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Quantification of Zinc and Lithium in Zinc Oxide Quantum Dots by Atomic Absorption Spectroscopy.

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ABSTRACT

Quantum dots have attracted tremendous interest in biomedical field. Zinc oxide quantum dots are well appreciated for their possible safety features over other quantum dots. Atomic absorption spectroscopy is considered to be a highly efficient quantitative technique for quantitative determination of chemical elements and thus would be very useful for quantification of metal in quantum dots. Therefore the objective of the present study was to carry out determination of zinc and lithium in prepared dispersion of quantum dots using atomic absorption spectroscopy. For this purpose, zinc oxide quantum dots were prepared by precipitation method. Atomic absorption spectroscopy was employed for the determination of zinc and lithium in prepared zinc oxide quantum dots. The standard plots for both zinc and lithium were found to be linear in the selected range of concentrations. Zinc and lithium were found to be present in the prepared dispersion of zinc oxide quantum dots at concentrations of 22.05 and 6.287 mg/L respectively. The developed method could be of great help for developing novel drug and gene delivery systems based on zinc oxide quantum dots.

Keywords: Quantum dots, Zinc oxide, Atomic absorption spectroscopy

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INTRODUCTION

Recently, quantum dots (QDs) have attracted tremendous interest as luminescent probes in biological and medical researches due to their unique optical and chemical properties [1]. At present QDs in drug delivery are focused on two major areas: using QDs as carriers and labeling therapeutics or drug carriers with QDs [2]. Applications of quantum dots include imaging cancer cells, drug discovery [3] surgical guidance and detection of virus [4]. Zinc oxide is considered as GRAS (generally recognized as safe) substance by FDA and could be very useful for delivery of drug and gene. Therefore an accurate quantification technique for zinc in its quantum dots will be of immense use. A general method for the preparation of zinc oxide quantum dots includes the use of lithium hydroxide [5]. Hence there are chances that residual lithium could be present in the final quantum dots even after purification. The residual lithium present in prepared zinc oxide quantum dots could be considered as impurity and thus its concentration in the final product should be monitored. Atomic absorption spectroscopy is considered to be a highly efficient quantitative technique for quantitative determination of metals [6,7]. Therefore the objective of the present study was to carry out determination of zinc and lithium in prepared quantum dots using atomic absorption spectroscopy.

MATERIALS AND METHODS

Materials

Zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) and lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$) were purchased from Sigma-Aldrich Co., (MO, USA). Ethanol (99.9%) was purchased from Jiangsu Huax Co., Ltd., Jiangsu, China.

Preparation of zinc oxide quantum dots

Zinc acetate (44 mg) was added to 20 mL of absolute ethanol. The mixture was dissolved completely by being stirred at room temperature for 30 min. Lithium hydroxide (36 mg) was dissolved in 20 mL of absolute ethanol. The zinc acetate solution was then added to the LiOH solution and stirred well for reaction. The pH value of the solution was measured to be 12. After reaction for 2 h, the solution became turbid, indicating formation of zinc oxide quantum dots (QDs). The obtained ZnO QDs were first washed thrice using absolute ethanol to remove unreacted precursors. The purified quantum dots were then dispersed in 20 mL absolute ethanol for storage till use [5].

Atomic absorption spectroscopy

The zinc and lithium content of zinc oxide quantum dot solution was quantified via atomic absorption spectroscopy (AAS), using an AAS NovAA 400 G device (Analytik Jena) via graphite furnace.

Preparation of standard stock solution of zinc

Measured out accurately 1 mL of zinc concentrate AAS standard, having concentration 1000 mg/L and was transferred into a 100 mL standard flask. It was dissolved in Nanopure[®] water (Thermo Scientific, Ottawa, ON, Canada) (resistivity $\geq 18 \text{ M}\Omega\text{-cm}$) and made upto the volume. This solution had a concentration of 10 mg/L of zinc (Solution A).

Accurately pipette out 1ml of solution A and was transferred into a 100 mL standard flask and made upto the volume with Nanopure[®] water. This solution had concentration of 100 $\mu\text{g/L}$ of zinc (Solution B).

1, 1.5, 2 and 2.5 ml of solution 'B' was accurately pipetted out into a 10 mL standard flask and made upto the volume with Nanopure[®] water to get concentrations of 10, 15, 20 and 25 $\mu\text{g/L}$ of zinc respectively.

