DETERMINATION OF COBALT AT ng ml⁻¹ LEVEL IN WATER USING THE ELECTROPHILIC SUBSTIUTION COMPLEXATION BETWEEN Co(II) AND CHLOROPHOSPHONAZO- p-Cl-Cu(II) COMPLEX

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Summary -The chromophore chlorophosphonazo-*p*-Cl (PCCPA) was used to complex Co(II) and Cu(II) at pH 9.18. The formation of Co(PCCPA)$_2$ and Cu(PCCPA)$_2$ complexes were characterized by the spectral correction technique. Co(II) could competitively substitute Cu(II) from the Cu(II)-PCCPA complex via electrophilic effect. With the assistance of the light-absorption ratio variation approach, the electrophilic substitution complexation showed a high selectivity and good sensitivity with 1.9 ng mL⁻¹ of LOD. The proposed method has been applied to the direct detection of Co(II) in surface water and wastewater with good percent of recovery.

INTRODUCTION

Cobalt is known to be essential at trace levels to man, animals, and plants for metabolic processes.[1-3] Though cobalt is not considered to be as toxic as some other heavy metals, it is an equally harmful element.[4] Toxicological effects caused by the intake of excess cobalt include interstitial lung disease vasodilatation, flushing, and cardiomyopathy in humans and animals.[5-7] Recently, it was found that cobalt would influence the proliferation and function of human osteoblast-like cells.[8] Moreover, at higher concentrations, it may become genotoxic and mutagenic.[9]

Cobalt is often used in the manufacture of alloys, catalysts, catalytic converters, and paint pigments.[10] Thus, the high consumption of cobalt-containing products in industry inevitably leads to environmental pollution at all stages of production, recycling, and disposal. Normally, cobalt founded in natural water is at low concentrations. However, the concentration may increase due to the discharge of industrial wastewater. So it is very important and necessary to develop reliable, rapid, and sensitive methods for cobalt determination in water matrices.

A number of well-established methods for the determination of trace cobalt in water have been developed, such as catalytic adsorptive stripping voltammetry[11], FI-FAAS[12], ICP-OES[13] and delayed neutron activation analysis (DNAA) technique[10]. Compared with these methods, spectrophotometry as a kind of conventional method has its own advantages such as simple operation, low-cost instrumentation, and wide owning throughout the world. Especially, the

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development of some spectrophotometric techniques *e.g.* light-absorption ratio variation approach (LARVA)[14] remarkably improves the analytical sensitivity and therefore expands the availability of spectrophotometry.

The chromophore, chlorophosphonazo–*p*-Cl (PCCPA), was synthesized and used in detection of scandium and bismuth about twenty years ago.[15-16] Nevertheless, due to its poor selectivity, this chromophore was seldom applied to metal determination later. In the current work, its novel usage was found. Trace amounts of Co(II) can competitively substitute Cu(II) from the Cu-PCCPA complex in alkaline medium via electrophilic substitution complexation (ESC). The combination of LARVA and ESC showed a high sensitivity and good selectivity. The proposed method has been applied to determine trace amounts of Co(II) in surface water and wastewater with satisfactory percent of recovery .

PRINCIPLE

Spectral correction technique [17]

A metal-ligand complexation is often used in analysis of trace metals. The reaction of Co/Cu with PCCPA can be expressed as follows:

$$N \text{ PCCPA} + \text{Co/Cu} \rightleftharpoons \text{Co(PCCPA)}_N/\text{Cu(PCCPA)}_N$$
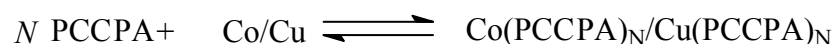
Initial state	C_{PCCPA0}	C_{Co0}/C_{Cu0}	*0*
Corresponding to	$A_{\lambda1}^{PCCPA}$ and	$A_{\lambda2}^{PCCPA}$	
Equilibrium	C_{PCCPA}	*~0*	C_{Co0}/C_{Cu0}
Corresponding to	*(1-η)* $A_{\lambda1}^{PCCPA}$ and	*(1-η)* $A_{\lambda2}^{PCCPA}$	A_c

where C_{PCCPA0} ,C_{Co0} and C_{Cu0} are the initial molarities of PCCPA , Co and Cu. η is the effective fraction of PCCPA and *N* is the coordination number of PCCPA with Co or Cu. The symbol A_c indicates the real absorbance of the Co-PCCPA or Cu-PCCPA complex at wavelength λ_2. Both $A_{\lambda1}^{PCCPA}$ and $A_{\lambda2}^{PCCPA}$ are the absorbances of PCCPA solution measured at wavelengths: λ_1 and λ_2 against water reference. The complex reaction was characterized according to the relations below:

$$A_c = \frac{A_{\lambda 2} - \beta A_{\lambda 1}}{1 - \alpha \beta} \tag{1}$$

where

$$\beta = \frac{A_{\lambda 2}^{PCCPA}}{A_{\lambda 1}^{PCCPA}} \tag{2}$$

and

$$\alpha = \frac{A_{\lambda 1}^{Co-PCCPA}}{A_{\lambda 2}^{Co-PCCPA}} \quad \text{or} \quad \alpha = \frac{A_{\lambda 1}^{Cu-PCCPA}}{A_{\lambda 2}^{Cu-PCCPA}} \tag{3}$$

