Analysis of Nickel Chelate solution with *m*-Chloroazoantipyrine and Determination of Trace Amounts of Nickel in Wastewater

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The chelate of Ni with *m*-chloroazoantipyrine (CAA) has been studied. Its characteristic factors were analysed for example, instability constant, complexation ratio and practical molar absorptivity. The new usage of β-correction principle has been built here. By means of the disscused ligand, the determination of trace amounts of nickel has been improved at pH 6. Results showed that Ni/CAA = 1:2 in their chelate, its practical molar absorptivity was equal to 3.52×10^4 L. mol^{-1} cm^{-1} at 630 nm and its total instability constant to 3.62×10^{-12} at pH 6 and 32°C with ions strength equal to 0.1. The analysis to wastewater show that the recovery of Ni was between 92.0 and 111% and the relative standard deviations less than 3.8%.

INTRODUCTION

Nickel often exists in waters polluted by, for example the metallurgical, electroplating and other industries. Its conventional spectrophotometric determinations involve with HINAP[1], TAN[2], TTA[3], etc. The reaction of Ni^{2+} and *m*-chloroazoantipyrine (CAA) is sensitive at pH 6 but the inaccurate determination of trace of Ni was brought out from the single wavelength spectrophotometry, because of the effect of the excess ligand on measurement of the real absorbance of the formed chelate. The updated method, nemed β-correction Spectrophotometry[4–6] is the first eliminate completely the excess of a ligand to give the real absorbance of the chelate. It is different in principle from one of other dual-wavelength methods[7–9]. By means of this principle, not only the trace amounts of nickel determined accurately but also the chelate's characteristic parameters may be calculated with the more easy equations and simpler operation than that obtained by the usual methods, for example molar ratio[10], equilibrium movement[11], continuous variation[12] and so on. Results showed that Ni : CAA = 1:2 in this chelate and its practical molar absorptivity is equal to 3.52×10^4 L. mol^{-1} cm^{-1} at 630 nm and its instability to 3.62×10^{-12} at pH 6, temperature 32°C and with ions strength 0.1.

Principle

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

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$$aM + bR \longrightarrow bMR_\gamma + cR$$
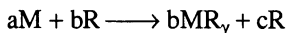
where, a is the molar concentration of M added at the reaction begining and b is that of R; c is the concentration of the excess of R at the reaction equilibrium; γ is the composition ratio of the formed chelate MR_γ. At the wavelength λ_2 the real absorbance (Ac) of chelate MR_γ may be expressed by[4]

$$Ac = \frac{\Delta A - \beta \Delta A'}{1 - \beta \alpha} \tag{1}$$

where ΔA and $\Delta A'$ are the absorbance of the above solution, respectively against a reagent blank at λ_2 and λ_1. Both α and β are named the correction coefficients and their expressions are followed, respectively by

$$\beta = A_0/A_0' \tag{2}$$

and $$\alpha = A_\alpha'/A_\alpha \tag{3}$$

where A_0, A_0', A_α and A_α' are shown in Fig. 1 with the easily understandable meanings.
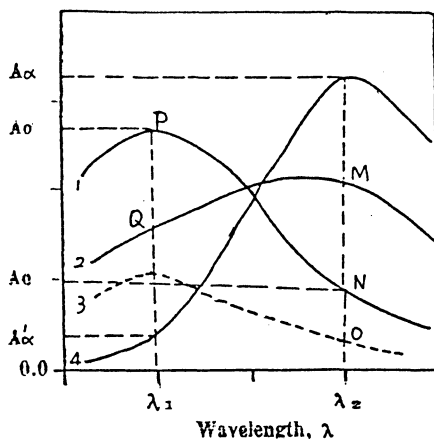
Fig. 1   Spectra of R and its M chelated solution: 1, R (b concentration); 2, MR_γ(a) + R(c); R (c); 4, MR_γ all against water.

