Spectral Correction Technique for Determination of Property Constants of Cadmium Complex with *o*-Nitrobenzenediazoaminoazobenzene and Determination of Trace Amounts of Cadmium

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The ligand, *o*-nitrobenzenediazoaminoazobenzene (*o*-NBDA) was synthesised and its reaction with cadmium(II) was sensitive in basic solution in presence of the non-ionic surfactant emulsifier OP. Because of the serious influence of excess of the ligand, the spectral correction technique was used in place of ordinary spectrophotometry. This method gave the simple determination of property constants of the Cd-*o*-NBDA complex and the results showed the complex was Cd(*o*-NBDA)$_4$, its real molar absorptivity $\varepsilon^{480 \text{ nm}} = 1.02 \times 10^5$ L mol^{-1} cm^{-1} and its cumulative stability constant $K = 2.15 \times 10^{23}$. For analysis of samples, the recovery was between 91.0 and 08.5% and the relative standard deviation (RSD) is less than 6%.

INTRODUCTION

Cadmium is one of the harmful pollutants to environment. It often exists in water polluted by, for example, metallurgical, chemical, electrolytic and other industries. Such ligands or chromogenic agents, *viz.*, cadion[1, 2], dithizone[3], 5-Cl-β-PAN[4], crystal violet[5], GBHA[6], di-2-pyridyl-methanone-2-(5-nitropyridyl) hydrazone[7] were ever studied and applied for the determination of trace cadmium by spectrophotometry. In our laboratory, we have synthesised a new ligand, *o*-nitrobenzenediazoamino-azobenzene (*o*-NBDA) and its structure is as follows:
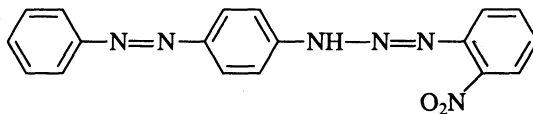
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It is very sensitive to complex Cd(II) over pH 12. The non-ionic surfactant emulsifier OP is helpful to increase the solubility of the Cd-*o*-NBDA complex in aqueous solution. Because the excess of *o*-NBDA interferes in the measurement of absorption of the complex, an ordinary single wavelength spectrophotometry was limited for use. The updated dual-wavelength spectrophotometric method, named spectral correction technique, was earlier established and applied to the investigation of many metal-complex solutions[8–14]. This method may eliminate the influence of excess of ligand in its metal-complex solution to give the real absorbance of complex produced. It is different from other dual-wavelength methods[15, 16] in operation and principle. In the present work, the technique was used in the determination of property constants of the Cd-*o*-NBDA complex and determination of trace amounts of Cd in wastewater with satisfactory results.

EXPERIMENTAL

Absorption spectra were recorded with a TU1221 UV/VIS dual-beam spectrophotometer (Puxi Instruments, Beijing, China), in a 10 mm glass cell.

Standard Cd(II) (1 g/L) solution was prepared with 1 g high-purity metal cadmium by dissolving in 20 mL of 2 M hydrochloric acid and diluted to 1000 mL.

Standard Cd(II) (5 mg/L) use solution was prepared daily by diluting the above solution.

Ligand solution, 0.50 mM *o*-NBDA was prepared by dissolving 173 mg of *o*-nitrobenzenediazoaminoazobenzene (*o*-NBDA, synthesized and purified by us) in 50 mL of acetone and then diluting to 1000 mL with acetone. It was stored in a dark bottle.

KOH solution, 5% (m/v).

The masking reagent solution was prepared by mixing 0.002 M triethanolamine (AR, Shanghai Solvent) and 0.02 M sodium citrate (AR, Shanghai Reagent) in equal volume and then adjusting the solution to pH 12 with 0.2 M sodium hydroxide.

Emulsifier OP (Shanghai Organic Chemicals) solution, 5%.

