Asian Journal of Chemistry Vol. 11, No. 3 (1999), 728–733

β-Correction Spectrophotometry to Improve the Determination of Trace Amounts of Cobalt with 1-(2-Pyridylazo)-2-Naphthol

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Cobalt has been determined in ammoniacal solution with 1-(2-pyridylazo)-2-naphthol (PAN) by β-correction spectrophotometry. The reaction is sensitive and very selective in the presence of thiourea to mask other ions. β-correction spectrophotometry is a new analytical method and it can eliminate completely the effect of excess PAN in its Co(II) coloured solution to give out the real absorbance of the produced Co-PAN complex. All of the sensitivity, precision and accuracy are increased. With the help of the updated principle the complex-ratio of the formed chelate and its true molar absorptivity and its instability constant have been still determined. Results for cobalt showed that the detection limit was 0.014 mg/L and Beer's law was obeyed over the concentration range 0–1.20 mg/L Co at 620 nm. It has been applied to the determination of trace amounts of cobalt in environmental water with satisfactory results.

INTRODUCTION

Cobalt often exists in water polluted by, for example, the metallurgical, chemical, machine-making and other industries. The traditional spectrophotometric determination of cobalt involves with PAR[1], 5-Br-PADAB[2], dithizone[3], NaS-[(4-diethylamino-2-hydroxyphenyl) azo]-1,2,4-triazole-3-carboxylate[4], etc. The reaction of cobalt(II) with 1-(2-pyridylazo)-2-naphthol (PAN) at pH 10 was utilized for the determination of trace amounts of Co in environmental water with an updated β-correction spectrophotometry[5, 6]. It is very selective and almost all of metal ions are allowed to co-exist in the presence of thiourea. β-correction spectrophotometric method was studied for the determination of trace amounts of cobalt in environmental water, using these reactions. The method may eliminate the effect of excess colorant to get real absorbance of a formed complex, increasing analytical sensitivity and decreasing error. It is different from other dual-wavelength colorimetries[7–9]. By means of this principle the complex-ratio of PAN with Co(II) can be improved to determine and it is more accurate in value

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and more easy in principle than that for the usual methods, for example molar ratio[10], equilibrium movement[11], continuous variation[12], etc. In addition, the chelate's characteristic parameters have been first to be worked out, for example, the true molar absorptivity (ε_t) and its instability constant (pK). Results showed for the determination of Co(II) that the detection limit was only 0.014 mg/L and the analysis of waste water showed the recovery of Co(II) was between 95.0 and 107% with the RSD of less than 3.2%.

Principles

The following reaction example of a metal (M) and a complexing ligand (R) is utilized to express the β-correction principle.

$$aM + bR \longrightarrow aMR_\gamma + cR$$

where a and b are the initial concentrations of M and R added, respectively, and c is the excess concentration of R. The term γ represents the complexation ratio of R to M. The real absorbance (A_c) of the chelate MR_γ at the wavelength λ_2 is expressed by[5]

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

where ΔA and $-\Delta A'$ are the absorbances of the above coloured solution at λ_2 and λ_1, respectively, determined against the reagent blank. α and β are named the correction coefficients. They are calculated from

$$\alpha = A'_\alpha/A_\alpha \quad (2)$$

and

$$\beta = A_0/A'_0 \quad (3)$$

where A_α, A'_α, A_0 and A'_0 can all be measured directly from the chelate solution and reagent blank, respectively.

The effective complexation percentage (η%) of R and its M chelate's complex ratio (γ) may be expressed[6] by equations 4 and 5 respectively

$$\eta = (A_c - \Delta A)/(\beta A'_0) \times 100\% \quad (4)$$

and

$$\gamma = 0.01\eta\, M_1V_0/M_2 \quad (5)$$

where M_1 represents the molarity of R solution in mmol/L and M_2 is the molar number of M added in μmol. V_0 is the addition volume, in mL, of solution R.

The apparent molar absorptivity (ε_a) of chelate MR_γ at λ_2 should be computed from a ΔA value. Therefore, it is true that ε_t may be worked out from an A_c value by the following equation:

$$\varepsilon_t = A_c/(\delta C) \quad (6)$$

where δ represents the thickness, in cm, of a cell used and C is the molarity, in mol/L, of M in the above coloured solution.

