

Development of β -Correction Spectrophotometric Principle and Analysis to Chelates Characteristics

HONG-WEN GAO

Huaibei Institute of Environmental Science

Huaibei, AH 235 000, PR China

A new analytical principle, named β -correction spectrophotometric principle, has been developed for the determination of trace amounts of metal and the analysis of its chelates' characteristic parameters. It is first to eliminate completely the interference of the excess of a ligand from its coloured solution with a metal ion give out the real absorbance of the formed chelate. The reactions of gold(III) and silver(I) with *p*-dimethylaminobenzal rhodanine (PDR) have been used for the determination of their chelates' composition ratio (γ) and practical molar absorptivity (ϵ_p) and the determination of trace amounts of copper has been made with the calculation of the above characteristic parameters, using the new reaction of copper and the ligand, *o*-bromobenzenediazoaminobenzene-*p*-azobenzene (OBDA) at pH 12. Results showed that the chelates formed are $\text{Au}_2(\text{PDR})$, $\text{Ag}(\text{PDR})$ and $\text{Cu}(\text{OBDA})_2$, their respective ϵ_p to 2.79×10^9 , 1.31×10^8 both at 550 nm and $9.41 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 500 nm. The determination for the analysis to practical samples showed that the relative standard deviations were less than 3.1% and the recovery of copper is between 91 and 106%.

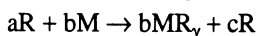
INTRODUCTION

In the modern spectrophotometry, a ligand with high absorptivity is often produced by synthesis because of its highly sensitive reaction with a metal ion. However, because of its high absorption at the working wavelength the single wavelength spectrophotometry is usually limited for the determination of trace amounts of a metal ion and its chelates' characteristic parameters. Otherwise the high error will be brought out. An updated theory named β -Correction Principle has been developed with the detailed procedure in this paper. It is the first method to eliminate completely the effect of the excess of a ligand from its metal coloured solution to bring out the real absorbance of the formed chelate. The method established in this principle is a dual-wavelength method but different in principle and in operation from one of other dual-wavelength methods¹⁻³. Recently, its results were applied for the determination of some metals^{4,5}. Here the author use the two reactions between gold(III) and *p*-dimethylaminobenzal rhodanine (PDR) and silver(I) and PDR at pH 12 in aqueous solution and their chelates' characteristic parameters have been determined by the β -correction spectrophotometry, for example the composition ratio (γ), practical molar absorptivity (ϵ_p) and the instability constant (K). In addition, in order to further prove its universality the reaction of copper(II) and the ligand *o*-bromobenzenediazoaminobenzene-*p*-azobenzene (OBDA) produced by synthesis, was also used to realize the accurate determination of trace amounts of copper with the

analysis of its chelate solution. Results show that γ is more understandable and more acceptable in theory and simpler in operation than one of the usual and present methods, for example, the molar ratio⁶, equilibria movement⁷, continuous variation⁸ and slope ratio, etc. The analysis of the above reactions shows that the formed chelates may be expressed as $\text{Au}_2(\text{PDR})$, $\text{Ag}(\text{PDR})$ and $\text{Cu}(\text{OBDA})_2$, and their respective ϵ_p equal to 2.79×10^3 , 1.31×10^4 both at 550 nm and $9.14 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 500 nm. The determined results for several geological samples were found satisfactory in this method.

Principle

Development of β -Correction Principle: The dual-wavelength principle can be illustrated by the following reaction example of ligand (R) with metal (M):



where a is the added molar concentration of ligand (R) at the reaction in beginning and b is that of metal (M); c is the concentration of the excess of ligand (R) at the reaction equilibrium; γ is the composition ratio of the formed chelate MR_γ . The spectra are drawn in Figure 1. We see that at the wavelength λ_2 the real absorbance (A_c) of chelate MR_γ should be equal to the interval M_5M_7 . We believe

