

## Reanalysis of Silver Chelate Solution and Determination of Trace Amounts of Silver in Waste Water

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$\beta$ -correction spectrophotometry is a new analytical method that is different from the known dual wavelength techniques.  $\beta$  corrected absorbance can eliminate completely the interference of excess colorant to get real absorbance of a complex produced. With the help of such a principle the complex ratio may still be determined and the result can be more accurate than with other methods. In this paper the reaction of silver (I)-ethyl violet in acidic solution was developed and studied to determine trace amount of Ag(I) in waste water by  $\beta$  correction spectrophotometry. The compound of EDTA-2Na is effective for masking other metal ions. Experimental results have shown that the complex ratio of Ag(I) with EV is 1/2. Beer's law was obeyed over the concentration range from 0 to 40.0  $\mu\text{g}$  of Ag(I) per 25 mL of final solution. The detection limit is 0.03  $\mu\text{g}/\text{mL}$ .

### INTRODUCTION

$\beta$ -correction spectrophotometry is a new analytical method that is developed from spectra of both the colorant and formed complex<sup>1, 2</sup>. The principle is different from one of other dual-wavelength colorimeters<sup>3-5</sup>.  $\beta$ -correction absorbance can eliminate the effect of excess of colorant in the colored solution to get real absorbance of the complex. With this theory to determine microcomponents, high levels of precision, sensitivity and accuracy can be achieved. It was found that the complex ratio can be determined and the result is more accurate compared to the traditional methods such as mole ratio method. In acidic solution Ag(I) can react with ethyl violet (EV) to change the color of the solution from yellow-green to blue. EDTA-2Na can mask other metal ions so that the direct determination of silver is not affected. The method is sensitive and selective. Based on this reaction,  $\beta$ -correction spectrophotometric method was studied for the determination of trace amount of Ag(I) and its complex ratio. Experimental results show that the complex ratio of Ag(I)-EV equals to 1/2, the recovery is between 94.7–107% and the detection limit is 0.03  $\mu\text{g}/\text{mL}$ . The method is suitable for the determination of waste water and polluted water.

### EXPERIMENTAL

Visible spectra were recorded with a spectrophotometer, Model 722, 2 cm glass

cell. Standard silver(I) solution, 10.0 mg/L; ethyl violet solution,  $1.00 \times 10^{-3}$  mol/L: dissolve 49.3 mg ethyl violet (EV, AR, Shanghai, China) in 100 mL of sulfuric acid solution, 0.5%; potassium iodide (KI, AR, Bengbu, China) solution, 10%; sulfuric acid solution, 5%; masking solution of ethylenediamine triacetic disodium salt (EDTA-2Na; AR, Xuzhou, China) solution 5%.

## Procedures

A known volume of waste water containing less than 40.0  $\mu\text{g}$  of Ag(I) was taken in a 25 mL standard flask. 1.0 mL of sulfuric acid solution, 1.0 mL of potassium iodide solution, 0.5 mL of EDTA-2Na solution and 2.0 mL of ethyl violet solution were added. Dilute with water to the desired concentration and shake well. After 10 min measure the absorbances ( $A'$  and  $A$ ) at 440 nm and 560 nm, respectively in a 2 cm cell for the reference by the reagent blank and calculate  $A_c$  from equation (1).

## RESULTS AND DISCUSSION

### $\beta$ -correction principle and absorption spectra

The absorption spectra of both reagent blank and Ag(I)-EV complex are shown in Fig. 1. Graph III is a suppositional curve which shows the absorption spectra of excess reactant in an Ag(I)-EV colored solution.

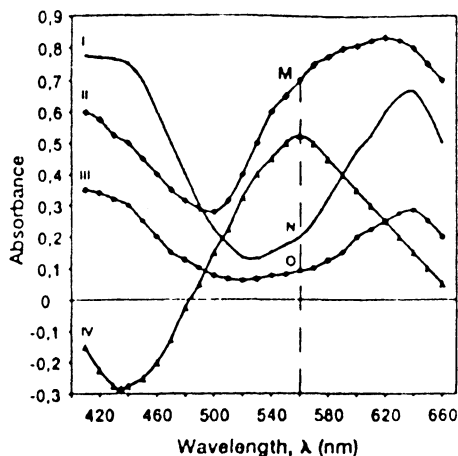


Fig. 1. Absorption spectra of EV-I and Ag(I)-EV-I: I, reagent blank, ref. water; II, Ag(I), ref. water; III, excess EV, ref. water, IV, Ag(I), ref. reagent blank

From graph I to III it can be seen that the absorbance of Ag(I)-EV complex at the wavelength  $\lambda_2$  equals MO but not MN, in order to make  $A_c = MO$  which is called  $\beta$  correction absorbance,  $A_c$  is expressed by the following equation:

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

$A$  and  $A'$  are the absorbances of reacted solution at the wavelength of  $\lambda_2$  and  $\lambda_1$  respectively, which is determined with the blank as a reference.  $\alpha$  and  $\beta$  are constants and computed from the equations

