Short Communication

Application of Carboxylic Carbon Nanotubes for the Rapid Determination of Lead by Spectrophotometry

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A novel spectrometric method for determination of lead was developed with the application of carboxylic carbon nanotubes (CNTs). 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 application of carboxyl CNTs exhibit the obvious hyperchromic effect: the absorbance of the complex was increased by nearly 52.2% through optimizing the technological parameters; the coloration system showed the maximum absorbance at 580.4 nm with a molar absorptivity value of 1.35×10^5 L mol^{-1} cm^{-1}; the calibration graph was linear in the range 1–24.0 μg/25.0mL and the limit of detection was 10.4 ng/mL. The proposed method is simple, sensitive and direct for the determination of lead.

Keywords: Lead; Carbon nanotubes; Spectrometric determination

1. INTRODUCTION

Lead as a typical heavy metal has been used in the various industries. However, it is accumulated through the biogeochemical cycle and ultimately reaches in water, which can cause serious health or environmental problems [1-3]. Determination of lead is very important and required with great consideration.

Carbon nanotubes (CNTs) have been used in the analytical field due to their unique structure and surface characteristics [4]. For example, CNTs were used as assisted matrix for laser depsorption/ionization time-of-flight mass spectrometry or infrared detector to the determination of

small molecules [5, 6]. Furthermore, CNTs were used for determination of the heavy metals in the preconcentration-separation procedures [7]. However, it suffers from tedious operation, time-consumption and so on.

In our previous research, CNTs were used as a toner for direct determination of copper, and carboxylic CNTs shows excellent hyperchromic effect to the coloration system[8]. In this work, the carboxylic CNTs was directly used in the determination of lead. 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. Lead nitrate, 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 lead ions was prepared from appropriate amounts of the lead nitrat as 10 μg mL^{-1} in doubly distilled water prior to use. 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 8-10.1) was used for pH adjustment.

2.3 Procedures

All experiments were carried out at room temperature. To the 25mL flask were added 2 mL of Pb^{2+} solution, 1mL of PF ethanol solution, 1mL of carboxylic CNTs solution and 11mL of boric buffer solution (pH=9.8) in turn. The flasks were filled with doubly distilled water to the top up mark. After 20min, absorption spectra were recorded from 500-650nm 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 Pb^{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.
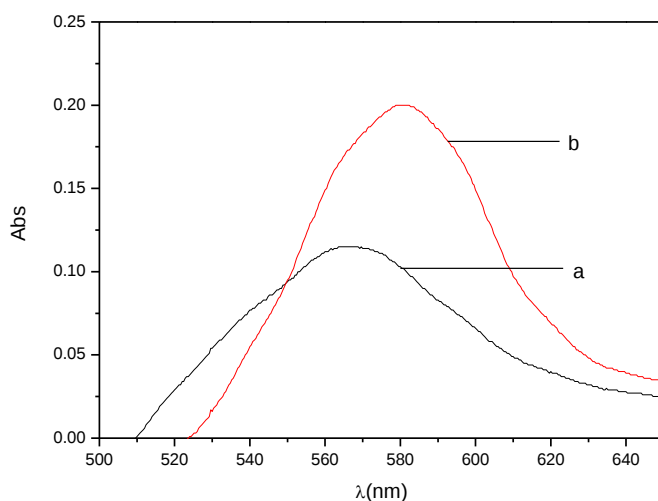
Figure 1. Absorption spectra of different chromogenic system a. Pb^{2+}-PF complex b. Pb^{2+}-PF-carboxylic CNTs complex
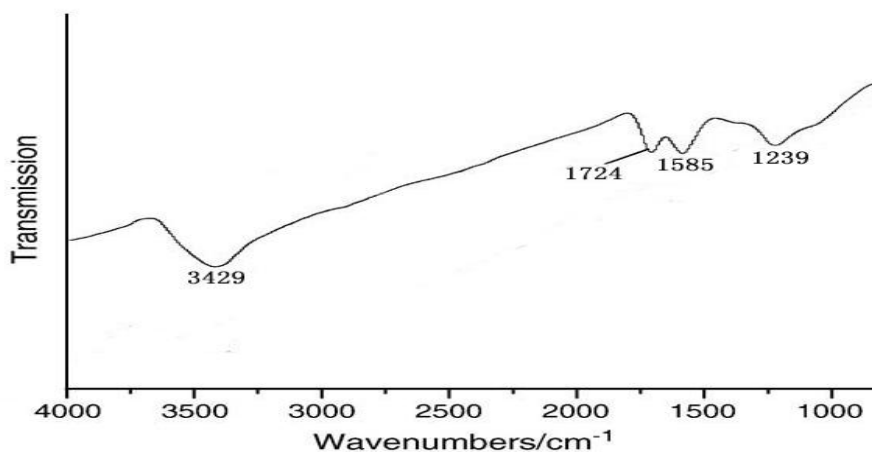
Figure 2. FTIR spectra of carboxylic CNTs

