Int. J. Electrochem. Sci., 7 **(2012)** 12992 - 12998

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Application of Carbon Nanotubes and CTMAB for the Rapid Determination of Zinc by Spectrophotometry

Qiang Yin [1, 2,*] *Yurong Liu* [2] *Linlin Wang* [1] *Zunpeng Ke* [1] *and Yue Yang* [1]

[1] Fundamental Science on Radioactive Geology and Exploration Technology Laboratory, East China Institute of Technology，NanChang, Jiangxi, 330013, China
[2] Chongqing Key Laboratory of Micro / Nano Materials Engineering and Technology, Chongqing 402160, China
[*]E-mail: sknyq@163.com

Received: 18 October 2012 / *Accepted:* 16 November 2012 / *Published:* 1 December 2012

A novel, rapid and sensitive spectrometric method for determination of zinc 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 effectthrough optimizing the technological parameters, the calibration graph was linear over the range 0–11.0μg/25.0mL and the limit of detection was 1.8 ng/mL. Moreover, the method is easy and direct to perform for the determination of zinc.

Keywords: Zinc; carbon nanotubes; cetyltrimethyl ammoniumbromide; spectrometric determination

1. INTRODUCTION

Zinc is a trace element that is essential for the living organisms' metabolism and plays an important role in some biochemical progresses [1, 2]. However, superfluous zinc can be toxic would bring some noxious effects to human body [3, 4]. Thus, a sensitive and accurate method fot determination of zinc is required with great consideration.

Carbon nanotubes (CNTs) have attracted much attention in the analytical field due to their unique structure and surface characteristics [5]. 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 [6]. Marian report CNTs can improve the spectral tenability and scalability of infrared detector[7]. Furthermore, Carbon nanotubes (CNTs) have been used as an absorbent for preconcentration and separation of zinc prior to determination [8-10]. However, it suffers from time-consumption, high labor intensity and toxic organic solvents needed, which brings great threat to the environment.

In our previous research, CNTs were used as a toner for direct determination of copper and lead [11, 12], and carboxylic CNTs in the presence of cetyltrimethyl ammoniumbromide (CTMAB) can further improve the sensitivity of the coloration system [13, 14]. In this work, the carboxylic CNTs and CTMAB were 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. CTMAB was kindly provided by Hunan Xiangzhong geological institute. 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. 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. 0.2g CTMAB was dispersed in 100mL of doubly distilled water to obtain 2.0 g L^{-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

1 mL of Zn^{2+} solution, 1.5 mL of PF ethanol solution, 1mL of carboxylic CNTs solution, 2.0mL of CTMAB solution and 6mL of boric buffer solution (pH=9.6) were introduced to the 25mL flask 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 chromogenic systems are shown in Fig.1. It is seen from the images that the maximum absorbance of the spectrum undergoes a redshift, and increases with the application of carboxylic CNTs and carboxylic CNTs -CTMAB.

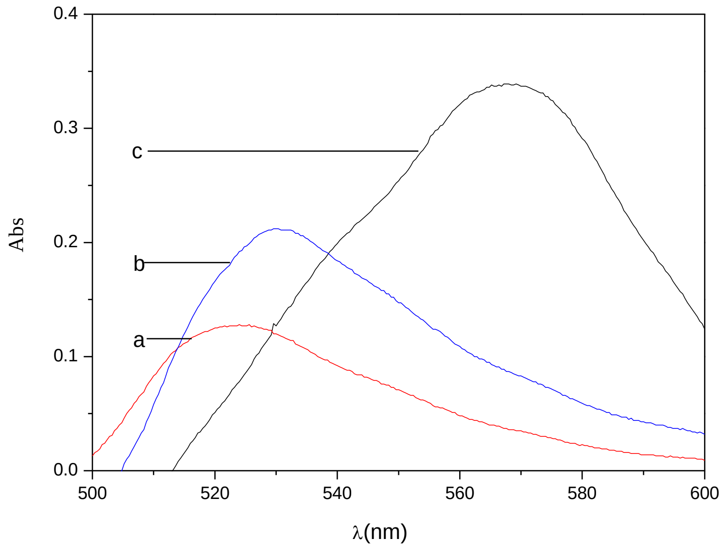

Figure 1. Absorption spectra of different chromogenic system (a. Zn^{2+}-PF complex (b. Zn^{2+}-PF-carboxylic CNTs (c. Zn^{2+}-PF-carboxylic CNTs-CTMAB

