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Short Communication

Spectrophotometric Determination of Zinc Using Carboxylic Carbon Nanotubes

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A novel, simple, and sensitive spectrometric method for determination of Zinc was developed using carboxylic carbon nanotubes (CNTs) as a toner. The optimum operating conditions including pH, volume and addition order of reagents solution were established. The nature of the novel complex was also investigated. Comparative experiments proved that the carboxyl CNTs exhibit the obvious hyperchromic effect: the absorbance of the complex was increased by nearly 70.3% through optimizing the technological parameters; the coloration system showed the maximum absorbance at 529.6 nm with a molar absorptivity value of 1.12×10^5 L mol^{-1} cm^{-1}; Beer's law is obeyed over the zinc concentration range 0–11 μg/25.0mL.

Keywords: Zinc; Carboxylic carbon nanotubes; Spectrometric determination

1. INTRODUCTION

Zinc is an essential micronutrient of great importance for the living organisms' metabolism [1, 2]. However, superfluous zinc would bring some noxious effects to human body, including alteration in the immune response, disturbance in energy metabolism, increase in oxidative stress, weight loss and retardation of growth[3, 4]. Thus, a sensitive and accurate determination of zinc is very important and required with great consideration.

Spectrophotometry is one of widely used technique for the analysis of metallic elements, which is attibuted to the adequate sensitivity, running cost of the instrument and ease to operation [5]. However, it is not sufficient when the zinc concentration levels are very low in water samples or biological samples. To solve this problem, various preconcentration procedures are often involved prior to analysis to improve the sensitivity of spectrophotometry [6]. Carbon nanotubes (CNTs) were used for determination of zinc in the preconcentration-separation procedures [4, 7-9].But these methods suffer from time-consumption, high labor intensity and toxic organic solvents needed, which brings great threat to the environment [10, 11].

In our previous research, CNTs were used as a toner for direct determination of copper and lead, and carboxylic CNTs shows excellent hyperchromic effect to the coloration system[12, 13]. In this work, the carboxylic CNTs was directly used in the determination of zinc. The analytical parameters including pH, addition and volume order of reagents on the absorbance of coloration system were investigated and optimized. The analytical feature of the novel coloration system was also investigated.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Carboxylic CNTs with an average external diameter of 40-60nm were provided by Shenzhen Nanoport Company; Phenylfluorone (PF) was obtained from Shanghai Yuanye Bio-technology Co., Ltd. Zinc sulfate, Hydrogen Peroxide (H_2O_2), Sodium tetraborate ($Na_2B_4O_7\cdot 10H_2O$) and sodium hydroxide (NaOH) were obtained from Tianjin Damao chemical Co., Ltd.

2.2. Solutions

Stock solution for zinc ions was prepared from appropriate amounts of the Zinc sulfate as 1.0 mg mL^{-1} in doubly distilled water, and the solution was further diluted to 10 μg mL^{-1} prior to use. Phenylfluorone(PF) ethanol solution with a concentration of 100 μg mL^{-1} was selected. Weighed amounts (0.0100 g) of carboxylic CNTs were dispersed by the KQ3200E ultrasonic instrument (Jiangsu Kunshan Ultrasonic Instrument Co., Ltd) in 100mL of doubly distilled water for 30 min to obtain a 100 μg mL^{-1} solution. A boric buffer solution (pH 7.4-10.1) was prepared by using $Na_2B_4O_7\cdot 10H_2O$ and NaOH at appropriate concentrations.

2.3. Procedures

All experiments were carried out at room temperature. To the 25mL flask were introduced 1 mL of Zn^{2+} solution, 2mL of PF ethanol solution, 1mL of carboxylic CNTs solution and 6mL of boric buffer solution (pH=9.6) in turn. The flasks were filled with doubly distilled water to the same volume. After 20min, absorption spectra were recorded from 500-600nm on T6 spectrophotometer with 1.0-cm silica quartz matched cell (Beijing Purkinje General Instrument Co., Ltd). The major parameters which could influence the performance of the method were varied to arrive at the wavelength of maximum absorbance. The absorbance change with the volume of Zn^{2+} solution was measured to obtain the analytical feature of the chromogenic system under the optimum conditions.

3. RESULTS AND DISCUSSION

3.1 Absorption spectra

The absorption spectra of different coloration systems are shown in Fig.1. It shows strong evidence that the absorbency of the coloration system increases with the application of carboxylic CNTs. As we known, carboxylic CNTs can provide more chemical adsorption sites due to the introduction of functional groups, which exhibit absorption capacities to Zn^{2+} and small molecules. The Zn^{2+}-PF complex can be closely absorbed onto the sidewall of carboxylic CNTs to form a novel and structural stable complex (shown in Fig.2) with the the addition of carboxylic CNTs, which can reduce the adverse effects caused by the hydrolysis reaction of Zn^{2+}. Then the absorbance of the system increased.

