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Determination of Copper by Spectrophotometry with Carbon Nanotubes

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Using carbon nanotubes(CNTs) as a toner, a novel, rapid and inexpensive spectrometric determination method for copper was developed in this work. Several factors affecting the absorbance of the coloration system, such as pH, kind of CNTs, concentration and addition order of reagents were investigated and optimized. The nature of the coloration system was also investigated. Comparative experiments prove that the absorption was increased by 74.1% due to the additing of CNTs into the coloration system. The calibration graph was linear in the range of 10-1100ng mL^{-1} and the limit of quantification (10s) was 5.8ng mL.

Keywords: Carbon nanotubes; Spectrophotometry; Copper

1. INTRODUCTION

Copper plays a different role in the human body. It is an essential nutrient or a toxic element for human beings, depending on the concentration level[1, 2]. Therefore, a sensitive and accurate determination of copper is of great importance and required with great consideration.

Carbon nanotubes (CNTs) have attracted much attention in the analytical field due to their unique structure and surface characteristics [3]. CNTs were used as assisted matrix for laser depsorption/ionization time-of-flight mass spectrometry, which can eliminated the interference of intrinsic matrix, transfer energy to the analyte, then improve the sensitivity and reproducibility of the spectrum signals[4]. Marian report CNTs can improve the spectral tenability and scalability of infrared detector[5]. Furthermore, Carbon nanotubes (CNTs) have been used as an absorbent for preconcentration and separation of heavy metals prior to determination[6]. However, it suffers from time-consumption, high labor intensity and so on.

By contrast, CNTs were used as a toner for direct determination of copper to increase the absorbance of the coloration system in this work. The analytical parameters including pH, volume and addition order of reagents on the absorbance of coloration system were investigated and optimized. Otherwise, the hyperchromic mechanism of CNTs was also investigated.

2. EXPERIMENTAL

2.1. Apparatus

A T6 UV–vis spectrophotometer with a quartz of 1.0-cm path length (Beijing Purkinje General Instrument Co., Ltd) was used for the absorption spectra and the absorbance measurements. A JEM Transmission electron microscopy was used to analyze the morphology of the CNTs. 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. Surface treatment of CNTs

In this work, the H_2O_2-ultraviolet treatment was used to improve the water solubility and adsorptive capacity of CNTs. 0.1g CNTs and 100 mL H_2O_2 were added in a vessel, and kept for 30min or 60min under the UV lamp (20W, 254nm) 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, and dried in a vacuum chamber at 110 ℃ for 12 h.

2.3. Solutions

Stock solution for copper ions was prepared from appropriate amounts of the $CuSO_4 \cdot 5H_2O$ 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 different CNTs were dispersed in 100mL of doubly distilled water for 30 min to give 100 μg ml^{-1} solutions. A buffer solution of pH around 6 was prepared by using potassium dihydrogen phosphate and potassium acid phosphate at appropriate concentrations.

2.4. Procedures

To the 25 mL flask were introduced 1 mL of copper solution, 2 mL of PF ethanol solution, 0.5 mL of different CNTs solution and 3 mL of phosphat buffer solution (pH=6) in turn. The flasks were filled with doubly distilled water to the same volume. After 20 min, absorption spectra were recorded from 500 to 650 nm in 1-cm cuvettes against the blank. The major parameters which could influence the performance of the method were varied to arrive at the wavelength of maximum absorbance.

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 can be improved with the addition of different CNTs.

