

## Aggregation of Dye on Polymer: Naphthochrome Green/PVP/Cu(II) Interaction and Determination of Cu Traces

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### ABSTRACT

The interaction of naphthochrome green (NCG) with polyvinylpyrrolidone (PVP) and the complexation of NCG with Cu on PVP chain were investigated in basic medium by the spectral correction technique. The binding of NCG on PVP by the electrostatic attraction obeys the Langmuir isothermal adsorption in aqueous solution. Both the NCG–PVP aggregate and Cu–NCG–PVP ternary complex was characterized at 20°C, 40°C, and 60°C. The presence of PVP sensitized the complexation between Cu and NCG. This novel approach is sensitive and selective in the presence of citrate and has been applied to the quantitative detection of Cu traces in samples with satisfactory recovery.

*Key Words:* Spectral correction technique; Polyvinylpyrrolidone; Naphthochrome green; Langmuir aggregation; Determination of Cu traces.

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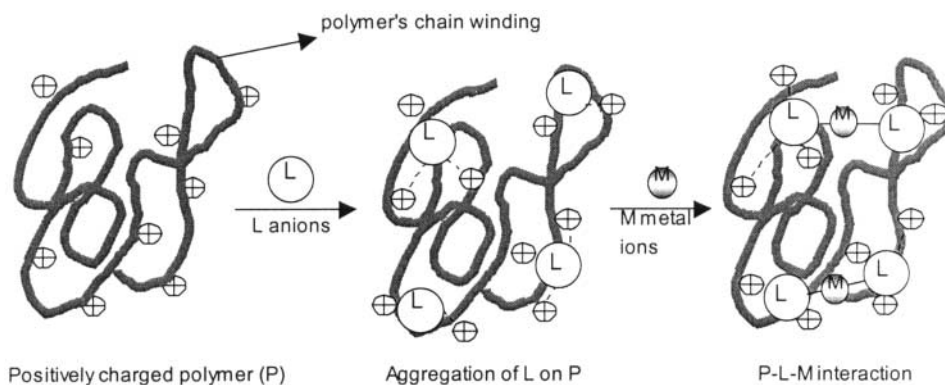
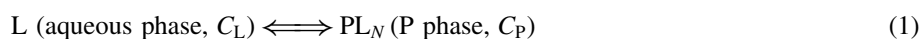
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## INTRODUCTION

In a sensitive analysis of trace components analytical chemists are always interested in the participation of a surfactant as a synergistic agent. Some synergistic mechanisms have been reported, such as synergism perturbation<sup>[1]</sup> and hydrogen bond formation.<sup>[2]</sup> Some polymers are surface-active and they can decrease the surface tension of a solution. The polymeric chain is often very long and carries many charges in an acidic or basic solution. For instance, a poly(maleic acid) chain will carry many negative charges in neutral and basic media and polyaniline carries great amounts of positive charges in acidic media due to the protonation of its amino groups. Though, winding and bending the chain will form a large and densely charged particle. The particle attracts and enriches small oppositely charged molecules or small counterions on its charged chain, so we believe that some of polymers have synergistic functions as surfactants too.<sup>[3]</sup> Recently, the study of the polymer–biomacromolecule interaction, e.g., protein and DNA,<sup>[4–7]</sup> another polymer,<sup>[8,9]</sup> and surfactant<sup>[10]</sup> was disclosed. The design and preparation of a solid dye-polymer thin film was reported too.<sup>[11–13]</sup> In fact, it is quite possible that a suitable polymer as synergistic agent will make a complexation more sensitive than any surfactant.

## PRINCIPLE AND CALCULATION

The interaction of a polymer (P) with a dye (L) is sketched in Fig. 1. The winding of P molecules in solution forms a large electrostatic body (Fig. 1, left). The electrostatic attraction of L with opposite charge occurs on the P chain until a kinetic equilibrium is attained (Fig. 1, middle). As a result, a much higher L in the P phase than in the aqueous phase. Certainly, the addition of a metal (M) will cause a more sensitive complexation of M with L fixed on P chain (Fig. 1, right) and the coordination reaction becomes more easy and rapid too. Like a catalyst carrier, P sensitizes the M–L complexation. The following equilibrium occurs:



**Figure 1.** Sketch of the electrostatic adsorption of dye probe (L) on polymer (P) chain and its complexation with a metal (M).



