Spectrophotometric Determination of Iron (III) with Quercetin and Polyvinylpyrrolidone

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Summary. A method for the spectrophotometric determination of iron (III) with quercetin in the presence of protective colloid, PVP was presented. Stable yellow complex was formed in the pH range 4.2 - 4.7 in acetate buffer medium. The molar composition of iron: quercetin in the complex was 1:3 with stability constant 4.6 x 10^{13}. The molar absorptivity of the complex was 5.4×10^4 l.mol^{-1}.cm^{-1} at 431 nm and Beer's law was obeyed over the concentration range 0.04 - 1.34 µg of iron (III). Some masking agents such as phosphate, citrate and sulphide were used to improve the selectivity of the proposed method. The method has been successfully applied to the determination of iron (III) in drinking water, River Nile, sea water and industrial wastewater samples.

Introduction

Several methods have been reported for the determination of iron, based on enhancing the absorbance of the formed complexes with surfactants and micellar systems[1]. Some organic reagents such as, 1,10-phenanthroline[2], thiocyanate[3], 8-hdroxyquinoline[4], bromopyrogallol red[5], methylthymol blue[6], phenylfluorone[7], 5-Br PADAP[8] and morin[9] have been used for the determination iron in micellar media.

Experimental

Apparatus

All absorbance measurements were conducted on SHIMADZU UV-VIS-NIR scanning spectrophotometer using 1 cm matched quartz cells. A Crison Digit Model 501 ion analyzer equipped with glass-calomel electrode was used for pH measurements and pH adjustment, respectively.

Reagents

All chemicals used in the proposed method were of analytical grade. Aqueous solutions were prepared with bi-distilled water. Stock iron (III) solution of 1×10^{-2} M

was prepared by dissolving 1.9607 g of ferrous ammonium sulphate Fe $(NH_4)_2$ $(SO_4)_2.6 H_2O$ in water containing 10.0 ml of concentrated sulphuric acid and the solution was diluted to 500 ml with water in a volumetric flask. Quercetin (3, 3`, 4`, 5, 7-pentahydroxyflavone) of 1×10^{-2} M was prepared by dissolving 0.84565 g of quercetin dihydrate in ethanol and diluted to 250 ml in a volumetric flask with the same solvent. PVP of 2% w/v concentration was prepared by dissolving 10.0 g of PVP in warm water and diluting to 500 ml with water in a volumetric flask. Acetate buffer solution of pH 4.5 was prepared by adjusted the pH of 0.2 M acetic acid with 0.2 M sodium acetate to the desired value.

Procedures

Determination of iron (III) in standard samples

Introduce a suitable aliquot of the sample solution containing 33.5 μg of iron (III) into a 25 ml volumetric flask. Add 0.5 ml of quercetin of 1×10^{-2} M maintaining 10% v/v of ethanol as final volume, followed by 0.5 ml of PVP solution of 5% w/v and completed to the mark with acetate buffer solution of pH 4.5. Stand for 25 minutes, and then measure the absorbance against a blank at 431 nm. Construct a calibration graph using a set of standards under the same conditions.

Determination of iron (III) in water and industrial wastewater samples

To an aliquot of water sample containing not more than 33.5 μg of iron (III) in 25 ml calibrated flask. The above steps for the determination of iron (III) with quercetin and PVP in the presence of suitable masking agents is followed to determine iron (III) in drinking water, River Nile water, sea water and industrial wastewater samples.

Results and Discussion

Effect of surfactants and protective colloids

In aqueous medium, iron (III)-quercetin complex is sparingly soluble. Some protective colloids and surfactants such as cationic, anionic and non-ionic types were tested to solubilize this complex. The utilized surfactants were CTAB, CBP, CPC,

Zephiramine, Tween 20, Tween 40, Tween 60, Tween 80, SLS, SDBS and SAS; as well as PVA, PVP, Gelatin and Arabic gum as aprotective colloids. The study was carried out at the optimum conditions.and showed that,the cationic surfactants, CTAB, CPB, CPC, Zephiramine and the protective colloids, Gelatin and Arabic gum did not solubilize the complex. However, other surfactants and protective colloids exerted a solubilizing effect on the complex. Maximum enhancement of the complex absorbance was obtained in the presence of protective colloid, PVP and was used for further studies.

Absorption spectra

The absorption spectra of the solubilized iron (III)-quercetin binary complex and its reagent blank are given in Fig.1. The solubilized complex has an absorption maximum at 431 nm. At this wavelength the absorbance of the blank is minimum.
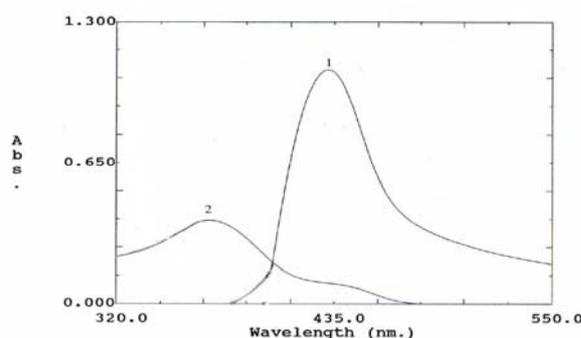

Fig.1. Absorption spectra of iron (III)-quercetin complex in the presence of PVP and its reagent blank. Curve 1, iron (III) complex; Curve 2, its reagent blank.