and

$$\gamma = \eta \times \frac{C_{PCCPA\ 0}}{C_{Co\ 0}} \quad \text{or} \quad \gamma = \eta \times \frac{C_{PCCPA\ 0}}{C_{Cu\ 0}} \tag{4}$$

where

$$\eta = \frac{A_c - A_{\lambda 2}}{A_{\lambda 2}^{PCCPA}} + 1 \tag{5}$$

where both β and α are the spectral correction constants, γ is the complexation ratio of PCCPA to Co or Cu. $A_{\lambda 1}^{Co-PCCPA}(A_{\lambda 1}^{Cu-PCCPA})$ and $A_{\lambda 2}^{Co-PCCPA}(A_{\lambda 2}^{Cu-PCCPA})$ are the absorbances of the Co-PCCPA(Cu-PCCPA) solution and Co-PCCPA (Cu-PCCPA) complex solution without free PCCPA, respectively measured at λ_1 and λ_2 against water reference. So A_c, η and γ can be calculated by Equations (1)-(5).

Light-absorption ratio variation approach [14]

The light absorption ratio variation approach (LARVA) were established for determination of trace amounts of Co(II). Its principle can be described by following equations:

$$\Delta A_r^{-1} = p C_{Co0}^{-1} + q \tag{6}$$

$$\Delta A_r = p' C_{Co0} + q' \tag{7}$$

The symbols ΔA_r and C_{Co0} is the absorbance ratio variation and the initial concentration of Co(II), respectively. From Equations (6) and (7), plots of ΔA_r^{-1} vs. C_{Co0}^{-1} are always linear, plots ΔA_r vs. C_{Co0} is linear only when the molarity of Co is at a lower concentration. Both p, q and p', q' are constants when the wavelengths λ_1 and λ_2 and the reaction conditions, such as the pH, temperature and reaction time, were fixed. Such Equations (6) and (7) can be equally used in the quantitative detection of trace amounts of Co(II).

EXPERIMENTAL

Apparatus

A Model Lambda 25 (PerkinElmer Instruments, USA) Spectrometer, which was connected to a computer with UV Winlab software (version 2.85.04) installed, was used to record the

adsorption spectra and absorbances of the reaction solutions. A Model pHS-25 meter (Shanghai Precise Instruments, Shanghai, China) was used to adjust the acidity of the solutions. A Model Anke TGL-16C centrifugal machine (Shanghai AnTing Science Instruments, Shanghai, China) was used for sample pretreatment.

Reagents and solutions

Co(II) and Cu(II) standard solutions containing 200 mg L^{-1} Co(II) and 200 mg L^{-1} Cu(II) respectively were prepared from their stock solutions: 1000 mg L^{-1} Co(II) (GSB07-1255-2000) and Cu(II) (GSB07-1257-2000), which were purchased from the Institute for Reference Materials of State Environmental Protection Agency (SEPA), Beijing, China. The standard use solutions containing 1.00 and 10.0 mg L^{-1} Co(II) and 10.0 mg L^{-1} Cu(II) were prepared by diluting the above solutions, respectively. PCCPA standard solution, 0.0500 mmol L^{-1} PCCPA was prepared by dissolving 33.86 mg of PCCPA (purchased from Changke Reagents Institute of Shanghai) in 1000 mL deionized water. A Cu-PCCPA complex solution containing 0.0500 mmol L^{-1} Cu-PCCPA complex was prepared by mixing 2% copper chloride (A. R, grade Silian Chemical Plant of Shanghai, Shanghai, China) and 0.100 mmol L^{-1} PCCPA together. The molar ratio of Cu(II) to PCCPA was kept at about 15:1. It was used as a chromogenic reagent in the determination of Co(II) later. All the solutions above were stored at less than 5 °C.

In addition, a series of ammonium buffer solutions were prepared with ammonia water and ammonium chloride. Each of the solutions was measured accurately with pH meter, and their pH values were 7.98, 8.57, 9.18, 9.72, 10.44 and 10.93, respectively. All the sodium oxalate, nitric acid, sulfuric acid, and sodium hydroxide used in pretreatment of water samples and sodium fluoride, potassium sodium tartrate used as masking reagents were in A. R. grade and purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

Experimental procedures

Characterization of the composition of PCCPA complexes

Into a series of 10 mL calibrated flask were added 1.00 μg of Co(II), 1 mL of pH 9.18 buffer solution, and a known volume of 0.0500 mmol L^{-1} PCCPA. The solution were diluted to 10 mL with deionized water and mixed thoroughly. After three hours, the absorbances of the solutions were measured at both 560 nm and 650 nm against water reference.

Using the same method, 5.00 μg of Cu(II) was added by replacing Co(II). The absorbances of Cu-PCCPA complex solutions were measured at 657 nm and 613 nm. Thus, the composition of the PCCPA complexes could be characterized by the relations (1)-(5).