The aggregation of L on P obeys the Langmuir isothermal adsorption<sup>[14]</sup> as follows:

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_L} \quad (2)$$

where  $K$  is the equilibrium constant and  $C_L$  the concentration of the excess L and  $\gamma$  is the molar ratio of L adsorbed to P. With an increase in L concentration,  $\gamma$  will approach a maximum, called the adsorption ratio  $N$ .  $\gamma^{-1}$  vs.  $C_L^{-1}$  is a linear function from which we can calculate  $N$  and  $K$ . Both  $C_L$  and  $\gamma$  are calculated by means of:<sup>[15,16]</sup>

$$\gamma = \eta \times \frac{C_{L0}}{C_P} \quad (3)$$

$$C_L = (1 - \eta)C_{L0} \quad (4)$$

where

$$\eta = \frac{A_c - \Delta A}{A_0} \quad (5)$$

where  $C_P$  and  $C_{L0}$  are the initial concentrations of the P and L, and  $\eta$  indicates the effective fraction of L.  $A_c$ ,  $A_0$ , and  $\Delta A$  are the real absorbance of the P–L product, the measured absorbance of the reagent blank against water, and that of the P–L solution directly measured against reagent blank at the peak wavelength  $\lambda_2$ , respectively.  $A_c$  is calculated by means of:<sup>[17]</sup>

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta} \quad (6)$$

where  $\Delta A'$  indicates the absorbance of the P–L solution measured at the valley absorption wavelength  $\lambda_1$ . Both  $\alpha$  and  $\beta$  are the correction constants; they are calculated by directly measuring directly  $PL_N$  and L solutions.

In the present work, the interaction of the polymer, polyvinylpyrrolidone (PVP), and naphthochrome green (NCG) was investigated. In aqueous solution, the amide-N atoms of PVP carries many positive charges and they can attract NCG anions by electrostatic attraction. Thus, the complexation of Cu with NCG on PVP becomes sensitive. The cooperation of both the Langmuir isothermal adsorption and the spectral correction technique may provide a very helpful experimental strategy to study the interaction of a dye with a polymer.

## EXPERIMENTAL

### Apparatus and Reagents

Absorption spectra were recorded on a TU1901 Spectrophotometer (PGeneral, Beijing) and independent absorbance was measured on a Model 722 spectrophotometer. DDS-11A conductivity meter, (Tianjin Second Analytical Instruments, Tianjin, China) was used to measure conductivity together with DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Devices, Shanghai, China) in deionized water of less than  $0.5 \mu\Omega^{-1} \text{cm}^{-1}$ . The pH of the solution was measured with a pH5-2C



acidity meter (Leici Instruments, Shanghai, China) and Model 630D pH Pen (Shanghai Ren's Electronics, Shanghai, China). The temperature was maintained constant in a Model 116R electrically heated thermostatic bath, (Changjiang Test Instruments of Tongjiang, China).

