

Spectrometric Determination of Copper With Carbon Nanotubes

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In this work, a novel and sensitive spectrometric method for determination of copper was developed with carbon nanotubes (CNTs) as a toner. The optimum operating conditions regarding kind of CNTs, concentration of reagents and pH were established. The enhancing mechanism of CNTs was also investigated. Comparative experiments prove that the application of carboxyl CNTs has the optimum hyperchromic effect: the absorbance of the complex was increased by nearly 100% through optimizing the technological parameters. The coloration system showed maximum absorbance at 578nm with a molar absorptivity value of $2.75 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$; the calibration graph was linear over the range 0.1–11.0 $\mu\text{g}/25.0\text{ml}$ and the limit of detection was 158ng/25ml. The enhancing mechanism of CNTs is that the copper-PF complex can be closely absorbed onto the sidewall of CNTs to form a novel and structural stable complex, which can reduce the adverse effects caused by the hydrolysis reaction of copper, and improve the sensitivity of the coloration system.

Keywords: Copper; Carbon nanotubes; Spectrometric determination; Enhancing mechanism

1. INTRODUCTION

Copper is an essential element for human beings, which can activate many enzymes and play an important role in the human body [1, 2]. But the excessive ingestion of copper can be toxic and lead to vomiting, diarrhea, liver or kidney damage and death from bleeding [3, 4]. Therefore, a sensitive and accurate determination of copper is very important and required with great consideration.

Different methods have been used for the determination of copper, such as spectrophotometry [5], electrothermal atomic absorption spectrometry (ET-AAS) [6, 7], flame atomic absorption spectrometry (FAAS) [8, 9], inductively coupled plasma-mass spectrometry (ICP-MS) [10, 11],

inductively coupled plasma optical emission spectrometry (ICP-OES) [12-14], microwave-induced plasma (MIP) [15]. Compared with other methods, spectrophotometry is often preferred since it is cheap and simple to implement in laboratories, which is based on the reaction between copper with chromogenic reagents. However, it is not sufficient when the copper concentration levels are very low in water samples or biological samples. To solve this problem, various preconcentration procedures including liquid-liquid extraction (LLE) [5, 16-18], solid phase extraction (SPE) [19, 20] and cloud point extraction (CPE) [21, 22], are often involved to improve the sensitivity of spectrophotometry prior to determination. However these methods suffer from time-consumption, high labor intensity and toxic organic solvents needed, which brings great threat to the environment [23, 24]. Hence, the development of more direct and sensitive spectrophotometry for determination of copper is still sought.

Carbon nanotubes (CNTs) have attracted much attention in the analytical field due to their unique structure and surface characteristics [25]. For example, Carbon nanotubes (CNTs) were used for determination of the heavy metals in the preconcentration-separation procedures [26, 27]. However, to the best of our knowledge, there has been no report on the application of CNTs as a toner for the determination of copper by spectrophotometry. Besides, it is known that the CNTs are not compatible with solvents due to the poor dispersion capability and weak interfacial interactions [28]. Therefore, Ultraviolet photolysis combined with hydrogen peroxide (H_2O_2 -ultraviolet) treatment was used to improve the compatibility and dispersion capability of CNTs in our research.

The aim of this work was to establish a novel, sensitive and direct method for determination of copper with the application of CNTs. The characteristics and performance parameters of the method were optimized, including kind of CNTs, concentration of reagents and pH. Otherwise, the enhancing mechanism of CNTs was also investigated.

2. EXPERIMENTAL

2.1. Apparatus

A T6 UV-vis spectrophotometer with 1.0-cm silica quartz matched cell (Beijing Purkinje General Instrument Co., Ltd) was used in all the spectral and absorbance measurements. The Vertex 80v vacuum FT-IR spectrometer (Bruker Optics) was used to measure infrared spectra of CNTs. The KQ3200E ultrasonic instrument (Jiangsu Kunshan Ultrasonic Instrument Co., Ltd) was used to disperse the CNTs solutions.

