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## Determination of ethylenediaminetetraacetic acid base on the reversion of fluorescence quenching of 2-pyridinecarbaldehyde-*p*-phenyldihydrazone by ferric iron



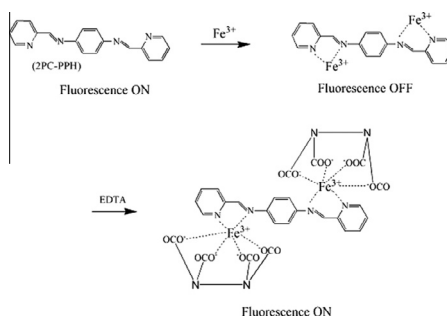
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### HIGHLIGHTS

- A fluorometric method for determination of EDTA is proposed.
- The method bases on EDTA recover the fluorescence of a Schiff base quenched by Fe<sup>3+</sup>.
- The fluorescence recovery mechanism is formation of a ternary complex.
- The method shows high specificity and high sensitivity for EDTA detection.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A fast and sensitive fluorometric method for determination of an emerging pollutant, ethylenediaminetetraacetic acid (EDTA), was proposed based on the reversion of fluorescence quenching of 2-pyridinecarbaldehyde-*p*-phenyldihydrazone by ferric iron. It was found that Fe<sup>3+</sup> could selectively quench the fluorescence of 2PC-PPH, while EDTA could recover it due to its strong coordination ability with Fe<sup>3+</sup>. Based on this, we established an “Off and On” fluorescence method for determination of EDTA. Under the optimum conditions, the linear range and detection limit (3S/N) for EDTA determination were  $2.0 \times 10^{-6} \sim 1.4 \times 10^{-5} \text{ mol L}^{-1}$  and  $1.5 \times 10^{-7} \text{ mol L}^{-1}$ , respectively. The relative standard deviation for the determination of  $7.0 \times 10^{-6} \text{ mol L}^{-1}$  EDTA was 3.7% ( $n = 11$ ). The method was successfully applied to determination of EDTA in tap water, lake water and investigating degradation of EDTA by TiO<sub>2</sub>/UV process.

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### Introduction

Ethylenediaminetetraacetic acid (EDTA) is widely used as an extremely good metal-chelating agent in copy industry, textile industry, paper-making industry, metal manufacturing and power plant boiler cleaning, etc. The excessive effluent [1] and low biodegradability [2] of EDTA have led to the spread of EDTA in water environment [3,4]. Although EDTA is believed to be non-toxic to mammals at micrograms per liter level, there is greatly concern about the

possibility of EDTA that released with wastewater streams to remobilize toxic heavy metals out of river/lake sediments [5]. Hence, EDTA is regarded as one of emerging pollutants, monitoring and controlling the effluents of EDTA is significantly important in environmental protection.

Various analytical methods had been developed for EDTA determination, such as titrimetry [6], electrochemistry [7–9], spectrophotometry [10], and chromatography [11–13]. Among them, gas chromatograph and HPLC were extensively used techniques. While gas chromatographic methods [11] always included a time-consuming derivatization step, in which EDTA was converted into methyl, ethyl, propyl or butyl esters. Similarly, HPLC methods

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[12,13] were mainly based on a pre-column derivatization step by coordinating with  $\text{Cu}^{2+}$  or  $\text{Fe}^{3+}$ . Fluorometric methods were usually used owing to its excellent selectivity and high sensitivity. Zhu et al. [14] established fluorometric methods for the determination of  $\text{Lu}^{3+}$ ,  $\text{Y}^{3+}$  and EDTA based on formation of strong fluorescent ternary complex of  $\text{Lu}^{3+}$  or  $\text{Y}^{3+}$ , EDTA and 7-(1'-naphthylamine-azo)-8-hydroxyquinoline-5-sulfonic acid (NAOX). Similarly, a fast method for determination of EDTA in microtiter plate based on increasing fluorescence of Terbium-Salicylate complex by adding EDTA had been reported [15]. Kawasaki [16] developed a fluorometric method for determination of EDTA based on that EDTA could decrease the fluorescence of  $\text{Ca}^{2+}$ -fluo-3 complex. However, so far still rare fluorescence methods of determining EDTA had been reported and those reported methods were mainly established based on the increase of fluorescence intensity of lanthanide complexes caused by EDTA.