Recommended Procedure

A known volume of a sample containing less than 25 μg of Cd was taken in a 25 mL volumetric flask and added ion exchange water to about 20 mL. Added 0.5 mL of the masking solution, 2 mL of the ligand solution and 0.5 mL of KOH solution. Diluted to volume and mixed well. After 10 min, measured its absorbances ΔA at 480 (λ_2) and $\Delta A'$ at 560 nm (λ_1) against a reagent blank, respectively. The real absorbance (A_c) of the formed complex was calculated by the relation[8]

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

α and β are the correction constants and they can be calculated by measuring independently the complex and the ligand solutions.

$$\alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda_1}}{\varepsilon_{ML_\gamma}^{\lambda_2}} \quad \text{and} \quad \beta = \frac{\varepsilon_{L}^{\lambda_2}}{\varepsilon_{L}^{\lambda_1}}$$

$\varepsilon_{ML_\gamma}^{\lambda_1}$, $\varepsilon_{ML_\gamma}^{\lambda_2}$, $\varepsilon_{L}^{\lambda_1}$ and $\varepsilon_{L}^{\lambda_2}$ are the molar absorptivities of complex (ML_γ) and ligand (L) at wavelengths λ_1 and λ_2 respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the absorption spectra of the *o*-NBDA and its Cd complex solution. From curve 3, two wavelengths should be selected such that the differences in absorbances were maximum 560 and 460 nm. The calculated value of β is found to be 0.790 from curve 1 and α to be 0.446 from curve 2. Hence, the following expression was applied in the successive determination:

$$A_c = 1.54(\Delta A - 0.790\Delta A')$$
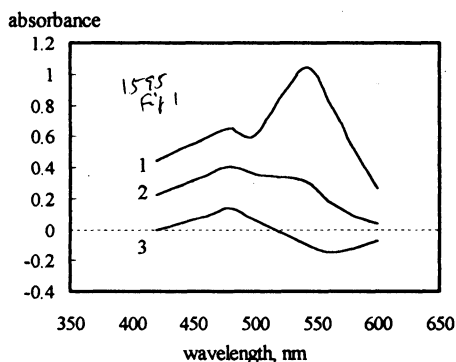
absorbance

Fig. 1. Absorption spectra of the *o*-NBDA and its Cd complex solution in the presence of OP and at pH 12.5: (1) 0.040 mM *o*-NBDA against water; (2) Cd (more than 100 µg) complex solution with *o*-NBDA (0.010 mM), against water; (3) Cd (10 µg) complex solution with 0.040 mM *o*-NBDA against reagent blank.

Effect of addition of *o*-NBDA solution: Fig. 2 shows the effect of the addition of the *o*-NBDA solution on the absorbance of the *o*-NBDA and its Cd complex solutions. From curve 2, it is difficult for the complex ratio of *o*-NBDA to Cd to be obtaind by the conventional molar ratio method[17] by reason of unclearness of the inflexion point. The molar ratio (γ') of the effective L to M was calculated by the relation below and its curve is shown in Fig. 3.

$$\gamma' = \eta \times \frac{C_L}{C_M} \quad \text{where} \quad \eta = \frac{A_c - \Delta A}{A_0}$$

The symbol η indicates the fraction of the effective L in its Cd solution. Both C_M and C_L are the molar concentrations of M and L in the beginning. The symbol A_0 is the absorbance of the L solution without Cd, measured at λ_2.

From curve 2, γ' approaches the maximum 4 when the addition of the *o*-NBDA solution is more than 1.5 mL. Therefore, the Cd(*o*-NBDA)$_4$ was formed. From curve 1, the real molar absorptivity of the complex was calculated to be $\varepsilon_{Cd(o\text{-}NBDA)_4}^{480\ nm} = 1.02 \times 10^5$ L mol^{-1} cm^{-1} at pH 12.5 in the presence of OP. However, from curve 2 in Fig. 2, the molar apparent absorptivity of the complex was $\varepsilon_{Cd(o\text{-}NBDA)_4}^{480\ nm} = 8.24 \times 10^4$ L mol^{-1} cm^{-1}.
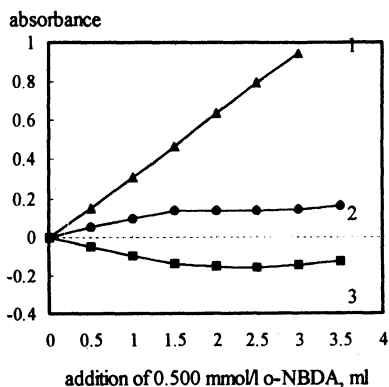

