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Updated β-correction Spectrophotometric Investigation of Zinc Chelate Solution with Acid Chrome Blue K and Determination of Zinc

HANG-WEN GAO
Huaibei Institute of Environment Science
Huaibei, AH 235 000, P.R. China

The updated analysis of zinc chelate solution with acid chrome blue K (ACBK) of pH 8.5 has been studied using β-correction spectrophototmetry. In the determination of this chelate characteristic factors are involved containing the complexation ratio, the real molar absorptivity (ε_γ) and effective percentage of ligand. Besides, because of high sensitivity the chelate reaction is used for the determination of trace amounts of zinc. The results show that the chelate formed is expressed as $Zn(ACBK)_2$ and its $\varepsilon_\gamma = 4.37 \times 10^4$ L·mol^{-1} cm^{-1} at 530 nm which is 3.6 times of its apparent value.

INTRODUCTION

In the field of spectrophotometric analysis one ligand is often selective to chelate a certain metal ion but perhaps not sensitive because of the interference of excess ligand in its metal chelate solution. To increase the sensitivity such an interference must be eliminated. One of the methods is to separate the excess ligand using a physical method, but it is usually very complicated and not practical. Because of this elimination, β-correction principle was established in 1994[1] and later it was improved[2, 3]. It applies the calculation formula to work out the real absorbance of chelate formed and give the effective percentage of ligand in its metal solution. So the effect of excess of ligand is eliminated. This principle has been accepted and widely used[4-8] for the analysis of metal chelates.

The present spectrophotometric determination of zinc involves biacetyl mono-(2-pyridyl)-hydrazone[9], tetraiodofluorescein[10], etc. The ligand, acid chrome blue-K (ACBK) is old one but sensitive and it is often used in titrametric analysis instead of in colorimetric determination because of the serious interference of the excess of ligand. In this paper, the ligand ACBK has been used first for the determination of trace zinc by the described β-correction spectrophotometry. The updated method is different from other dual-wavelength methods[11-13] in principle. It can eliminate the interference of excess ligand to give out the real absorbance of formed chelate. All of the sensitivity, precision and accuracy are higher than those by the single wavelength method. In addition, with β-correction theory, the effective complex percentage of ligand and the metal chelate composition ratio and its real molar absorptivity may be all formulated. Here, it has been found that other metal ions may be separated by extraction with methyl isobutylketone in the presence of potassium thiocyanate and thiourea. The results have shown that the chelate formed is $Zn(ACBK)_2$. Beer's law is obeyed over the concentration range

0.0–1.0 mg/L. Zn and the real molar absorptivity of $Zn(ACBK)_2$ at 530 nm equals 4.37×10^4 L. mol^{-1} cm^{-1}. The average recovery of zinc is between 90.5 to 100% and the relative standard deviation (RSD) is less than 11%.

Principle

The dual-wavelength principle may be illustrated by the following reaction example of ligand (L) with metal (M).

$$aL + bM \rightarrow bML_\gamma + cL$$

where a and b are the molar concentrations of L and M at the beginning, respectively; c is the concentration of excess of L in its M equilibrium solution and the term γ is the stoichiometric ratio of L to M. The real absorbance (Ac) of chelate ML_γ at wavelength λ_2 should be expressed by

$$Ac = (\Delta A - \beta \cdot \Delta A')/(1 - \alpha \cdot \beta) \quad (1)$$

where ΔA and $\Delta A'$ are the absorbances of the chelated solution against its reagent blank at λ_2 and λ_1, respectively, and β and α are named correction coefficients. They can be expressed by, eqn 4 and 5 respectively.

$$\beta = Ao/Ao' \quad (2)$$

and

$$\alpha = A'_\infty/A_\infty \quad (3)$$

where A_0, A_0', A_∞ and A'_∞ are absorbances of L solution and ML_γ solution (when M concentration is much more than L concentration) against water at λ_2 and λ_1 respectively.

The effective percentage (η%) of L and its M complexation ratio (γ) may be expressed by eqns. (4) and (5) respectively.

$$\eta = (Ac - \Delta A)/\beta A_0' \times 100\% \quad (4)$$

and

$$\gamma = M_1(0.01\eta)/M_2 \quad (5)$$

where M_1 and M_2 are the molar concentrations of L and M at the beginning of the reaction.

From ΔA the apparent molar absorptivity (ε_a) of the chelate may be calculated; therefore its real molar absorptivity (ε_γ) should be expressed by

$$\varepsilon_\gamma = \frac{Ac}{\delta \cdot c} \quad (6)$$

where c is the molar concentration of its chelate solution and δ is the thickness (1 cm) of the used cell.

EXPERIMENTAL

Apparatus and Reagents

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai Third Analytical Instruments Plant, China), using a 1 cm cell.

Standard zinc solution, 10.0 mg/L; ACBK (Beijing Chemical, China) solution, 2.00 mmol/L; ammonia buffer solution, pH 8.5; potassium thiocyanate (A.R., Shanghai Chemical); thiourea solution (A.R., Beijing Chemical) solution, 5%; methyl isobutylketone (A.R., Shanghai Organic Chemical); sodium fluoride (A.R., Shanghai Chemical).