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

$$\varepsilon_p = A_c/(\delta_a) \tag{4}$$

where δ is the thickness of a used cell in cm and a is the same as the above reaction, in mol/L.

The effective percentage (η) of R for complexation is expressed by[5]

$$\eta = (A_c - \Delta A)/A_0 * 100\% \tag{5}$$

From a η value we may calculate the complexation ratio (γ) according to the following equation, if the added M will be reacted completely.

$$\gamma = 0.01\eta b/a \tag{6}$$

where a and b have the same meanings as the above reaction. When γ value will reach maximum and remain constant, we believe this complexation is complete and this reaction reaches the maximum sensitivity. Therefore, this maximum γ value presents the composition ratio of chelate MR_γ.

In order to the instability constant (K) of chelate MR_γ, we discuss the following equilibria using the reaction of b concentration R and a concentration M (in mol/L):

$$\underset{\substack{b \quad\quad a \quad\quad 0}}{\gamma R + M \overset{K^{-1}}{\rightleftharpoons} MR_\gamma}$$

at beginning

At equilibrium, there are R, M, MR, $MR_2 \ldots MR_\gamma$ in chelated solution and every equilibrium exists. Therefore we can list the following equation:

$$s + K_1 b0(s - 1) + K_1 K_2 b0^2(s - 2) + \ldots + K_1 K_2 \ldots K_n b0^n(s - n) = 0 \qquad (7)$$

where s = the computed γ (for example $\gamma_1, \gamma_2, \gamma_3, \ldots$), $b0 = (1 - 0.01 \cdot \eta)b$ and $K_1, K_2, \ldots$ are equilibrium constants, this is stability constant, corresponding each step equilibrium. The total stability constant can be expressed by[13]

$$K = K_1 \cdot K_2 \cdot \ldots \cdot K_1 \cdot \ldots \cdot K_n \qquad (8)$$

and chelate's instability constant $\zeta = K^{-1}$.

The above $K_1, K_2, \ldots$ may be worked out from 0 point tangent line of γ curve against ligand (R) initial concentration (b), by the help of a computer program[13].

EXPERIMENTAL

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

Preparation of the following solution were made. Standard Ni(II) solution, 10.0 mg/L was made by dissolving pure metal nickel in concentrated nitric acid and then diluting it. CAA solution, 1.50 mmol/L was prepared for complexing Ni(II), provided by Shanghai Changke Reagents Station. The masking solution was made by dissolving 5 g of thiourea and 2 g of acsorbic acid in 100 mL of water, for masking other metal ions. The acetate buffer solution, pH 6 was prepared for adjusting the constant pH value of the chelated solution.

Recommended Procedure: A known volume of a sample water containing less than 20 μg of nickel was taken in a 25 mL volumetric flask. Added 3 mL of buffer solution, 1 mL of the masking solution and 1.00 mL of CAA solution, successively. Diluted to volume and mixed well. After 10 min, measures the absorbance at 630 and 540 nm, respectively, against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra: Figure 2 showed the absorption spectra of CAA, Ni—CAA chelate and their chelated solution. From curve 3 two wavelengths should be selected to bring out te maximal sensitivity: 540 and 630 nm, which represent the curve's peak and valley, respectively. $\beta = 0.223$ from curve 1 and $\alpha = 0.631$ from curve 2. Therefore, from equation 1
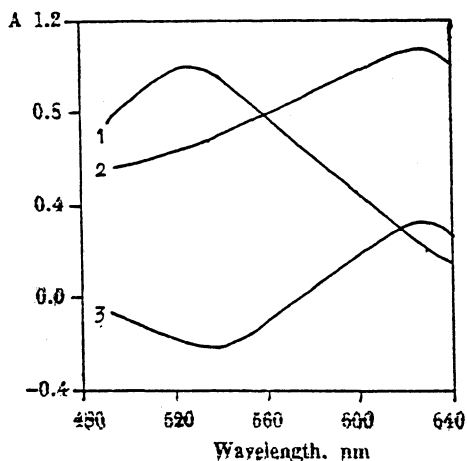
$$Ac = 1.16(\Delta A - 0.223\Delta A')$$

Fig. 2   Absorption spectra of CAA and its nI chelated solution at pH 6: 1, 0.06 mmol/L CAA against water; 2, Ni-CAA chelate against water, formed by 100 mg/L Ni(II) + 0.06 mmol/L CAA (in this solution, CAA is complete to complex Ni and the excess of CAA equals to zero.); 3, 0.06 mmol/L CAA + 0.80 mg/L Ni(II) against a reagent blank.

