Quantitative Detection of Fe\(^{3+}\) and F\(^{-}\) based on the Fluorescence “OFF-ON” of Quinine Sulfate

Peng Xie\(^1\), Liang Tian\(^2\), Jianhui Zhang\(^1\), Ting Li\(^3\) and Canhui Xiang\(^*\)

\(^1\)School of Chemical Engineering and New Energy Materials, Zhuhai College of Jilin University, Zhuhai, Guangdong, 519041, China

\(^2\)Department of Bioengineering, Zunyi Medical University, Zhanzhou Campus, Zhanzhou, Guangdong, 519041, China

\(^*\)Corresponding author’s e-mail: xp@jluzh.edu.cn

Abstract. In this experiment, a method for continuous detection of Fe\(^{3+}\) and F\(^{-}\) based on the fluorescence "OFF-ON" of quinine sulfate was designed. Through the addition of Fe\(^{3+}\), the fluorescence spectrum of quinine sulfate appeared “OFF”. Then, when F\(^{-}\) was added, the fluorescence appeared "ON" again. By this method, we can get the quantitative detection of Fe\(^{3+}\) and F\(^{-}\) continuously. The detection limit of Fe\(^{3+}\) is 1.0×10\(^{-5}\) mol/L and the linear range is 4×10\(^{-5}\) mol/L-8×10\(^{-4}\) mol/L. The detection limit of F\(^{-}\) is 4.4×10\(^{-5}\) mol/L and the linear range is 1.2×10\(^{-4}\) mol/L-2.4×10\(^{-3}\) mol/L.

1. Introduction
Iron is an important trace element in life, which is widely involved in a variety of life processes, such as cell metabolism, proton transfer, enzyme catalysis, DNA and RNA synthesis\(^{[1-3]}\).

Fluorine is also an important trace element in human body, which is of great significance to bone tissue, tooth glaze, calcium, phosphorus metabolism and so on\(^{[4]}\). However, excessive intake of F\(^{-}\) can cause fluorosis of bone, and low intake of F\(^{-}\) for long-term can also cause harm to the stomach and kidney\(^{[5, 6]}\).

At present, UV-vis spectrophotometry, atomic absorption spectrometry, electrochemical method, ion chromatography, colorimetric method are commonly used to detect Fe\(^{3+}\) and F\(^{-}\). However, there are some problems on these methods above, such as low specificity, high detection limit, complex operation or high detection cost. The method of fluorescence sensors has become an important method to detect the Fe\(^{3+}\)\(^{[7-9]}\) and F\(^{-}\)\(^{[10-12]}\) due to its uniqueness, high sensitivity, low detection limit, simple operation and low cost.

In this experiment, a method for continuous detection of Fe\(^{3+}\) and F\(^{-}\) based on the fluorescence "OFF-ON" of quinine sulfate (QS) was designed.

2. Experimental

2.1. Preparation of solution
Took 1 mL of 0.4 g/L QS solution, 0.05 mol/L sulfuric acid was added to a volume of 100 mL, then 5×10\(^{-6}\) mol/L QS solution was obtained.

Weighed 0.0964 g of NH\(_4\)Fe(SO\(_4\))\(_2\)-12 H\(_2\)O, 0.05 mol/L sulfuric acid was added to 10 mL, and 0.02 mol/L Fe\(^{3+}\) solution was obtained.
Weighed 0.2220 g of NH$_4$F which was under vacuum at 40 °C for 24 h, and made up to 10 mL with ultrapure water to obtained 0.06 mol/L F$^-$ solution.

Weighed 0.094 g of NH$_4$Fe(SO$_4$)$_2$·12 H$_2$O to 100 mL of 5×10$^{-6}$ mol/L QS solution to obtained a QS-Fe$^{3+}$ complex solution which has the Fe$^{3+}$ concentration of 2.00×10$^{-3}$ mol/L.

2.2. Determination of fluorescence quenching spectrum of QS by Fe$^{3+}$ (OFF)

All experiments were performed at pH = 1.52. Took 10 mL of 5×10$^{-6}$ mol/L QS solution in a small beaker and took out 3 mL in a 1 cm quartz cuvette. Set the excitation and emission grating slits to 5 nm. Set the excitation wavelength to $\lambda_{ex} = 347$ nm. 20 $\mu$L of 0.02 mol/L Fe$^{3+}$ solution was added everytime (10 times in total) by the method of fluorescence titration. Then we could got the solution to be measured which contained the concentration of Fe$^{3+}$ 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 6.0, and 8.0×10$^{-4}$ mol/L respectively. The fluorescence emission spectrum of QS was measured.

2.3. Determination of fluorescence enhanced spectrum of QS-Fe$^{3+}$ by F$^-$ (ON)

Took 10 mL of 8.0×10$^{-4}$ mol/L QS-Fe$^{3+}$ solution above to the small beaker and took out 3 mL in a 1 cm quartz cuvette. Set the excitation and emission grating slits to 5 nm. Set the excitation wavelength to $\lambda_{ex} = 347$ nm. 20 $\mu$L of 0.06 mol/L F$^-$ solution was added everytime (10 times in total) by the method of fluorescence titration. Then we could got the solution to be measured which contained the concentration of F$^-$ 0, 1.2, 2.4, 3.6, 4.8, 6.0, 7.2, 8.4, 9.6, 10.8, 12.0, 24.0×10$^{-4}$ mol/L respectively. The fluorescence emission spectrum of QS-Fe$^{3+}$ was measured.