Determination of cobalt in water samples

Cobalt does not necessarily exist in terms of Co(II) in natural water. So prior to determination，the samples must be pretreated by digesting with nitric acid and sulfuric acid in order to convert various states of cobalt, *e.g.* bounded cobalt to colloid or suspended particulates, to Co(II) and Co(III). In acidic and neutral solutions, Co(III) is very unstable and can easily be changed into Co(II) within twenty-four hours. The digestive method is as follows: 100 mL water sample, 1.00 mL of concentrated sulfuric acid and 5.00 mL of nitric acid were mixed thoroughly in a 250 mL beaker. The solution was then boiled and digested at 100 °C until SO$_3$ fumes appeared. After the solution was cooled-down, 80 mL of deionized water was added and boiled for three minutes. Then 1.00 mol L^{-1} NaOH was added drop by drop until pH approached 7. Afterwards, the cooled solution was diluted to 100 mL with deionized water.

After twenty-four hours, into a 10 mL centrifugal tube were added less than 5.00 mL of the solution above, 0.500 mL of 0.200 mol L^{-1} sodium oxalate. The solution was centrifuged for 10 min at 15000 rpm to remove the majority of calcium ions in water sample and the supernatant fluid was

collected.

Into a 10 mL calibrated flask were added a known volume of the supernatant fluid above, 0.5 mL of pH 9.18 buffer solution, 0.500 mL of 0.500 mol L^{-1} sodium fluoride, 0.500 mol L^{-1} potassium sodium tartrate, and 0.600 mL of 0.0500 mmol L^{-1} Cu-PCCPA complex. The solution was diluted to 10 mL with deionized water and mixed thoroughly. After three hours, the absorbances of the solution, A_{570nm} and A_{658nm}, were measured at 570nm and 658 nm against deionized water. At the same time, the absorbance of the reagent blank, $A_{570nm}^{Cu-PCCPA}$ and $A_{658nm}^{Cu-PCCPA}$ were measured at 570nm and 658 nm against deionized water. The absorbance ratio variation (ΔA_r) was calculated by equation (8):

$$\Delta A_r = A_r - A_{r0}$$
$$= \frac{A_{658\,nm}}{A_{570\,nm}} - \frac{A_{658\,nm}^{Cu-PCCPA}}{A_{570\,nm}^{Cu-PCCPA}} \qquad (8)$$

ΔA_r was obtained from Equation (8) and C_{Co0} in the sample can be calculated from Equation (7).

RESULTS AND DISCUSSION

pH dependence of absorption spectra

The absorption spectra of the Co-PCCPA and Cu-PCCPA solutions were shown in Fig.1 in a series of various buffer solutions from pH 7.98 to 10.93. The complexation between Co(II) or Cu(II) and PCCPA becomes increasingly sensitive with the increase of the peak-valley interval of their corresponding absorption spectra. From the left curves, all the Co-PCCPA complexations are very sensitive in the range of pH examined. However, Co(II) was found to replace Cu(II) from the Cu-PCCPA complex only when pH was higher than 9. Meanwhile, the binding force of Cu-PCCPA complex is relatively weak when the pH of the solution is more than 9.5, so as to affect the determination selectivity. Based on the above mentioned factors, 9.18 was selected as the optimal pH for the whole reaction. From curve 3 in the left, the peak of Co-PCCPA solution is located at 650 nm and the valley at 560 nm. From curve 3 in the right, the peak of Cu-PCCPA solution is located at 613 nm and the valley at 657 nm. Such four wavelengths were selected for subsequent characterization of the Co-PCCPA and Cu-PCCPA complexes.
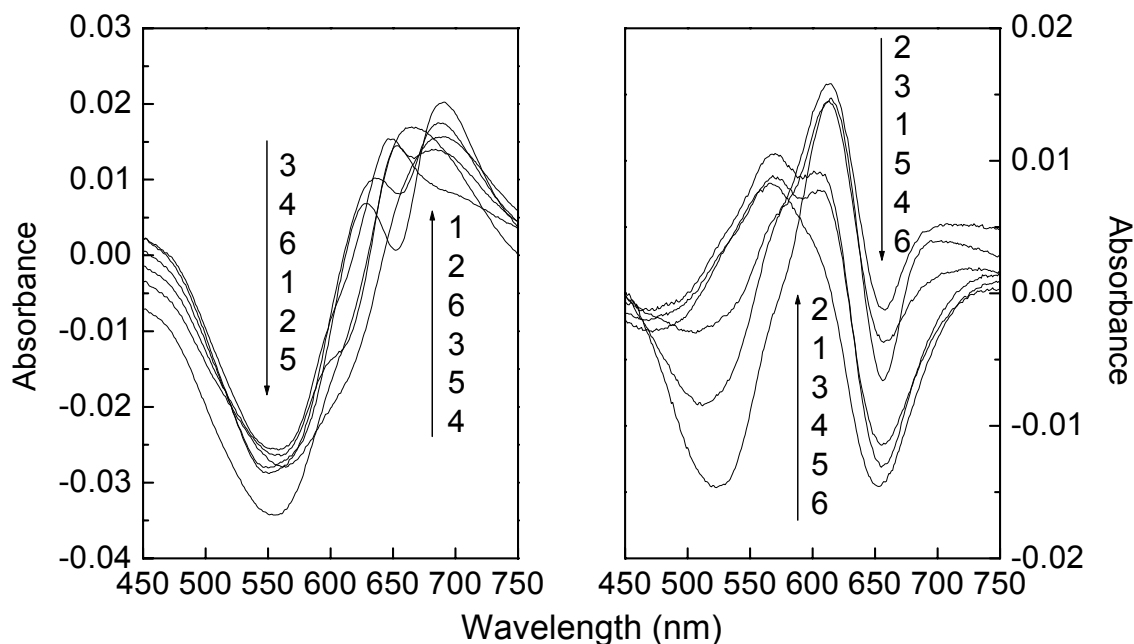
FIGURE 1. - Effect of pH on the absorption spectra of Co-PCCPA (left) and Cu-PCCPA (right) solutions against the regent blank without Co(II) or Cu(II), in which 1.00 mL of 0.0500 mmol L^{-1} PCCPA, 0.500 mL of 1.00 mol L^{-1} different buffer solution of pH 7.98 (1), pH 8.57 (2), pH 9.18 (3), pH 9.72 (4), pH 10.44 (5) and pH 10.93 (6), 2.00 μg of Co(II) (left) or 30.0 μg of Cu(II) (right) are added to a series of calibrated flask and then diluted to 10 mL.