Fig. 2.   Effect of *o*-NBDA on absorbances of the reagent blank and its Cd complex solution at pH 12.5 in the presence of OP: (1) *o*-NBDA solution at 480 nm against water; (2) Cd (10 µg)-*o*-NBDA solution at 480 nm against *o*-NBDA solution; (3) same as (2) but at 560 nm.
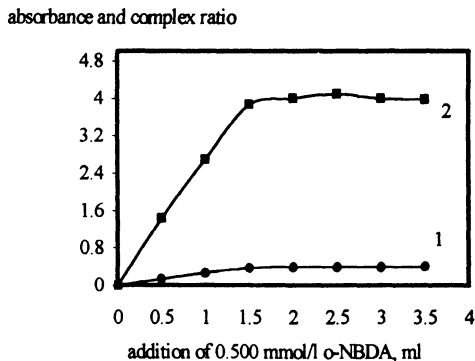

Fig. 3.   (1) A_c and (2) γ'.

Effect of addition of 5% OP: By varying the addition of 5% OP, its effect on the absorbance of the Cd-*o*-NBDA solution was shown in Fig. 4. We observe that A_c reaches a maximum when the addition of the OP solution is more than 0.2 mL. In this study, 1 mL of the OP solution was added.

Effect of pH: By varying pH of solution, the solution color has no change besides pH over 12. We changed the addition of 5% KOH and its effect on both ΔA and A_c is shown in Fig. 5. The A_c approaches maximum when the addition of the KOH solution is more than 0.5 mL. In this study, 1 mL of 5% KOH was used.

Effect of Reaction Time: The effect of the reaction time on ΔA and A_c of

the Cd-*o*-NBDA solution is shown in Fig. 6. We observe that the reaction was completed in 35 min. The color remains almost constant for at least 4 h.
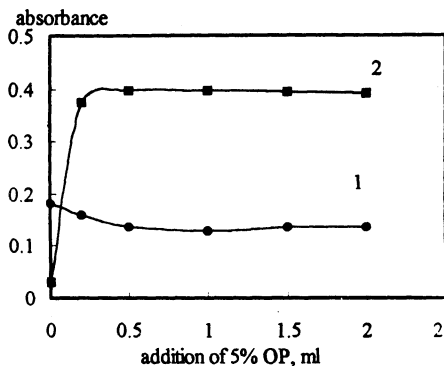

Fig. 4.   Effect of the addition of 5% OP on absorbance ΔA (1) and A_c (2) of the Cd (10 µg)-*o*-NBDA solution.
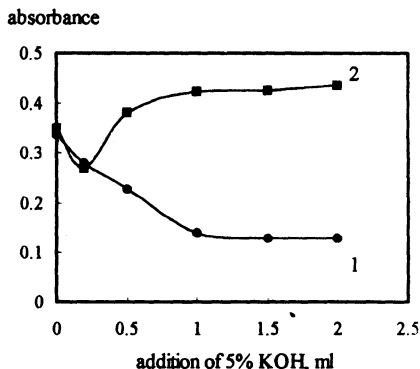

Fig. 5.   Addition of 5% KOH on absorbance ΔA (1) and A_c (2) of the Cd (10 µg)-*o*-NBDA solution in the presence of OP.

Calibration Graph: A series of standard Cd (0–25 µg/25 mL) solutions were prepared and the absorbance of each was measured. A_c of each solution was calculated. The calibration curves are shown in Fig. 7. We find that all points around line 2 (the correlation coefficient, r = 0.9997) is much more linear than those around curve 1 (r = 0.990). As a result, the spectral correction technique has higher accuracy than single wavelength spectrophotometry. The regression equation of curve 2 is expressed by:

$$A_c = 0.0341X - 0.009$$

Precision, Accuracy and Detection Limit: Eight replicate determinations of the standard solution containing 10 µg of Cd were carried out. The results showed that the average is 10.6 ± 0.6 µg and the relative errors (REs) between
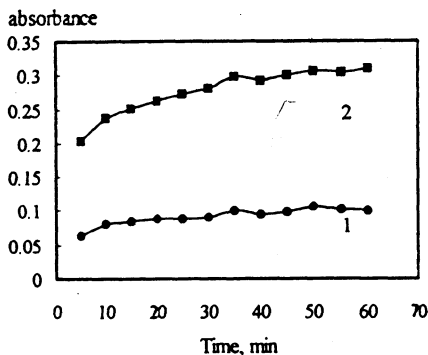
Fig. 6. Effect of the reaction time on absorbance ΔA (1) and A_c (2) of the Cd (7 µg)-*o*-NBDA solution in the presence of OP.
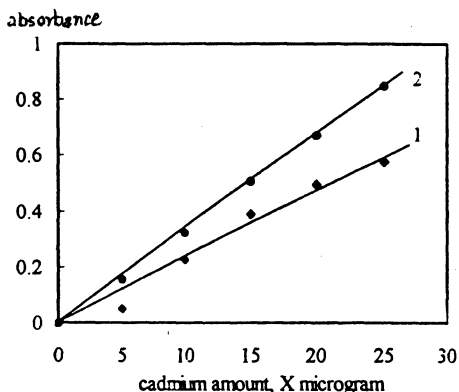