Effect of CAA: The effect of CAA concentration has been drawn in Figure 3 on the absorbance of the reagent blanks at 540 nm against water and on that of 0.80 mg/L Ni(II) at 540 and 630 nm against the reagent blank. From curve 2 we found that it is difficult to calculate the accurate complex-ratio of CAA to Ni with the Molar Ratio method because the inflexion point cannot be decided. Both η and γ can be computed from Eqns 5 and 6 and their curves against CAA concentration have been shown in Fig. 4. From curve 1 when the added volume of CAA solution is more than 0.50 mL γ remains constant to be 2. The formed chelate ion should be expressed by $[Ni(CAA)_2]^{2+}$. From curve 2 we found that at
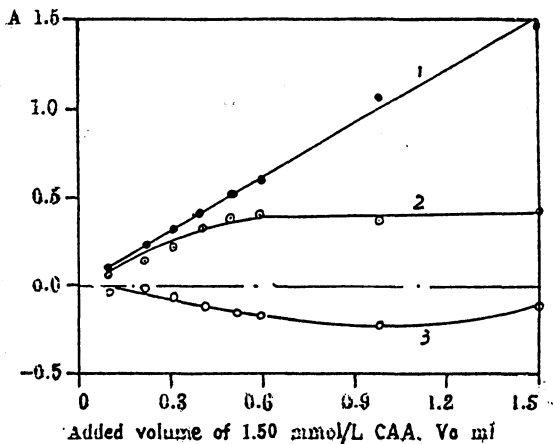
Fig. 3   Effect of CAA on reagent blnaks and their Ni(II) chelated solutions at pH 6: 1, reagent blanks at 540 nm against water; 2, the chelated solution containing 0.80 mg/L Ni at 630 nm against the reagent blank; 3, same as 2 but at 540 nm.

the working volume of CAA solution, 1.00 mL, η was equal to only 50%. It showed that the excess of CAA occupied 50% in 0.80 mg/L Ni(II). It is therefore undoubtedly that the above excess CAA will affect the accurate measurement of the absorbance of the formed chelate and its molar absorptivity.

Calculation of Equilibrium Constant: From curve 1 in Figure 4, we can calculate the tangent line's gradient value of 0 point, $d\gamma/dC_{CAA} = 6.67 \times 10^4$. In addition, we also know $a = 1.36 \times 10^{-5}$ mol/L and $\gamma = 2$. The step equilibrium constant is therefore calculated using Eqn. 7 and the recommended computer program, as follows: $K_1 = 7.17 \times 10^5$ and $K_2 = 3.85 \times 10^5$. In further, the total stability constant $K = 2. 76 \times 10^{11}$ from Eqn. 8 and its instability that $\zeta = 3.62 \times 10^{-12}$. The above constants are all based on the following conditions: pH = 6 and experimental temperature 32°C and ions strength as 0.1.
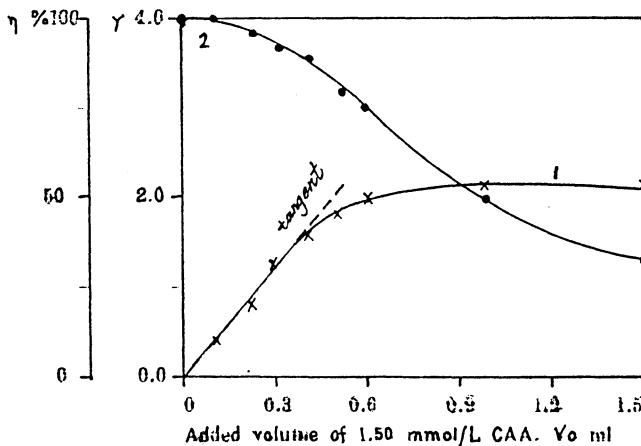

Fig. 4   Curves of γ and η: 1, γ; 2, η%.