$$M_5M_7 = M_5M_6 + M_6M_7, \quad M_1M_3 = M_1M_2 + M_2M_3$$

and

$$M_6M_7/M_6M_8 = M_1M_3/M_1M_4$$

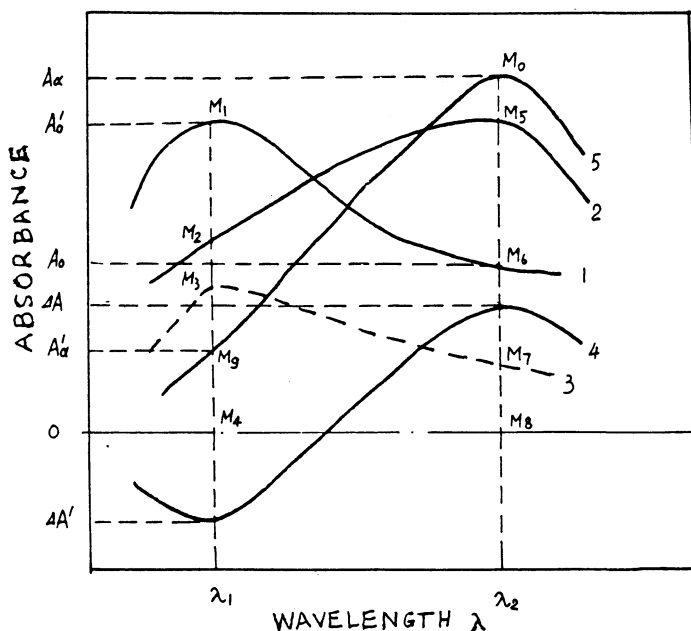


Fig. 1 Spectra of R and its M solution: 1, R (a concentration) against water; 2, $R(b) + M(a)$, against water; 3, excess $R(c)$, against water; 4, same as 2 but against a reagent blank; 5, chelate MR_γ , against water.

and make $\Delta A = M_5M_6$ and $-\Delta A' = M_1M_2$, $A_0 = M_6M_8$ and $A'_0 = M_1M_4$. ΔA and $\Delta A'$ are the absorbance of the above coloured solution, respectively against a reagent blank at λ_2 and λ_1 , and A_0 and A'_0 are that of a reagent blank against water. We design the following relation:

$$\beta = A_0/A'_0 \quad (1)$$

where β is a correction coefficient. From the above equations,

$$A_c = \Delta A - \beta\Delta A' + \beta M_2M_3 \quad (2)$$

We know that the interval between curves 2 and 3 presents the absorbance of chelate MR_γ . From the spectra of a certain concentration, MR_γ without the excess R, which should be formed when b is much more than a, we believe

$$M_5M_7/M_0M_8 = M_2M_3/M_4M_9$$

We make $A_\alpha = M_0M_8$, $A'_\alpha = M_4M_9$, and

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

where A_α and A'_α are the absorbance of concentration MR_γ against water at λ_2 and λ_1 , and α is named the other correction coefficient. From Eqn. (2) we develop the following formula

$$A_c = \frac{\Delta A - \beta\Delta A'}{1 - \beta\alpha} \quad (4)$$

We know that A_c value is in direct proportion to M concentration b. For a reaction if its every operation's conditions have been fixed we believe the $\alpha\beta$ value is constant. Therefore the correction absorbance (A_β)

$$A_\beta = \Delta A - \beta\Delta A'$$

is also directly proportional to b value. We see that if

$$-\beta\Delta A' < 0.1A_\beta \quad (5)$$

the corrected absorbance $-\beta\Delta A'$ may be omitted¹⁰. ΔA is considered to be also directly proportional to M concentration.

From the A_c value we can calculate the practical molar absorptivity (ϵ_p) of chelate MR_γ at λ_2 by the following equation:

$$\epsilon_p = A_c/(\delta b) \quad (6)$$

where δ is the thickness of a used cell in cm and b is M concentration in mol/L.

To see the above coloured solution, at λ_2 the division absorbance (A_d) of the excess R can be computed from the equation: $A_d = A_0 + \Delta A - A_c$. Hence, the effective percentage (η) of R for complexation is equal to $(1 - A_d/A_0) \times 100\%$. Further,

$$\eta = (A_c - \Delta A)/A_0 \times 100\% \quad (7)$$

where all parameters have the same meanings as the above equations.