Recommended Procedure

To 100 mL of a solution containing less than 25 μg of zinc, add 1 g of NaF, 10 g of potassium thiocyanate and 1 mL of thiourea solution, successively. The solution is transferred into a separating funnel and zinc ion is extracted with two 5 mL portions of methyl isobutylketone. After removing the aqueous layer, zinc ions are stripped with two 5 mL portions of 0.1 mol/L hydrochloric acid. The aqueous layer is taken in a 25 mL volumetric flask. After adjusting pH to about 8 with 1 mol/L sodium hydroxide, add 2 mL of buffer solution and 1.50 mL of ACBK solution. Dilute to required volume with distilled water and mix well. After 5 min, measure the absorbances at 530 and 610 nm, respectively, against a reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra

Fig. 1 shows the absorption spectra of ACBK, Zn(II) chelate and its Zn chelated solution at pH 8.5. From curve 3, we select 530 and 610 nm as the work wavelengths because the sensitivity will reach a maximum. From curve 1, β value has been computed to be 0.768 and from curve 2, α to be 0.456. Therefore,

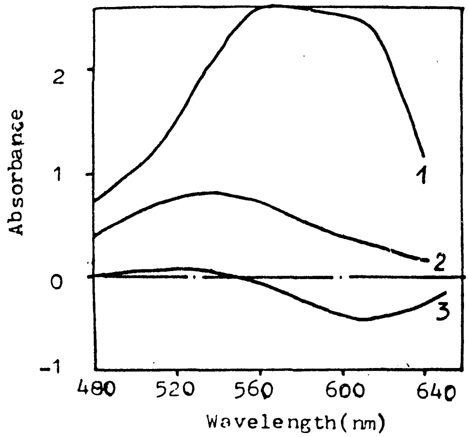

Fig. 1. The absorption spectra of ACBK and its Zn(II) chelated solution at pH 8.5: (1); 0.12 mmol/L ACBK against water (2); $Zn(ACBK)_2$ chelate (measure from the solution containing 0.040 mmol/L ACBK and 0.04 mol/L Zn^{2+} against water) (3); 0.80 mg/L Zn(II) plus 0.12 mmol/L ACBK against a reagent blank.

$$A_c = 1.54(\Delta A - 0.768\Delta A') \qquad (7)$$

Effect of ACBK and Determination of η and γ

Fig. 2 shown the effect of ACBK concentration on the absorbance of ACBK solution at 530 nm against water, that of zinc chelated solution at 530 nm and 610 nm against reagent blank and Ac of Zn-ACBK chelate at 610 nm. From curve 3 because it is difficult to find accurately the inflexion point; the chelate's composition ratio calculation is not possible by the usual method, such as molar ratio[14] method. From curves 1, 2 and 3 both η and γ values can be worked out. Their curves have been drawn in Fig. 3. From curve 2 we see that when the addition (V_0) of ACBK solution is more than 1.0 mL, γ value reaches maximum and remains constant to be 2. The produced chelate may be therefore expressed as $Zn(ACBK)_2$. At the work addition volume, 1.5 mL of ACBK solution, η value

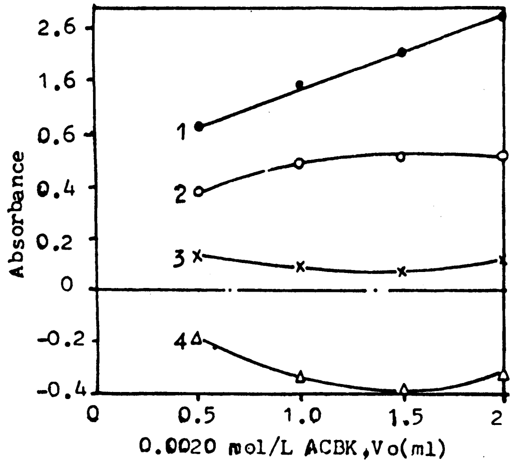

Fig. 2. Effect of ACBK on absorbances at pH 8.5: (1) ACBK solution at 530 nm against water, (2) Ac of Zn-ACBK chelate calculated from curves (3) and (4); (3) 0.80 mg/L Zn solution at 530 nm against a reagent blank; (4), same as 3 at 610 nm.

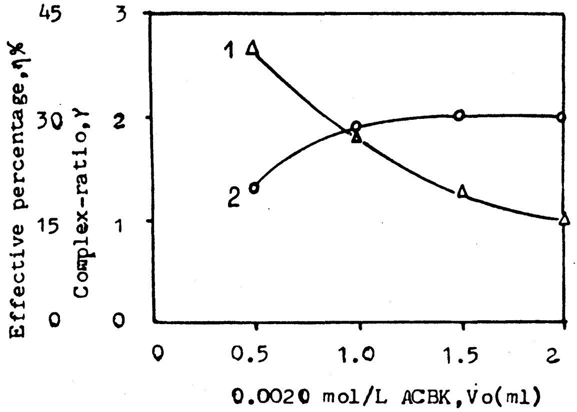

Fig. 3. Curves η and γ against ACBK addition (V_0 mL): (1) η%; (2) γ.

equals about 20% from curve 1. Therefore, the excess of ACBK in 0.80 mg/L Zn(II) will take up 80%. Hence, the excess of ACBK can make a serious effect on the determination of trace zinc and its elimination will increase certainly the analytical accuracy and sensitivity of zinc. The quantitative analytical results will be shown in the sections below.

