Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1148-1152

Spectrophotometric Determination of Trace Amount of Oxalic Acid Based on Zirconium(IV)-(DBM-Arsenazo)-Oxalic Acid System

QING-ZHOU ZHAI
Research Center for Nanotechnology, Changchun University of Science and Technology, Weixing Road, Changchun-130022, P.R. China
E-mail: zhaiqingzhou@sohu.com, zhaiqingzhou@hotmail.com

In hydrochloric acid medium (0.2 mol L^{-1}), zirconium (IV) and DBM-arsenazo (DBM-ASA) form a blue-green complex with a 1 : 1 mole ratio. The addition of oxalic acid can quantitatively replace the DBM-arsenazo in the complex, which makes the coloured solution with enhance absorbance. At 520 nm, the concentration of oxalic acid is proportional to the increase of absorbance. Beer's law is obeyed over the concentration range of oxalic acid 1.0×10^{-5} - 3.0×10^{-4} mol L^{-1} with a correlation coefficient of 0.9968. The apparent molar absorptivity of the method is $\varepsilon_{520\,nm} = 1.85 \times 10^3$ L mol^{-1} cm^{-1}. The detection limit of the method for oxalic acid is 0.549 μg/mL. The effect of fifty-eight diverse substances on the determination of oxalic acid was examined. The method has good selectivity. It was directly applied to the determination of trace amount of oxalic acid in urine samples with satisfactory results.

Key Words: Oxalic acid, Spectrophotometry, DBM-arsenazo, Zirconium(IV), Urine sample.

INTRODUCTION

Oxalic acid and its salt extensively exist in various kind of biological samples, usually exist in plants in the form of potassium or calcium salt. As a metabolin, oxalic acid exists in the body tissue of mankind and animal. It gets rid of body from urine in the form of calcium salt with the oxalic acid assimilated by food. If the confusion of mineral supersession happens, oxalate attends the formation of kidney calculus and bladder calculus. Most of the patients of urine calculus result from high contents of oxalic acid in the body. Mankind assimilating a large amount of foods that contains the high contents of oxalic acid will increase the danger that suffers from the urine calculus. Therefore, the accurate and rapid determination of the amount of oxalic acid, especially in body, has very important significance. It has, especially in clinical medical analysis, much more value of application. The analytical methods of oxalic acid have the following ones. For macro

amount of oxalic acid, permanganimetric titration method is used[1]. For the determination of micro and trace amount of oxalic acid, extraction-photometry[2], chemiluminescence method[3], fluorometry[4] are used. However, for all these methods, there exist different drawbacks such as low sensitivity, poor selectivity, sample process time-consuming, complex instrument operation, high analytical cost, *etc.*

DBM-Arsenazo (DBM-ASA)[5] has been used for the spectrophotometric determination of rare earth elements. In present studies, a novel method was developed for the determination of trace amount of oxalic acid. In hydrochloric acid medium (0.2 mol L^{-1}), DBM-ASA and zirconium (IV) can form a blue-green complex. After oxalic acid was added to the system, the DBM-ASA in the complex could be replaced by the oxalic acid and the absorbance of the coloured solution increased. The concentration of oxalic acid is linearly related to the increase value of absorbance. The effects of fifty-eight coexisting substances were observed and found that the present method has very good selectivity for common substances. The method is of high sensitivity, the apparent molar absorptivity being $\varepsilon_{520\ nm} = 1.85 \times 10^3$ L mol^{-1} cm^{-1} at 520 nm and the detection limit of the present method 0.549 μg/mL. Compared with other analytical methods[1-4], the present method has the advantages of operation simplicity, rapidity, high sensitivity, high selectivity, *etc.* The developed method was used in the direct determination of trace amount of oxalic acid in urine samples and satisfactory results were obtained. The present method may be used as routine analysis in clinical laboratory.

EXPERIMENTAL

Oxalic acid standard solution [5.0×10^{-3} mol L^{-1}]: A 0.0629 of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$, Beijing Chemical Plant, A.R.) was dissolved in a beaker with a small amount of water, then transferred to a 100 mL of calibrated flask and diluted to the mark with water.

Zirconium(IV) working solution [5.0×10^{-4} mol L^{-1}]: A 0.0161 g of $ZrOCl_2 \cdot 8H_2O$ (Shanghai Chemical Reagent Company, G.R.) was dissolved in a small amount of 1 mol L^{-1} nitric acid, then transferred to 100 mL of calibrated flask and diluted to the mark with water.

DBM-arsenazo (DBM-ASA) chromogenic solution [5.0×10^{-4} mol L^{-1}]: A 0.0420 g of DBM-ASA (Shanghai Changke Research Institute for Reagent, A.R., China) was dissolved in 100 mL of water.