From a η value we may calculate the chelate's complex ratio (γ) according to the following equation, if the added M will be reacted completely:

$$\gamma = 0.01\eta b/a \quad (8)$$

where both a and b have the same meaning as in the above reaction.

When γ value will reach maximal and remain constant, we believe that this complexation is complete, M ions will be compounded completely and this reaction reaches the maximal sensitivity. Therefore, this maximal γ value presents the composition ratio of chelate MR_γ .

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai 3rd Analytical Instruments, China) in 1 cm cell.

The standard gold solution, 0.100 g/L was prepared by dissolving 0.2092 g of gold chloride in analytical reagent grade (Shanghai First Reagents Plant) in 10 mL of 5 mol/L hydrochloric acid, then diluted to 1000 mL with distilled water. Prepared the standard silver solution, 0.100 g/L, by dissolving 0.1575 g of silver nitrate in analytical reagent grade (Shanghai Reagents Plant) in 5 mL of 10 mol/L sulfuric acid, then diluted to 1000 mL and to place in a brown bottle. 2.00 mmol/L PDR was prepared by dissolving 0.132 g of *p*-dimethylaminobenzal rhodanine (PDR) in analytical reagent grade (Shanghai Third Reagent Plant) in 250 mL of aqueous ammonia (A.R., Huainan Chemical Reagents Plant, China). The following solutions were prepared for the determination of copper and analysis of copper chelate solution: standard copper solution, 1.00 mg/L; OBDA solution, 2.00 mmol/L (provided by Chemistry Department of Huaibei Coal Normal College); Tween 80 solution 2% for dissolving Cu-OBDA chelate and increasing the sensitivity; the tetraborate buffer, pH 12; the diantipyrylmethane solution, 10%, dissolved in chloroform; hydrogen peroxide solution, 2% for oxidizing Cu(I); ascorbic acid solution, 3% for reducing Cu(II); ammonium chloride solution, 20% and ammonia solution, 0.5 mol/L.

Recommended Procedures: Placed 0.100 mmol of standard silver (or gold) in a 25 mL volumetric flask. Added 1 mL of 10% sodium hydroxide and 1.50 mL of PDR solution. Then diluted to volume with distilled water and mixed well. After 16 min, measured the absorbance at 420 and 550 nm, respectively, against a reagent blank. Finally, A_c value can be calculated from the above equation .

Dissolved at first 1 g of a solid sample in solution containing 0.5 mol/L nitric acid and 8 mol/L sulfuric acid and evaporated out the excess acid molecules. Then, dissolved the excess sample with 10 mL of 1 mol/L hydrochloric acid and diluted to 100 mL. A known volume of this solution containing less than 0.005 mg of copper was placed in a 200 mL separating funnel. Added 8 mL of concentrated hydrochloric acid (37% HCl), 10 mL of ascorbic acid solution, 10 mL of ammonium chloride solution and 20 mL of diantipyrylmethane solution. After this solution was shaken strongly, the metal ion Cu(I) was stripped. Then, the back-extraction of copper was carried out with two 10 mL portions of ammonia solution. The final aqueous layer was taken in a 25 mL volumetric flask. Then, added 0.5 mL of hydrogen peroxide solution, 2 mL of the tetraborate buffer solution, 2 mL of Tween 80 solution and 0.50 mL of OBDA solution, successively.

Diluted to volume and mixed well. After 5 min, measured the absorbance at 410 nm and 500 nm, respectively, against a reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: The absorption spectra of PDR, OBDA and that of Ag-PDR, Cu-OBDA coloured solutions and that of their chelate solutions all at pH 12 have been drawn in Figure 2. From curves 3 and 3', the following wavelengths should be selected at the peak and the valley: 550 nm and 420 nm for the reaction between Ag and PDR as well as 410 nm and 500 nm for the reaction between Cu and OBDA, in order to obtain the maximal sensitivity. The calculation of β from curves 1,1' and that of α from curves 2,2' have been resulted: $\beta = 0.061$ and $\alpha = 1.22$ for the reaction of Ag and PDR and $\beta = 0.079$ and $\alpha = 0.31$ for the reaction of Cu and OBDA. In this study, Au(III) coloured solution with PDR had the same spectra as silver solution that with the same α and β .