2.4. Determination of UV-vis absorption spectrum

The Fe$^{3+}$ was continuously added to the 5×10$^{-6}$ mol/L QS solution, so that the Fe$^{3+}$ concentration was 0, 0.4, and 1.6×10$^{-4}$ mol/L respectively. Then the F$^-$ was continuously added, so that the F$^-$ concentration was 3.6, 9.6×10$^{-4}$ mol/L respectively. The UV-vis absorption spectrum was continuously measured.

3. Results and discussion

3.1. Fluorescence quenching spectrum (OFF) and fluorescence Enhanced spectrum (ON)

In the experiment, the fluorescence quenching spectra of Fe$^{3+}$ on QS and the fluorescence enhanced spectra of F$^-$ on QS-Fe$^{3+}$ were investigated. The results are shown in figures 1 and 2. It can be seen from that, the fluorescence of QS was regularly quenched (OFF) with the addition of Fe$^{3+}$. When F$^-$ was added to QS-Fe$^{3+}$ system, the fluorescence was enhanced regularly (ON). Therefore, the fluorescence quenching spectra of QS can be used to quantitatively detect Fe$^{3+}$. The fluorescence enhanced spectra of QS-Fe$^{3+}$ system can quantitatively detect F$^-$. 
3.2. Research on UV-vis absorption spectrum

The UV-vis absorption spectra of Fe$^{3+}$ and F$^-$ determined by QS system were investigated experimentally. As shown in Figure 3, when Fe$^{3+}$ was added to QS solution (curve b, c), the UV absorption of QS (curve a) at 250 and 317 nm increased significantly. The addition of F$^-$ made the peaks at 250 and 317 nm decreased, and coincided with the peaks at a certain concentration of Fe$^{3+}$. Through this phenomenon,
the "OFF-ON" phenomenon of QS fluorescence is confirmed.

![Figure 3. UV-vis spectra of determination of Fe\(^{3+}\) and F\(^-\) in QS System](image)

3.3. Fluorescence curve and quantitative detection of QS fluorescence "OFF-ON"

The relationship between ion addition and fluorescence variation can be obtained by fluorescence curve. So that Fe\(^{3+}\) and F\(^-\) can be quantitatively detected. The linear equation of Fe\(^{3+}\) is \(|\Delta F| = 4.17273 \times 10^5 [Q] + 3.74\), \(R = 0.9997\), and the linear equation of F\(^-\) is \(|\Delta F| = 9.49959 \times 10^4 [Q] - 3.7867\), \(R = 0.9995\). Both of the curves have good linearity.

3.4. Research on ion response

In order to investigate the ionic response of QS to Fe\(^{3+}\)[13], we studied the response characteristics of QS to metal ions by adding Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\), Fe\(^{2+}\), Cr\(^{3+}\), Ni\(^{2+}\), Cd\(^{2+}\), Al\(^{3+}\), Cu\(^{2+}\), Mn\(^{2+}\) respectively with the same concentration as Fe\(^{3+}\). As the results shown, the response of QS to Fe\(^{3+}\) is much higher than that of other ions, and QS can be used as an effective sensor for detecting Fe\(^{3+}\).

The ionic response of QS-Fe\(^{3+}\) system to F\(^-\) was also investigated. The ionic response characteristics of QS-Fe\(^{3+}\) system to anions were studied by adding Cl\(^-\), PO\(_4^{3-}\), C\(_2\)O\(_4^{2-}\), CO\(_3^{2-}\), NO\(_3^-\), CH\(_3\)COO\(^-\), respectively. The results shown that the response of QS to Fe\(^{3+}\) system to F\(^-\) is higher, but Cl\(^-\) can cause interference. After precipitation titration with silver nitrate, the interference of Cl\(^-\) can be eliminated.

3.5. Detection limit and linear range

By dividing three times of the instrument noise by the slope of the curve, the detection limit of Fe\(^{3+}\) is \(1.0 \times 10^{-5}\) mol/L. The experiment shows good linearity in the range of Fe\(^{3+}\) concentration of \(4 \times 10^{-5}\) mol/L- \(8 \times 10^{-4}\) mol/L. The detection limit of F\(^-\) is \(4.4 \times 10^{-5}\) mol/L, and the linearity is good in the range of F\(^-\) concentration of \(1.2 \times 10^{-4}\) mol/L- \(2.4 \times 10^{-3}\) mol/L.

4. Conclusion

A fluorescent switch based on QS was designed in this experiment. Using the "OFF-ON" mechanism of
QS fluorescence, the quantitative detection of Fe$^{3+}$ by QS and the quantitative detection of F$^{-}$ by QS-Fe$^{3+}$ were investigated. And the quantitative detection of Fe$^{3+}$ and F$^{-}$ can be realized under specific conditions. The detection limit of Fe$^{3+}$ is $1.0 \times 10^{-5}$ mol/L and the linear range is $4 \times 10^{-5}$ mol/L-$8 \times 10^{-4}$ mol/L. The detection limit for F$^{-}$ is $4.4 \times 10^{-5}$ mol/L and the linear range is $1.2 \times 10^{-4}$ mol/L-$2.4 \times 10^{-3}$ mol/L. This study will provide a good idea and data support for the design of fluorescent sensors based on quinine sulfate functionalization.

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