In this work, we established a new fluorescent probe 2PC-PPH(2-pyridinecarbaldehyde-*p*-phenylenedihydrazone)- $\text{Fe}^{3+}$  for EDTA detection. According to our previous work [17], the fluorescence of Schiff base 2PC-PPH could be selectively quenched by ferric ion. In our further study, the fluorescent intensity of 2PC-PPH- $\text{Fe}^{3+}$  could be recovered by EDTA and recovering intensity was linear with the amount of EDTA. Based on this, a fast and sensitive fluorometric method for determination of EDTA was proposed.

## Materials and methods

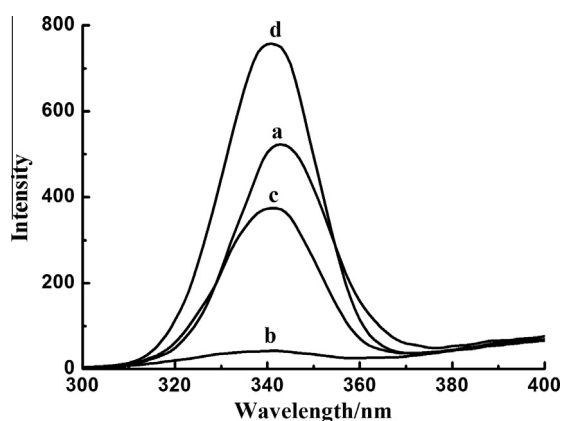
### Reagents

2PC-PPH was synthesized in our previous work [17]. HCl,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , HAC, NaAc, EDTA- $\text{Na}_2$  were of analytical grade and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

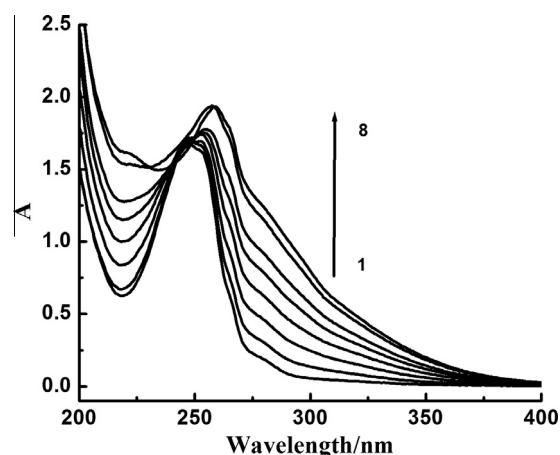
### Preparation of stock solution and dilution standards

2PC-PPH solution ( $2.0 \times 10^{-4} \text{ mol L}^{-1}$ ): 5.7 mg 2PC-PPH was dissolved by doubly distilled water and 1 mL of  $1.0 \text{ mol L}^{-1}$  HCl was added to improve its solubility, and then diluted to 100 mL.

$\text{FeCl}_3$  stock solution ( $1.0 \times 10^{-2} \text{ mol L}^{-1}$ ): Dissolved 0.2703 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 100 mL of doubly distilled water (containing 1 mL  $1.0 \text{ mol L}^{-1}$  HCl to avoid hydrolysis of  $\text{FeCl}_3$ ); The  $\text{FeCl}_3$  solution ( $4.0 \times 10^{-4} \text{ mol L}^{-1}$ ): Pipetted 400  $\mu\text{L}$  stock solution to 10 mL colorimetric cylinder, added 200  $\mu\text{L}$   $0.10 \text{ mol L}^{-1}$  HCl, and diluted to volume.