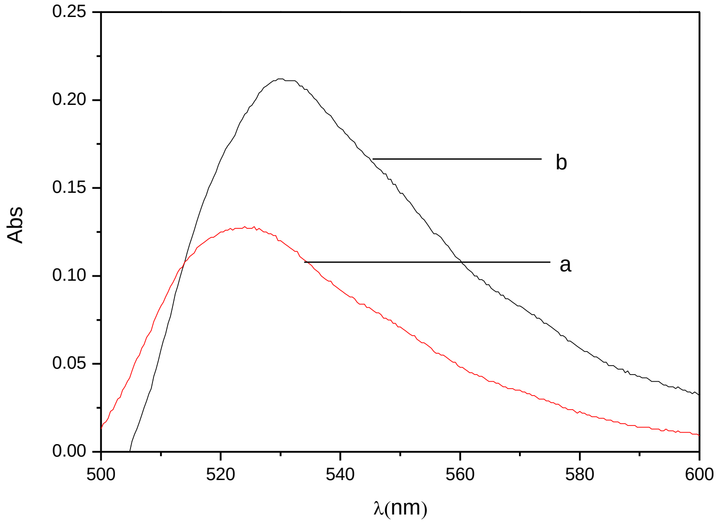

Figure 1. Absorption spectra of different chromogenic system; a. Zn^{2+}-PF complex b. Zn^{2+}-PF-carboxylic CNTs complex

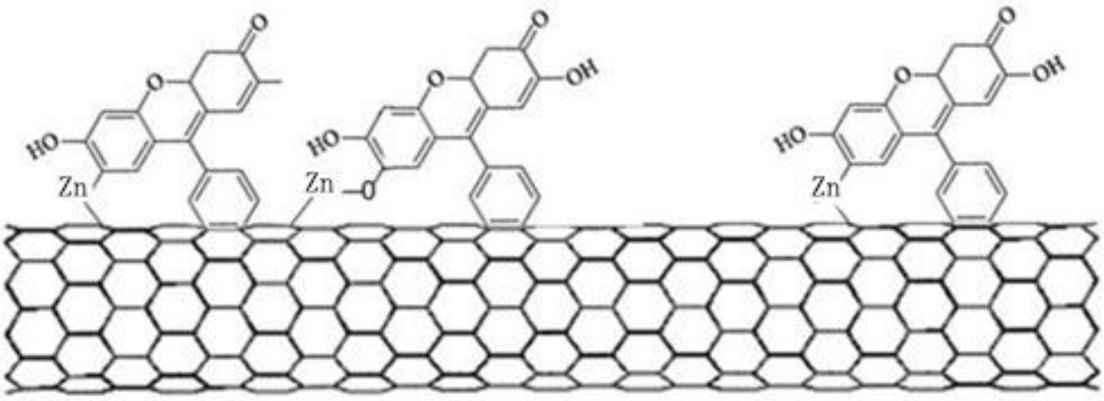

Figure 2. The Zn^{2+}-PF complex absorbing onto the sidewall of carboxylic CNTs

3.2 Effect of pH of buffer solution

The pH plays a important role on the metal-chelate formation and the absorption of CNTs [12, 14]. Then, finding the proper pH is one of the most crucial issues in the optimization of working conditions. For this reason, the effect of pH on the determination of zinc was investigated. The mixture solution was measured in the range of 7.4-10.1 at 529.4 nm. As it is clearly seen from Fig.3, the pH of the coloration system in the range of 9.4-9.8 was sufficient. Therefore later samples were buffered to pH 9.8.

