

A Simple and Highly Sensitive Spectrometric Determination of Lead by Using Carboxylic Carbon Nanotubes and Cetyltrimethyl ammoniumbromide

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A novel and sensitive spectrometric method for determination of lead was developed with the application of carboxylic carbon nanotubes (CNTs) and cetyltrimethyl ammoniumbromide (CTMAB). The optimum operating conditions regarding pH, volume and addition order of reagents solution were established. The nature of the complex was also investigated. Comparative experiments proved that the application of carboxyl CNTs and CTMAB had the obvious hyperchromic effect: the absorbance of the complex was increased by nearly 90% through optimizing the technological parameters. The coloration system showed the maximum absorbance at 600.4nm with a molar absorptivity value of $0.70 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$; the calibration graph was linear over the range 0.5–11.0 $\mu\text{g}/25.0\text{mL}$ and the limit of detection was 17.8ng/mL. Moreover, the method is easy and direct to perform for the determination of lead.

Keywords: Lead; Carbon nanotubes; cetyltrimethyl ammoniumbromide; spectrometric determination

1. INTRODUCTION

As a typical heavy metal, lead (Pb^{2+}) has been widely used in variety of electrochemical and industrial applications [1-3]. However, lead is known as a toxic element, which can cause serious hazardous effect to human health, including neuropathy, encephalopathy, and kidney damage [4, 5]. Thus, a sensitive and accurate determination of lead is very important and required with great consideration.

Spectrophotometry is a relatively sensitive method for lead since it is cheap and simple to implement in laboratories, which is based on the reaction between lead with chromogenic reagents [6,

7]. However, the complex is unstable due to the hydrolysis reaction of Pb^{2+} especially when the lead concentration levels are very low in water samples or biological samples, which leads to the low-sensitivity of the analytical method (molar absorptivity value $<10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$). To solve this problem, various preconcentration procedures including liquid-liquid extraction (LLE), solid phase extraction (SPE) and cloud point extraction (CPE), are often involved to improve the sensitivity of spectrophotometry prior to determination [8-11], whose molar absorptivity value is in the range of $10^4 \sim 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. However these methods suffer from time-consumption, high labor intensity and toxic organic solvents needed, which brings great threat to the environment [12, 13]. Hence, the development of more direct and sensitive spectrophotometry for determination of lead is still sought.

Carbon nanotubes (CNTs) have been used in the analytical field due to their unique structure and surface characteristics [14]. For example, CNTs were used for determination of the heavy metals in the preconcentration-separation procedures [15, 16]. But, the mixture of CNTs and heavy metals must be desorbed before the determination, which also suffers from tedious operation, time-consumption and so on. By contrast, carboxylic CNTs in the presence of cetyltrimethyl ammoniumbromide (CTMAB) were selected to be used in the direct determination of copper in our resent research, which can simply the practical steps and improve the sensitivity of the coloration system [17]. The present work is dedicated to determination of lead by using carboxylic CNTs and CTMAB.

In this work, a simple, direct, sensitive and spectrometric method for determination of lead with the application of CNTs has been developed. The analytical parameters including pH, volume and addition order of reagents on the absorbance of coloration system were investigated and optimized. The nature of the complex was also investigated.

2 EXPERIMENTAL

2.1 Reagents and chemicals

Carboxylic CNTs with an average external diameter of 40-60nm were kindly provided by Shenzhen Nanoport Company; Phenylfluorone (PF) was obtained from Shanghai Yuanye Biotechnology Co., Ltd. CTMAB was kindly provided by Hunan Xiangzhong geological institute. Lead nitrate, Hydrogen Peroxide (H_2O_2), Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were obtained from Tianjin Damao chemical Co., Ltd.

2.2 Solutions

A 1.0 mg mL^{-1} standard solution of Pb^{2+} was prepared by dissolving lead nitrat in doubly distilled water and the solution was further diluted to $10 \mu\text{g mL}^{-1}$ before being used. PF ethanol solution with a concentration of $100 \mu\text{g mL}^{-1}$ was selected. Weighed amounts (0.0100 g) of carboxylic CNTs were dispersed by the KQ3200E ultrasonic instrument (Jiangsu Kunshan Ultrasonic Instrument Co., Ltd) in 100 mL of doubly distilled water for 30 min to obtain a $100 \mu\text{g mL}^{-1}$ solution. 0.2 g

CTMAB was dispersed in 100mL of doubly distilled water to obtain 2.0 g L^{-1} solution. A boric buffer solution (pH 8.4-10.1) was used for pH adjustment.