**Fig. 1.** Synchronous fluorescence emission spectra ( $\Delta\lambda = 55 \text{ nm}$ ) of 2PC-PPH- $\text{Fe}^{3+}$  in the absence and presence of EDTA. (a)  $5.0 \times 10^{-6} \text{ mol L}^{-1}$  2PC-PPH; (b)  $5.0 \times 10^{-6} \text{ mol L}^{-1}$  2PC-PPH,  $1.4 \times 10^{-5} \text{ mol L}^{-1}$   $\text{Fe}^{3+}$ ; (c) b +  $7.0 \times 10^{-6} \text{ mol L}^{-1}$  EDTA; and (d) b +  $1.4 \times 10^{-5} \text{ mol L}^{-1}$  EDTA. Above solutions all at pH4.4 which were regulated by HAC-NaAc buffer solution.



**Fig. 2.** UV-Vis spectra of 2PC-PPH- $\text{Fe}^{3+}$  system in the presence of EDTA with increasing concentrations.  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  2PC-PPH;  $1.4 \times 10^{-4} \text{ mol L}^{-1}$   $\text{Fe}^{3+}$ ; EDTA with the concentrations of 0, 2, 4, 6, 8, 10, 12,  $14 \times 10^{-5} \text{ mol L}^{-1}$ ; pH = 4.4 HAC-NaAc.

EDTA stock solution ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ): Dissolved 0.0372 g of disodium salt of EDTA in 100 mL of doubly distilled water. The EDTA solution ( $2.0 \times 10^{-4} \text{ mol L}^{-1}$ ): Diluted the concentration of this stock solution for 5 times.

All water used in this experiment was doubly distilled water.

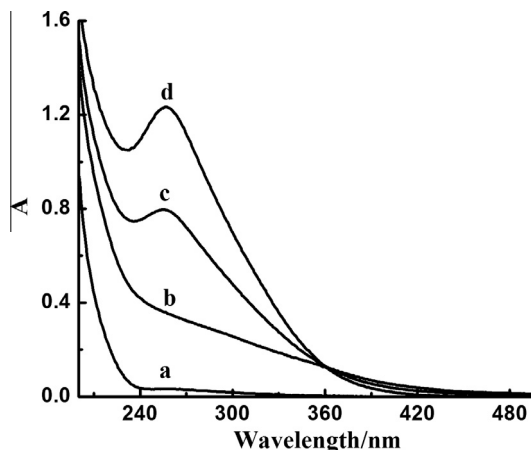
### Apparatus

RF-5301PC fluorescence spectrophotometer (SHIMADZU, Japan) with a  $1 \times 1 \text{ cm}$  cuvette. UV-2401 ultraviolet-visible spectrophotometer (SHIMADZU, Japan). Photoreactor with a 20-W low pressure Hg lamp and a crystallizing dish (diameter is 9 cm). TGL-16C desktop centrifuge (Anke, Shanghai, China).

### Experimental procedure

#### Assay of standard EDTA solution

Successively added 250  $\mu\text{L}$  of 2PC-PPH stock standard solution, 350  $\mu\text{L}$   $\text{FeCl}_3$  ( $4.0 \times 10^{-4} \text{ mol L}^{-1}$ ) aqueous solution, appropriate volumes of EDTA ( $2.0 \times 10^{-4} \text{ mol L}^{-1}$ ) and 1 mL HAC-NaAc ( $0.10 \text{ mol L}^{-1}$ , pH 4.4) buffer solution in 10 mL graduated tubes



**Fig. 3.** UV-Vis spectra of  $\text{FeCl}_3$ , EDTA and  $\text{FeCl}_3$ -EDTA systems. (a)  $1.4 \times 10^{-4} \text{ mol L}^{-1}$  EDTA; (b)  $1.4 \times 10^{-4} \text{ mol L}^{-1}$   $\text{Fe}^{3+}$ ; (c) b +  $7.0 \times 10^{-5} \text{ mol L}^{-1}$  EDTA; (d) b +  $1.4 \times 10^{-4} \text{ mol L}^{-1}$  EDTA. Above solutions all at pH4.4 which were regulated by HAC-NaAc buffer solution.

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