Determination of concentration of zinc in zinc oxide quantum dots

Towards the determination of concentration of zinc in zinc oxide quantum dots a standard plot at 213.9 nm were obtained by plotting absorbance on y-axis and concentration of zinc on x-axis. Then the solution containing the zinc oxide quantum dots was initially digested with hydrochloric acid and was suitably

diluted with water. Then the absorbance of the as prepared sample was taken. The concentration of zinc present in the quantum dot solution was calculated relative to the standard plot of zinc.

Preparation of standard stock solution of lithium

Measured out accurately 1 mL of lithium concentrate AAS standard, having concentration 1000 mg/L and was transferred into a 100 mL standard flask. It was dissolved in Nanopure® water (resistivity $\geq 18 \text{ M}\Omega\text{-cm}$) and made upto the volume. This solution had a concentration of 10 mg/L of lithium (Solution A).

Accurately pipette out 1ml of solution A and was transferred into a 100 mL standard flask and made upto the volume with Nanopure® water. This solution had concentration of 100 $\mu\text{g/L}$ of zinc (Solution B).

1, 1.5, 2, 2.5 and 3 mL of solution 'B' was accurately pipetted out into a 10 mL standard flask and made upto the volume with Nanopure® water to get concentrations of 10, 15, 20, 25 and 30 $\mu\text{g/L}$ of lithium respectively.

Determination of concentration of lithium in zinc oxide quantum dots

Towards the determination of concentration of lithium in zinc oxide quantum dots a standard plot at 670.8 nm were obtained by plotting absorbance on y-axis and concentration of lithium ($\mu\text{g/L}$) on x-axis.

Then the sample of optimized solution containing the zinc oxide quantum dots was initially digested with hydrochloric acid. Then the absorbance of the as prepared sample was taken after suitable dilution with water. The concentration of lithium present in the quantum dot solution was calculated relative to the standard plot of lithium.

RESULTS AND DISCUSSION

Preparation of zinc oxide quantum dots

Zinc oxide quantum dots were prepared as detailed in the experimental section. Figure 1 shows the photograph of the obtained zinc oxide QD dispersion in ethanol.

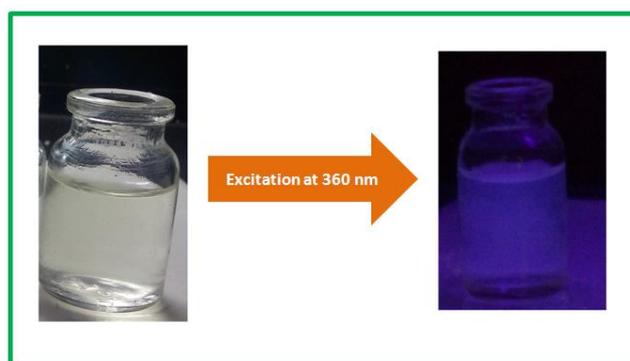


Figure 1: Photograph of zinc oxide quantum dot dispersion in ethanol

Atomic absorption spectroscopy

The concentration of zinc and lithium in the dispersion of quantum dots were quantified by atomic absorption spectroscopy.

Standard plot of zinc

The standard plot of zinc was obtained, at 213.9 nm with the concentrations in the range of 0– 25 $\mu\text{g/L}$. The mean value ($n=3$) of absorbance obtained was plotted against concentration of zinc (Fig. 2).

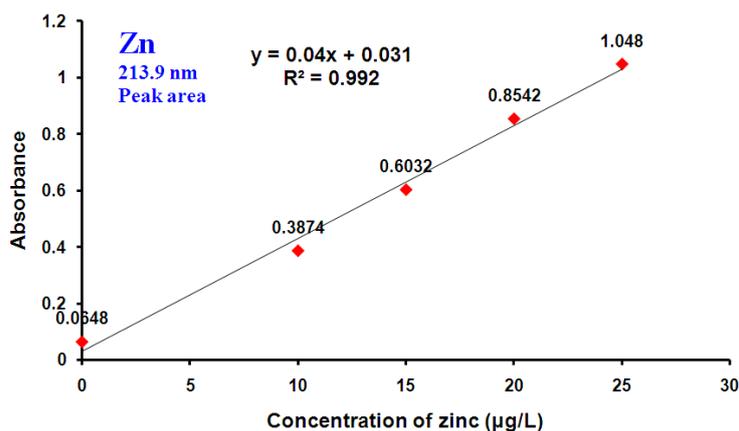


Figure 2: Standard plot for zinc

Determination of concentration of zinc in zinc oxide quantum dot samples

The concentration of zinc in zinc oxide quantum dot dispersion was quantified by taking the absorbance of the sample at 213.9 nm and then evaluated using the standard plot of zinc. The regression analysis data is shown in Table 1.