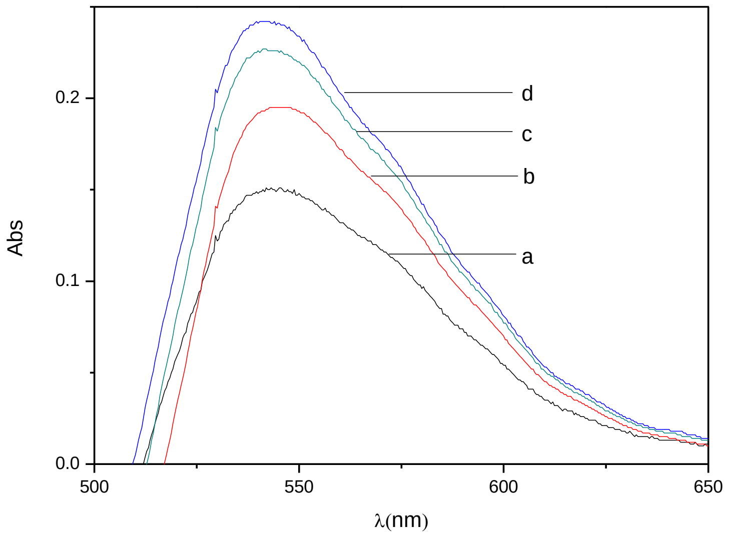

Figure 1. Absorption spectra of different chromogenic systems; a. Cu-PF complex b. Cu-PF-pristine CNTs complex; c. Cu-PF-hydroxylic CNTs complex d. Cu-PF-carboxylic CNTs complex

3.2. Hyperchromic Mechanism of Carboxylic CNTs

CNTs have been used as absorbent materal due to their unique structure and large specific surface area. Much previous work suggested that carbon nanotubes show high efficiency for copper. Meanwhile, the bonding of CNTs is essentially sp^2 hybridized and the π orbital is more delocalized outside the tube. The PF with the conjugate structure can interact strongly with the sidewalls of CNTs via π-stacking [7, 8]. As a result, copper and PF molecules could be absorbed onto the sidewall of CNTs.

The copper can react with PF molecules to form a complex as they were added into the colorimetric cylinder. the copper-PF complex formed can be closely absorbed onto the sidewall of CNTs to form a novel and structural stable complex as the addition of CNTs (shown in Fig.2), which can reduce the adverse effects caused by the hydrolysis reaction of copper, and raise the absorbance of the coloration system. Then the sensitivity of the system was improved.

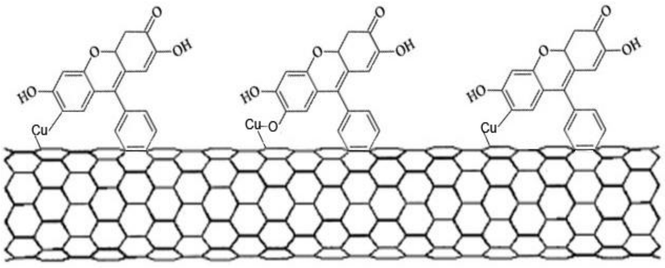

Figure 2. The copper-PF complex absorbing onto the sidewall of CNTs

3.3. Effect of different kinds of CNTs

CNTs are practically insoluble and difficult to disperse in the solvents[9]. The H_2O_2-ultraviolet treatment was used to improve the water solubility and adsorptivity of CNTs in our research.The variation of absorbance with the addition of different CNTs was also shown in Fig.1. It exhibited the addition of different CNTs can lead to different hyperchromic effects, and the absorption spectra of copper-PF-carboxylic CNTs complex showed the maximum absorbance at 543 nm.

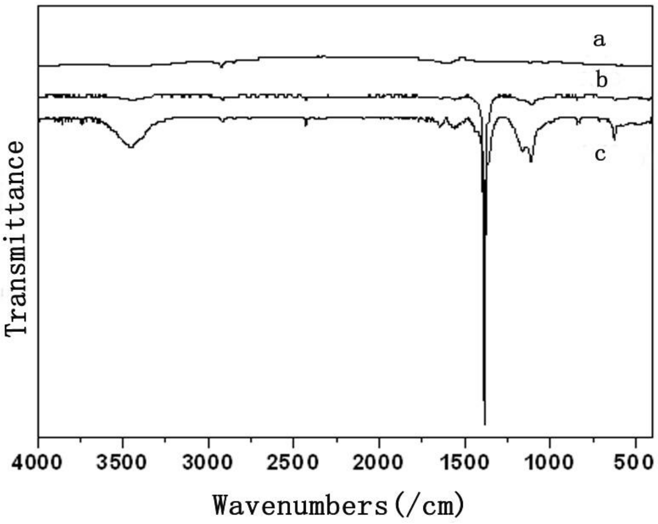

Figure 3. FTIR spectra of different CNTs a) pristine; b) modified for 30min c) modified for 60min