2.3 Procedures

All experiments were carried out at room temperature. To the 25mL flask were added 1 mL of Pb^{2+} solution, 0.6mL of PF ethanol solution, 0.6mL of carboxylic CNTs solution, 2.0mL of CTMAB solution and 11mL of boric buffer solution (pH=10.0) in turn. The flasks were filled to the top up mark with doubly distilled water. Absorption spectra were recorded from 500-650nm on T6 spectrophotometer with 1.0-cm silica quartz matched cell (Beijing Purkinje General Instrument Co., Ltd) after 20min. The major parameters which could influence the performance of the method were varied to arrive at the wavelength of maximum absorbance against a reagent blank as a reference.

The absorbance change with the volume of Pb^{2+} solution was measured to obtain the nature of the chromogenic system under the optimum conditions.

3. RESULTS AND DISCUSSION

3.1 Absorption spectra

The absorption spectra of different chromogenic systems are shown in Fig.1. It is seen from the images that the maximum absorbance of the spectrum undergoes a redshift (from 577.2 nm to 600.4 nm), and increases with the application of carboxylic CNTs and CTMAB.

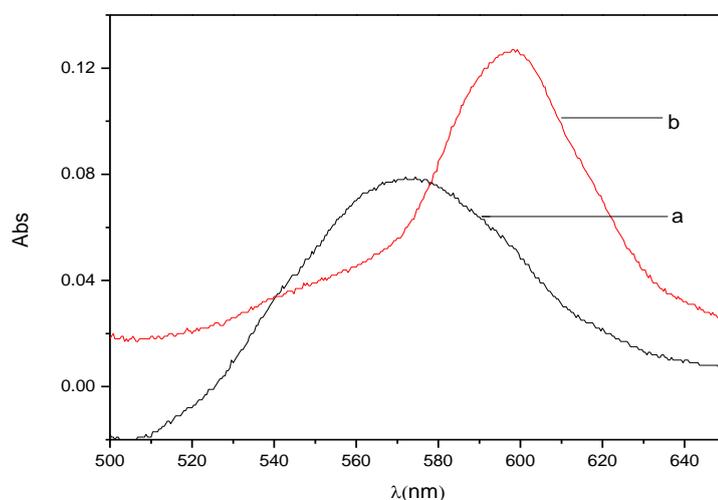


Figure 1. Absorption spectra of different chromogenic system a. Pb^{2+} -PF complex measured against blank PF b. Pb^{2+} -PF-carboxylic CNTs-CTMAB complex measured against blank PF-carboxylic CNTs-CTMAB

As we known, the Pb^{2+} can be binded on the chromophore (-OH) of PF molecule to form a complex [18]. However, the complex is unstable due to the hydrolysis reaction of Pb^{2+} , which is a principle reason for low-sensitivity of the coloration system. With the addition of carboxylic CNTs, 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.2), which can reduce the adverse effects caused by the hydrolysis reaction of Pb^{2+} . As CTMAB was added subsequently, it can improve the homogeneity and dispersity of the coloration system, which can further reduce the hydrolysis reaction of Pb^{2+} . Then the absorbance of the system increased.

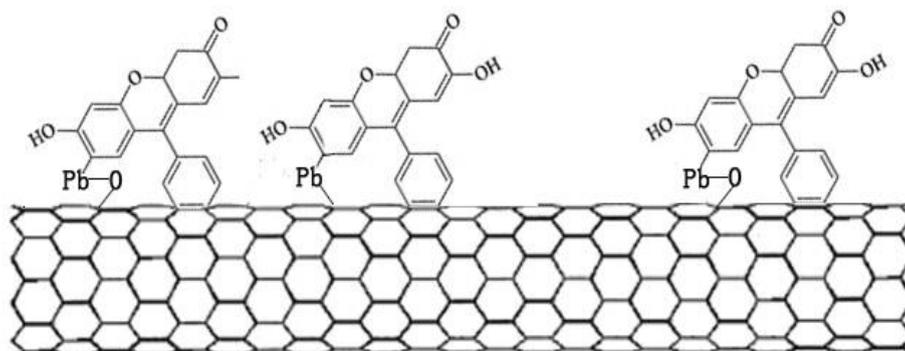


Figure 2. The Pb^{2+} -PF complex absorbing onto the sidewall of carboxylic CNTs

3.2 Effect of pH of buffer solution

The pH plays a unique role on metal-chelate formation [19, 20], which was adjusted with the buffer solution. Keeping all 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 8.4-10.1 at 600.4nm. As it is clearly seen from Fig.3, the pH of the coloration system in the range of 9.6-10.0 was sufficient. Therefore for further studies all samples were buffered to pH 9.8.