Table 1: Regression analysis data of standard plot for zinc

Regression analysis data	
Slope	0.039999
Intercept	0.031547
Regression coefficient (R2)	0.992

The concentration of zinc in zinc oxide quantum dot dispersion was calculated by using the regression analysis data. The concentration of zinc in prepared dispersion of zinc oxide quantum dot was found to be 22.05 mg/L.

Standard plot of lithium

The standard plot of lithium was obtained, at 670.8 nm with the concentrations in the range of 0-30 µg/L. The mean value (n=3) of absorbance obtained was plotted against concentration of lithium (Fig. 3).

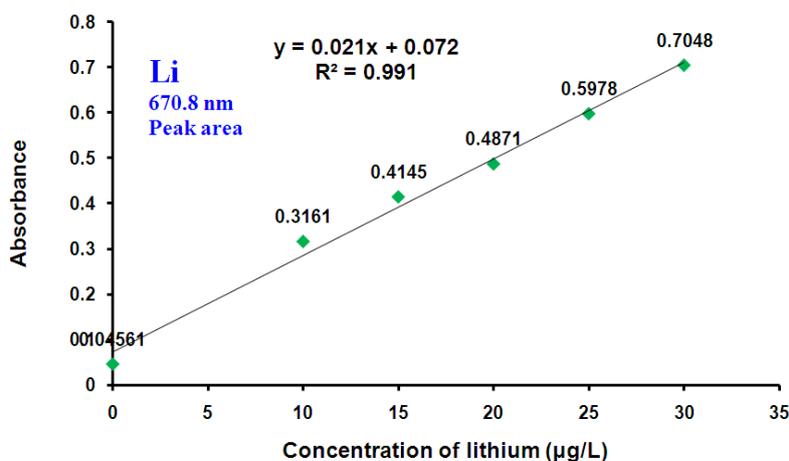


Figure 3: Standard plot for lithium

Determination of concentration of lithium in zinc oxide quantum dots

The concentration of lithium in zinc oxide quantum dot dispersion was quantified by taking the absorbance of the sample at 670.8 nm and then evaluated using the standard plot of lithium. The regression analysis data is shown in Table 2.

Table 2: Regression analysis data of standard plot for lithium

Regression analysis data	
Slope	0.021
Intercept	0.072
Regression coefficient (R2)	0.991

The concentration of zinc in zinc oxide quantum dot dispersion was calculated by using the regression analysis data. The concentration of zinc in prepared dispersion of zinc oxide quantum dot was found to be 6.29 mg/L.

CONCLUSIONS

Atomic absorption spectroscopy was successfully employed for the determination of zinc and lithium in prepared zinc oxide quantum dots. The standard plots for both zinc and lithium were found to be linear in the selected range of concentrations with regression coefficient (R2) values of 0.992 and 0.991 respectively. The R2 values close to 1 indicated high linearity for the standard plots. Lithium was present in very low concentration of 6.29 mg/L in the prepared dispersion of zinc oxide quantum dots. The developed method could be of great help while developing novel drug and gene delivery systems based on zinc oxide quantum dots.

REFERENCES

- [1] Selim KMK, Xing ZC, Choi MJ, Chang Y, Guo H, Kang IK. *Nanoscale Res Lett* 2011; 528: 1-9.
- [2] Qi L, Gao X. *Expert Opin Drug Deliv* 2008; 5: 263-267.
- [3] Azzazy HME, Mansour MMH, Kazmierczak SC. *Clin Biochem* 2007; 40: 917-927.
- [4] Peng J, Chen HL, Zhu XB, Yang GF, Zhang ZL, Tian ZQ, Pang DW. *J Nanosci Nanotechnol* 2011; 11(11):9725-9730.
- [5] Tang X, Choo ESG, Li L, Ding J, Xue J. *Chem Mater* 2010; 22: 3383-3388.
- [6] Ali SL. *J Pharm Biomed Anal* 1983; 1(4): 517-523.
- [7] Qadir MA, Ahmed M, Haq I, Ahmed S. *Pak J Pharm Sci* 2015; 28(3): 875-879.