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SHORT COMMUNICATION

SPECTROPHOTOMETRIC DETERMINATION OF TRACE OXALIC ACID WITH ZIRCONIUM(IV)-DIBROMOCHLOROARSENAZO COMPLEX

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ABSTRACT. Based on the property that oxalic acid has the effect on the replacement of dibromochloroarsenazo in zirconium(IV)-dibromochloroarsenazo complex to produce hyperchromic effects in 1.26 M hydrochloric acid medium, a novel method for the determination of trace oxalic acid by spectrophotometry was developed. The concentration of oxalic acid is linearly related to the absorbance at 500 nm. Beer's law is obeyed over the range of 5.0 x 10^{-5} - 3.0 x 10^{-4} M for oxalic acid. The apparent molar absorptivity of the determination of oxalic acid is $\varepsilon_{500\ nm} = 1.52 \times 10^{3}\ M^{-1}\cdot cm^{-1}$ with a correlation coefficient of 0.9994. The detection limit of the present method is 1.73 $mg.L^{-1}$ of oxalic acid. The method was used in the determination of trace amounts of oxalic acid in a few of kinds of tea leaves with satisfactory results.

KEY WORDS: Oxalic acid, Zirconium(IV)-dibromochloroarsenazo, Spectrophotometry

INTRODUCTION

Oxalic acid is found in some biological samples and it can be absorbed by the people through the food chain. Oxalic acid and calcium can easily form kidney calculus in people's bodies. If its intake is high, oxalic acid is harmful to humans. Therefore, the determination of the content of oxalic acid is of interest to the identification of the nutritional quality of fruits and vegetables or to the evaluation of clinical analysis [1]. Tea leaves contain oxalic acid and oxalic acid can be absorbed by humans by means of drinking tea water. Thus, the determination of oxalic acid in biological samples such as tea is significant. At present the methods for the determination of oxalic acid include chemical luminescence [2], fluorimetry [3,4], and permanganimetric titration [5]. These methods have different extent of defects, such as instrumental operation complexity, high analytical cost, and poor selectivity [2-4], or they are suited only for the macro analysis of oxalic acid [5]. Vanadium(V)-mandelohydroxamic acid-oxalate complex spectrophotometry was also used for the determination of oxalate [6]. However, toluene is needed in this method for extraction of the complex. This causes unconvenience for the operation. DBC-arsenazo, namely dibromochloroarsenazo (DBC-ASA, $C_{22}H_{14}AsBr_2ClN_4O_{11}S_2$), whose full name is 3-[2,6-dibromo-4-chlorophenylazo-6-(2-arsenophenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid, is an unsymmetric bis-arylazo derivative of chromotropic acid that has been used for the spectrophotometric determination of rare earths [7]. In this paper, the authors found that Zr(IV) and DBC-ASA can form a red-purple complex in 1.26 M hydrochloric acid medium and oxalic acid has a stable complexation effect on the zirconium(IV), whereas the DBC-ASA can be replaced after the addition of oxalic acid to the Zr(IV)-(DBC-ASA) complex. Based on these characteristics, a new simple and rapid spectrophotometric method for the determination of oxalic acid has been developed. The colored system is stable for 12 h. Compared with other

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methods of the determination of oxalic acid [1-6], the present method is characterized by operation simplicity, rapidity, and good selectivity. The trace oxalic acid was determined in a few kinds of tea by the proposed method with satisfactory results.

EXPERIMENTAL

Reagents and apparatus

A 5.0 x 10^{-3} M oxalic acid solution was prepared by dissolving 0.0629 g of oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) (Beijing Chemical Plant, China) in water, transferred into a 100 mL calibrated flask and diluted up to the mark with water. A 5.0 x 10^{-4} M of zirconium(IV) solution was prepared by dissolving 0.0161 g of $ZrOCl_2 \cdot 8H_2O$ (Shanghai Chemical Reagent Company, China) with 10 mL of 1.0 M HNO_3 in a beaker. The solution was placed into a 100 mL of calibrated flask and diluted up to the mark with distilled water. A 5.0 x 10^{-4} M of DBC-ASA ($C_{22}H_{14}AsBr_2ClN_4O_{11}S_2$) (Shanghai Changke Research Institute for Reagent, China) solution was prepared by dissolving 0.0420 g of the reagent in 100 mL of water. A 6.0 M hydrochloric acid (Jilin Yitong Chemical Plant, China) solution was used for adjusting the acidity of the system. All reagents were of analytical grade and the water was distilled. A 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China) was used for absorbance measurements with 1 cm cells.