Effect of pH and type of buffer

The effect of pH on the soluilized iron (III)-quercetin complex in the pH range 2.5–5.5 has been studied. Some acidic buffer solutions such as acetate, formate, succinate and phthalate were tested for adjusting the medium pH. The maximum absorption was observed when the pH was maintained between 4.2–4.7 by the addition of acetate buffer solution. Therefore, acetate buffer solution of pH 4.5 was used for further investigations.

Effect of ethanol

The dependence of the absorbance of the iron (III)-quercetin complex on ethanol content has been studied at the optimum experimental values. The binary

complex exerted maximum absorbance in the presence of 4.0-45% v/v of ethanol thus, 10% v/v of ethanol was utilized in the proposed method for further studies.

Effect of quercetin concentration

A study on the influence of quercetin concentration on the absorbance of the iron (III)-quercetin complex was carried out at the optimum experimental values. The reagent concentration ranged between 2.8×10^{-5} M and 1.0×10^{-3} M throughout the study maintaining 10% v/v of ethanol as final volume. Maximum color was developed using a reagent concentration ranging between 1×10^{-3} M and 1×10^{-4} M. Therefore, 0.5 ml of 1×10^{-2} M quercetin was used in the procedure.

Effect of polyvinylpyrrolidone concentration

The effect of PVP concentration on the absorbance of iron (III)-quercetin binary complex was examined at the optimum conditions using variable concentrations of PVP ranging between 0.04 and 0.5% w/v. The results revealed that, the solubilization of the binary complex in the presence of $\geq$ 0.05% w/v of PVP. Moreover, the complex exerted maximum and constant absorbance in the presence of PVP concentration ranging between 0.05-0.5% w/v as final concentration. In the recommended procedure for iron (III) determination, 0.5 ml of 5% w/v PVP was used.

Effect of time

The influence of time on the formation and stability of iron (III)-quercetin complex has been studied at the optimum conditions of the proposed method. The study showed that, the absorbance of the complex reaches its maximum value within 20 minutes after mixing and remained constant for more than two days. Consequently, a standing time of 25 minutes was recommended for the determination of iron (III) in the binary complex.

Calibration graphs and statistical analysis of data

The calibration graph for the determination of iron (III)-quercetin complex was obeyed Beer's law in the concentration range 0.04-1.34 ppm. The value of the molar absorptivity, as determined by a least squares method was 5.4×10^{4} l.mol^{-1} .cm^{-1} for the iron (III) at 431 nm. The linear regression equation for calibration graph as calculated with a least squares fit relation for fourteen readings was A=0.012+ 5.4×10^{4}C with a

correlation coefficient of 0.9998, where C is the concentration of iron (III) in mg/l. The sensitivity index of the method was 1.04 ng.cm^{-2}.

Stoichiometry of the complex

The molar ratio and continuous variation methods have been used to determine the stoichiometry of the iron (III)-quercetin complex. The study showed that, the ratio of iron (III)-quercetin was 1:3 at maximum absorption 431 nm. The method of continuous variation has been used to determine the stability constant (β) of the iron (III) complex. The determined value of the stability constant (β) is 4.6×10^{13} and log β is 13.46.

Effect of interfering ions

The effect of foreign ions on the determination of iron (III) was studied at the optimum conditions. The tolerance limit was taken as the amount that cause $\pm$ 0.02 error in the absorbance value. However, some metal ions such as aluminium, beryllium, lead, molybdenum, scandium, tin, titanium, uranium and zirconium which form colored complexes with the same reagent were seriously interfered. The selectivity of the proposed method has been improved by adding masking agents such as phosphate of 4×10^{-3} M for Zr(IV) and ammonium citrate of 2×10^{-4} M for Al(III), Be(II) and U(IV). On the other hand, the interference of Be(II), Pb(II), Mo(VI), Sc(III) and Sn(II&IV) were eliminated by prior separation of them. The separation was performed by precipitation with hydrogen sulphide in the presence of As(III) as collector[10]. The precipitated metal sulphides were separated by centrifugation before measuring the absorbance of iron (III) complex.

Application of the method

The developed method was used to determine iron (III) in water samples. The analyzed water samples were collected from River Nile, Ismailia canal and drinking water in Shoubra El-Kheima area and sea water in Suez gulf whereas, industrial wastewater samples from plants in Helwan and Shoubra El-Kheima power station. A suitable volume of each water sample containing 0.02-0.6 μg of iron (III) was transferred into a 25 ml volumetric flask and the recommended procedure for iron (III) determination was followed. On the other hand, for industrial wastewater samples,

suitable masking agents were added before measuring iron (III) concentration. The results obtained were in good agreement between the suggested spectrophotometric method and the standard one.

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