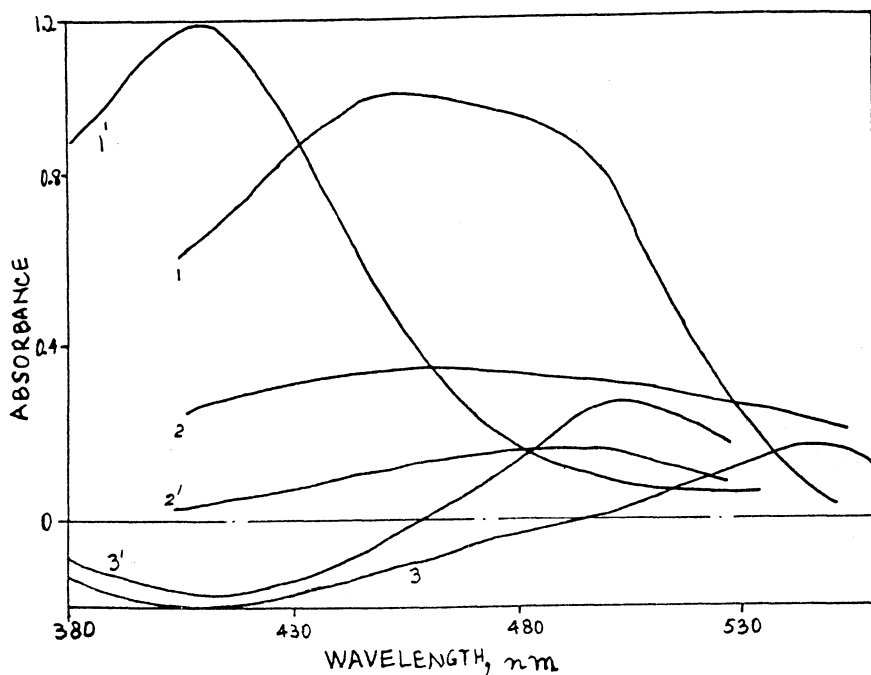


Fig. 2 Absorption spectra of the following solutions at pH 12: 1, 0.120 mmol/L PDR against water; 1', 0.020 mmol/L OBDA against water; 2, 0.016 mmol/L PDR + 2 mmol/L Ag^+ against water; 2', 0.01 mmol/L OBDA + 1 mmol/L Cu^{2+} against water; 3, 0.040 mmol/L Ag(I) + 0.120 mmol/L PDR against a reagent blank; 3', 0.10 mg/L Cu(II) + 0.040 mmol/L OBDA against a reagent blank

Effect of Ligand Solution: The effect of the added volume (V_0) of PDR and OBDA solutions have been shown in Figure 3 on the absorbance of Ag (0.0400 mmol/L)-PDR, Au (0.0400 mmol/L)-PDR and Cu-OBDA solutions and that of