Standard procedure

In a 10 mL calibrated flask, 2.1 mL of 6.0 M ydrochloric acid solution, 1.0 mL of 5.0 x 10^{-4} M zirconium(IV) solution, 1.0 mL of 5.0 x 10^{-4} M DBC-arsenazo solution, and 0.50 mL of 5.0 x 10^{-3} M oxalic acid were added in turn, the flask was filled to the mark with distilled water and mixed well. After 20 min, the absorbance was measured at 500 nm against a corresponding reagent blank in 1-cm cells.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows the absorption spectra of DBC-ASA and the corresponding colored systems. It can be seen from Figure 1 that the maximum absorption peak of DBC-ASA solution against water is at 480 nm, the maximum absorption of (DBC-ASA)-Zr(IV) complex against water is at 500 nm, and the maximum absorption peak of zirconium(IV)-(DBC-arsenazo) oxalic acid against water is at 480 nm. After oxalic acid was added, the absorbance of zirconium(IV)-(DBC-arsenazo) complex against water at 500 nm rises and the peak moves to 480 nm. Oxalic acid can replace the DBC-ASA from the zirconium(IV)-(DBC-arsenazo) complex and coordinates with the zirconium(IV). The maximum absorption peak of zirconium(IV) + (DBC-arsenazo) + oxalic acid system against a corresponding reagent blank is located at 500 nm. In the further measurement of oxalic acid, the wavelength of 500 nm was selected. The chemical reactions which take place in the corresponding systems can be expressed as follows:

$$ZrOCl_2 + C_{22}H_{14}AsBr_2ClN_4O_{11}S_2 \rightarrow Zr(C_{22}H_{10}AsBr_2ClN_4O_{11}S_2) + 2HCl + H_2O$$

$$Zr(C_{22}H_{10}AsBr_2ClN_4O_{11}S_2) + 2H_2C_2O_4 \rightarrow Zr(C_2O_4)_2 + C_{22}H_{14}AsBr_2ClN_4O_{11}S_2$$

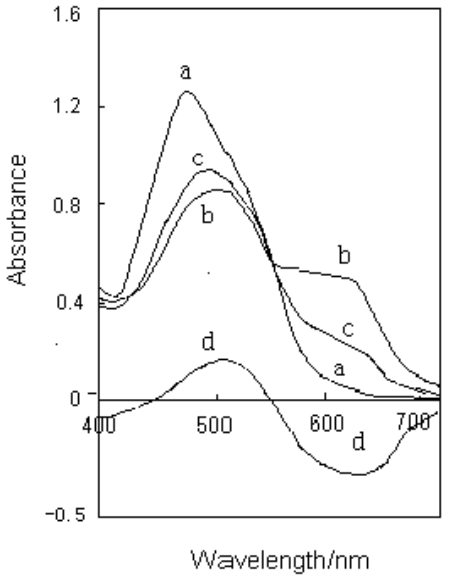

Figure 1. Absorption spectra. a: DBC-ASA (against H_2O), b: Zr(IV)-(DBC-ASA) (against H_2O), c: Zr(IV)+(DBC-ASA)+$H_2C_2O_4$ (against H_2O), d: Zr(IV)+(DBC-ASA)+$H_2C_2O_4$ (against corresponding reagent blank); [$H_2C_2O_4$] = 2.5 x 10^{-4} M, [Zr(IV)] = 5.0 x 10^{-5} M, [DBC-ASA] = 6.0 x 10^{-5} M, [HCl] = 1.26 M.

Optimization of experimental variables

The acidity studies showed that the maximum and constant absorbance was obtained in the range of 1.08-2.00 M hydrochloric acid. Beyond this range, the sensitivity of the determination of oxalic acid is lower. A 1.26 M solution of hydrochloric acid was selected for the final procedure. In the experiments, 2.1 mL of 6.0 M hydrochloric acid solution was added to control the acidity of the system. The hydrochloric acid has an effect on the replacement of the DBC-ASA in the Zr-(DBC-ASA) complex by oxalic acid as described in the chemical reactions of the absorption spectra section.

The effect of the amount of DBC-ASA on the absorbance was observed by determining different concentrations of DBC-ASA. The results showed that with increase in the amount of DBC-ASA, the absorbance gradually raised. When the amount of DBC-ASA solution was in the range of 0.8-1.5 mL, the absorbance was at a maximum. Thus, 1.0 mL of 5.0 x 10^{-4} M DBC-ASA solution was selected.

The effect of the amount of Zr(IV) on absorbance showed that the absorbance gradually rises with the increase in the concentration of Zr(IV). When the concentration of Zr(IV) was 2.5 x 10^{-5} - 1.0 x 10^{-4} M, the absorbance was maximal and constant. Therefore, the concentration of 1.0 mL of 5.0 x 10^{-5} M Zr(IV) was selected for the subsequent studies.

It was found that after the various reagents were mixed for 20 min, the absorbance attained a maximum. The variation of absorbance was less than 5% within 12 h. The measurement of absorbance was conducted after 20 min after the addition of all reagents was carried out.

Calibration curve, sensitivity, precision and detection limit

Under the optimum experimental conditions, the calibration curve of oxalic acid showed that the linear relationship of the concentration of oxalic acid is in the range of 5.0 x 10^{-5} - 3.0 x 10^{-4} M. The linear regression equation was found to be A = 7.2 x 10^{2} C + 0.1052, with a correlation coefficient γ = 0.9994, where C is the molar concentration of oxalic acid. The apparent molar absorptivity of oxalic acid is $\varepsilon_{500\ nm}$ = 1.52 x 10^{3} $M^{-1}{\cdot}cm^{-1}$. By using three multiple standard deviation of 11 blank values as the limit of detection, the detection limit of the method was calculated to be 1.73 mg L^{-1} of oxalic acid. The precision of the present method was evaluated by determining 2.0 x 10^{-4} M oxalic acid standard solution 11 times. The relative standard deviation was 0.38%, indicating that the method is highly precise.