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

(Mole ratio)  $Mr \rightarrow 0$

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

$A_0$  and  $A'_0$  are the absorbances of reagent blank at  $\lambda_2$  and  $\lambda_1$  with water as a reference, respectively.  $A_\alpha$  and  $A'_\alpha$  are the absorbances of a colored solution. The mole ratio ( $Mr$ ) of a colorant reagent with analysed component is extrapolated to zero such as 0.01 at the wavelengths of  $\lambda_2$  and  $\lambda_1$ . We can calculate the complex ratio ( $\gamma$ ) from  $A_c$  value

$$\gamma = M_1 V_0 (A_c - A) / (M_2 A_0) \quad (4)$$

$M_1$  is moles of colorant molecules in 1.0 mL solution.  $M_2$  is moles of testing silver.  $V_0$  is the added volume of colorant solution in mL.

From graph IV, we can see that  $\lambda_1$  and  $\lambda_2$  are selected at the valley and the peak of such a function to optimize the analytical sensitivity. The relation between  $A_c$  and silver (I) concentration ( $x$ ) is a linear function and is expressed by the following equation:

$$A_c = kx + b \quad (5)$$

Here both  $k$  and  $b$  are constants calculated from standard Ag(I) solution. An analytical method following this model is called  $\beta$  correction spectrophotometry.

The absorption spectra of silver(I)-EV are shown in graph IV in figure 1 with maxima and minima at 440 nm ( $\lambda_1$ ) and 560 nm ( $\lambda_2$ ), respectively. From graph I the  $\beta$  value was calculated to be 0.292. When  $Mr$  is extrapolated to zero,  $\alpha = 0.251$ .

*Determination of complex ratio of Ag(I)-EV:* Determinations of the blank and coloured solutions of 40.0  $\mu\text{g}$  of Ag(I) were made. The relations of determined absorbance with the volume of added colorant solution are shown in graphs I, II, III in Fig. 2.

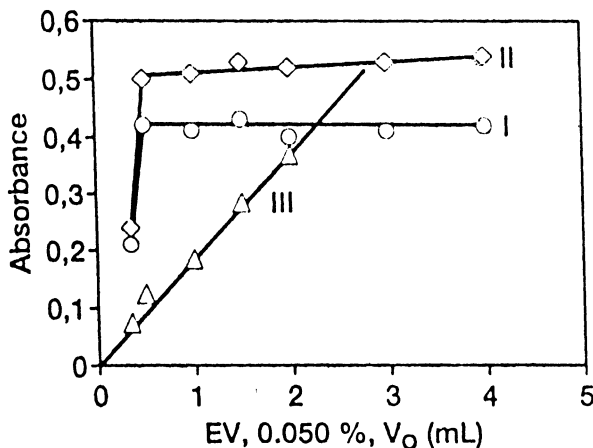


Fig. 2. Effect of colorant solution: I, Ag(I), 40.0  $\mu\text{g}$ , 560 nm, ref. blank; II, real absorbance ( $A_c$ ) of complex; III, reagent blank, 560 nm, ref. water

It can be shown that the complex ratio cannot be calculated accurately by mole ratio method. From graphs I to III, the effective rate ( $\eta$ ) of the colorant molecules which are reacted off and the complex ratio can be calculated accurately. The results are shown in Fig. 3 with  $M_1 = 1.0 \times 10^{-6}$  and  $M_2 = 3.70 \times 10^{-7}$ .

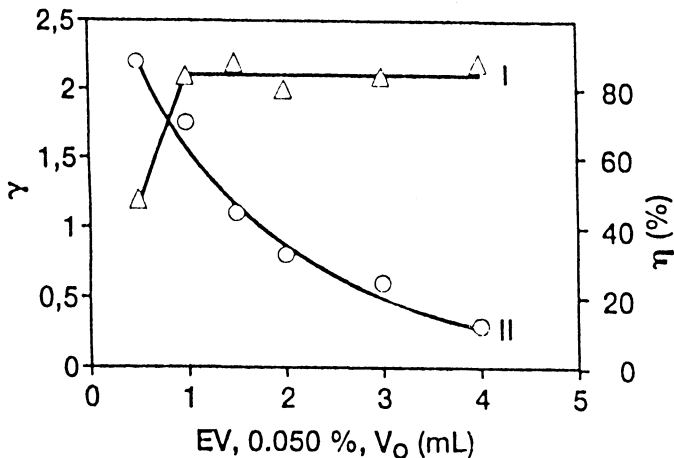


Fig. 3 Curves of calculated parameters: I,  $\eta - V_0$ , II,  $\gamma - V_0$

We see that if  $V_0$  is higher than 1.0 mL the complex ratio reaches a maximum and remains constant as 2. At this time the effective rate is less than 70%.

From graph II in Fig. 2, 2.0 mL of ethyl violet solution was selected as working volume.