Composition of the PCCPA complexes

In the reaction, excess PCCPA was added to complex Co and Cu completely. The free PCCPA often occupies a high fraction in the solution. Undoubtedly, an excess of PCCPA will affect the accurate measurement of the absorbance of the PCCPA complexes. It is hard for an ordinary spectrophotometry to solve such a problem, so the spectral correction technique was applied to eliminate the interference of excess PCCPA.

By varying the PCCPA molarity in the reagent blanks, β remained constant in the vicinity of 0.48 for A_{650nm}/A_{560nm} and in the vicinity of 1.61 for A_{613nm}/A_{657nm} with the increase of PCCPA molarity. This indicates that the self-aggregation of PCCPA molecules would not occur in aqueous solution at pH 9.18. By varying Co(II) or Cu(II) molarity in solutions with a constant PCCPA molarity, the absorbance ratio of the complex solutions could be calculated. Curve 1 in Fig. 2 shows the variation of the ratio A_{560nm}/A_{650nm}. The ratio value decreases rapidly when the molarity of Co(II) molarity is less than that of PCCPA and then remains almost constant at 0.746 when the molarity of Co(II) is more than PCCPA. Under such circumstances, all the PCCPA molecules should have coordinated with Co(II) completely. Therefore, the spectral correction constant α was obtained as 0.746 from the Co-PCCPA complex solution. The same method was applied to the determination of α for the Cu-PCCPA complex and the value of α is 0.226 from curve 2 in Fig. 2.
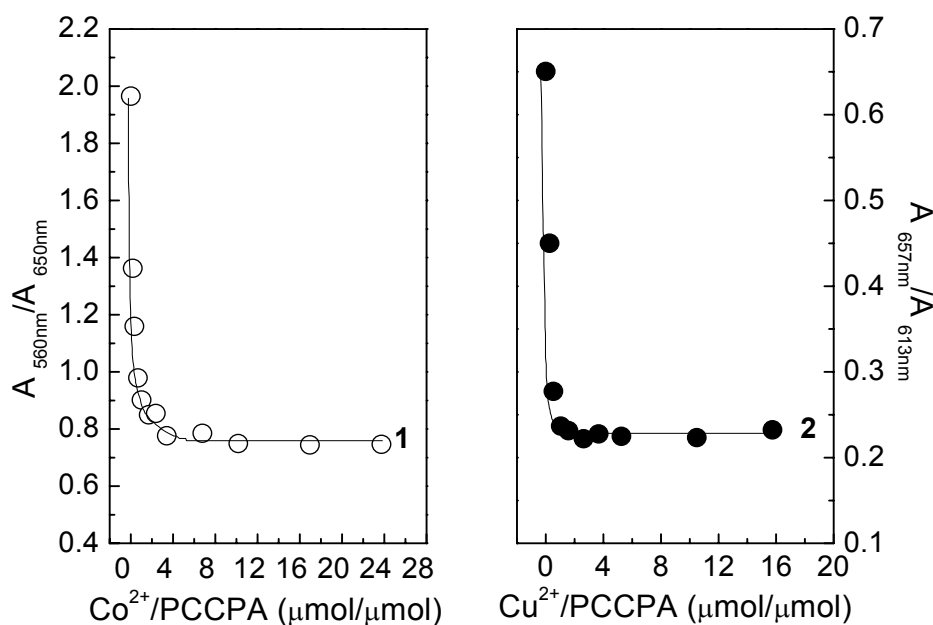
FIGURE 2. - Variation of the absorbance ratio of the Co-PCCPA solution and the Cu-PCCPA solution with the increase of the molar ratio of Co(II) or Cu(II) to PCCPA at pH 9.18. In Co-PCCPA and Cu-PCCPA complex solutions, PCCPA remains constant at 0.00500 or 0.00300 mmol L^{-1}, respectively. The absorbance ratios approach constant minima (α) when the molar ratio of Co(II) or Cu(II) to PCCPA is over 8.0 and 4.0 respectively.

