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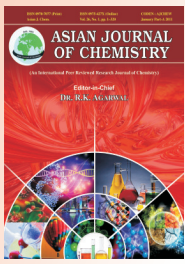

Spectrophotometic Determination of Trace Zinc in Milk Powder by Ethyl Rhodamine B†

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In the presence of the surfactant gum Arabic, the Zn(II)-SCN^--ERB (ERB = ethyl rhodamine-B) ternary chromogenic reaction system was studied. The results showed that, in the acetic acid-sodium acetate medium of pH 5.0, Zn(II)-SCN^--ERB forms a rose red complex of 1:4:2 at room temperature. The complex has a maximum absorption wavelength of 625 nm, a zinc content of 0.16-8.00 μg/25 mL conforming to the Lambert-Beer's law, a molar absorption coefficient ε_{625} of 1.02×10^5 L mol^{-1} cm^{-1} and a detection limit of 0.045 μg/25 mL. Using this method to determine the trace zinc in milk powder, the relative standard deviation is less than 2 % and the results are satisfactory.

Keywords: Zinc(II), Potassium thiocyanate, Ethyl rhodamine B, Spectrophotometry.

INTRODUCTION

Zinc is one of the important trace metal elements in the human body[1]. Zinc in milk powder is also necessary for the healthy growth of children. Its content is directly related to human health and infant growth and development. At present, methods for determination of zinc in milk powder include atomic absorption spectroscopy[2,3], electrochemical analysis[4], ICP-AES[5], ICP-MS[6], catalytic kinetic spectrophotometry[7], spectrophotometry[8], *etc*. In present study, it is noted that in presence of the surfactant gum Arabic, the Zn (II)-SCN^--ERB (ERB = ethyl rhodamine-B) ternary system can form a rose red complex with a maximum absorption at 625 nm in the acetic acid-sodium acetate medium of pH 5. The absorbance value of the system has a linear relationship with the zinc concentration in the solution within a particular range. A new ethyl rhodamine B spectrophotometry was thus established for rapid determination of the trace zinc in milk powder.

EXPERIMENTAL

722-P visible spectrophotometer (Shanghai Scientific Instrument Co., Ltd.); potassium thiocyanate solution of 20 %; acetic acid-sodium acetate buffer solution of pH 5.5; gum Arabic solution of 1 %; ethyl rhodamine B (ERB) solution of 0.05 %.

Standard solution of zinc(II) (1 mg/mL): In a small beaker, accurately weigh 0.1 g high purity zinc powder and add 5 mL HCl (3 mol/L). After dissolution, transfer the solution to a 100 mL volumetric flask. And then dilute it to the mark with deionized water and shake it up. When using, dilute it to zinc standard solution of 1 μg/mL.

All reagents were analytically pure and experimental water was deionized pure water.

Experimental method: In a 25 mL colorimetric tube, add 5 μg zinc standard solution, 2.00 mL potassium thiocyanate solution of 20 %, 3.50 mL acetic acid-sodium acetate buffer solution of pH 5.0, 3.00 mL gum Arabic solution of 1 % and 3.40 mL ethyl rhodamine B solution of 0.05 % in turn. Shake up every time after a reagent is added. Dilute the solution to the mark with water and settle it for 10 min at room temperature. And then measure the absorbance value in the spectrophotometer with a 1 cm cuvette at a wavelength of 625 nm by using the reagent blank as the reference.

RESULTS AND DISCUSSION

Absorption spectrum: According to the experimental method, within a wavelength of 480-680 nm, the absorbance value of the Zn (II)-SCN^--ERB complex was determined and the absorption curve (Fig. 1) was drawn.

Fig. 1 shows the maximum absorption wavelength of the ethyl rhodamine B solution is 554 nm and the maximum absorption wavelength of the Zn(II)-SCN^--ERB complex is 625 nm. It is because that Zn(II) forms complex anions with SCN^- and

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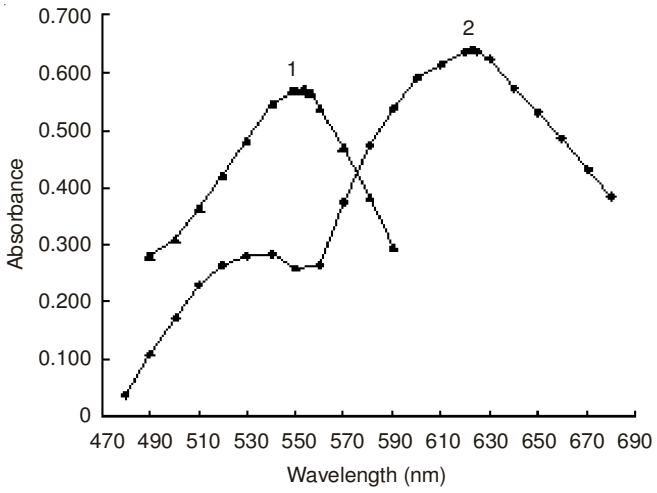

Fig. 1. Absorption curve. (1) Ethyl rhodamine B (with water as the reference), (2) Zn (II)-SCN^--ERB complex (with reagent blank as the reference), C_{ERB} = 0.05 %, $C_{Zn(II)}$ = 1 μg/mL, C_{SCN^-} = 20 %

then forms an ion association complex with ethyl rhodamine B, increasing the absorption area of light in the presence of a surfactant and causing red shift to the absorption wavelength of the complex. Therefore, 625 nm was selected as the determination wavelength in the experiment.