Stock solution of PVP (1 mg/L) was prepared by dissolving PVP K-30 (molecular weight 40,000, Shanghai Reagents, China Medical Group, Shanghai, China) in deionized water. Stock NCG solution (1 mg/mL) was prepared by dissolving 0.2500 g of NCG (C.I. 44,530, content 75%, Koch-Light Laboratories, Colnbrook, Berks, England) in 250 mL deionized water. This solution contains 1.38 mmol/L NCG and 0.100 mg/mL (0.138 mmol/L) NCG was prepared daily before use by diluting the stock solution above. The buffer solutions from pH 8.30 and 12.05 were prepared with ammonium and its salt, acetate and acetic acid, phosphate, and sodium hydrate, which were used to adjust the acidity of the solution. The PVP–NCG aggregate solution (L') was prepared by mixing 40 mL (55  $\mu$ mol) of NCG (1 mg/L), 1.1 g (27.5  $\mu$ mol) of PVP and 10 mL of pH 11.55 buffer solution and diluting to 250 mL with deionized water. In the solution, 0.220 mmol/L NCG<sub>2</sub>PVP aggregate was formed at room temperature. Then 2 mol/L NaCl was used to adjust the ionic strength of the aqueous solution. Standard stock Cu solution (100  $\mu$ g/mL) was prepared by dissolving 0.1000 g of pure copper metal (content > 99.95%) HNO<sub>3</sub> and then diluting to 1000 mL with deionized water. Standard Cu solution (5  $\mu$ g/mL) was prepared daily by diluting the above solution. Sodium citrate of 5% was used as the masking reagent to mask the other metal ions in detection of Cu.

## General Procedures

### Interaction of Polyvinylpyrrolidone with Naphthochrome Green

Into a 25-mL calibrated flask were added 8 mL of 1 mg/L PVP, 2.5 mL of the buffer solution and an appropriate volume of 0.100 mg/mL NCG. The mixture was diluted to 25 mL with de-ionized water and mixed thoroughly. After 5 min, the absorbances were measured at 544 and 633 nm, respectively, against the reagent blank treated in the same way, but without PVP, and  $A_c$ ,  $\eta$ ,  $\gamma$ , and  $C_L$  were calculated.

### Quantitative Detection of Cu

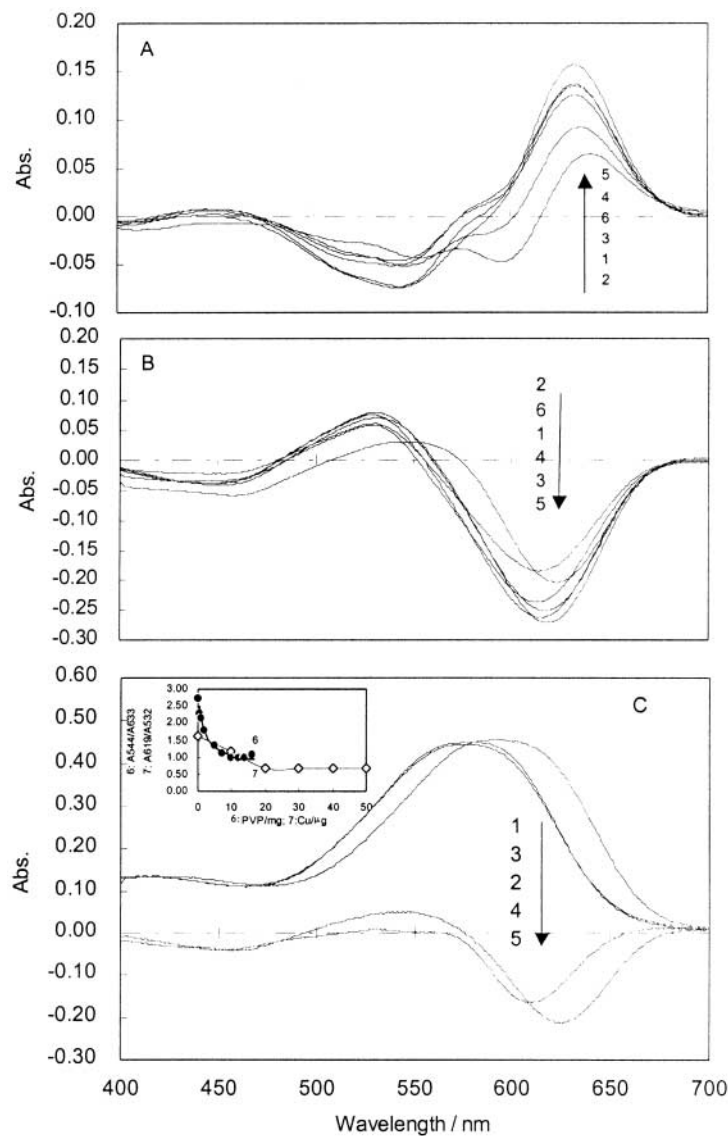
A sample of 10 mL containing less than 18  $\mu$ g of Cu(II), was added to a 25-mL calibrated flask followed by 2 mL of the masking reagent and 2.50 mL of L' solution. After 10 min, the absorbances were measured at 532 and 619 nm, respectively, against the reagent blank treated in the same way, but without Cu, and  $A_c$  of the ternary complex was calculated.