The FTIR spectra of different CNTs are shown in Fig.3. There are no significant functional groups detected on the pristine CNTs (Fig.1a). Fig.1b presents the FTIR spectra of CNTs modified for 30 min. The peak at 1374 cm^{-1} can be assigned symmetrical vibration of-CH_3. Meanwhile, the peak at 1100 cm^{-1} and 3400 cm^{-1} is associated with the C-O and –OH stretching mode respectively, which is corroborated that the hydroxyl groups are attached to the surface of the CNTs. Fig.1c presents the

FTIR spectra of CNTs modified by the H_2O_2-ultraviolet treatment for 60min. Compared with Fig.1b, there appear some changes: it can be found a new peak appeared at 1712 cm^{-1} (-C=O stretching mode), a more intense peak appeared at 3200-3600 cm^{-1} and 1080-1115 cm^{-1}. It proves that further more hydroxyl groups and a few of carboxyl groups were attached to the surface of CNTs. It is concluded that the hydroxylic and carboxylic CNTs can be obtained by the H_2O_2-ultraviolet treatment for 30min and 60min, respectively.

The introduction of functional groups as hydrophilic radical can improve the solubility of CNTs, which can be concluded from the TEM images of different CNTs (Fig.4). On the other hand, it can provide numerous chemical adsorption sites for the copper-PF complex. Thus, the addition of the modified CNTs shows the better absorbance than that of pristine CNTs in the coloration system. The carboxylic CNTs exhibit more functional groups on the sidewall in relation to the hydroxylic CNTs. Futhermore, the absorption capacity of carboxyl groups is better than that of hydroxyl groups [10]. So, the coloration system with carboxylic CNTs has the best absorbance.

3.4. Effect of addition order

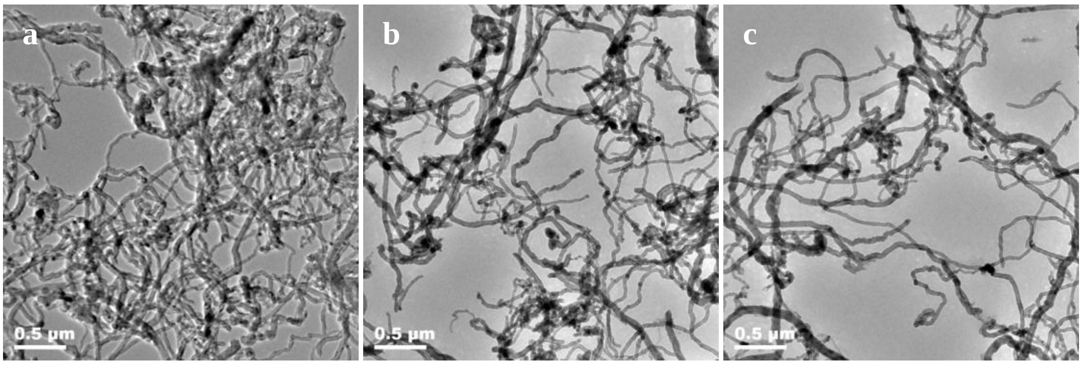

Figure 4. TEM images of pristine CNTs (a), hydroxylic CNTs(b) and carboxylic CNTs (c)