By changing the PCCPA molarity in solutions containing Co(II) or Cu(II), variations of A_c, η and γ values are shown in Fig. 3. From curves 1 and 2, both η decrease from about 70 to 20% for Co-PCCPA complex and from about 90 to 50% for Co-PCCPA complex with increase of the PCCPA molarity, indicating that a high fraction of PCCPA did not reacted with Co(II) or Cu(II). As mentioned before, the excess of PCCPA will influence the measurement of absorbance of the Co-PCCPA and Cu-PCCPA complex. It is impossible for ordinary spectrophotometry to measure the accurate light-adsorption of each color compounds in the reaction solution. However, utilizing the spectral correction technique, both the real light-absorption of Co-PCCPA/Cu-PCCPA complex and the composition of complexes can be obtained from Equations (1)-(5).

From curve 3 in Fig.3, γ of the Co-PCCPA complex approaches a maximum constant at 2.0 when PCCPA is more than 0.0150 mmol L^{-1}. This confirms that the complex $Co(PCCPA)_2$ is formed at pH 9.18. Similarly, the complex $Cu(PCCPA)_2$ is formed, as shown by curve 4.
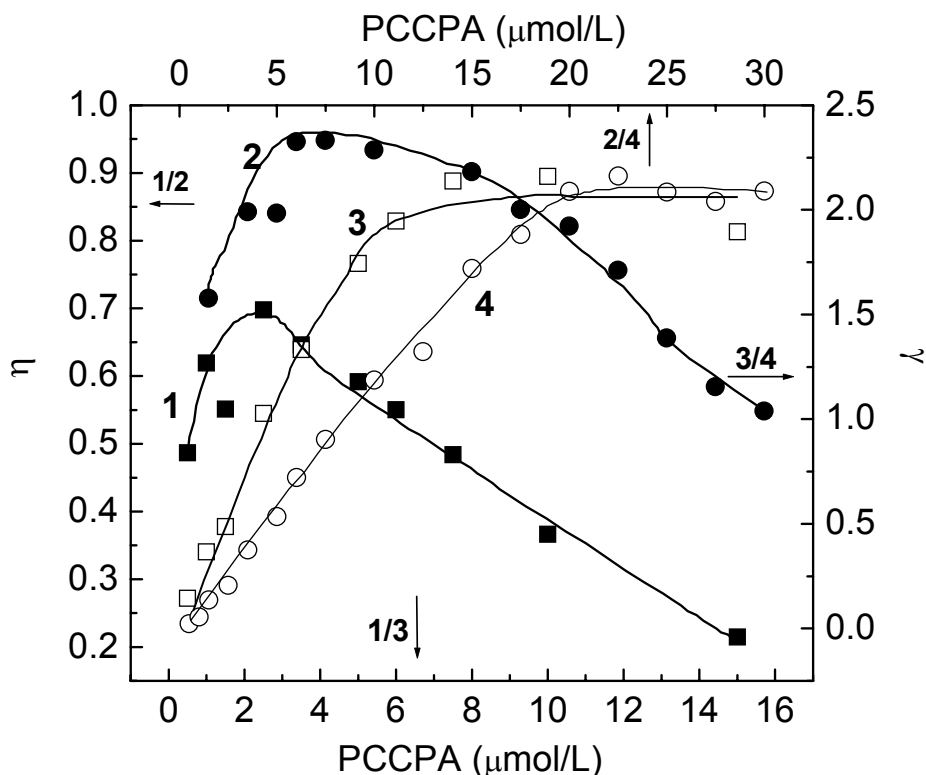
FIGURE 3. - Variation of η and γ with PCCPA molarity: Co-PCCPA complex solution containing 0.100 μg mL^{-1} of Co(II), Cu-PCCPA solution containing 0.500 μg mL^{-1} of Cu(II). Curve 1 and 3 refer to variation of η and γ of Co-PCCPA solution, respectively and curve 2 and 4 refer to variation of η and γ of Cu-PCCPA solution, respectively. The decrease of η is correlated with increased excess of PCCPA. γ increases up to a maximum constant at 2.0 for both Co-PCCPA solution and Cu-PCCPA solution The upper horizontal axis is for curves 2 and 4, the lower horizontal axis is for curves 1 and 3. The same rule is applied to vertical axis.

