Detection of Mercury Ions in Aqueous Solution by Fluorescence Spectrometry

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Abstract. This paper proposes a simpler and operable method to replace the traditional detection method and detect the mercury ion in water samples quickly and easily. Firstly, the rhodamine derivatives are synthesized, then a rhodamine derivative fluorescent molecular probe is constructed and adopted to detect mercury ions in water samples.

1. Introduction
Due to the simple operation, high sensitivity and superior selectivity of fluorescence analysis, it has been widely used to detect metal ions. With the invention of a large number of new drugs and the development of science and technology, traditional fluorescence analysis methods are facing new and more superior challenges and it is necessary to develop new fluorescence analysis technologies with higher sensitivity and higher efficiency. This paper studied the mechanism of fluorescence probes in detail and researched the rare earth fluorescent probes with strong specificity, high sensitivity and easy preparation. By comparing various detection technologies, this paper explored a fast and accurate multi-component large sample detection method and developed a more automated and intelligent fluorescence analysis based on computer technology to complete the qualitative and quantitative analysis of drugs. Rhodamine-type fluorescent probes have considerable development prospects. The application of fluorescence analysis technology in heavy metal detection has an important role in human health and environmental protection. The operation process of the experiments will be briefly described below [1-3].

Rhodamine and its derivatives have the advantages of photostability, high yield of fluorescent quantum, long excitation wavelength, and high light consumption coefficient. Therefore, this paper chose rhodamine as the experimental fluorescent molecular probe to detect mercury ions in aqueous solution. The purpose of this experiment is to study the conditions of mercury ion probes. Mercury pollution mainly comes from volcanic eruption, gold mining, and solid waste incineration. Due to the high toxicity of mercury, strictly restricted mercury content standards have been established around...
the world for drinking water, such as the standard content of $\text{Hg}^{2+}$ in drinking water stipulated by US Environmental Protection Agency is within 2 $\mu$g/L, the standard content of $\text{Hg}^{2+}$ in drinking water in China is within 1 $\mu$g/L. Therefore, the Rhodamine-$\text{Hg}^{2+}$ fluorescent probe designed has to be within the above-mentioned detection limits [4-8].

In 2012, Wang designed and synthesized a new probe with vanillin rhodamine 6G hydrazone as structure. This probe has a photometric response rather than fluorescence response in the presence of Cu$^{2+}$ in aqueous ethanol solution. Its performance changes completely when $\text{Hg}^{2+}$ is added. It has a fluorescence response and no photometric response in the presence of $\text{Hg}^{2+}$. The cell experiments have shown that rhodamine probes have broad application prospects in organisms and the environment.

Based on the mechanism of thiomercury and thiosemicarbazide derivatives and the conversion of $\text{Hg}^{2+}$ into hydrazine derivatives, Zhang synthesized a new $\text{Hg}^{2+}$ ion probe (R6G1), and investigated the water solubility, spectrum of R6G1 and its selectivity to common ions in the aqueous phase in 2014. The detection of $\text{Hg}^{2+}$ by fluorescent probe in aqueous solution was realized without being affected [9-11].

In summary, rhodamine and its derivatives have the advantages of stable photostability, high yield of fluorescent quantum, long excitation wavelength, and high light consumption coefficient which makes it very suitable to be used as the fluorescent molecular probe for this experiment. Besides, its mature technology and long history of development have provided great convenience for this experiment. Therefore, rhodamine was selected as the fluorescent molecular probe for the detection of mercury ions in aqueous solutions so as to make contributions to the environmental safety and the drinking water health of the people.

2. Experiment

2.1. Construction of $\text{Hg}^{2+}$ Rhodamine Derivative Fluorescent Probe

In order to obtain standard solution of rhodamine derivatives, rhodamine, hydrazine hydrate, and triethoxymethane were sequentially added to the flask for heating and refluxing, filtering and washing. Then vacuum rotary evaporation was performed, and vacuum drying was carried out on the crude product. A new powdered rhodamine derivative solid was obtained, and the generated rhodamine derivative was used to get a standard solution of rhodamine derivative with a concentration of $20 \times 10^{-6}$ mol/L.

Take an appropriate amount of mercury chloride and the prepared standard solution of rhodamine derivative compound to prepare a fluorescent reaction system with the concentration of metal $\text{Hg}^{2+}$ ion and rhodamine derivative of $5 \times 10^{-6}$ mol/L, and leave it for about 50 minutes to obtain the $\text{Hg}^{2+}$ rhodamine derivative fluorescent probe system.

2.2. Fluorescence Method

Appropriate amount of the standard solution of the derivative was added in a series of 10 ml colorimetric tubes, and then the mercury chloride solution was added with a volume ratio of ethanol to water of 2:1. After being left for 40 minutes, the fluorescence detection was performed on the samples. With the excitation wavelength of 491 nm, the fluorescence emission spectrum in the wavelength range of 500-700 nm was measured, and the excitation and emission slits were 5 nm.