Effect of changing other conditions: The reaction bewteen Ni(II) and CAA can proceed fairly at pH between 4.5 and 7. pH 6 was selected with the maximum sensitivity in this work. The formation of the chelate was complete in 10 min at the room temperature, 32°C. The measurement of absorbance was therefore carried out 10 min, the colours remaining constant for at least 2 h.

Calibration graph: A series of standard Ni(II) solutions were prepared and the absorbance of each was measured. Curve of Ac and ΔA against Ni concentration (x mg/L) have been shown in Fig. 5. Curve 1 (the relative coefficinet, R = 0.9994) is more linear than curve 2 (R = 0.995) at 630 nm. It shows that the accuracy for the β-correction method is better than that obtained by the single wavelength spectrophotometry. From curve 1 we can compute the chelate's practical molar absorptivity (ε_p) at 630 nm is equal to 3.52×10^4 L. mol^{-1} cm^{-1} but its ε_a to 2.68×10^4 from curve 2. Therefore, the sensitivity with the β-correction method is also higher than that obtained by the single wavelength spectrophotometry.

Precision and Detection Limit: Ten replicate determinations of 0.10 mg/L Ni^{2+} were made, the relative standard deviation (RSD) being 1.7%. However, the RSD obtained by the single wavelength method was equal to 3.5%. The precision
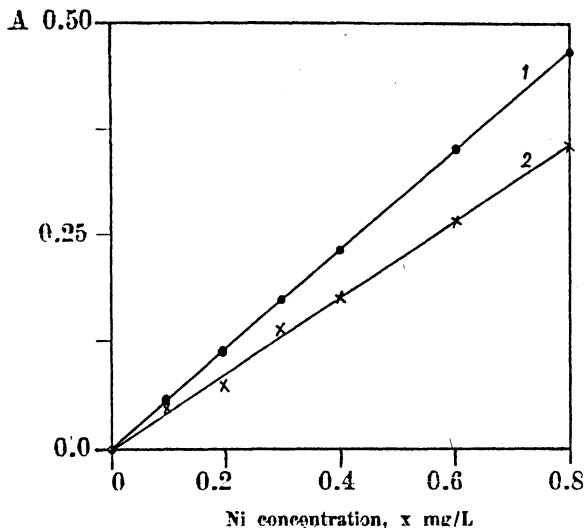
Fig. 5   Standard curves at 630 nm for the determination of nickel using the reaction of Ni(II) and CAA at pH 6: 1, Ac – x; 2, ΔA – x.

obtained by the β-correction method is higher than that obtained by the single wavelength spectrophotometry.

We use 0.010 of a real absorbance to compute the detection limit of nickel to be 0.02 mg/L.

Effect of Foreign Ions: Once the recommended masking solution had added to 0.1 mg/L Ni^{2+}, none of the following ions affected the direct determination: 100 mg/L Ca^{2+}, Mg^{2+}, Ba^{2+}; 10 mg/L Al^{3+}, Be^{2+}, Ti^{4+}, Zn^{2+}, Pb^{2+}, Sn^{2+} and 1 mg/L Cu^{2+}, Fe^{2+}. The metals ions, Co^{2+}, Cd^{2+} and Hg^{2+} were found to interfere the determination of Ni(II).

Samples Analysed: As a test of the method, nickel has been determined in several wastewaters samples. The results showed that the RSDs were less than 3.8% and the recovery of standard nickel between 92.0 and 111%.

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