Electrophilic substitution complexation[17] and effect of time on reaction

Fig. 4 gives a series of absorption spectra of PCCPA, Co-PCCPA and Cu-PCCPA complexes. Interestingly, curve 2 is almost completely coincident with curve 4, indicating that there should be only a kind of coloured complex Co-PCCPA in the two reaction solutions. Therefore, it is rational that Co(II) can competitively replace Cu(II) from the Cu-PCCPA complex via the electrophilic substitution effect. Actually, both Co(II) and Cu(II) could react with PCCPA and form the green Co-PCCPA complex and deep blue Cu-PCCPA complex, respectively. The addition of plenty of Co(II) could then turn the deep blue color of the Cu-PCCPA solution into green color as that of the Co-PCCPA solution. Such a color transition process exactly confirmed the existence of electrophilic substitution complexation between Co(II) and Cu(II) with PCCPA. Thus, the Cu-PCCPA complex could be regarded as a new chromophore and used to detect trace amounts of Co(II). Curve 5 in Fig. 4 was obtained by scanning the absorption spectra of solution containing Co(II) and Cu-PCCPA complex against the corresponding reagent blank without Co(II). From curve 5, the valley is located at 570 nm and the peak at 658 nm, and the two wavelengths were selected as the operation wavelength for LARVA.
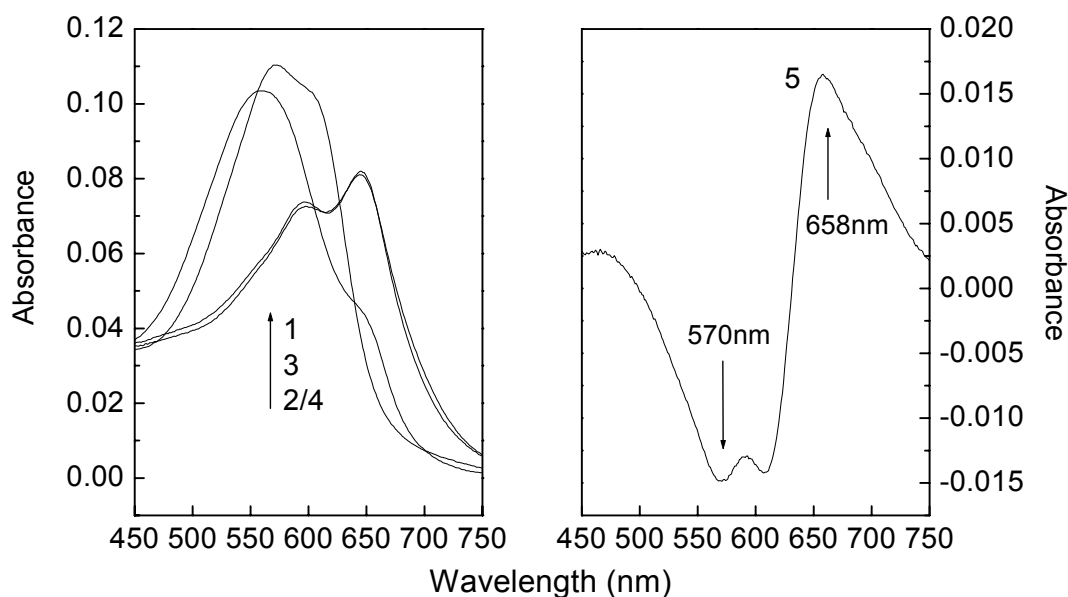
FIGURE 4. - The absorption spectra of different metal-PCCPA complexes' solutions: (1) containing 0.00500 mmol L^{-1} PCCPA plus 0.0500 mol L^{-1} buffer solution at pH 9.18, (2) the same as (1) plus 3.00 μg mL^{-1} Co(II), both against water(3) the same as (1) plus 10μg mL^{-1} Cu(II), (4)the same as (3) plus 3.00 μg mL^{-1} Co(II), both against the solution containing 10.0 μg mL^{-1} Cu(II) and 0.0500 mol L^{-1} pH 9.18 buffer solution, (5) containing 0.0500 mol L^{-1} pH 9.18 buffer solution, 0.00500 mmol L^{-1} Cu-PCCPA complex solution, 1.00 μg of Co(II) against corresponding blank without Co(II).
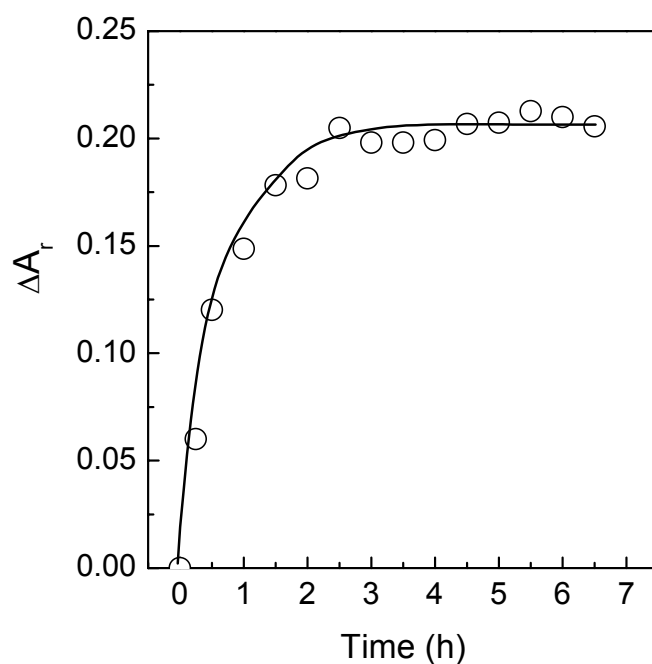