Hydrochloric acid solution: 16.7 mL of conc. HCl (Jilin Weilong Chemical Reagent Company, A.R.) was transferred to a 100 mL of calibrated flask and then diluted to the mark with water, mixed well. A 2.0 mol L^{-1} of hydrochloric acid was obtained. All other reagents were of analytical grade and water was distilled twice and used throughout the experiment.

A 722S spectrophotometer (Shanghai Lingguang Technique Co. Ltd., China) with 1 cm cells was used for absorbance measurements.

Procedure: Place 1 mL of HCl (2.0 mol L^{-1}) into a 10 mL of calibrated flask. In the following order, add 0.50 mL of zirconium (IV) solution (5.0×10^{-4} mol L^{-1}), 1.2 mL of DBM-ASA solution (5.0×10^{-4} mol L^{-1}), 0.50 mL of oxalic acid solution (5.0×10^{-3} mol L^{-1}) and then dilute to the mark with water. Leave for 20 min, then measure the absorbance of the coloured solution against a corresponding reagent blank at 650 nm with 1 cm cells.

RESULTS AND DISCUSSION

Absorption spectra: Fig. 1 shows the absorption spectra of DBM-ASA and the corresponding system. As can be seen from the Fig. 1, the maximum absorption peak of DBM-ASA solution against water is at 520 nm, the maximum absorption peak of Zr (IV)-(DBM-ASA) complex against water is at 540 nm and the maximum absorption peak of $H_2C_2O_4$-Zr(IV)-(DBM-ASA) system against water is at 540 nm. After oxalic acid was added, the absorbance of the Zr(IV)-(DBM-ASA)-$H_2C_2O_4$ system against water raised at 540 nm. As the addition amount of oxalic acid increases, the peak location moves to 520 nm. Because oxalic acid has the complexation with the Zr(IV) in the Zr(IV)-(DBM-ASA) complex, the DBM-ASA was replaced by the oxalic acid. At this time, the free DBM-ASA produced in the solution resulted in the absorption peak location change and absorbance change. The maximum absorption peak of $H_2C_2O_4$-Zr(IV)-(DBM-ASA) system against a corresponding reagent blank locates at 520 nm. In all the subsequent experiments, 520 nm was selected as measurement wavelength.

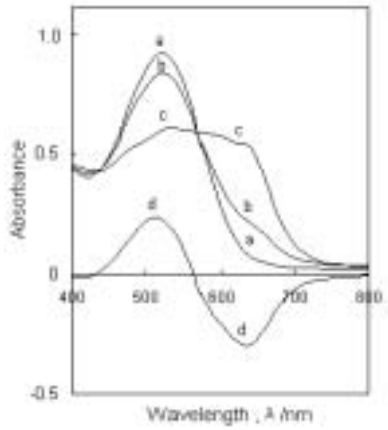

Fig. 1. **Absorption spectra:** a) DBM-ASA (against H_2O); b) $H_2C_2O_4$-Zr(IV)-(DBM- ASA) (against H_2O); c) Zr(IV)-(DBM-ASA) (against H_2O); d) $H_2C_2O_4$-Zr(IV)- (DBM-ASA) against corresponding reagent blank); [$H_2C_2O_4$] = 2.5×10^{-4} mol L^{-1}, [Zr(IV)] = 2.5×10^{-5} mol L^{-1}, [DBM-ASA] = 7.2×10^{-5} mol L^{-1}, [HCl] = 0.20 mol L^{-1}

Optimization of experimental variables

Effect of acidity: The experimental results showed (Fig. 2) that the optimum hydrochloric acid concentration fall in the range of 0.1-0.3 mol L^{-1}. Over the above range, the maximum and constant absorbance was obtained. Outside this range of acidity, the absorbance decreased. In the following work, 0.2 mol L^{-1} hydrochloric acid was chosen. 1 mL of HCl (2.0 mol L^{-1}) was added to control the acidity in the experiments.

Effect of the amount of reagents: The results of the amount of DBM-ASA showed as the amount of DBM-ASA increases, the absorbance gradually increases. When the amount of DBM-ASA solution was 1.0-1.5 mL, the absorbance can attain the maximum. 1.2 mL of DBM-ASA solution (5.0×10^{-4} mol L^{-1}) was recommended.

Effect of zirconium(IV) concentration: The effect of the amount of zirconium(IV) on absorbance was tested. With the increases of the amount of zirconium(IV), the absorbance gradually increases. When the concentration of zirconium(IV) was 0.3-0.8 mL, the maximum absorbance was attained. 0.50 mL of zirconium(IV) solution (5.0×10^{-4} mol L^{-1}) was selected.

Effect of reaction time and the stability of system: The experimental results showed that the maximum and constant absorbance can be obtained after the various reagents were mixed for 20 min. The variation of absorbance was less 5% within 7 h and the system kept stable.