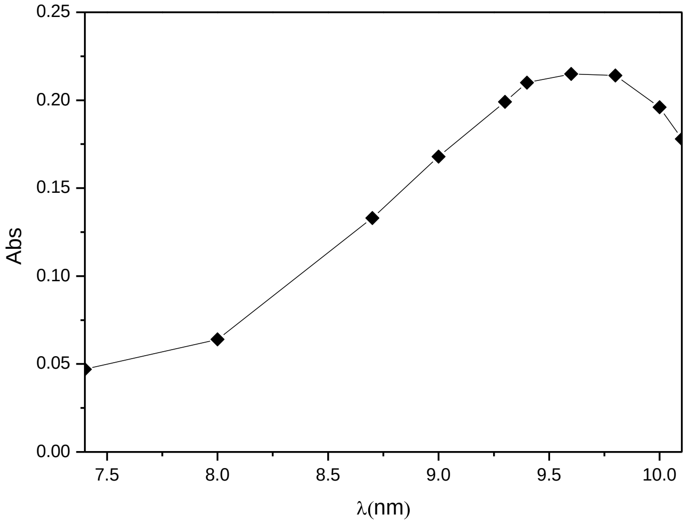

Figure 3. Effect of pH of buffer solution on the absorbance

3.3. Effect of volume of reagents solution

3.3.1. Carboxylic CNTs

The concentration of carboxylic CNTs has a direct effect on the formation of the complex. In order to study the influence of its concentration on analytical response for zinc, different concentrations of carboxylic CNTs were obtained by added 0.5-1.0 mL 100 μg ml^{-1} solutions into the colorimetric cylinder. It shows that the absorbance increases up to 0.8mL carboxylic CNTs solution, reaching a plateau, and that the signals decrease with increase of the carboxylic CNTs volume above 1.2 mL. The carboxylic CNTs solution volume of 1.0 mL was used in the later experiments.

3.3.2. PF

As an excellent chromogenic agent, PF have been used in the determination of heavy metals. Keeping other experimental parameter constant, the effect of volume of PF solution (0.5-3.0 mL) on the determination of Zn^{2+} was investigated spectrophotometrically. According to experiment, the volume of PF solution above 2.0 mL was sufficient. Hence, 2.0 mL of PF solution was chosen in the later experiments.

3.4 Effect of addition order

The effect of addition order of other reagents was also studied on condition that the buffer solution was added finally. The results are shown in Fig.4. The color of the system was more intense and stable with the addition order of Zn^{2+}–PF-carboxylic CNTs than the order of Zn^{2+}–carboxylic CNTs–PF. If the carboxylic CNTs had been added to the Zn^{2+} solution before PF, Zn^{2+} was firstly absorbed onto the surface of the carboxylic CNTs, which could affect the formation of the Zn^{2+}-PF complex, and then the absorbency of Zn^{2+}–carboxylic CNTs–PF would not be as strong as that of Zn^{2+}–PF- carboxylic CNTs.

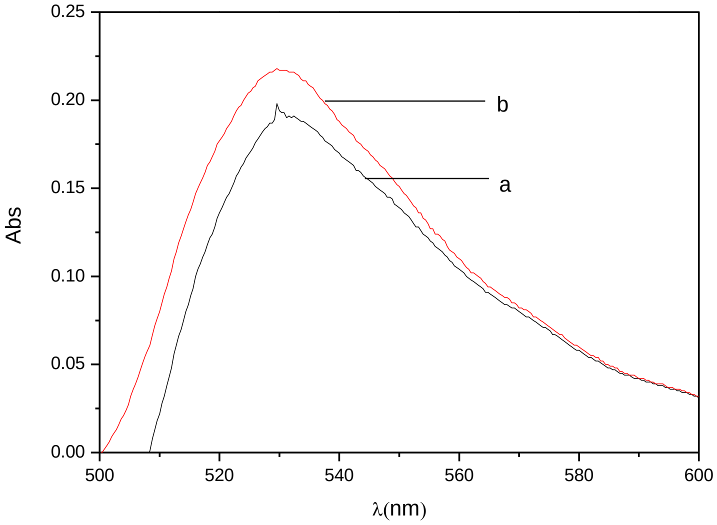

Figure 4. Effect of different addition order on absorption spectrum; a Zn^{2+}–carboxylic CNTs–PF b Zn^{2+}–carboxylic CNTs–PF

3.5 Nature of the complex and the linearity of Zn^{2+}

The composition of the examined complex was established by Job's method. The result is shown in the Table 1. It was found that stoichiometry of the chelate Zn:PF is 1:2 at the optimum conditions.

Table 1. Absorbance of coloration system with different addition order

$c(Zn^{2+})$/ c(PF)	1 : 3	1 : 2.5	1 : 2	1 : 1.5	1 : 1
A	0.153	0.174	0.218	0.208	0.210

Under the optimized conditions, the effect of concentration of Zn^{2+} was studied to obtain the calibration curve. The calibration curve was linear over the range 0–11.0 μg/25.0mL of Zn^{2+}, which obey the Beer's law. The regression equation for zinc determination was $A=0.02182C+0.00082$

(where A is the absorbance and C is the zinc concentration in ng mL^{-1}) with the correclation coefficient (r^2) of 0.9994. The molar absorptivity of the complex is 1.12×10^5 L mol^{-1} cm^{-1} at 529.6nm.

4. CONCLUSION

In this study, a noval method for determination of Zn^{2+} by using carboxylic CNTs is developed. An advantage of this method is a direct and simple spectrophotometric measurement of absorbance of the analysed solution. Moreover, the elaborated method is precise and has good sensitivity, which proves that it can be used for determination of Zn^{2+}.

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