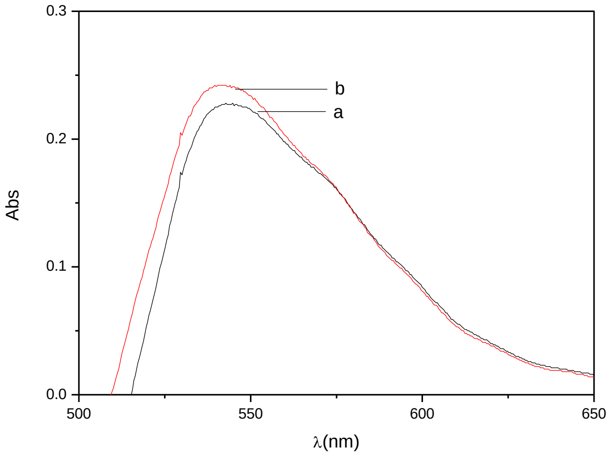

Figure 5. Effect of different addition order on absorption spectrum; a Cu^{2+}–carboxylic CNTs–PF b Cu^{2+}–carboxylic CNTs–PF

On condition that the buffer solution was added finally, it was observed that the addition order of other reactants was also important during research (shown in Fig.5). The color of the system was more intense and stable with the addition order of copper–PF- carboxylic CNTs than the order of copper–carboxylic CNTs–PF. It was expected as the copper–PF complex is formed firstly, and then the complex can be absorbed onto the surface of the carboxylic CNTs. If the carboxylic CNTs had been added to the copper solution before PF, copper was absorbed onto the surface of the carboxylic CNTs, which could affect the formation of the copper-PF complex, and then the absorbency of copper–carboxylic CNTs–PF would not be as strong as that of Cu^{2+}–PF- carboxylic CNTs.

3.4. Effect of pH

The pH plays a unique role on metal-chelate formation [11, 12]. 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 copper was investigated. The mixture solution was measured in the range of 5.6-7.0 at 543 nm. According to the experiment result, the pH of the coloration system in the range of 6.2-6.7 was sufficient. Therefore for further studies all samples were buffered to pH 6.4.

3.5. Effect of volume of carboxylic CNTs solution

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 copper, different concentrations of carboxylic CNTs were obtained by added 0.2-0.8 mL 100 μg ml^{-1} solutions into the colorimetric cylinder. The results are shown in Fig.6. It shows that the absorbance increases up to 0.4 ml carboxylic CNTs solution, reaching a plateau, and that the signals decrease with increase of the carboxylic CNTs volume above 0.6 ml.

3.6. Analytical feature

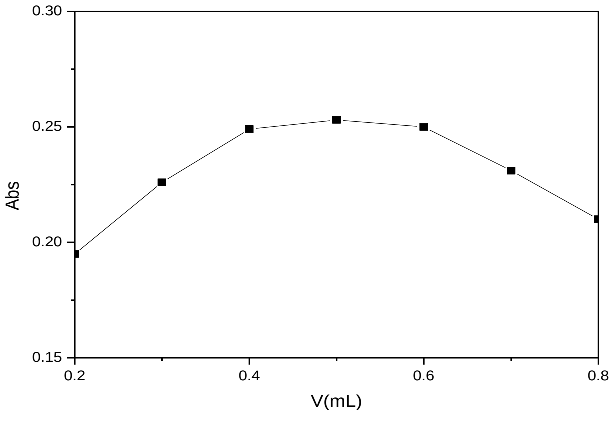

Figure 6. Effect of the volume of carboxylic CNTs on the absorbance

Under the optimized conditions, the analytical feature of the method was evaluated. The calibration graphs were linear over the range 10–1100 ng mL^{-1} of copper. The regression equation for copper determination was $A=0.0324C-0.0016$(where A is the absorbance and C is the copper concentration in ng mL^{-1}) with the correclation coefficient (r^2) of 0.9997.

The limit of detection (LOD) shows an indication of the lowest concentration of copper 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 (LOD=3SD/b). The calculated LOD was 5.8 ng mL^{-1} of copper.

4. CONCLUSION

Application of CNTs, which can reduce the adverse effects caused by the hydrolysis reaction of copper, improve the sensitivity of the coloration system. An advantage of this method is direct spectrophotometric measurement of absorbance of the analysed solution. The elaborated method is precise and has good sensitivity.

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