detection, sb is the standard deviation, and m is the slope of the calibration curve). Using this formula, the detection limit of this method was calculated to be 3.58×10^{-7} mol/L (S/N = 3).

Predicting the concentration of heavy metals using the changes in FI required selecting the FI at the optimal wavelength band, that is, screening for characteristic wavelengths. This study used the correlation coefficient method to select the characteristic band. Fig. 5 shows a correlation coefficient graph between the concentration of heavy metal ions and the FI in the 400- to 800-nm band.

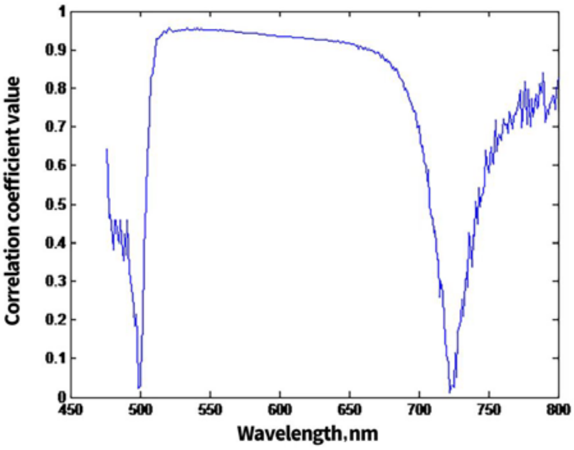

Fig. 5. Correlation coefficient between Cu^{2+} concentration and fluorescence spectrum

3.3. Principal component regression model

Principal component analysis (PCA) is a method of transforming a set of data into a set of unrelated variables by orthogonal transformation. In the PCA process, the independent-variable spectral matrix was first decomposed and then the principal components that met the requirements were selected for multiple regression modeling analysis. According to the actual needs, the selected principal component should be able to represent most of the original spectral information. When the number of principal components was 1, 2, and 3, the contribution rate of the principal component equation was 68.6147 %, 96.4761 %, and 98.070 %, respectively.

The regression analysis was performed on the first three principal components extracted. The results showed that the determination coefficient of the correction set model was 0.8916, the root mean square prediction error of correction was 8.8423 μmol/L, the verification set determination coefficient was 0.7391, and the root mean square error of prediction was 16.800 μmol/L.

3.4. Partial least squares regression model

In this study, different preprocessing methods and partial least squares (PLS) regression models were used to compare related indicators so as to obtain a better prediction model. The prediction set was used to evaluate the prediction performance of the model, and the modeling set used the data set for modeling. The preprocessing methods used were polynomial smoothing algorithm (SG), multiple scattering correction (MSC), standard normal variate (SNV), first-order differential, second-order differential, and cross-validation method to obtain the main factors of PLS modeling. Fig. 6 shows the correlation between the true value and the predicted value of the calibration set of the univariate regression model.

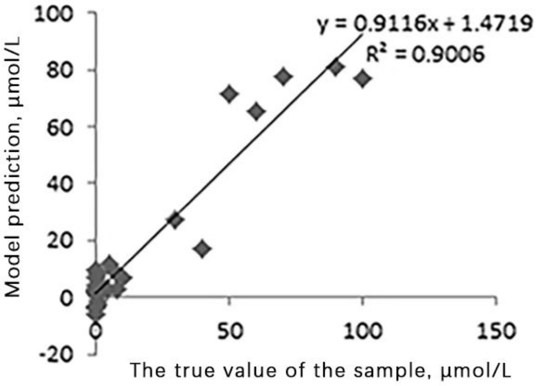

Fig. 6. Correlation diagram between the true and predicted values of the calibration set of the univariate regression model

3.5. Method validation

The quantitative analysis of Cu^{2+} in the calibration material was performed to illustrate further the reliability of the detection method. The results are shown in Table 1. The relative standard deviation (RSD) reflected the stability of the test. As shown in Table 1, the detection error range was between 1.33 % and 3 %, the RSD was between 0.65 % and 2.41 %, and the recovery rate was between 97 % and 101.33 %, indicating that the method had high detection accuracy and stability.

Table 1. Cu^{2+} quantitative analysis

Sample	Calibration value, nmol/L	Measured value, nmol/L	Relative error, %	RSD, %	Recovery rate, %
Sample 1	10 ± 0.3	9.8 ± 0.2	2.00	1.32	98.00
Sample 2	15 ± 1.4	15.2 ± 1.1	1.33	2.41	101.33
Sample 3	20 ± 1.7	19.4 ± 1.7	3.00	0.65	97.00
Sample 1	10 ± 0.3	9.8 ± 0.2	2.00	1.32	98.00
Sample 2	15 ± 1.4	15.2 ± 1.1	1.33	2.41	101.33

4. DISCUSSION

In summary, this study explored the feasibility of using cysteine and glutathione/CdTe quantum dot solutions to detect Cu^{2+} in water quantitatively [24]. The univariate analysis of Cu^{2+} detection experimental data and the comparison of the results of PCA and PLS modeling methods showed that the simplest univariate regression model (at 598 nm) had a higher correction set decision coefficient (0.9006) and more predictive power (standard deviation was 5.4320). Although the selected wavelength was a single wavelength, the simplest univariate regression model was also a modeling method in the actual hardware development process [25, 26]. The principal component regression analysis had good self-predictive ability (decision coefficient reached 0.8916), but the actual predictive ability was lower than that of the PLS model. The PLS model of the characteristic frequency band usually had a better self-predictive ability. After the preprocessing of the characteristic zone, its self-prediction ability was lower than that of PCA, but the actual prediction ability was better. Among these, MSC preprocessing was performed on the characteristic zone, and then PLS modeling and analysis were performed. The predicted decision-making coefficient was 0.8389, and the actual predicted decision-making coefficient was 0.8046. The detection range of Cu^{2+} was 3×10^{-5} to 8×10^{-3} mol/L. These results indicated that the method exhibited excellent selectivity [27]. The combination of cysteine and glutathione/CdTe quantum dot detection and spectroscopy was successfully used to detect Cu^{2+} in water. Therefore, it has broad application prospects in the field of water quality monitoring and environmental pollution analysis.

5. CONCLUSIONS

1. The study of the physical and chemical properties of quantum dots and optimization of related conditions produced the best experimental scheme [28].
2. The innovation of the article lies in: using the method of cysteine and glutathione/CdTe quantum dots, using the fluorescence spectrum value to show a correlation with the content of heavy metal common ions, to quantitatively predict the content of copper ions in the water.
3. Under optimized conditions, the principal component regression analysis of characteristic bands and PLS modeling were carried out for different preprocessing methods [29]. The results showed that the SNV preprocessing of the characteristic frequency band and then the PLS modeling could obtain better self-predictability and actual prediction ability.

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