*Effect of other operating conditions:* the reaction between Ag(I) and ethyl violet can proceed rapidly in acid solution and potassium iodide is necessary for increasing the analytical sensitivity (Fig. 4). In this study 1.0 mL of sulfuric acid solution and potassium iodide solution was selected. The formation of the colored

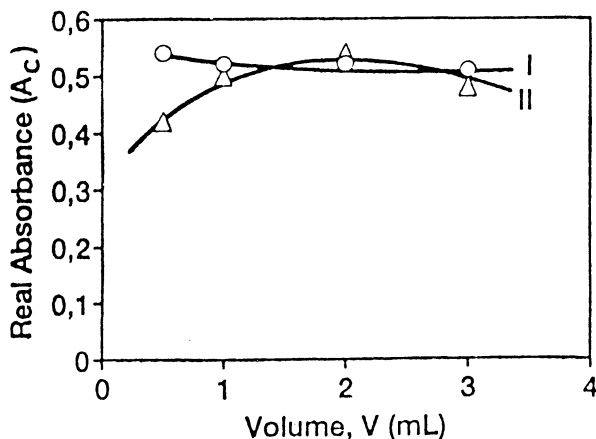


Fig. 4. Effect of  $H_2SO_4$  and KI: I,  $H_2SO_4$  solution; II, KI solution

complex of Ag(I) with ethyl violet and KI is completed after 10 min. Measurement of the absorbance was therefore carried out 10 min after the addition of ethyl violet solution.

**Standard curve [ $A_c(X)$ ]:** A series of standard Ag(I) solutions were prepared and the absorbance of each was measured and plotted in the standard curve. Beer's law was obeyed over the concentration range of 0–40.0  $\mu\text{g}$  of Ag(I) in 25 mL of final solution (Fig. 5). Two curves of  $A_c(x)$  and  $A(x)$  were drawn. From Fig. 5 we can see that graph I [ $A_c(X)$ ,  $r = 0.9993$ ] is more linear than graph II [ $A(x)$ ,  $r = 0.995$ ]. Hence, the sensitivity of the recommended procedure is increased due to higher rate  $k$ .

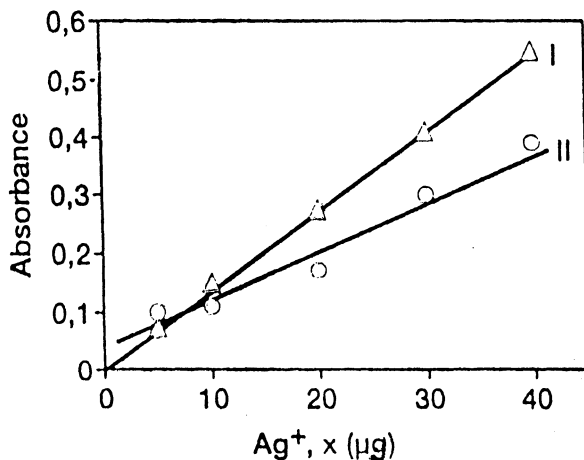


Fig. 5. Standard curves I,  $A_c(X)$ ; II,  $A(X)$ , 560 nm

Consequently,  $A_c(x)$  can be expressed by the following regression equation:  $A_c = 0.0135x - 0.005$ .

**Effect of interfering ions:** After EDTA-2Na solution was added the following concentrations of anions and cations do not affect direct determination: 40  $\mu\text{g}$  of Ag(I); 10.0 mg of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Ti(IV)}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ; 1.0 mg of  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ; 500  $\mu\text{g}$  of  $\text{Cd}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{As(III)}$ ,  $\text{Cu}^{2+}$  and 100  $\mu\text{g}$   $\text{Hg}^{2+}$ .

**Precision and detection limit:** Replicate (6 times) determinations of one standard Ag(I) solution of 20.0  $\mu\text{g}$  are performed with a relative standard deviation (RSD) and maximum relative error (MRE) was 3.5% and 9.6%, respectively. However, RSD and MRE by single wavelength method are 13% and 22%. Therefore, both the precision and accuracy by  $\beta$  correction spectrophotometry are higher than by the single wavelength spectrophotometry. A real absorbance ( $A_c$ ) of 0.010 is used to calculate the detection limit of Ag(I) as 0.03  $\mu\text{g}/\text{mL}$ .

**Samples analyzed:** To prove the validity of the methods Ag(I) was deter-

mined in polluted water. The results summarized in Table-1 show that RSD is less than 4.4% and the recovery was between 94.7–107%.

TABLE-1  
ANALYTICAL RESULTS OF Ag(I) IN WASTEWATER

Wastewater from	Added (mg/L)	found (mg/L) (average of 6 times)	RSD (%)	Recovery (%)
Electroplating	0	0.913	2.1	94.7
	1.00	1.860		
Chem. Lab.	0	0.113	4.4	107.0
	0.10	0.220		
Printing	0	0.416	2.9	98.4
	0.50	0.908		

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