## RESULTS AND DISCUSSION

### Effect of pH on Absorption Spectra

The effect of pH on the absorption spectra of the PVP–NCG and PVP–NCG–Cu solutions is shown in Fig. 2. From the curves in Fig. 2(A) and 2(B), we observe that both





**Figure 2.** Absorption spectra of NCG, NCG-PVP, and Cu-NCG-PVP solutions at pH 11.55: (A) from 1 to 6: NCG (0.400 mg)-PVP (8.0 mg) in 25 mL solution at pH 8.30, 9.56, 9.86, 10.9, 11.55, and 12.02 against the reagent blank; (B) from 1 to 6: NCG (0.400 mg)-PVP (8.0 mg)-Cu (20  $\mu$ g) in 25 mL solution at pH 8.30, 9.56, 9.86, 10.9, 11.55, and 12.02 against the reagent blank; (C-1) NCG (0.400 mg) in 25 mL solution against water; (C-2) NCG (0.400 mg)-PVP (14 mg) in 25 mL solution against water; (C-3) NCG (0.400 mg)-PVP (14 mg)-Cu (40  $\mu$ g) solution against water; (C-4) NCG (0.400 mg)-Cu (10  $\mu$ g) in 25 mL solution against a reagent blank; (C-5) NCG (0.400 mg)-PVP (14 mg)-Cu (10  $\mu$ g) in 25 mL solution against a reagent blank; (C-6) effect of PVP on the ratio of absorbances of the 25 mL solution containing 0.400 mg of NCG, measured at 544 and 633 nm; and (C-7) effect of Cu(II) on the ratio of absorbances of the solution containing 0.400 mg of NCG and 14 mg of PVP, measured at 619 and 532 nm.



the PVP–NCG and PVP–NCG–Cu interactions are more sensitive in basic solution. Among them, spectrum 5 gives the maximal peak and valley in a pH 11.55 buffer solution. From curve C-1, the peak absorption of the NCG solution is located at 580 nm. From curve C-6, we observe that the absorbance ratios of the solution measured at 544 and 633 nm approach a minimum when PVP is over 10 mg in a solution containing 0.400 mg of NCG. So, this solution is composed of only PVP–NCG aggregate and excess PVP, but not any longer of free NCG. Curve C-2 gives the spectrum of the PVP–NCG aggregate; its peak is located at 600 nm. The spectral red shift of the PVP–NCG aggregate is only 20 nm. Similarly, from curve C-7, the absorbances ratio of the solution measured at 619 and 532 nm approaches a minimum when Cu(II) is over 20  $\mu\text{g}$ . This solution contains only Cu–PVP–NCG aggregate, excess PVP, and free Cu(II), but no longer contains free NCG. Curve C-3 gives the spectrum of the Cu–PVP–NCG aggregate; its peak is located at 580 nm. The spectral blue shift of the Cu–PVP–NCG aggregate is 20 nm; it is revealed by comparing curve C-2. By comparison of curves C-4 and C-5, we observe that the NCG–Cu reaction is more sensitive in the presence of PVP. Therefore, PVP is used as a sensitizer because it provides a charge carrier to enrich NCG. From curve A-5, the peak of the PVP–NCG solution is located at 633 nm and its valley is at 544 nm. These two wavelengths were used in investigation of the NCG–PVP interaction. In the same method, the peak of the Cu–NCG–PVP solution is located at 532 nm and its valley is at 619 nm, from curve B-5. These two wavelengths were used to characterize the Cu–NCG–PVP complex and to detect Cu. From curves C-1 and C-2, the correction coefficients were calculated to be  $\beta_{\text{NCG}} = 0.365$  and  $\alpha_{\text{NCG-PVP}} = 1.01$ . In the same way,  $\beta_{\text{NCG-PVP}} = 0.612$  from curve C-2 and  $\alpha_{\text{Cu-NCG-PVP}} = 0.667$  from C-3. Therefore, real absorbance ( $A_c$ ) of the PVP–NCG aggregate is calculated by  $A_c = 1.58(\Delta A - 0.365\Delta A')$  and that of the Cu–NCG–PVP complex by  $A_c = 1.69(\Delta A - 0.612\Delta A')$ .