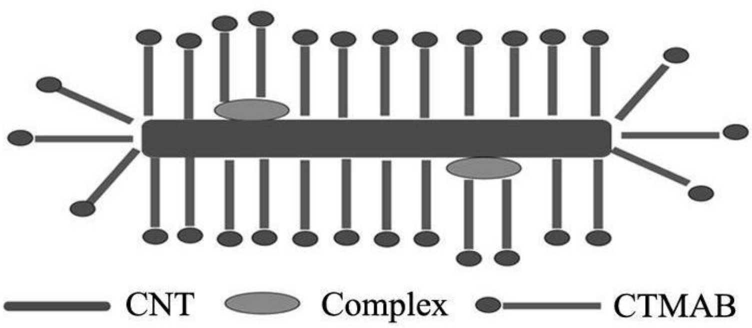

Figure 2. Structure of Zn^{2+}-PF-CNTs-CTMAB complex

Carboxylic CNTs 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 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. As CTMAB was added subsequently, it can improve the homogeneity and dispersity of the coloration system, which can further reduce the hydrolysis reaction of Zn^{2+} (shown in Fig.2). Then the absorbance of the system increased furtherly.

3.2 Effect of pH of buffer solution

The pH plays a important role on the metal-chelate formation and the absorption of CNTs [15, 16]. which was adjusted with the buffer solution. Keeping all other experimental parameter constant, the effect of pH on the determination of Zn^{2+} was investigated spectrophotometrically. The mixture solution was measured in the range of 7.4-10.1 at 569.6nm. As it is clearly seen from Fig.3, the pH of the coloration system in the range of 9.3-9.8 was sufficient. Therefore for further studies all samples were buffered to pH 9.3.

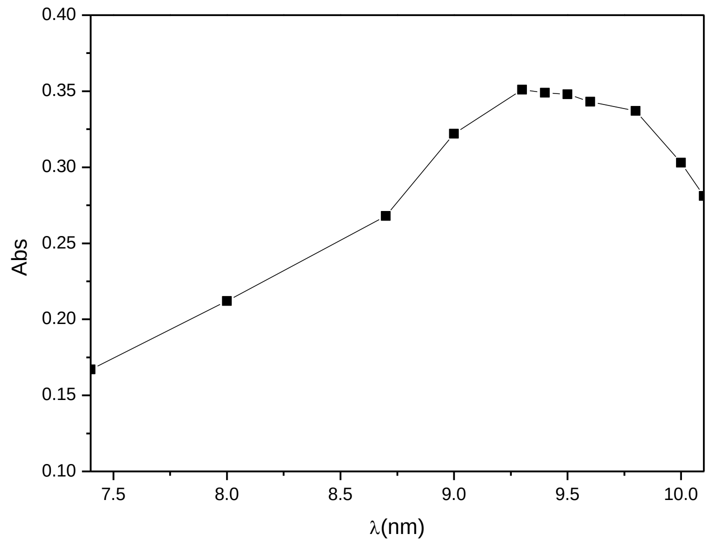

Figure 3. Effect of pH of buffer solution on the absorbance

3.3 Effect of volume of reagents solution

3.3.1. Carboxylic CNTs

The effect of the carboxylic CNTs solution volume (0.1-1.5 mL) on the absorbance was studied as other experimental variables remained unchanged. 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 1.0 mL. The carboxylic CNTs solution volume of 0.5 mL was used in the later experiments.

3.3.2 PF

The effect of volume of PF solution (1.0-3.0mL) 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 1.3-1.8 mL was sufficient. Hence, 1.5 mL of PF solution was used in the later experiments.

3.3.3 CTMAB

CTMAB regents were used in our research to improve the homogeneity and dispersity of the coloration system. Keeping other experimental parameter constant, the effect of volume of PF solution (2.0-10.0 mL) on the determination of Zn^{2+} was investigated spectrophotometrically. According to experiment, the absorbance increases up to CTMAB volume of 6.0mL, reaching a plateau. Thus, CTMAB volume of 6.0mL 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 Zn^{2+}→PF→carboxylic CNTs→CTMAB shows the maximum absorbance. As the reagents were added by the order of Zn^{2+}→carboxylic CNTs→PF→CTMAB, Zn^{2+} was absorbed onto the surface of the carboxylic CNTs, which can affect the formation of the Zn^{2+}-PF complex, then the absorbance of the coloration system decreased.