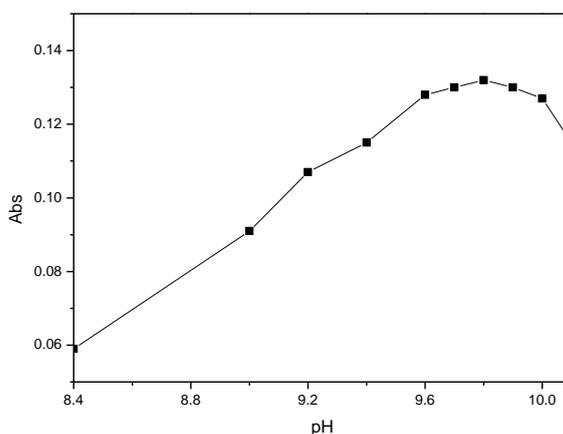


Figure 3. Effect of pH of buffer solution on the absorbance

3.3 Effect of volume of reagents solution

3.3.1 Carboxylic CNTs

The effect of the carboxylic CNTs solution volume on the absorbance was studied as other experimental variables remained unchanged.

The results are shown in Fig.4. It shows that the absorbance increases up to 0.5mL carboxylic CNTs solution, reaching a plateau, and that the signals decrease with increase of the carboxylic CNTs volume above 0.8mL.

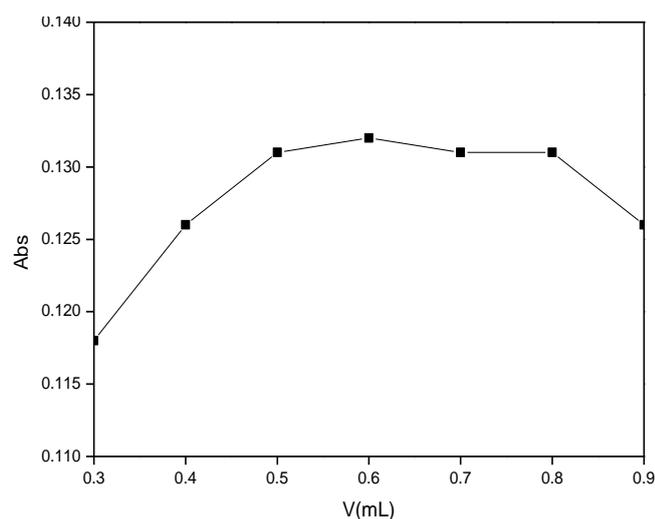


Figure 4. Effect of the volume of carboxylic CNTs on the absorbance

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 0.5mL. 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. Carboxylic CNTs volume of 0.6mL was therefore chosen in order to obtain a good absorbance.

3.3.2 PF

The effect of volume of PF solution (0.3-1.5mL) was studied to obtain information of the absorbance as other experimental parameters were kept constant. According to experiment, the volume of PF solution in the range of 0.5-1.1mL was sufficient. Hence, 0.6mL of PF solution was used in the later experiments.

3.3.3 CTMAB

CTMAB reagents were used in our research to improve the homogeneity and dispersity of the coloration system, and the effect of volume of CTMAB solution (1.5-4.0mL) was studied to obtain information of the absorbance. The absorbance increases up to CTMAB volume of 1.9mL, reaching a plateau. Thus, CTMAB volume of 2.0mL was chosen in order to obtain the optimum absorbance.