### Effect of Ionic Strength and Temperature

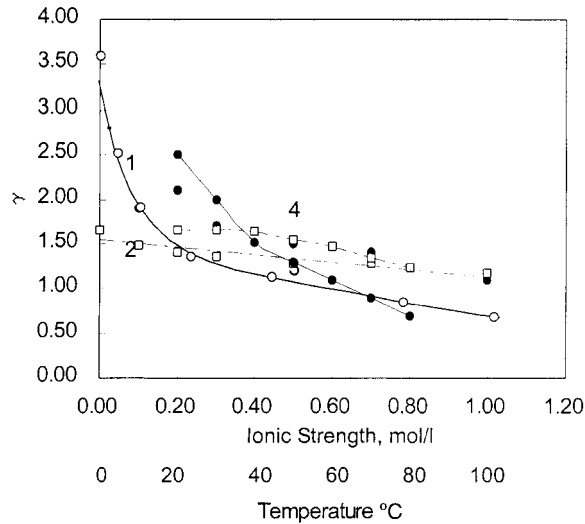
In order to investigate the effect of ions on the Cu–NCG–PVP interaction, NaCl was added; its effect is shown in Fig. 3. From curve 1, the binding ratio of NCG to PVP decreases quickly with increasing in ionic strength. This is attributed to the fact that more  $\text{Cl}^-$  will bind on the positively charged PVP chain screening more positive charges. From curve 2,  $\gamma$  of NCG to Cu hardly changes because the Cu–NCG coordination bond is much stronger than the electrostatic attraction.

From curve 3 in Fig. 3, the binding ratio of NCG to PVP decreases rapidly with an increase in temperature. This is attributed to the fact that the electrostatic attraction is weak and is easily destroyed by high temperature. To the contrary, from curve 4 we find that change of  $\gamma$  of NCG to Cu is small with temperature change because of their coordination connection.

### Characterization of the Naphthochrome Green–Polyvinylpyrrolidone Aggregate

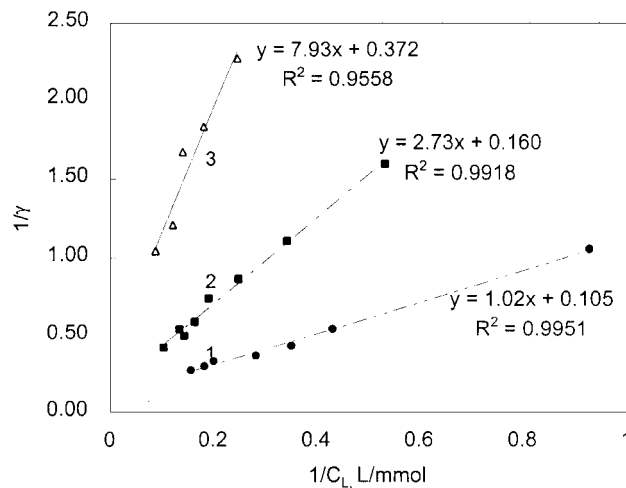
To a solution containing 4 mg of PVP, the NCG added was varied with the addition of NCG between 0.10 and 0.45 mg at pH 11.55, at three temperatures.  $C_L$  and  $\gamma$  were