The coloured solution containing a mol/L M and γa mol/L R is used for the determination of the instability constant (K). Its negative logarithm, pK, can be expressed by[13]

$$pK = \log [\eta/(100 - \eta)] - \gamma \log [a\gamma(1 - 0.01\eta)] \quad (7)$$

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai, China), in a 3 cm glass cell.

Standard cobalt(II) solution, 10 mg/L; PAN solution, 0.030%: dissolve 30 mg of PAN (Shanghai Chemicals, China) in 100 mL of ethanol. Thiourea solution, 2% (A.R., Shanghai Reagents); ammonium buffer solution, pH 10.

Recommended Procedures: A known volume of a water sample containing less than 0.030 mg of cobalt was taken in a 25 mL volumetric flask. Then, added 2 mL of the buffer solution, 0.5 mL of thiourea solution and 0.80 mL of PAN solution, successively. Diluted to volume with distilled water and mixed well. After 20 min, measures the absorbance at 490 and 620 nm, respectively, against a reagent blank and calcualted A_c value from the above equation.

RESULTS AND DISCUSSION

The adsorption spectra of PAN and its Co(II) coloured solution have been shown in Fig. 1. From curve 3, two wavelengths should be selected such that the difference of absorbance is maximum: 490 and 620 nm, with the maximum sensitivity. We may calculate β to be 0.249 from curve 1 and α to be 0.472 from curve 2. Therefore, Equations (1) and (4) can be expressed by equation (8) and (9) respectively

$$A_c = 1.13(\Delta A - 0.249\Delta A') \quad (8)$$

and

$$\eta = 1.13(0.472\Delta A - \Delta A')/A_0' \times 100\% \quad (9)$$

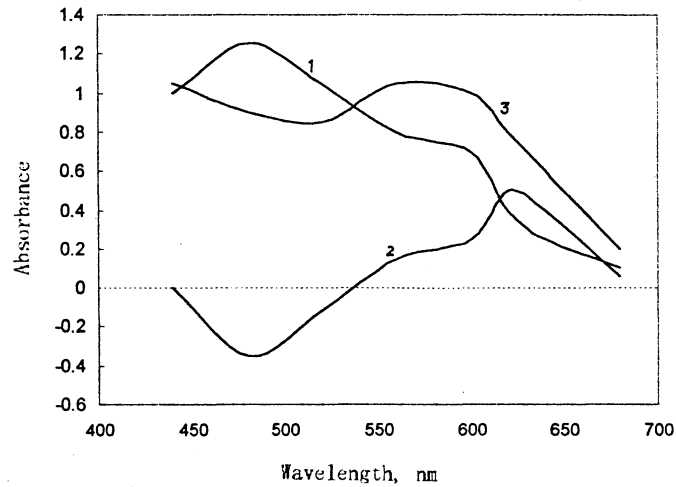

Fig. 1. Absorption spectra of PAN and its Co(II) coloured solution at pH 10: 1, 12 mg/L PAN against water; 2, 0.80 mg/L + 12 mg/L PAN against a reagent blank; 3, only chelate of Co(II) with PAN against water.

Effect of PAN: Fig. 2 shows the effect of the added volume of 0.03% PAN on the absorbance. From curve 2 we find $V_0 \geq 0.5$ mL A_c remains almost constant and reaches maximum. In this work, 0.80 mL was selected. From equations (9) and (5) we can compute η and γ at any V_0, where $M_1 = 1.20$ mmol/L and $M_2 = 0.339$ μmol. Their curves have been shown in Fig. 3 and 4, respectively. From Fig. 4 when $V_0 \geq 0.7$ mL, γ remains constant and maximum to be 1. The

