Chinese Chemical Letters Vol. 11, No. 10, pp. 893–894, 2000

Development of Multi-Wavelength Spectral-Correction Method

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Abstract: This investigation developed a new method for determining metal complex's property containing the stepwise real absorptivity (ε) and stability constant (K_m). The correction equation of the multi-wavelength spectral absorption was established for the simultaneous determination of various complexes to give high accuracy for trace analysis. This method was more acceptable in theory and simpler in operation than the classical methods.

Keywords: Simultaneous determination, multi-wavelength spectral-correction, complex property.

Beta-correction theory has been applied extensively for the analysis of metal complex solution[1-3]. Recently, we found that the beta-correction principle was very useful to the determination of metal complex's properties, for example the stepwise real absorptivity (ε) and stability constant (K_m). The new equations were established as follows:

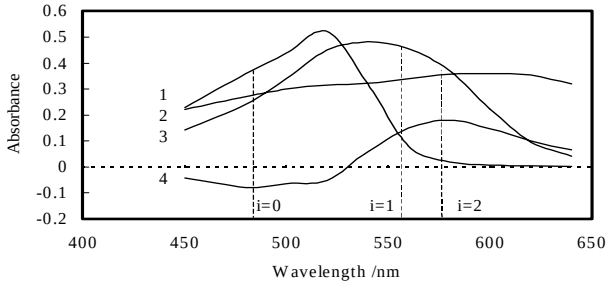
$$K_m = \frac{\gamma'+1-m}{(m-\gamma')(C_{Ligand}-\gamma' C_M)} \quad \text{and} \quad \varepsilon_{ML_m} = \frac{A_c}{\delta C_M(\gamma'+1-m)} - \frac{m-\gamma'}{\gamma'+1-m}\varepsilon_{ML_{m-1}}$$

where $A_c=(\Delta A-\beta\Delta A')/(1-\alpha\beta)$. The term, A_c indicated the real absorbance of complex ML_γ (α, β and γ were all constants), C_{ligand} and C_M were the molarity of ligand and metal, respectively, *m* indicated the *m*-th step complex and γ' the complexation ratio of ligand to metal. The new method was more acceptable in principle and simpler in operation than the ordinary methods such as molar ratio [4], continuous variation [5], equilibrium movement [6], *etc*.

In addition, we studied the multi-reactions between various metals and single ligand. The following correction equation was established: $\sum_{j=1}^{n} a_{ij}x_j = \Delta A_i - \beta_i \Delta A'_0$ ($i=1, 2,\ldots n$) or the matrix expression: $\begin{pmatrix} a_{11} & a_{12} & \ldots & a_{1n} \\ a_{21} & a_{22} & \ldots & a_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ a_{n1} & a_{n2} & \ldots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \ldots \\ x_n \end{pmatrix} = \begin{pmatrix} \Delta A_1 - \beta_1 \Delta A'_0 \\ \Delta A_2 - \beta_2 \Delta A'_0 \\ \ldots\ldots\ldots\ldots \\ \Delta A_n - \beta_n \Delta A'_0 \end{pmatrix}$. Where $\beta_i = \varepsilon_{Ligand}^{\lambda i} / \varepsilon_{Ligand}^{\lambda o}$ and $a_{ij}=A_{\beta i}/x_j$. The term β_i was measured from L solution at wavelengths λ_i and λ_0. The term a_{ij} indicated the linear slope or sensitivity of *j*-th metal at *i*-th wavelength λ_i, which was regressed from the standard solutions. The corrected absorption eliminated the effect of other complexes and the excess of ligand in such a complicated system. This method brought out higher accuracy and better precision than the classical methods [7, 8] in the simultaneous determination of various trace components. The new reactions between ferrous, copper and new ligand dibromo-*o*-nitrophenylfluorone (DBNPF) were

investigated at pH 8 in detail. The absorption spectra were shown in **Figure 1.**

Figure 1 Absorption spectra of DBNPF and its Fe, Cu complex solutions:0.70 μmolDBNPF; 2- Fe (8.0 μmol) - DBNPF (0.70 μmol) complex; 3- Cu(8.0 μmol)-DBNPF (0.70 μmol) complex; 4 - Fe(10.0 μg) - Cu(10.0 μg) – DBNPF (0.70 μmol). 4 against a reagent blank and the others against water



The following calibration equation was established for the simultaneous determination of trace amounts of Fe between 0-5.00 μg/25ml and Cu between 0-10.0 μg/25ml.

$$\begin{pmatrix} 0.0188 & 0.0090 \\ 0.0252 & 0.0092 \end{pmatrix} \begin{pmatrix} x_{Fe} \\ x_{Cu} \end{pmatrix} = \begin{pmatrix} \Delta A_{560nm} - 0.223\Delta A'_{480nm} \\ \Delta A_{580nm} - 0.053\Delta A'_{480nm} \end{pmatrix}$$

Table 1 gave out the determination results of stepwise stability constant (K_j) and stepwise real molar absorptivity($\varepsilon_j^{\lambda i}$) of Fe (j=1) and Cu (j=2) complexes

Table 1 the determination of stability constant and absorptivity of Fe and Cu complexes

j-th step	K_j *(in 0.025 ion strength and 10 ℃)*		$\varepsilon_j^{\lambda i}$ $lmol^{-1}cm^{-1}$	
	$Fe(DBNPF)_3$	**Cu(DBNPF)**	**$Fe(DBNPF)_3$** at 580 nm	**Cu(DBNPF)** at 560 nm
1	5.95×10^6	1.98×10^6	1.20×10^4	1.62×10^4
2	6.05×10^5	/	2.45×10^4	/
3	2.45×10^5	/	3.67×10^4	/

Acknowledgment

This work was supported by the Natural Science Foundation of Anhui Province (No. 99045332).

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Received 13 March 2000