**Figure 3.** Effect of ionic strength and temperature of solution on the binding ratio of NCG to PVP (1) and that of NCG to Cu (2) in 25 mL solution. 1–0.400 mg of NCG plus 4 mg of PVP and 2–0.400 mg of NCG plus 14 mg of PVP plus 20  $\mu\text{g}$  of Cu, 3–0.400 mg of NCG plus 4 mg of PVP and 4–0.400 mg of NCG plus 14 mg of PVP plus 20  $\mu\text{g}$  of Cu.

calculated in each case and the curves ( $C_L^{-1}$  vs.  $\gamma^{-1}$ ) are shown in Fig. 4. We observe that all of them are linear. This means that the aggregation of NCG on the PVP chain obeys the Langmuir isothermal adsorption. From the line intercept the binding constants of the NC–PVP aggregates were calculated as given in Table 1. By calculation, we know that, statistically, each of the 36 amide-N’s of PVP bind 1 NCG molecule. Figure 5 shows the



**Figure 4.**  $\gamma^{-1}$  vs.  $C_L^{-1}$  of the solutions containing 4 mg of PVP and NCG between 0.10 and 0.45 mg at pH 11.55 in 25 mL solution: 1–20°C, 2–40°C and 3–70°C.

**Table 1.** Determination of the binding constants of the PVP–NCG aggregate at pH 11.55.

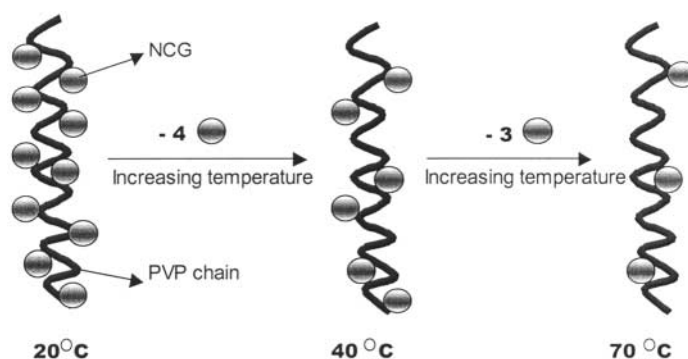
Temperature (°C)	<i>N</i>	<i>K</i>	$\epsilon^{633\text{ nm}}, \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
20	10	98.0	13.9
40	6	59.1	9.53
70	3	46.7	4.27

desorption process of NCG with temperature. Four of NCG molecules fall from one of PVP when it rises from 20°C to 40°C and there again three others leave the chain when raised to 70°C. This phenomenon accords with the common nature of surface adsorption. By considering *K* in Table 1, we observe that *K* decreases from 98.0 to 46.7 with an increase of temperature from 20°C to 70°C. So, the binding of NCG with the PVP chain becomes more and more unsteady. Similarly, the real molar absorptivity ( $\epsilon$ ) of the aggregate decreases from  $1.39 \times 10^5$  to  $4.27 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 633 nm with increase of temperature because of the corresponding decrease of the binding ratio of NCG to PVP. For the characterization of the adsorption product, we find the spectral correction technique is preferable in operation and principle to the classical methods such as the Scatchard model,<sup>[18]</sup> molar ratios, and others.

### Naphthochrome Green–Cu Complexation and Calibration Graph for Determination of Cu

By varying the addition of *L'*, the complexation ratio of NCG to Cu is 1 from  $\gamma$  change curve. Therefore, complex Cu–NCG<sub>2</sub> was formed in the presence of PVP at pH 11.55. The ternary complex is expressed as Cu–NCG<sub>2</sub>–PVP.

A series of standard solutions of Cu(II) between 0 and 30  $\mu\text{g}$  in 25 mL solution were prepared and their absorbances were measured at 532 and 619 nm. The calibration graph is shown in Fig. 6; all *A<sub>c</sub>* points are highly linear in the range between 0 and 18.0  $\mu\text{g}$  of Cu.