2.2. Reagents and chemicals

CNTs with an average external diameter of 40-60nm were kindly provided by Shenzhen Nanoport Company; Phenylfluorone (PF) was obtained from Shanghai Yuanye Bio-technology Co., Ltd. Cetyltrimethyl ammoniumbromide (CTMAB) was kindly provided by Hunan Xiangzhong geological institute. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), Hydrogen Peroxide (H_2O_2),

Potassium dihydrogen phosphate (KH_2PO_4) and Potassium acid phosphate (K_2HPO_4) were obtained from Shantou Xilong chemical Co., Ltd.

2.3. Surface treatment of CNTs

0.1g of CNTs and 100 ml H_2O_2 were added in a vessel under the UV lamp (20W, 254nm), and kept for 30min or 60min at room temperature, Then the CNTs were respectively collected on a 200-nm-pore membrane and washed with distilled water until pH value of the filtrate was about 6-7. Finally the black solid powders were respectively dried in a vacuum chamber at 110 °C for 12 h.

2.4. Solutions

A 1.0 mg ml^{-1} standard solution of copper (II) was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 different CNTs were dispersed in 100mL of doubly distilled water for 30 min to give 100 $\mu\text{g ml}^{-1}$ solutions. 0.2g CTMAB was dispersed in 100ml of doubly distilled water to obtain 2.0 g l^{-1} solution. A phosphat buffer solution (pH 5.8-7.0) was used for pH adjustment.

2.5. Procedures

All experiments were carried out at room temperature. To the 25ml flask were added 1.0ml of copper (II) solution, 2.0ml of PF ethanol solution, 0.5ml of different CNTs solution, 2.0ml of CTMAB solution and 3.0ml of phosphat buffer solution (pH=6) in turn. The flasks were filled to the top up mark with doubly distilled water. Absorption spectra were recorded from 500 to 650nm on T6 spectrophotometer 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 copper (II) solution was measured to obtain the nature of the chromogenic system under the optimum conditions.

3. RESULTS AND DISCUSSION

3.1 Effect of different treatments on the surface of CNTs

CNTs are practically insoluble and difficult to disperse in the solvents, which has been a large barrier for their significant applications. Surface treatment of CNTs is the key breaking the barrier. Hence, the H_2O_2 -ultraviolet treatment was used in our research. It is well known that the H_2O_2 -ultraviolet treatment is a relatively simple and effective process for modifying CNTs due to the

oxidizability and electrophilic addition properties of hydroxyl radical ($\text{HO}\cdot$) generated in the reactions (as shown in the follow equation)[29, 30].



The FTIR spectra of different CNTs are shown in Fig.1. There are no significant functional groups detected on the pristine CNTs (Fig.1a). Fig.1 (b) presents the FTIR spectra of CNTs modified by the H_2O_2 -ultraviolet treatment for 30min. The peaks at 1100cm^{-1} start appearing, which can be assigned symmetrical vibration of $-\text{CH}_3$. Meanwhile, it exhibits a little peak at 3400cm^{-1} , which is attributed to the formation of $-\text{OH}$ stretching. It is further corroborated by appearance of peak at 1100cm^{-1} that corresponding to the C-O stretching mode. This additional evidence proves that the hydroxyl groups were attached to the surface of the CNTs. Fig.1 (c) presents the FTIR spectra of CNTs modified by the H_2O_2 -ultraviolet treatment for 60min. It shows the presence of further more hydroxyl groups and a few of carboxyl groups on the surface of CNTs due to a typically broad peak at $3200\text{--}3600(-\text{OH})\text{cm}^{-1}$ and $1080\text{--}1115(\text{C-O})\text{cm}^{-1}$, a little peak at $1712(-\text{C=O})\text{cm}^{-1}$. It was concluded that the hydroxylic and carboxylic CNTs can be obtained by the H_2O_2 -ultraviolet treatment for 30min and 60min, respectively.