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 \rightarrow CTMAB shows the maximum absorbance. As the reagents were added by the order of $Pb^{2+} \rightarrow$ carboxylic CNTs \rightarrow PF \rightarrow CTMAB, Pb^{2+} was absorbed onto the surface of the carboxylic CNTs, which can affect the formation of the Pb^{2+} -PF complex, then the absorbance of the coloration system decreased. The Pb^{2+} -PF complex can form the micelle in the presence of CTMAB as the reagents were added by the order of $Pb^{2+} \rightarrow$ PF \rightarrow CTMAB \rightarrow carboxylic CNTs, which offered no hyperchromic effect with the addition of carboxylic CNTs. If the pre-blended solution of carboxylic CNTs and CTMAB was added into the $Pb^{2+} \rightarrow$ PF solution, the dispersity of carboxylic CNTs can be improved by the existence of CTMAB, but carboxylic CNTs can be encased in the CTMAB, which can reduce their absorption to the Pb^{2+} -PF complex. Thus, the optimum addition order of reagents is $Pb^{2+} \rightarrow$ PF \rightarrow carboxylic CNTs \rightarrow CTMAB.

Table 1. Absorbance of coloration system with different addition order

NO.	addition order of reagents	Absorbance
1	$Pb^{2+} \rightarrow$ PF \rightarrow carboxylic CNTs \rightarrow CTMAB	0.132
2	$Pb^{2+} \rightarrow$ carboxylic CNTs \rightarrow PF \rightarrow CTMAB	0.121
3	$Pb^{2+} \rightarrow$ PF \rightarrow CTMAB \rightarrow carboxylic CNTs	0.103
4	$Pb^{2+} \rightarrow$ PF \rightarrow (carboxylic CNTs + CTMAB)	0.111

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

The composition of the examined complex was established by Job's method. It was found that stoichiometry of this chelate Pb^{2+} : PF is 1:2 at the optimum conditions. The colored solution was attained within 10min, and the intensity remained constant for at least 6h.

Keeping all other experimental parameter constant, the effect of concentration of Pb^{2+} was studied to obtain the calibration curve (shown in Fig.5), which can be represented by a linear regression equation:

$$A = -0.00113 + 0.01351C \quad (r^2 = 0.9994)$$

Here, A is the absorbance and C is the Pb^{2+} concentration in μg per 25.0 mL. The calibration curve was linear over the range 0.5–11.0 $\mu\text{g}/25.0\text{mL}$ of Pb^{2+} , which obey the Beer's law. The molar absorptivity of the complex, calculated in terms of Pb^{2+} , is $0.70 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 600.4nm.

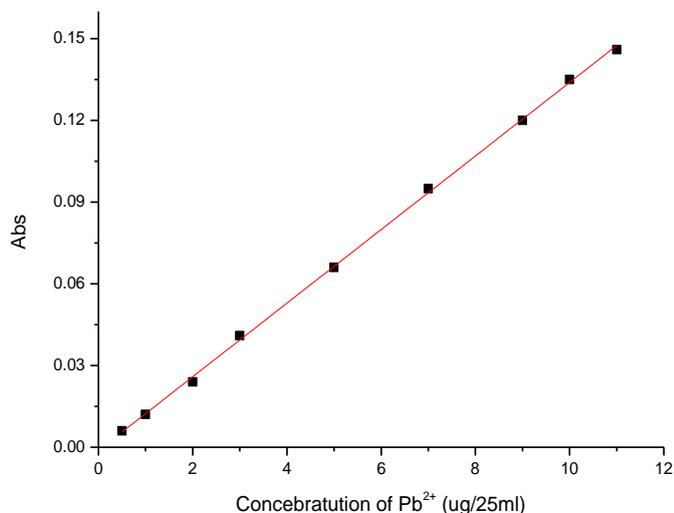


Figure 5. The calibration curve for Pb^{2+}

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, defined as the analyte concentration which resulted in a response equivalent to three times the standard deviation (SD) of the blank ($n=10$) divided by the angular coefficient (b) of the calibration curve ($\text{LOD}=3\text{SD}/b$). The calculated LOD was 17.8ng/ml of Pb^{2+} .

4. CONCLUSION

Application of carboxylic CNTs and CTMAB, which can reduce the adverse effects caused by the hydrolysis reaction of Pb^{2+} , creates better conditions for determination. An advantage of this method is a direct and simple spectrophotometric measurement of absorbance of the analysed solution. Beer's law is obeyed for Pb^{2+} concentrations in the range of 0.5-11 $\mu\text{g}/25.0\text{mL}$. The elaborated method is precise and has good sensitivity, which proves that it can be used for the direct determination of Pb^{2+} .

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