FIGURE 5. - Effect of the reaction time on ΔA_r of electrophilic substitution complexation

In addition, in order to further optimize the reaction conditions, the effects of time and

temperature on the electrophilic substitution complexation were then explored simultaneously. The absorption-ratio variation of the substitution solution at different reaction time was showed in Fig. 5. From the curve in Fig. 5, the ΔA_r of the reaction solution approaches maximum and remains constant after three hours at room temperature. Therefore, the substitution solutions should be kept at room temperature for at least three hours before measurement.

Effect of the Cu-PCCPA complex on ΔA_r

Fig. 6 gives the effect of the Cu-PCCPA complex on ΔA_r of the reaction solutions. From curve 2 with a constant ratio of Co(II) (1.00 μg) to Cu-PCCPA complex (0.0500 μmol) , ΔA_r changes slightly when the Cu-PCCPA complex solution (0.0500 mmol L^{-1}) added is more than 0.400 mL. On the other hand, when Cu-PCCPA solution added is less than 0.600 mL, the sensitivity factor $\Delta A_r/M_{Co}$ increases rapidly as curve 1 indicates. The primary reason is that the self-aggregation of Cu-PCCPA complex would not occur in such an extremely diluted solution. Thus, the less the Cu-PCCPA complex is added, the lower the amounts of Co(II) can be detected. However, if the concentration of the Cu-PCCPA complex is too low, the interference from instrumental noise may directly affect the accurate measurement of the absorbances of reaction solutions. In the successive calibration experiments, four series of the Cu-PCCPA solution were prepared with Co(II) added to obtain the most satisfactory calibration graph and to give the lowest limit of detection of Co(II).
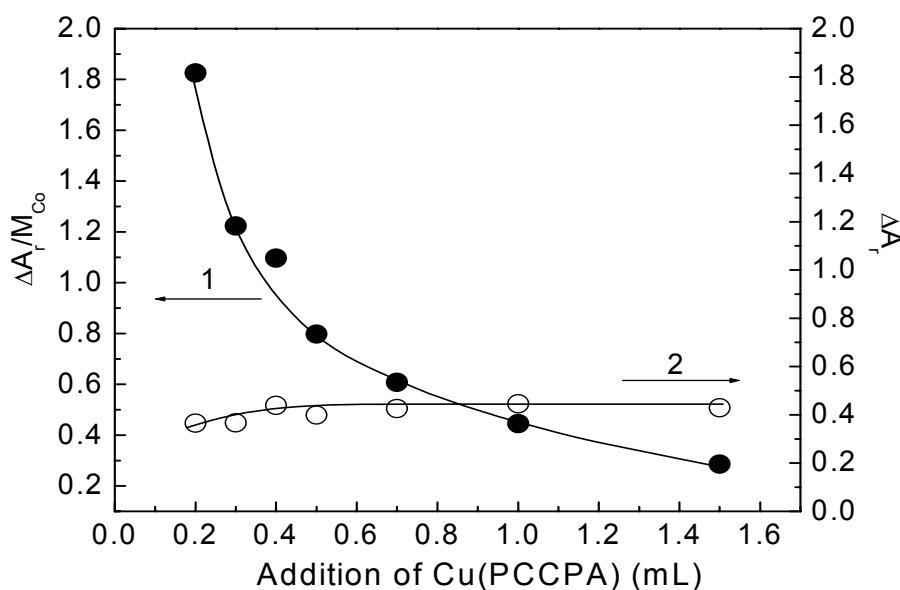

FIGURE 6. - Effect of the addition of 0.0500 mmol L^{-1} Cu-PCCPA complex (from 0.200 mL to 1.50 mL) on $\Delta A_r/M_{Co}$ (curve 1) and ΔA_r (curve 2)of Cu-PCCPA-Co(II) solution at pH 9.18, where Co(II) was added according to the constant ratio of Co(II) (1.00 μg) to Cu-PCCPA complex (0.0500 μmol)

Calibration graph and limit of detection

Four series of solutions containing standard Co(II) between 0 and 0.300, 0 and 0.500, 0 and 0.400, 0 and 0.500 μg were prepared, 0.300, 0.500, 0.600 and 0.700 mL of the Cu-PCCPA solution were then added, respectively. According to the recommended procedures, ΔA_r could be calculated from Equation (7). The regression equations of plots ΔA_r vs C_{Co} and their corresponding limit of detection (LOD) of Co(II) were calculated and listed in Table 1. By comparing the four series of

data, the third series has the best linearity and the lowest LOD of 1.9 ng mL^{-1}. Therefore, 0.600 mL of the Cu-PCCPA solution was deemed as the optimal volume added, and the third regression equation was chosen for the subsequent analysis of water samples.