As we known, CNTs have been used as absorbers, which exhibit absorption capacities to Pb^{2+} and small molecules[9, 10]. Furthermore, carboxylic CNTs can provide more chemical adsorption sites due to the introduction of functional groups (shown in Fig.2) [11]. The Pb^{2+}-PF complex can be closely absorbed onto the sidewall of carboxylic CNTs to form a novel and structural stable complex

(shown in Fig.3) with the the addition of carboxylic CNTs, which can reduce the adverse effects caused by the hydrolysis reaction of Pb^{2+}. Then the absorbance of the system increased.
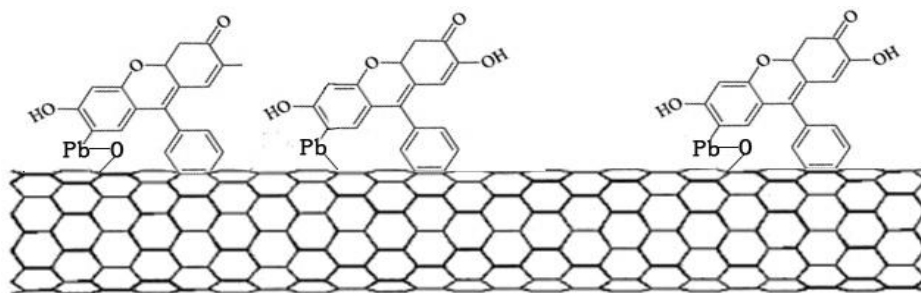
Figure 3. The Pb^{2+}-PF complex absorbing onto the sidewall of carboxylic CNTs

3.2 Effect of pH of buffer solution

The pH plays a important role on the metal-chelate formation and the absorption of CNTs [8, 12], which was adjusted with the buffer solution. Keeping other experimental parameter constant, the effect of pH on the determination of Pb^{2+} was investigated spectrophotometrically. The mixture solution was measured in the range of 8.0-10.1 at 580.4 nm. As it is clearly seen from Fig.4, the pH of the coloration system in the range of 9.6-9.9 was sufficient. Therefore later samples were buffered to pH 9.8.
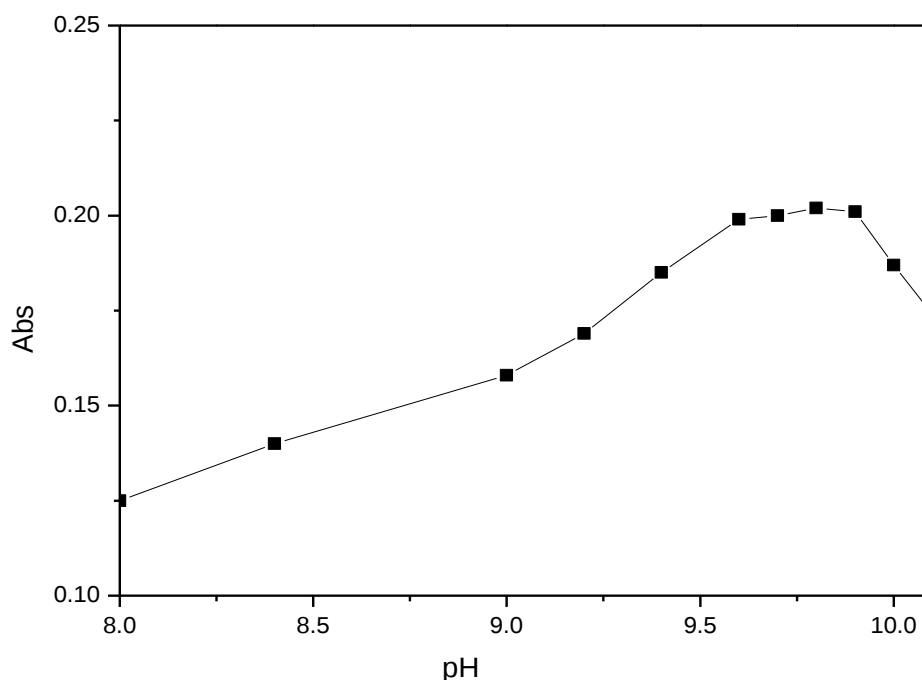
Figure 4. Effect of pH of buffer solution on the absorbance

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. The effect of the carboxylic CNTs solution volume(0.4-1.4 mL) on the absorbance was studied. The results are shown in Fig.6. 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 1.1 mL.