Linear range, sensitivity, precision and detection limit: The calibration graph, prepared by the procedure, is linear over the range of 1.0×10^{-5}-3.0×10^{-4} mol L^{-1} for oxalic acid under the optimum experimental conditions. The linear regression equation and regression coefficient are found to be, respectively, $A = 9.70 \times 10^{2}C + 0.0991$ (C: mol L^{-1}), the correlation coefficient y = 0.9968. The apparent molar absorptivity, calculated from the calibration graph, is $\varepsilon_{520nm} = 1.85 \times 10^{3}$ L mol^{-1} cm^{-1}. The determinations of 1.0×10^{-4} mol L^{-1} oxalic acid were carried out 12 times and the calculated relative standard deviation was 0.88 %, indicating that the present method has excellent precision. By using three times of standard deviation of eleven blank as detection limit, the detection limit calculated was 0.549 μg/mL of oxalic acid.

Composition of the complex: Molar ratio and equimolar continuous variation methods were used to determine the composition of the zirconium(IV)-(DBM-ASA) complex. A zirconium (IV)-(DBM-ASA) (1:1) complex was indicated by both methods. After oxalic acid was added, oxalic acid can coordinate with the zirconium (IV) in the Zr(IV)-(DBM-ASA) complex and replaces a part of the DBM-ASA to make the absorbance increase at 520 nm.

Effect of diverse ions: The effect of 58 diverse substances including cations, anions, organic acids, saccharides, *etc*. was investigated. The most commonly encountered ions are individually added to a solution containing 2.5×10^{-4} mol L^{-1} oxalic acid was investigated. The tolerance limits (> 5 % maximum error) are shown as follows (m/m): Na^+ (1000); K^+ (800); Li^+ (400); Ag^+ (0.05); NH_4^+(120); Mn^{2+}(500); Fe^{2+} (100); Cu^{2+} (10); Cd^{2+} (4); Sn^{2+} (1); Zn^{2+}, Mg^{2+} (0.1); Ba^{2+}, Ca^{2+} (0.5); Sr^{2+} (0.3); Co^{2+}, Ni^{2+} (0.4); Pb^{2+} (0.01); Al^{3+} (300); Fe^{3+} (0.5); Cr^{3+} (0.8); Bi^{3+} (1); B^{3+} (3); La^{3+}, Eu^{3+} (0.05); Y^{3+} (0.1); Th^{4+} (0.004); Cl^- (100); NO_3^- (150); Br^-, I^- (50); NO_2^-, F^- (10); VO_3^- (1); BrO_3^- (0.05); MnO_4^- (0.0005); WO_4^- (0.1); SO_4^{2-} (1); $S_2O_7^{2-}$ (8); $Cr_2O_7^{2-}$, SiO_3^{2-} (5); PO_4^{3-} (15); $Mo_7O_{24}^{6-}$ (0.07); EDTA (2); urea (800); citric acid (600); glucose (400); ascorbic acid (150); leucine (6); lysine, glycine, acetic acid, salicylic acid (5); alanine, tartaric acid (4); apple acid (3); bovine serum albumin (20); bovine red albumin (8). The method has very good selectivity and can meet the need of determining oxalic acid in some biological samples.

Analysis of urine samples: Place 10.00 mL of urine sample into a 50 mL of calibrated flask, and dilute to the mark with distilled water. Transfer an appropriate amount of solution into colorimetric tubes. Oxalic acid was determined according to the experimental procedure. The analytical results are shown in Table-1. The relative standard deviations of six determinations for the present method are less 1 %. The recovery of the method is between 99.4-102.0%. It can meet the need of clinical routine analysis.

TABLE-1
ANALYTICAL RESULTS OF SAMPLES

Urine Sample	Found (μg/g)	Average (μg/g)	Relative standard deviation (%)	Added (mol L^{-1}) $\times 10^{-5}$	Recovered (mol L^{-1}) $\times 10^{-5}$	Recovery (%)	Contrast result[6] (μg/g)
No. 1	21.1,20.9,21.2, 21.0,21.2,21.3	21.1	0.70	5.00	5.10	102.00	21.0
No. 2	24.6, 24.5, 24.8, 24.6, 24.9, 24.6	24.7	0.63	5.00	4.97	99.40	24.9

REFERENCES

1. M.S.P. Rao, A.R.M. Rao and K.V. Raman, *Talanta*, **38**, 937 (1991).
2. F. Salinas, J.L. Martinez and V. Gonzalez, *Analyst*, **114**, 1685 (1989).
3. T.M. Downey and T.A. Nieman, *Anal.Chem.*, **64**, 261 (1992).
4. L.P. Long, *Chin. J. Anal. Lab.*, **21**, 80 (2002).
5. X.Y. Li, H.S. Zhang and J.C. Cui, *Chem. J. Chin. Univ.*, **9**, 661 (1988).
6. Q.Z. Zhai, X.X. Zhang and Q.Z. Liu, *Spectrochim. Acta*, **65A**, 1 (2006).

(*Received*: 24 November 2005; *Accepted*: 1 September 2006) AJC-5068