Composition of complex

The complex ratio of Zr(IV)-(DBC-ASA), determined by using both mole ratio method and equimolar continuous variation method is 1:1.

Effect of co-existing substances

At a concentration of 2.0 x 10^{-4} M oxalic acid and a relative error of less than 5%, the effects of fifty-six co-existing substances including organic acids, saccharides, cations, and anions were assessed. The results (weight ratio) are as follows: urea, citric acid (500); ascorbic acid (170); lysine, glycocoll, leucine, salicylic acid, acetic acid (7); alanine (5); malic acid (4); tartaric acid (2); glucose (300); bovine serum albumin (7); bovine red albumin (4); K^{+}, Na^{+} (700); Li^{+} (500); Ag^{+} (0.05); NH_4^{+} (120); Mn^{2+} (500); Fe^{2+} (50); Cu^{2+}, Cd^{2+} (5); Sn^{2+} (1); Ba^{2+} (0.5); Zn^{2+}, Ca^{2+}, Sr^{2+} (0.1); Co^{2+} (0.5); Ni^{2+}; Pb^{2+} (0.01); Al^{3+} (400); Fe^{3+}, Cr^{3+} (1); Bi^{3+} (0.2); B(III) (2); La^{3+} (0.05); Eu^{3+} (0.02); Y^{3+} (0.04); Th(IV) (0.005); NO_3^{-} (200); Br^{-} (100); I^{-} (50); NO_2^{-} (10); F^{-} (5); VO_3^{-} (0.5); BrO_3^{-} (0.01); WO_4^{-} (0.05); MnO_4^{-} (0.0005); $Cr_2O_7^{2-}$ (3); SO_4^{2-} (0.05); $S_2O_7^{2-}$ (6); SiO_3^{2-} (3); PO_4^{3-} (10); Mo_7O_{24}(VI) (0.05); EDTA (10). It can be seen that the present method has good selectivity for most common substances and the selectivity can meet the need of the determination of the content of the oxalic acid in common samples.

Analysis of samples

2.000 g of tea leaf was accurately weighted and soaked with 100 mL of boiled water for 30 min in a beaker. The mixture was filtered and the filtrate was placed into a storage bottle. An appropriate amount of the tea water sample was transferred into a 10-mL calibrated flask and the contents of oxalic acid were determined according to the standard procedure. The analytical results are shown in Table 1.

The recovery test was made according to the following procedure. In a 10 mL of calibrated flask, 2.1 mL of 6.0 M hydrochloric acid solution, 1.0 mL of 5.0 x 10^{-4} M zirconium(IV) solution, 1.0 mL of 5.0 x 10^{-4} M DBC-arsenazo solution, the testing aliquot solution and 1.0 mL of 5.0 x 10^{-4} M of zirconium(IV) solution were added in turn, and then the determination of oxalic acid was carried out according to the standard procedure. The total amount of oxalic acid was calculated according to the linear regression equation. The total amount subtracts the amount in the tea testing solution to obtain the amount of the recovered oxalic acid. This value is divided by the added amount of oxalic acid to obtain the recovery. The results showed that the recovery of the method was between 96.2-104.2%. The relative standard deviation of six determinations was less than 0.24-1.78%. The analytical results are in excellent agreement with

those obtained by the catalytic kinetic spectrophotometric method [8]. It is thus concluded that the present method may be used for the routine analysis of tea leaf.

Table 1. Analytical results of samples.

Sample	Found $mg \cdot g^{-1}$	Average $mg \cdot g^{-1}$	RSD %	Added 10^{-5} M	Recovered 10^{-5} M	Recovery %	Contrast method [8]*
Xueyajian tea	3.45, 3.48, 3.54, 3.58, 3.62, 3.55	3.54	1.78	5.00	4.95	99.00	3.54
Green tea	5.65, 5.67, 5.70, 5.81, 5.77, 5.79	5.73	1.17	5.00	5.07	101.4	5.71
Black tea	11.7, 11.8, 12.2, 12.1, 12.0, 12.5	12.1	0.24	5.00	4.94	98.80	12.2
Maojian tea	3.46, 3.54, 3.48, 3.50, 3.53, 3.55	3.51	1.02	5.00	5.10	102.0	3.50

*Oxalic acid-rhodaminB-potassium dichromate catalytic-kinetic spectrophotometry [8].

CONCLUSIONS

A novel spectrophotometric method for the determination of trace oxalic acid was developed with zirconium(IV)-(DBC-arsenazo) complex. The linear range for the determination of oxalic acid is 5.0×10^{-5} - 3.0×10^{-4} M. The detection limit of the present method is 1.73 g L^{-1} of oxalic acid. The present method is simple, rapid and has been satisfactorily applied to the determination of tea leaf.

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