Effect of Changing Other Conditions

The reaction between Zn(II) and ACBK cannot proceed while pH is less than 6, but zinc hydroxide precipitation will happen while pH is more than 10. Therefore, the working pH may be selected at pH 8.5, where the sensitivity reaches maximum. The formation of the chelate $Zn(ACBK)_2$ is complete in 3 min. Measurement of the absorbance may therefore be carried out in 5 min remaining constant for at least 1 h.

Calibration Graph

A series of standard zinc solutions are prepared and the absorbance of each is measured and plotted against concentration. Curves of Ac and ΔA against Zn concentration (x mg/L) at 530 nm have been drawn in Fig. 4. We see that curve 1 (its relative coefficient, r = 0.9997) is more linear than curve 2 (r = 0.9921). It shows that the accuracy by the β-correction method is higher than that by the single wavelength spectrophotometry. From the slope of curve 1, the real molar absorptivity of chelate $Zn(ACBK)_2$ at 530 nm has been computed to be $4{\cdot}37 \times 10^4$ L mol^{-1} cm^{-1} but it is apparent that it is only 1.21×10^4 L mol^{-1} cm^{-1} from the slope of curve 2. Therefore, the sensitivity by the β-correction method is 3.6 times that by the single wavelength method.

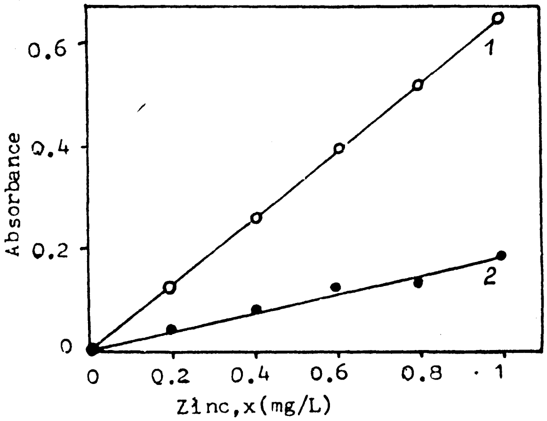

Fig. 4. Standard curves foro the determination of zinc with ACBK at pH 8.5 and at 530 nm: (1), Ac(x); (2) ΔA(x).

Effect of Foreign ions

In the analysis of a sample, the separation of other metal ions must be carried out by the recommended extraction and back-extraction so as to increase the selectivity for the determination of zinc. None of the following metal ions affect the determination of 0.80 mg/L Zn(II): 200 mg/L Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, Ti^{4+}; 10 mg/L Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Cr^{3+}; Be^{2+}, Pb^{2+}; 5 mg/L Cd^{2+}, Mn^{2+} and 2 mg/L Hg^{2+}.

Precision and Detection Limit

Ten replicate dterminations of two standard 0.10 and 0.80 mg/L Zn(II) solutions are made. The relative standard deviations (RSDS) and the maximal relative errors (MRS) were 6.5, 1.4% and 8.0, 4.6%, respectively. However, the RSDS and MRES by the single wavelength method are 15, 9.8% and 26, 14.3%, respectively. Therefore, both the precision and accuracy of β-correction spectrophotometry are higher than those for the ordinary one.

We use 0.010 of a real absorbance to calculate the detection limit of zinc. According to the preconcentration of zinc by the recommended extraction method with methyl isobutylketone, down to 2.0 μg/L, Zn can also be determined. It can satisfy the determination of ultratrace zinc existing in, for example, organisms, underground water, etc.

Analysis of Samples

As a test of the method, zinc was determined in some samples, for example, metallurgical waste water (1), medicinal herbs (2) and underground water (3), etc, The results have been listed in Table-1. The average recovery of zinc is between 90.5 to 100% and the relative standard deviations is less than 11%.

TABLE-1
DETERMINATION RESULTS OF ZINC IN SAMPLES

S. No.	Zn, mg/L		RSD(%)	Recovery(%)
	Added	Found		
1	0	11.4 12.8		
		11.7 12.3	4.1	
		12.0 11.9		
	10.0	23.1 24.1 21.7		109
2	0	1.66 1.58		
		1.49 1.61	3.8	
		1.53 1.58		
	1.00	2.39 2.51 2.54		90.5
3	0	0.073 0.069		
		0.073 0.075	6.8	
		0.076 0.063		
	0.10	0.163 0.171 0.167		95.5
4*	0	0.007 0.006		
		0.006 0.005	11	
		0.006 0.007		
	0.010	0.014 0.017 0.018		103

*Water for especial use

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