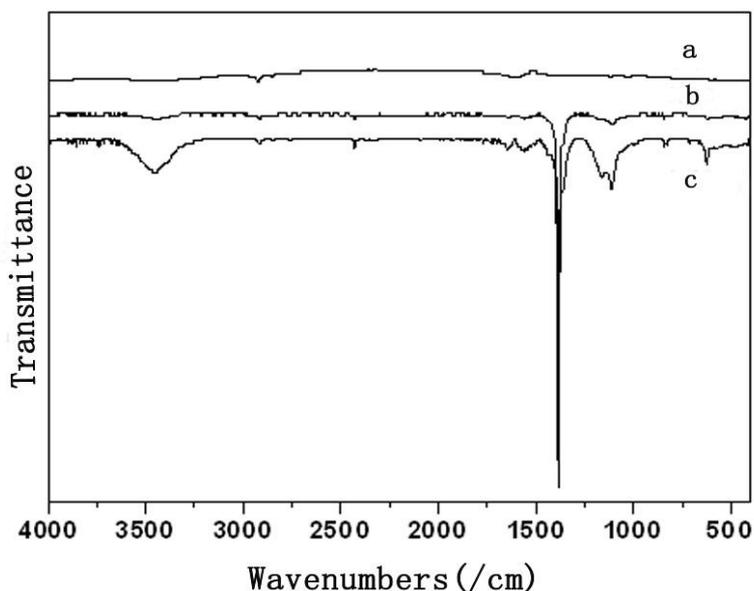


Figure 1. FTIR spectra of different CNTs a) pristine b) modified for 30min c) modified for 60min

3.2. Absorption spectra

The absorption spectra of different chromogenic system are shown in Fig.2. It is seen from the images that the absorbance increased in the presence of the CTMAB or CNTs-CTMAB, and the increase of absorbency is relatively limited with the only addition of CTMAB.

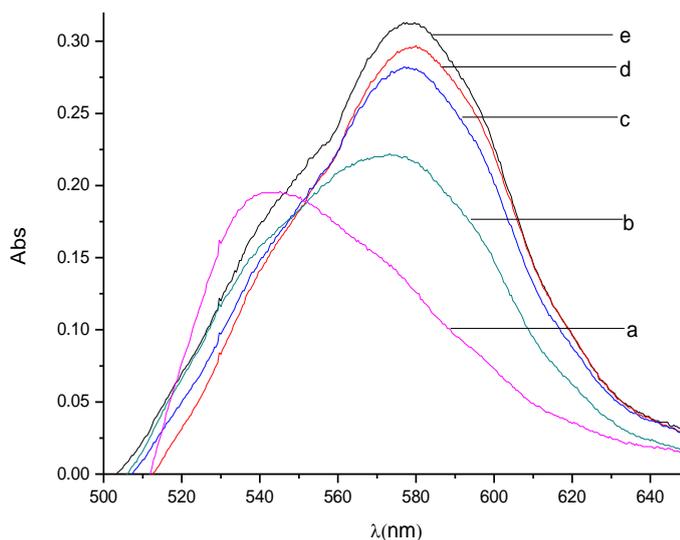


Figure 2. Absorption spectra of different chromogenic systema. Cu-PF complex measured against blank PF b. Cu-PF-CTMAB complex measured against blank PF-CTMAB c. Cu-PF-pristine CNTs-CTMAB complex measured against blank PF--pristine CNTs-CTMAB d. Cu-PF-hydroxylic CNTs-CTMAB complex measured against blank PF-hydroxylic CNTs-CTMAB e. Cu-PF-carboxylic CNTs-CTMAB complex measured against blank PF-carboxylic CNTs-CTMAB

3.3 Effect of addition of CNTs and enhancing mechanism of CNTs

Fig.2 also shows strong evidence that the absorbency of the chromogenic system can be further improved with the addition of CNTs. As is well known, the bonding in nanotubes is essentially sp^2 hybridized and the π orbital is more delocalized outside the tube. The aromatic molecules with the conjugate structure can interact strongly with the sidewalls of CNTs via π -stacking [31, 32]. The PF molecules happen to have the conjugate structure (shown in Fig.3), which could be absorbed onto the sidewall of CNTs (shown in Fig.4). Meanwhile, CNTs exhibit excellent adsorption capacities to copper (II) due to their unique structure [33]. As a result, copper (II) and PF molecules could be absorbed onto the sidewall of CNTs.