**Figure 5.** Variation of the binding number of NCG on PVP chain with temperature.



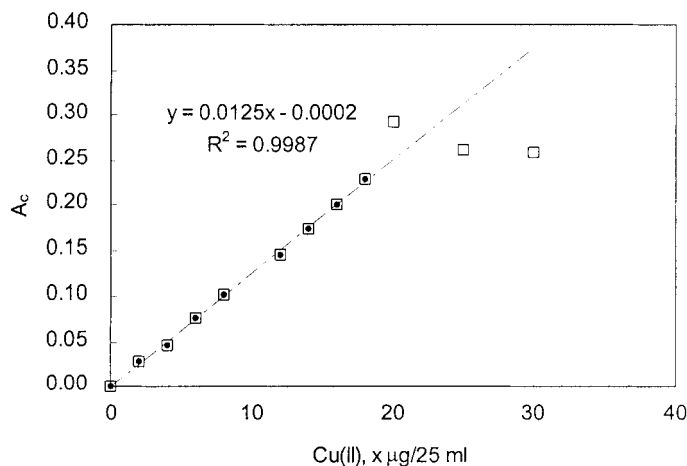


Figure 6. Plots  $A_c$  vs.  $x$  for the determination of Cu traces ( $x$   $\mu\text{g}$ ) in 25 mL solution at pH 11.55.

### Precision and Selectivity

Six replicated determinations of 10  $\mu\text{g}$  of Cu(II) gave as an average:  $9.59 \pm 0.24$   $\mu\text{g}$ . The relative standard deviation (RSD) is 2.5%. For  $A_c = 0.010$ , the detection limit of Cu was calculated to be about 0.8  $\mu\text{g}$  in 25-mL flask.

By adding the masking reagent, none of the following ions affected the direct determination of 10  $\mu\text{g}$  of Cu (II) (error less than 10%): 20  $\mu\text{g}$  of  $\text{Cr}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ag}^+$ ; 40  $\mu\text{g}$  of  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ; 50  $\mu\text{g}$  of  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Sn}^{4+}$ , and 100  $\mu\text{g}$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The ternary reaction reveals it is suitable for the direct detection of Cu traces and could be used for water.

### Determination of Cu in Samples

To test the novel method, three samples were collected and analyzed. Sample 1 was from a local sewage pipe, sample 2 from Huaihe River, and sample 3 from lake water. The relative standard deviation (RSD and recovery (Rec) of the samples are given as follows: 1:  $0.538 \pm 0.009$  mg/L, RSD = 1.67% and Rec = 108%, 2:  $0.105 \pm 0.005$  mg/L, RSD = 1.8% and Rec = 106% and 3:  $0.176 \pm 0.008$  mg/L, RSD = 4.83%, Rec = 103%.

### CONCLUSIONS

The investigation of the NCG–PVP interaction indicates the Langmuir isothermal adsorption of a dye on polymeric chain. Only the concentration of dye on the polymer sensitizes its coordination with metal ions. The analytical methods of heavy metal traces are numerous, for example, by spectrometry,<sup>[19]</sup> polarography,<sup>[20]</sup> and others. The chromogenic reagents, bidentate pyridylazo,<sup>[21]</sup> 2-nitroso-1-naphtholsulfonic acid,<sup>[22]</sup> and calcon<sup>[23]</sup> were all applied to the determination of Cu traces by spectrophotometry. The



present work is established on basis of the polymer–dye interaction. The recommended method is suitable for the analysis of water and wastewater.

### ACKNOWLEDGMENTS

Financial support from both the National High Technology Research and Development Program of China (863 Program, No. 2002AA601320) and the National Natural Science Foundation of China (No. 50008011) is gratefully acknowledged.

### ABBREVIATIONS

NCG naphthochrome green  
 PVP polyvinylpyrrolidone

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Received October 1, 2002

Accepted September 5, 2003

Manuscript JTMT02082



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