System acidity selection: H^+ is a key factor in the chromogenic reaction process. If H^+ is too high, ERB+ will be quickly protonated to produce $HERB^+$ and the formation reaction of the ion association complex cannot be carried through to the end. The absorbance of colorimetric solution decreases with the increase of H^+. According to the experimental method, the impact of different concentrations of hydrochloric acid, nitric acid, sulphuric acid, phosphoric acid and acetic acid-sodium acetate buffer solution on the reaction was tested, respectively. The results showed that acetic acid-sodium acetate buffer solution has better stability and sensitivity than the other media. Therefore, in this paper, it is selected as the reaction medium of the system. Meanwhile, when the dosage of acetic acid-sodium acetate of pH 5 is within 3-4 mL, the absorbance value of the system is maximum and stable. The optimal dosage selected is 3.5 mL.

Influence of potassium thiocyanate dosage: According to the experimental method, the impact of 1.5, 1.7, 1.9, 2.0, 2.1, 2.3 and 2.5 mL dosage of potassium thiocyanate (20 %) on the system was tested, respectively. The results showed that, when the dosage of potassium thiocyanate solution of 20 % is within 1.7-2.0 mL, the absorbance value of the Zn(II)-SCN^--ERB complex system is maximum and stable. Therefore, 2 mL was selected as the dosage of potassium thiocyanate in the experiment.

Influence of ethyl rhodamine B dosage: According to the experimental method, the impact of 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL dosage of ethyl rhodamine B (0.05 %) on the system was tested, respectively. The results showed that, when the dosage of ethyl rhodamine B solution of 0.05 % is within 3.2-3.6 mL, the absorbance value of the Zn(II)-SCN^--ERB complex system is maximum and relatively stable. Therefore, 3.4 mL was selected as the dosage of ethyl rhodamine B in the experiment.

Influence of surfactants: According to the experimental method, the impact of cationic surfactant CTMBA, anionic surfactant SDBS and nonionic surfactant OP, Tween-80, gum Arabic, gelatin, PVA124 and micro-emulsion (OP: *n*-amyl alcohol: *n*-heptane: water = 3.2: 2.3: 0.5:94) on the system was tested, respectively. The results showed that the gum Arabic has the best sensitization, solubilization and stabilization effect. When the dosage of gum Arabic solution of 1 % is within 2.5-4.0 mL, the absorbance value of the Zn(II)-SCN^--ERB complex system is maximum and stable. Therefore, 3 mL was selected as the dosage of gum Arabic solution in the experiment.

Composition and stability of complex: The composition of the Zn(II)-SCN^--ERB complex system was speculated by using the equilibrium shifting process. The research showed that the complex ratio of zinc and thiocyanate is 1:4, consisting of $[Zn(SCN)_4]^{2-}$ complex anions; the composition ratio of $[Zn(SCN)_4]^{2-}$ and ERB is 1:2, *i.e.*, the molecular structure of the simple complex formed with $[Zn(SCN)_4]^{2-}$ and ERB is $[ERB_2^+ \cdot Zn(SCN)_4^{2-}]$. The complex absorbance value tends to be stable at ten minutes.The stability of complex can last more than 1 h.

Interfering ions: To determine 5 μg Zn(II) in 25 mL solution, when the relative error is ± 5 %, the coexistence of the following ions (in mg) is allowed: Na^+, Mg(20); K^+(30); Ca^{2+}, Al^{3+}(15); NH_4^+(30); Cl^- (20); F^-, NO_3^-(20); $C_2O_2^{2-}$(30). The tolerance (in μg) of the following ions: Cd^{2+}, Pb^{2+}, Fe^{3+}, Mn^{2+}(2); Cr^{3+}(10); Cu^{2+}(4). Combined masking agent ($Na_2S_2O_3$ solution + tartaric acid solution + NaF solution) may be added to Cd^{2+}, Pb^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+} and Cu^{2+} for interference elimination. In the experiment, sodium fluoride of 5 % was used as the masking agent of Fe^{3+}.

Sample analysis

Working curve: According to the experimental method, 1, 2, 3, 4, 5, 6, 7 and 8 mL zinc standard solution (1 μg/mL) was, respectively transferred to a 25 mL colorimetric tube. And the working curve was drawn. The linear regression equation of the curve is A = 0.0627C + 0.0069 (C in μg/25 mL), the correlation coefficient is γ = 0.9997, the molar absorption coefficient $\varepsilon_{625} = 1.02 \times 10^5$ L mol^{-1} cm^{-1} and the detection limit is 0.045 μg/25 mL. The zinc content assumes a linear relationship within 0.16-8.00 μg/25 mL.

Sample analysis: Weigh 0.10-0.15 g Yili nutritional milk powder for middle-aged and old people and milk powder for primary and secondary school students in a small beaker. Add 10 mL concentrated nitric acid. Stir it with a glass rod until the initial reaction of the sample is stable and settle it overnight. And then add 5 mL perchloric acid. Heat and digest it on an electric stove until white smoke comes out and cool it. Transfer the solution to a 25 mL colorimetric tube and add 2 mL NaF solution of 5 % (Table-1).

Conclusion

It is simple and fast to use the Zn(II)-SCN^--ERB complex system for the determination of the trace zinc in milk powder. The relative standard deviation is less than 2 %. The results are accurate and reliable, consistent with the labeled values on the packing bags.

TABLE-1
SAMPLE ANALYSIS RESULTS

Sample	Labeled content (mg/100 g)	Determination results by the method (mg/100 g)					Average (mg/100 g)	RSD (%)
Milk powder for primary and secondary school students	2.00	2.05	2.03	1.96	2.01	1.98	2.01	1.98
Milk powder for middle-aged and old people	3.75	3.78	3.71	3.80	3.74	3.68	3.74	1.32

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