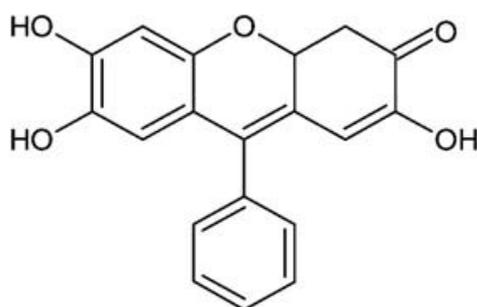


Figure 3. The structure of PF

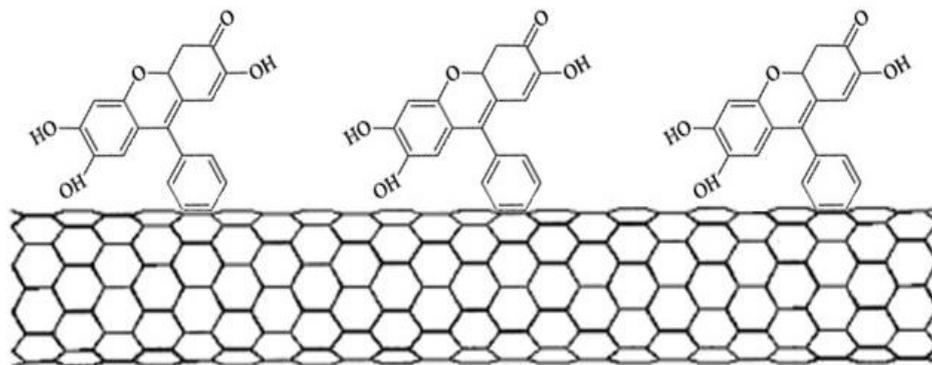


Figure 4. PF molecules absorbing onto the sidewall of CNTs via π -stacking

The copper (II) can react with PF to form a complex as they were added into the colorimetric cylinder. However, the complex is unstable due to the hydrolysis reaction of copper (II), which is a principle reason for low-sensitivity of the coloration system. With the addition of CNTs, the copper-PF complex can be closely absorbed onto the sidewall of CNTs to form a novel and structural stable complex (shown in Fig.5), which can reduce the adverse effects caused by the hydrolysis reaction of copper (II), and raise the absorbance of the coloration system. Then the sensitivity of the system was improved.

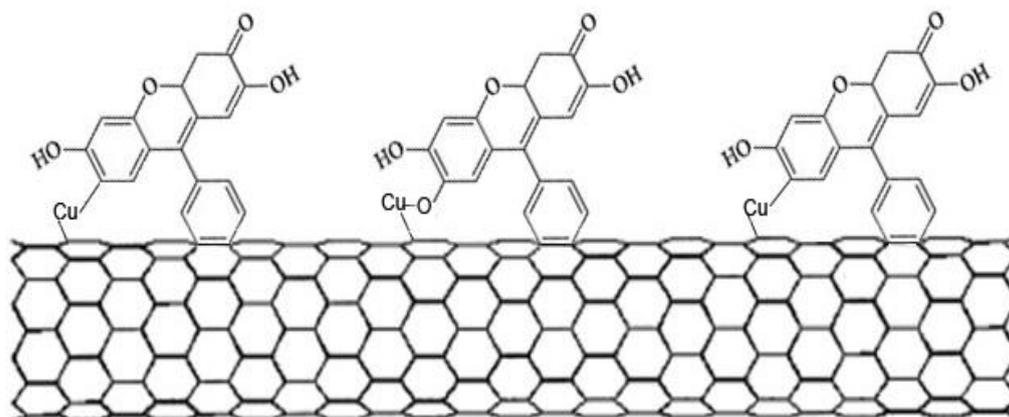


Figure 5. The copper-PF complex absorbing onto the sidewall of CNTs

3.4 Effect of different kinds of CNTs

The addition of different kinds of CNTs can lead to different hyperchromic effects (shown in Fig.2), and the absorption spectra of copper-PF-carboxylic CNTs-CTMAB complex shows the maximum absorbance at 578nm.

After the CNTs were modified, a great amount of carbon-containing defects along the sidewall of CNTs were detected, which can be easily introduced functional groups to the sidewall of CNTs

(shown in Fig.1). The introduction of functional groups as hydrophilic radical can improve the solubility of CNTs. On the other hand, it can provide numerous chemical adsorption sites for the copper-PF complex. Thus, compared with the pristine CNTs, the addition of the modified CNTs shows the better absorbance in the coloration system. It is also seen from Fig.1 that the carboxylic CNTs exhibit more functional groups on the sidewall in relation to the hydroxylic CNTs. Especially, the absorption capacity of carboxyl groups is better than that of hydroxyl groups [34]. So, the coloration system with the carboxylic CNTs has the best absorbance.