Table 1. Absorbance of coloration system with different addition order

NO.	addition order of reagents	Absorbance
1	Zn^{2+}→PF→carboxylic CNTs→CTMAB	0.351
2	Zn^{2+}→carboxylic CNTs→PF→CTMAB	0.303
3	Zn^{2+}→PF→CTMAB→carboxylic CNTs	0.215
4	Zn^{2+}→PF→(carboxylic CNTs +CTMAB)	0.267

The Zn^{2+}-PF complex can form the micelle in the presence of CTMAB as the reagents were added by the order of Zn^{2+}→PF→CTMAB→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 Zn^{2+}→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 Zn^{2+}-PF complex. Thus, the optimum addition order of reagents is Zn^{2+}→PF→carboxylic CNTs→CTMAB.

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

Under the optimized conditions, the effect of concentration of Zn^{2+} was studied, and the calibration graphs were linear over the range 0–11.0 μg/25.0mL of Zn^{2+}, which obey the Beer's law.. The regression equation for copper determination was $A=0.3947C+0.0001$ (where A is the absorbance and C is the zinc concentration in μg per 25.0 mL) with the correclation coefficient (r^2) of 0.9991.

The limit of detection (LOD) shows an indication of the lowest concentration of zinc 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 1.8 ng mL^{-1} of zinc.

4. CONCLUSION

Application of carboxylic CNTs and CTMAB, can reduce the adverse effects caused by the hydrolysis reaction of Zn^{2+}, creates better conditions for determination. An advantage of this method is a direct and simple spectrophotometric measurement of absorbance of the analysed solution. The elaborated method is precise and has good sensitivity, which proves that it can be used for the direct determination of Pb^{2+}.

ACKNOWLEDGEMENT
The authors gratefully acknowledge the financial support by the opening project Chongqing Key Laboratory of Micro / Nano Materials Engineering and Technology and the Foundation of East China Institute of Technology.

References

1. S. Tajik, M. A. Taher, *Desalination*, 278 (2011) 57.
2. S. M. Z. AL-Kindy, K. H. AL-Hinai, F. E. O. Suliman, et al., *Arabian J. Chem*. 4 (2011) 147.
3. N.F. Kolachi, T.G. Kazi, S. Khan,et al., *Food Chem. Toxicol.*, 49 (2011) 2548.
4. T. T. Hou, X. S. Zhu, *J. Mol. Liq., 166* (2012) 17.
5. Z. H. Wang, X. K. Chen, F. F. Zhang, L. Tian, Y. Z. Xia, *Mater. Sci. Eng. C*, 29(2009)341.
6. S. Y. Xu, Y. F. Li, H. F. Zou, *J. Am. Soc. Spectro*., 16(2005)263.
7. B. T. Marian, T. F. Kuo, D. A. Straus, A. J. Yin, Jimmy. J. Physic. Chem. C, 111(2007)5800.
8. M. Tuzen, K. O. Saygi, M. Soylak, *J. Hazard. Mater.*, 152 (2008) 632.
9. S. Tajik, M. A. Taher, *Desalination*, 278 (2011) 57.
10. A. Stafiej, K. Pyrzynska, *Microchem. J.*, 89 (2008) 29.

11. Q. Yin, Q. S. Chen, M. C. Sun, et al., *Int. J. Electrochem. Sci.*, accept.
12. Q. Yin, L. L. Wang, M. C. Sun, *Int. J. Electrochem. Sci.*, accept.
13. Q. Yin, R. Chen, Y. R. Liu, *Int. J. Electrochem. Sci.*, 6 (2011) 6620.
14. Q. Yin, Q. S. Chen, Y. R. Liu, et al., *Int. J. Electrochem. Sci.*, 6 (2011) 5005.
15. N. Satıro˘glu, C. Arpa, *Microchim. Acta*, 162 (2008) 107.
16. C. A. Sahin, I. Tokgoz, *Anal. Chim. Acta*, 667 (2010) 83.