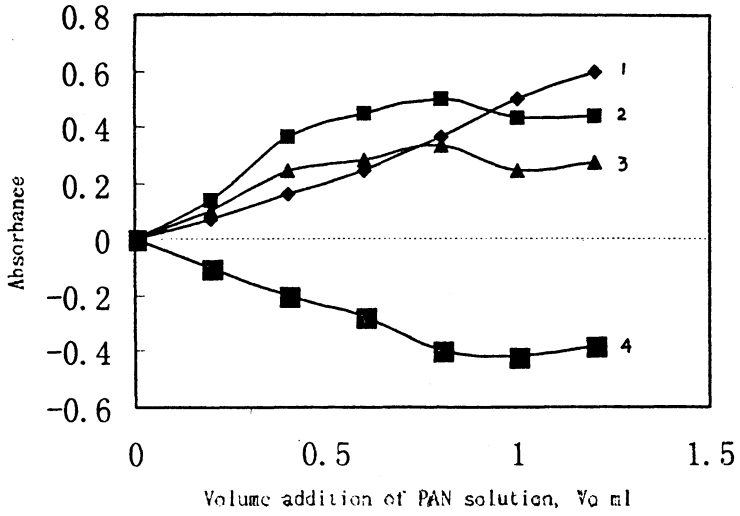

Fig. 2. Effect of PAN on the blanks and its Co(II) coloured solution at pH 10: 1, reagent blanks at 620 nm against water; 2, A_c of 0.80 mg/L Co(II) chelate with PAN, calculated from curves 3 and 4; 3, 0.80 mg/L Co(II) + 12 mg/L PAN at 620 nm against reagent blanks; 4, same as 3 but at 490 nm.

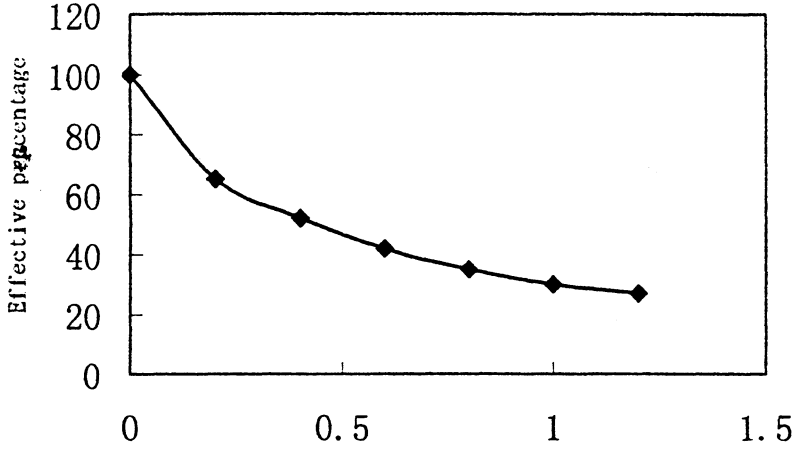

Fig. 3. Curve of η against V_0

formed chelate should be therefore expressed as Co(PAN). We see at $V_0 = 0.80$ mL, η is equal to only 40% from Fig. 3. It indicates that the excess ligand reaches 60% of PAN addition. It is andoubtedly that this excess ligand will affect the measurement of the chelate's absorbance.

Effect of changing other conditions:. The reaction between Co(II) and PAN proceeds rapidly in the pH range 3–11. The results showed that the sensitivity decreases at pH < 6 and the hydroxide precipitate appears at pH > 11. Therefore, pH 10 has been chosen in this study. The formation of the coloured chelate is

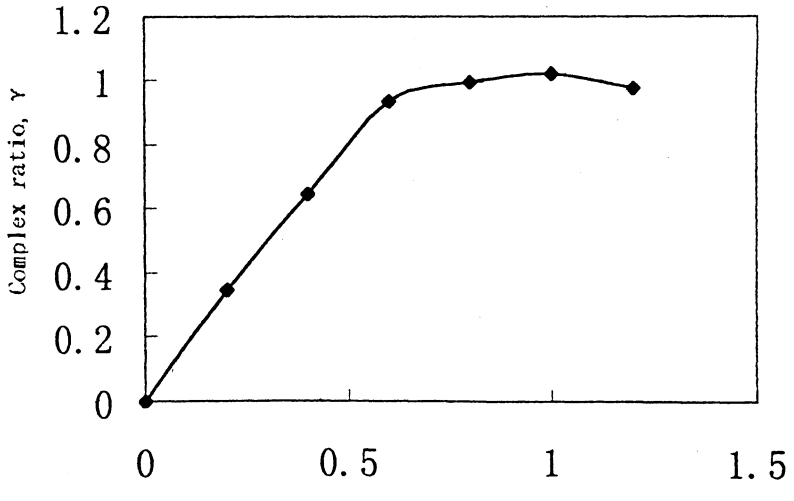

Fig. 4. Curve of γ against V_0

complete in 15 min. Measurement of the absorbacne was therefore carried out 20 min after the addition of PAN.