3.5 Effect of dosage of carboxylic CNTs solution

The effect of the volume of carboxylic CNTs solution on the absorbance was studied as other experimental variables remained unchanged. The results are shown in Fig.6. It shows that the absorbance increases up to 0.4ml carboxylic CNTs solution, reaching a plateau, and that the signals decrease with increase of the carboxylic CNTs volume above 0.6ml.

The amount of carboxylic CNTs is so little that some copper-PF complex can not be absorbed onto the sidewall of tubes as the volume of solution is below 0.4ml. Therefore, the absorbance increases with the volume of solution. The amount of carboxylic CNTs is excessive when the volume of solution is above 0.6ml. They tend to agglomerate, which lead to reduce the absorption capacity to the complex and decrease the absorbance of the coloration system. Carboxylic CNTs volume of 0.5ml was therefore chosen in order to obtain a good absorbance.

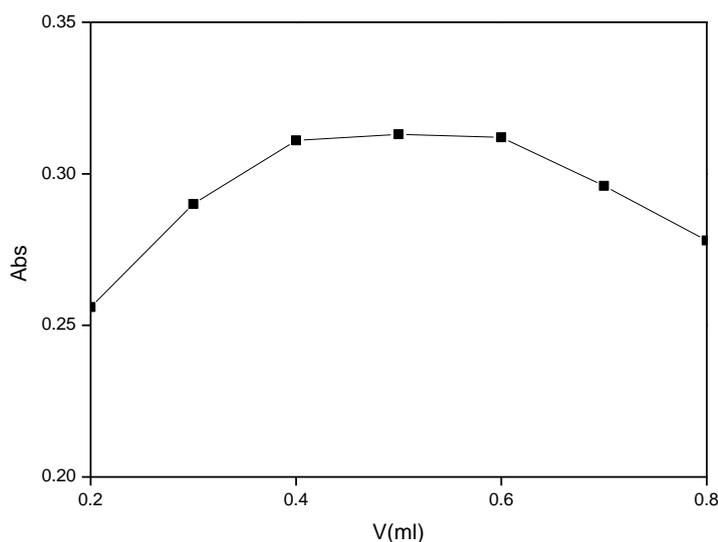


Figure 6. Effect of the volume of carboxylic CNTs on the absorbance

3.6 Effect of volume of PF solution

Keeping all other experimental parameter constant, the effect of volume of PF solution (1.0-2.5ml) was studied to obtain information of the absorbance. According to experiment, the volume of

PF solution in the range of 1.3-2.0ml was sufficient. Hence, 1.5ml of PF solution was used in the later experiments.

3.7 Effect of pH of buffer solution

The pH of the solution plays a unique role on metal-chelate formation [35, 36], which was adjusted with the buffer solution. The pH of buffer solution was varied in the range of 5.8-7.0, in order to find the optimal pH for the determination of copper (II). According to experiment, the pH in the range of 6.2-6.7 was sufficient. Therefore for further studies all samples were buffered to pH 6.5.

3.8 Effect of volume of CTMAB solution

Surface active agents were often used in the determination of metal ions, due to that it can improve the homogeneity and dispersity of the coloration system. CTMAB reagents were used in our research, and the effect of volume of CTMAB solution (1.0-8.0ml) was studied to obtain information of the absorbance (as shown in Fig.7). The absorbance increases up to CTMAB volume of 5.0 ml, reaching a plateau. CTMAB volume of 5.0ml was chosen in order to a good absorbance.

The absorbance of the complex was 0.422 through optimizing the technological parameters, which was increased by nearly 100% in the presence of carboxylic CNTs.