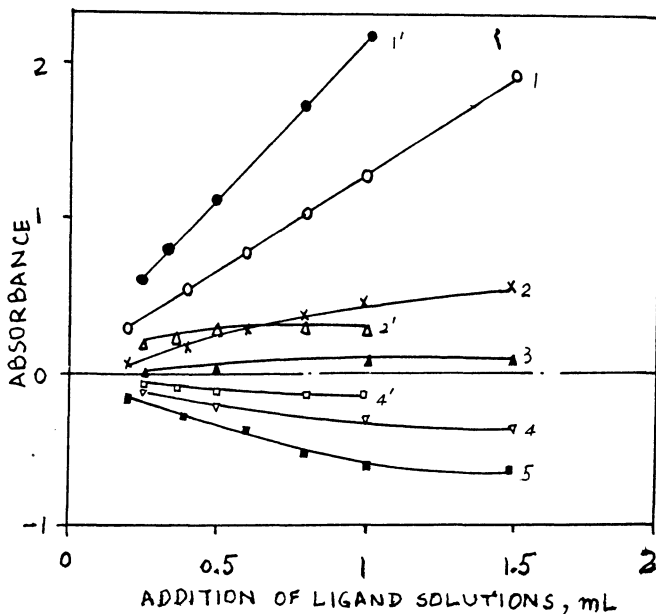


Fig. 3. Effect of ligand concentration on absorbance: 1, PDR solution at 420 nm against water; 1', OBDA solution at 410 nm against water; 2, A_c of 0.040 mmol/L Ag chelate at 550 nm; 3, A_c of 0.040 mmol/L Au chelate; 2', the coloured solution containing 0.20 mg/L Cu at 500 nm against the reagent blank; 4, 0.040 mmol/L Ag(I) + PDR at 420 nm against a reagent blank; 5, 0.040 mmol/L Au(III) + PDR against a reagent blank; 4', same as 2' but at 410 nm

the reagent blanks. Curves 2 and 3 represent A_c curves of Ag and Au chelates at 550 nm, respectively, calculated from the above equation. From curves 2, 3 and 3' because the inflexion point is difficult to be found accurately, the inaccurate determination of the chelate's composition ratio will be resulted by the molar ratio method. From curves 2, 3 and equation 6, we may calculate the chelate's practical molar absorptivity (ϵ_p) at 550 nm, as shown in Table-1 with its apparent

TABLE-1
DETERMINATION OF γ AND ϵ ($\times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$)

M-R	γ	Chelate	ϵ_p	ϵ_a
Au^{3+} -PDR	0.5	$\text{Au}_2(\text{PDR})$	2.79	2.05 (at 550 nm)
Ag^+ -PDR	1	$\text{Ag}(\text{PDR})$	13.10	11.30 (at 550 nm)
Cu^{2+} -OBDA	2	$\text{Cu}(\text{OBDA})_2$	91.40	85.10 (at 500 nm)

molar absorptivity (ϵ_a) calculated from Eqn. 6 but instead of A_c with ΔA . In the same way, both ϵ_p and ϵ_a of Cu-OBDA chelate at 500 nm may be computed and their results are presented in Table-1. From equations 6, 7 and curves

1, 1', 2, 2', 4, 4' and 5 in Figure 3, both η and γ at any V_0 may be calculated. Their curves were drawn in Figure 4. We see from curves 3, 4 and 5 when V_0 is

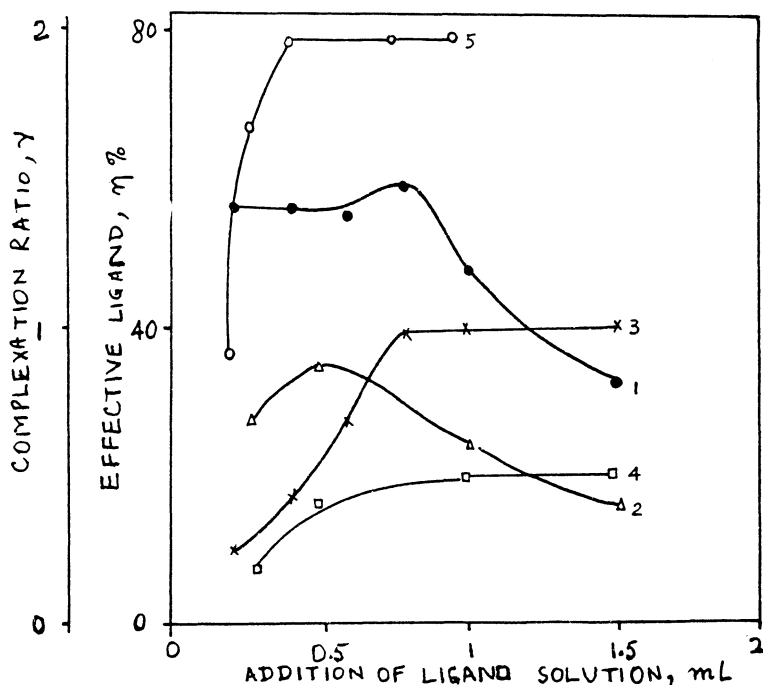


Fig. 4 Curves of η and γ : 1(Ag-ODR) and 2(Au-PDR), η %; 3(Ag-PDR), 4(Au-PDR) and 5(Cu-OBDA), γ