Fig. 7. Standard curves for the determination of cadmium using the Cd-*o*-NBDA reaction at pH 12.5: (1) ΔA and (2) A_c.

−2.1% and +17%. However, the single wavelength method gave the results as: 12.7 ± 3.0 µg of Cd and the REs between −13.1% and +69%. So both the precision and accuracy by the recommended method are higher than those by single wavelength spectrophotometry.

We used $\lambda_{min} = kS_b/S$ to calculate the detection limit of Cd to be 0.2 µg/25 mL (0.008 mg/L), where $k = 3$, the standard deviation $S_b = 0.007$ for the twenty replicate determinations of the *o*-NBDA solutions and the sensitivity $S = 0.0341$.

Effect of foreign ions: The recommended procedure was carried out; none of the following ions will affect the direct determination of 10 µg of Cd ($< 10\%$ error): 0.5 mg of SO_3^{2-}, $S_2O_3^{2-}$, Ca(II), Mg(II), 200 µg of Al(III), Zn(II), F^-, PO_4^{3-}, NH_4^+; 50 µg of Pb(II), Nd(III) and 10 µg of Co(II), Ni(II), Cu(II), Hg(II), Ag(I).

Determination of molar absorptivity and stability constant of complex: The following solutions were prepared for the determination of the stepwise molar absorptivity (ε) and stability constant (K) of the complex: 0.10 µ mol of Cd(II) with 0.10, 0.20, 0.5 and 0.75 µmol of *o*-NBDA. The results are given in Table-1. The stepwise molar absorptivity and stability constant of the Cd-*o*-NBDA complex were calculated by the equations:

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma' C_M)} \quad \text{and} \quad \varepsilon_{ML_n}^{\lambda_2} = \frac{A_c}{\delta C_M(\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n} \varepsilon_{ML_{n-1}}^{\lambda_2}$$

Here the symbol n indicates n-th step complex and δ is the cell thickness (cm). The results are given in Table-1.

TABLE-1

DETERMINATION OF THE STEPWISE ABSORPTIVITY AND STABILITY CONSTANT OF THE Cd COMPLEX WITH *o*-NBDA IN THE PRESENCE OF OP AT pH 12.5 (IONIC STRENGTH 0.01 M AND TEMPERATURE 25°C)

Solution containing 0.004 mM Cd and	A_c at 480 nm for three determinations	γ'	$K \times 10^6$	Mean ε_r^{480} L mol^{-1} cm^{-1}
0.004 mM *o*-NBDA	0.073	0.60	K_1 1.430	1st-step ML : 3.04 × 10^4
0.004 mM *o*-NBDA	0.166	1.65	K_2 1.400	2nd-step ML$_2$: 4.74 × 10^4
0.020 mM *o*-NBDA	0.263	2.70	K_3 0.254	3rd-step ML$_3$: 7.36 × 10^5
0.030 mM *o*-NBDA	0.377	3.86	K_4 0.422	4th-step ML$_4$: 9.80 × 10^5

Sample Analyzed

As a test of the method, Cd was determined in the three samples. The results were given in Table-2. The recovery of Cd is between 91.0 and 108.5%.

TABLE-2

DETERMINATION OF CADMIUM IN SAMPLES

Sample	Cd concentration, mg/L		Recovery, %
	Added	Found	
Waste water 1#	0	0.390	
		0.382	
		0.408	
		mean 0.393	
	0.500	0.848	91.0
		0.907	102.8
Waste water 2#	0	0.698	
		0.668	
		0.744	
		mean 0.703	
	1.00	1.68	97.7
		1.76	105.7
Sewage 3#	0	0.0292	
		0.2980	
		0.2940	
		mean 0.295	
	0.200	0.4860	95.5
		0.5120	108.5

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