TABLE 1. - Regression equations and LOD of Co(II)

Series	0.0500 mmol/L Cu(PCCPA) (mL)	Linear scope, Co(II) (μg)	Calibration graph	R [1]	σ [2]	LOD[3] (ng/mL)
1	0.300	0-0.300 (7) [4]	$\Delta A = 0.59\,C_{Co} + 0.0192$	0.9680	0.0130	6.6
2	0.500	0-0.500 (8)	$\Delta A = 0.4015\,C_{Co} + 0.0145$	0.9679	0.0069	4.3
3	0.600	0-0.400 (7)	$\Delta A = 0.465\,C_{Co} - 0.002$	0.9993	0.0029	1.9
4	0.700	0-0.500 (7)	$\Delta A = 0.4082\,C_{Co} + 0.0083$	0.9923	0.0037	2.7

[1] Linear correlation coefficient; [2] Standard deviation of 10 repetitive reagent blanks; [3] Limit of detection of Co(II) was calculated by LOD=3×σ×p(p=line slope of plots ΔA_r vs C_{Co}) ; [4] number of solutions

Interference study

The effects of potential interfering ions were examined by using the solutions containing 0.300 μg/mL Co(II) and one of the other ions. Sixteen foreign metal ions including bovine serum albumin (BSA) and sodium dodecyl benzene sulfonate (SDBS) were added into the reaction solutions, and the effect of these foreign ions on ΔA_r of the solutions was shown in Table 2. Because of the existence of plenty of Cu(II) in the reaction solution without free PCCPA, the majority of metal ions would not seriously affect the direct determination of Co(II). The addition of masking reagents, such as sodium fluoride, potassium sodium tartrate and sodium oxalate, could further enhance the selectivity by eliminating the interference from Ca(II), Mg(II), Al(III), Fe(III), Fe(II) and Mn(II). Hence, the recommended method should be suitable for the analysis of surface water and wastewater.

Compared with the other LARVA methods of cobalt detection[18-20] proposed by Gao et al, this work has some attributes: (a) sample pretreatment (no pretreatment for ref. 18-20); (b) using masking agents (no masking agents added for ref. 18-20); (c) relatively slow Esc reaction rate (rapid and finished within 30 min for ref. 18-20); (d) no need heating (60 ° C hot water bathing for ref. 20). But obtaining results are as good as or even better than the methods as far as limit of detection and linear correlation coefficient are concerned.

Analysis of water samples

In the present work, totally four water samples were analyzed. Each of the samples was pretreated according to the recommended procedures before measurement. All the results are listed in Table 3. The percent of recovery of Co(II) are between 84.0 and 100.9% with the R.S.D. less than 10%. Furthermore, the concentrations of Co(II) in the samples are comparable to those reported. Therefore, the proposed method is accurate and credible for practical analysis of cobalt at trace level.

TABLE 2. - Effect of foreign ions on ΔA_r of the solutions containing 0.300 μg Co(II) in 10 mL calibrated flask

No.	Foreign ion	Added (μg)	Error (%)
1	Cd(II)	1.00	-2.0
2	Zn(II)	1.00	1.0
3	Mg(II)	20.0	3.7
4	Sn(II)	1.00	9.0
5	Mo(VI)	2.00	-4.0
6	V(V)	2.00	1.0
7	Fe(II)	0.600	3.9
8	Fe(III)	1.00	5.0
9	Pb(II)	1.00	1.0
10	Ti(IV)	2.00	4.0
11	Ni(II)	1.00	7.0
12	Al(III)	0.600	5.1
13	Cr(III)	1.00	1.0
14	Ca(II)	20.0	7.0
15	Mn(II)	1.00	1.0
16	BSA	10.0	-3.0
17	SDBS	10.0	1.0

TABLE 3. - Determination of Co(II) in water samples

Sampled from	Co(II) added (μg / L)	Co(II) found (μg/ L)	R.S.D. (%)	Recovery (%)
Lake	0 20.0	<1.9 [1] 20.4 [2]	15	100.9
River	0 20.0	2.9 ± 0.3 [1] 23.7 [2]	10	92.1
Wastewater1	0 10.0	22.1 ± 1.7 [1] 30.4 [2]	7.8	84.0
Wastewater2	0 10.0	20.4 ± 1.3 [1] 30.4 [2]	6.2	99.1

[1] Average of 4 replicated determinations; [2] Average of 2 replicated determinations

CONCLUSIONS

In this work, the utilization of electrophilic substitution complexation (ESC) is based on the fact that Co(II) can competitively substitute Cu(II) from its PCCPA complex via electrophilic effect. The combination of ESC and LARVA can remarkably improve the selectivity of the chromophore PCCPA and achieve good sensitivity with the LOD of 1.9 ng mL^{-1}. Therefore, the proposed method is suitable for the direct determination of Co(II) in water. Utilizing this method, the trace amounts of Co(II) in surface water and wastewater was directly determined with reasonable percent of recovery . Therefore, it can be prospected that the present method will become an alternative cobalt

determination method besides of the techniques that are presently favored. Moreover, the sensitivity and limit of detection can be further improved if a sequential injection system is coupled.

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