more than a certain value γ reaches maximal and remains constant. Therefore, this constant value should be the composition ratio of metal ion to ligand. From curves 1 and 2 in Figure 4 we see at the recommended volume of PDR solution, $V_0 = 1.50$ mL, η is equal to 35% and 17%, respectively. Therefore, the excess of PDR occupies 65% and 83%, respectively, in 0.040 mmol/L Ag(I) and 0.040 mmol/L Au(III). It was undoubtable that for this excess of ligand to affect seriously the accurate measurement of the chelate's real absorbance and the determination of ϵ_p . In other words, the ordinary wavelength spectrophotometry cannot give out the satisfactory determination of a chelate's characteristic parameters.

Determination of Copper

Effect of Changing Other Conditions: The reaction between Cu(II) and OBDA can proceed fairly rapidly at pH between 11 and 12.5. At pH 12 copper hydroxide is not produced, when Cu concentration was less than 0.20 mmol/L. ΔA was found to remain constant for the addition of 2% Tween 80 between 1 and 6 mL. The formation of chelate $\text{Cu}(\text{OBDA})_2$ was complete in 5 min. The measurement of the absorbance was therefore carried out 5 min of after the addition of OBDA.

Calibration Graph: A series of standard copper solutions were prepared and the absorbance of each was measured and plotted. We calculated the corrected absorbance of Cu coloured solution containing 0.20 mg/L, $-\beta\Delta A'$ was equal to about 0.015 and its correction absorbance A_β to 0.28. From Eqn. 5 because $-\beta\Delta A' < 0.1A_\beta$, ΔA was therefore directly proportional to Cu concentration (x).

Effect of Foreign Ions: Once the recommended procedure was carried out, none of the following ions affected the determination of 20 mg/L copper (< 10% error): 100 mg/L Ca^{2+} , Mg^{2+} , Fe^{2+} , Al^{3+} ; 10 mg/L Cr^{3+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Ce^{3+} , V^{5+} , La^{3+} , Zr^{3+} , Ni^{2+} , Sn^{2+} , Ge^{4+} , Be^{2+} , Pb^{2+} and 0.1 mg/L Cd^{2+} .

Precision and Detection Limit: For ten replicate determinations of a standard solution containing 0.050 mg/L Cu(II), the relative standard deviation (RSD) was equal to 2.3%. The detection limit of copper was 0.007 mg/L for 0.010 of ΔA from the standard curve.

Determination of Sample: As a test of the method, copper was determined in some geological samples. The results were listed in Table-2. We see that the RSDs are less than 3.1% and the recovery of copper is between 91 and 106%.

TABLE-2
DETERMINATION OF COPPER IN SAMPLES

Sample No.	Copper, mg/g		RSD, %	Recovery, %
	Added	Found*		
1.	0	1.240	0.9	102
	1.0	2.260		
2.	0	0.073	2.6	91
	0.10	0.164		
3.	0	0.151	2.1	106
	0.10	0.257		
4.†	0	0.111	3.1	97
	0.10	0.208		

*Average of 6 determinations; †Wastewater in mg/L

REFERENCES

1. H.W. Gao; *Chem. Anal. (Warsaw)*, **39**, 699 (1995).
2. H.W. Gao and P.F. Zhang, *Analyst*, **119**, 2109 (1994).
3. H.W. Gao, *Chin. J. Environ. Sci.*, **13**, 82 (1993).
4. H. Watanabe and H. Ohmori, *Talanta*, **26**, 959 (1979).
5. M.C. Valencia, S. Boudra and M. Bosque-Sendra, *Analyst*, **118**, 1333 (1993).
6. L.C. Kamra, *Anal. Chim. Acta*, **78**, 423 (1975).
7. W. Likussar, *Anal. Chem.*, **45**, 1926 (1973).
8. W.H. Bu, *Kexue Tongbao*, **23**, 415 (1975).
9. B. Tamhina, *Anal. Chim. Acta*, **76**, 417 (1975).
10. H.W. Gao, *Anal. Proc.*, **32**, 225 (1995).