In order to investigate the selectivity to mercury ions, the changes of the fluorescence spectrum before and after adding different metal ions to the compound were measured. The results can be found in figure 1. It shows that after adding the metal mercury ion, there is a strong fluorescence peak at 583 nm, while there is no fluorescence peak when other metal ions are added under the same conditions, which proves that the fluorescence system has good response and selectivity to mercury ions.
3. Results and Discussion

3.1. Response of \( \text{Hg}^{2+} \) Derivatives to Metal Ions

In order to examine the selectivity and response effects of \( \text{Hg}^{2+} \) derivatives to different metals, this paper tested the changes of fluorescence intensity of the system under the action of metal ions after adding different metal ions to the compound. The response of the \( \text{Hg}^{2+} \) derivative fluorescence system to metal ions after adding different metal chlorides (magnesium chloride, cobalt chloride, sodium chloride, nickel chloride, manganese chloride, ferrous chloride, chromium trichloride (II), aluminum chloride, chloride Copper, zinc chloride, calcium chloride, potassium chloride) can be found in figure 1.

![Fluorescence emission spectra of Hg^{2+} derivatives in response to different metal ions.](image1)

**Figure 1.** Fluorescence emission spectra of \( \text{Hg}^{2+} \) derivatives in response to different metal ions.

3.2. Fluorescence Properties of \( \text{Hg}^{2+} \) Rhodamine Derivatives

In order to examine the fluorescence spectra of the compounds and the reaction system, metallic mercury ions were added to the solution. After the addition of metal mercury ion, a fluorescence peak appeared at 555 nm in the fluorescence system and the changes in fluorescence intensity at 555 nm was measured as the concentration of the detected metal mercury ion increased within \( 1 \times 10^{-6} - 50 \times 10^{-6} \). The equimolar method and the continuous variable method were used to determine the coordination ratio of the fluorescent system complex by fluorescence spectroscopy. As shown in figure 2, when the molar ratio of the derivative to the metal mercury ion is 1:1, its fluorescence is the strongest, so the coordination ratio of the fluorescence system of the \( \text{Hg}^{2+} \) rhodamine derivative in this experiment is 1:1.

![Coordination ratio of equimolar Hg^{2+} rhodamine derivative fluorescence system.](image2)

**Figure 2.** Coordination ratio of equimolar \( \text{Hg}^{2+} \) rhodamine derivative fluorescence system.
3.3. Fluorescence Spectrum of Hg$^{2+}$ Rhodamine Derivative Fluorescence System

Figure 3 shows the ultraviolet spectrum of Hg$^{2+}$ rhodamine derivative fluorescent probe system. It can be seen from the ultraviolet-visible absorption spectrum that an ultraviolet absorption peak appears at 527 nm. Rhodamine derivative compounds have no obvious fluorescence peak in the range of 500-700 nm. A strong fluorescence peak centered at 555 nm appears after the addition of metal mercury ions, indicating that the Hg$^{2+}$ rhodamine derivative fluorescent probe system has been successfully established.

![Figure 3. Ultraviolet absorption spectrum of Hg$^{2+}$ rhodamine derivative fluorescent probe system: (a) Hg$^{2+}$ derivative, (b) derivative.](image1)

![Figure 4. Ultraviolet absorption spectrum of Hg$^{2+}$ rhodamine derivative fluorescent probe: (a) Hg$^{2+}$ derivative, (b) derivative.](image2)

It can be seen from figure 3 that after the metal mercury ion is added, the ultraviolet absorption and fluorescence intensity of the fluorescent system are significantly enhanced. It is known from the UV-visible absorption spectrum that a UV absorption peak appears at 527 nm. As shown in figure 4, the rhodamine derivative compound has no obvious fluorescence peak in the range of 500-700 nm. After adding the metal mercury ion, a strong fluorescence peak appears at 555 nm, indicating that the Hg$^{2+}$ rhodamine derivative fluorescence probe system has been successfully established.

4. Conclusion

In order to detect mercury ions in aqueous solutions, the fluorescence spectroscopy was adopted in this experiment, and rhodamine derivatives were used as fluorescent molecular probes. The rhodamine and its corresponding derivatives were used to detect mercury ions in aqueous solutions. Different metal ions and different chlorides were added to the solution of the compound. Only the one with the addition of mercury ion shows a peak at 555 nm. Therefore, it is concluded that the mercury ion derivative has a better response to metal mercury ion. After the metal mercury ion was added, a fluorescence peak of 555 nm appeared in the fluorescence system, and as the concentration of the detected metal mercury ion increased, the coordination ratio of the fluorescent system complex determined by the equimolar method and the continuous variable method and the fluorescence spectrum was 1:1. Through the fluorescence detection under different pH conditions, the optimal pH value of the fluorescent system in this experiment was between 4-11, and the optimal reaction time of the fluorescent system was 50 min. This experiment was carried out according to the best conditions obtained. According to the ultraviolet spectrum and fluorescence spectrum of the Hg$^{2+}$ rhodamine derivative fluorescence probe system, the ultraviolet absorption and fluorescence intensity of the rhodamine derivative fluorescence system with the addition of metal mercury ion are significantly
enhanced and a strong fluorescence peak centered at 555 nm can be obtained, indicating that the Hg$^{2+}$ rhodamine derivative fluorescent probe system has been successfully established.

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