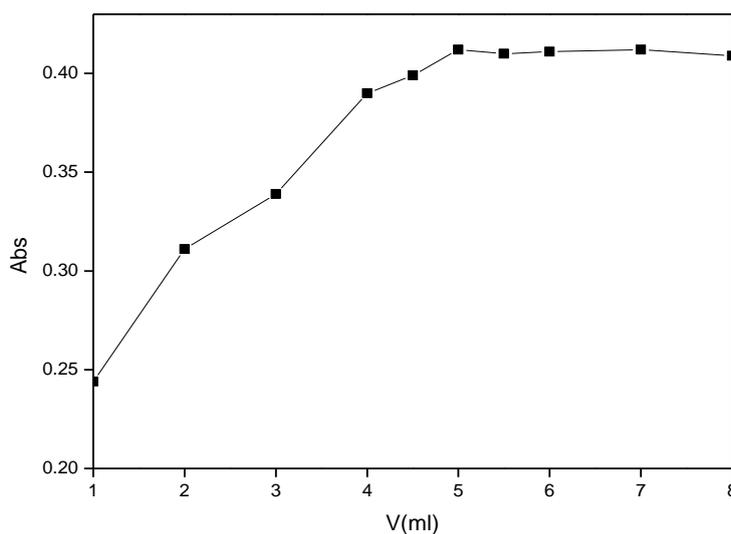


Figure 7. Effect of the volume of CTMAB on the absorbance

3.9 Nature of the complex and the linearity of copper (II)

The stoichiometric composition of the complex was ascertained by application of the Job's method of continuous variation and the molar-ratio method. According to the data, the complex was

formed by copper (II) and PF in the molar ratio 1:2. The colored solution was attained within 15min, and the intensity remained constant for at least 24h.

The calibration curve for the determination of the concentration of copper (II) was obtained under the optimum conditions (shown in Fig.8), which can be represented by a linear regression equation:

$$A = -0.0007 + 0.0426C \quad (r^2 = 0.9999)$$

Here, A is the absorbance and C is the copper (II) concentration in μg per 25.0ml. The calibration curve was linear over the range 0.1–11.0 $\mu\text{g}/25.0\text{ml}$ of copper (II), which obey the Beer's law. The molar absorptivity of the complex, calculated in terms of copper (II), was $2.75 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 578nm.

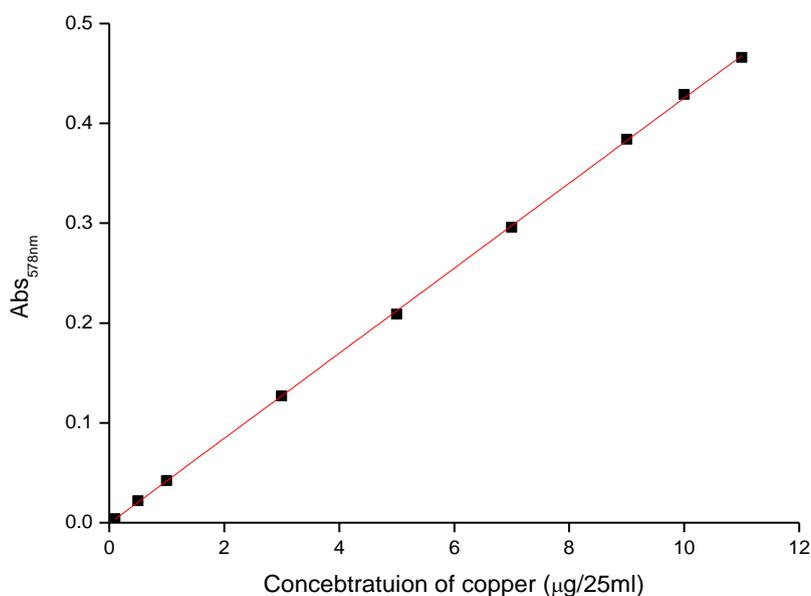


Figure 8. The calibration curve for copper

The limit of detection (LOD) shows an indication of the lowest concentration of copper (II) 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 158 ng/25.0ml of copper (II).

4. CONCLUSION

Using CNTs as a toner, a simple and sensitive spectrophotometric method for the determination of copper (II) has been developed. The copper-PF complex can be absorbed onto the sidewall of CNTs in

the presence of CTMAB, which can reduce the adverse effects caused by the hydrolysis reaction of copper (II), and improve the sensitivity of the coloration system. Beer's law is obeyed for copper (II) concentrations in the range of 0.1-11 μ g/25.0ml. The elaborated method is precise and has good sensitivity, which proves that it can be used for the direct determination of copper (II).

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