Calibration graph: A series of standard cobalt solutions were prepared and the absorbance of each was measured and plotted. Curves of A_c and ΔA against Co(II) concentration (× mg/L) at 620 nm have been drawn in Fig. 5. We find that the linearity of curve 1 is better than that of curve 2. Therefore, the accuracy from the β-correction method is higher than that from the single wavelength one. The contrast of the gradient rates shows that the sensitivity with β-correction method is higher than that with the ordinary one. From Equation (6) and curve 1 we are the first to calcualte ε_t of chelate Co(PAN) to be equal to 1.39×10^4 L mol^{-1} cm^{-1} at 620 nm but its ε_a to be 1.01×10^4.

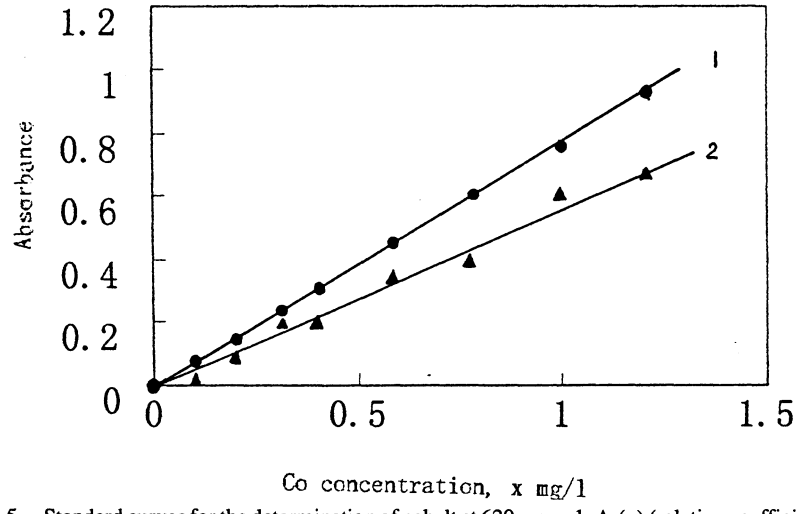

Fig. 5. Standard curves for the determination of cobalt at 620 nm: 1, $A_c(x)$ (relative coefficient, r = 0.9993); 2, $\Delta A(x)$ (r = 0.993).

TABLE-1
DETERMINATON OF COBALT IN WASTE WATER

Sample No.	Co, Mg/L			RSD, %	Recovery, %
	with PAR	Added	Found*		
1.	0.790	0	0.811	1.7	
		0.40	1.240		107
2.	0.066	0	0.069	3.2	
		0.02	0.088		95
3.	0.219	0	0.213	2.1	
		0.20	0.417		102

*Average of 6 determinations

Determination of K constant: Measure the absorbance of the coloured solution containing 0.0384 mmol/L PAN and 0.0384 mmol/L Co(II). The results showed that $\Delta A = 0.643$, $\Delta A' = -0.590$ and $A'_0 = 1.24$. Hence, $\eta = 81.4\%$ from eqn. (9) and $pK = 5.787$ from eqn. (7) and thus the value of K is equal to 1.63×10^{-6}.

Effect of foreign ions: Once thiourea reagent had been added to 0.80 mg/L Co(II), none of the followng ions will affect the direct determination (< 20% error): 100 mg/L Ca, Mg, K, Na, W, Be, Ti, Al, F^-, Cl^-, I^-, 10 mg/L Fe, Cu, Ni, Zn, V, Pb; 1 mg/L Sb, Se, Sn, As, Hg, Cd.

Precision and detection limit: Ten replicate determinations of standard cobalt solution containing 0.10 mg/L were made, the relative standard deviation (RSD) being 2.1%. However, the RSD with the single wavelength method was 8.2%. The precision for the β-correction method is therefore better than that for the ordinary spectrophotometric method. We use a real absorbance of 0.01 to compute the detection limit of cobalt to be equal to 0.014 mg/L.

Samples analysed: As a test of the method cobalt was determined in, for example, the chemical (1), metallurgical (2) and electroplating (3) waste waters. The results have been listed in Table-1. We see that the results by the recommended method are almost same as that with PAR[1].

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(*Received*: 2 November 1998; *Accepted*: 20 February 1999) AJC-1690