The amount of carboxylic CNTs is so little that some Pb^{2+} and PF can not be absorbed onto the sidewall of tubes as the volume of solution is below 0.8mL. Therefore, the absorbance increases with the volume of solution. The amount of carboxylic CNTs is excessive when the volume of solution is above 0.8mL. It results in fewer Pb^{2+} and PF absorbed onto the sidewall of each tube, which lead to incomplete reaction and decrease of absorbance. The carboxylic CNTs solution volume of 1.0 mL was used in the later experiments.
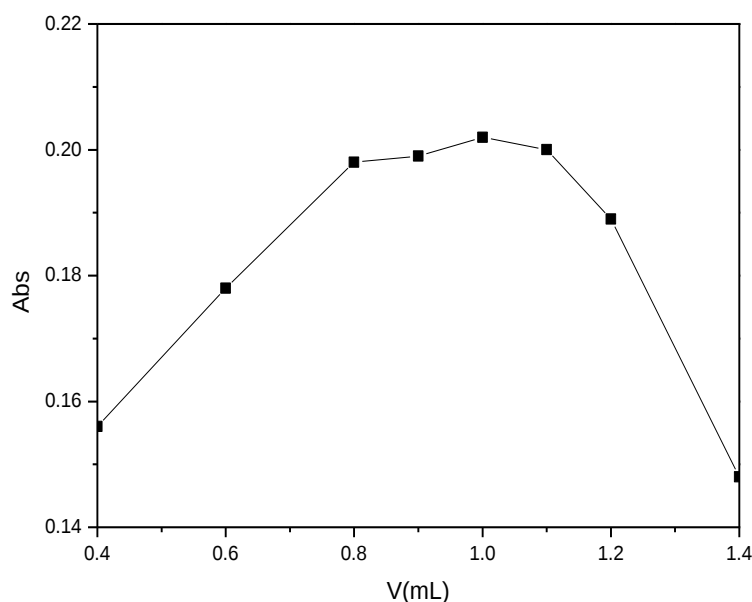
Figure 6. Effect of the volume of carboxylic CNTs on the absorbance

3.3.2 PF

As an excellent chromogenic agent, PF have been used in the determination of heavy metals. The effect of volume of PF solution (0.4-1.5mL) was studied to obtain information of the absorbance. According to experiment, the volume of PF solution above 1.0 mL was sufficient. Hence, 1.0 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 Table 1. The coloration system with the order of $Pb^{2+}\rightarrow PF\rightarrow$carboxylic CNTs shows the maximum absorbance. If the carboxylic CNTs had been added to the Pb^{2+} solution before PF, Pb^{2+} was firstly absorbed onto the surface of the carboxylic CNTs, which could affect the formation of the Pb^{2+}-PF complex, and then the absorbency of Pb^{2+}–carboxylic CNTs–PF would not be as strong as that of Pb^{2+}–PF- carboxylic CNTs.

Table 1. Absorbance of coloration system with different addition order

NO.	addition order of reagents	Absorbance
1	$Pb^{2+}\rightarrow PF\rightarrow$carboxylic CNTs	0.202
2	$Pb^{2+}\rightarrow$carboxylic CNTs$\rightarrow PF$	0.165

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

Keeping all other experimental parameter constant, the effect of concentration of Pb^{2+} was studied to obtain the calibration curve. The calibration curve was linear over the range 1–24.0 μg/25.0mL of Pb^{2+}, which obey the Beer's law. The regression equation for copper determination was *A=0.03451C-0.00134* (where A is the absorbance and C is the copper concentration in ng mL^{-1}) with the correclation coefficient (r^2) of 0.9995. The molar absorptivity of the complex is 1.35×10^5 L mol^{-1} cm^{-1} at 580.4nm.

The limit of detection (LOD) shows an indication of the lowest concentration of Pb^{2+} that can be determined from the blank absorbance with 95% certainty. The LOD was calculated by the equation: LOD=3SD/b (where, SD is the standard deviation of the blank (n=10), b is the angular coefficient of the calibration curve). The calculated LOD was 10.4ng/mL of Pb^{2+}.

4. CONCLUSION

In this study, an effecive method for determination of Pb^{2+} with the appliation of 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 Pb^{2+}.

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