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Study on Cadmium Complex Reaction with *p*-Acetyl-Benzenediazoaminoazobenze and Determination of Trace Amounts of Cadmium by β-correction Spectrophotometry

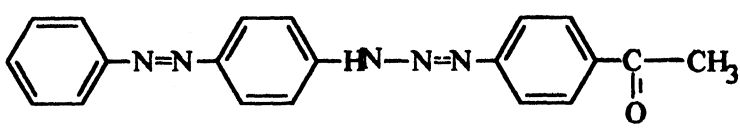
MEI LI†, MING-LIANG YE‡ and HONG-WEN GAO*
Huaibei Environmental Monitoring Centre, Huaibei-235 000, P. R. China

The synthesis of ligand, *p*-acetyl-benzenediazoaminoazobenzene (*p*-ABAA) was carried out and its complex reaction with cadmium was sensitive in basic solution and in the presence of the nonionic surfactant, emulsifier OP Because of the effect of excess of *p*-ABAA on the absorption of Cd-*p*-ABAA complex product, the ordinary spectrophotometry was limited for use. The current principle, named β-correction theory was applied instead of single wavelength method. It gave the simple determination of the composition ratio, molar absorptivity (ε) and stability constant (K) of Cd-*p*-ABAA complex. Results showed that complex Cd(*p*-ABAA)$_3$ was formed at pH 12.5, its real (not apparent) molar absorptivity was 1.28×10^5 L mol^{-1} cm^{-1} at 475 nm and its cumulative stability constant 7.78×10^{18}. For analysis of water samples, the recovery of cadmium was between 98.5 and 110% and the relative standard deviations less than 7.1%.

Key words: β-Correction principle, Cadmium complex, Trace amounts of cadmium, *p*-Acetyl-benzenediazoaminoazobenzene.

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. Ligands or chromogenic agents 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. The synthesis of the chromogenic reagent, *p*-acetyl-benzenediazoaminoazobenzene (*p*-ABAA) was carried out; its structure is given below:



The ligand is sensitive to react cadmium(II) at pH 12–13. In the presence of emulsifier OP, the complex solution was changed into redness from aurantium

†School of Chemistry and Chemical Engineering, Anhui University, Hefei-230039, P.R. China.
‡Zhejiang Conba Pharmacy Co. Ltd., Lanxi- 321100, P. R. China

because the absorption of the complex product is maximal at 475 nm but such a ligand at 565 nm. However, in absence of a surfactant, the complex solution appears clouding. The use of a surfactant was favor to increase the solubility of Cd-*p*-ABAA complex in aqueous solution and raising the reaction sensitivity. Because of two wavelengths difference between the peak and valley absorption of the complex solution only 90 nm the excess of *p*-ABAA will interfere the measurement of real absorbance of the formed complex. As a result, the single wavelength spectrophotometry is not capable to satisfy the analysis of trace Cd(II). The updated dual-wavelength spectrophotometry, named β-correction method[8] have been applied[9-14] for investigation of characteristic factors of the other complex solutions and determination of trace metals. In this report, it was found for β-correction method to eliminate almost completely the effect of excess of *p*-ABAA ligand from the complex solution to give out the real absorption of Cd-*p*-ABAA complex. Such a method is different from other dual-wavelength methods[15, 16]. By the help of the new principle some of the characteristic factors of Cd -*p*-ABAA complex can still be calculated easily for example complex ratio, real but not apparent molar absorptivity and step or cumulative stability constant. For the determination of trace amounts of cadmium, this work gave out all the satisfactory results. This complex reaction was one of most sensitive spectrophotometric determination of trace amounts of cadmium in water, which gave out the detection limit only 0.006 mg/l. The determination of cadmium in wastewater samples showed that the recovery was between 98.5 and 110% and the relative standard deviation less than 7.1%.

Principle

From the following expression[8, 17], the real absorbance (A_c) of a metal (M) complex (ML_γ) produced with a ligand (L) in solution is calculated.

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

Here ΔA and ΔA′ are the absorbances of the mixed solution of ML_γ and L measured at wavelengths λ_2 and λ_1 against the reagent blank (only L solution), respectively and both α and β are named correction factors which are calculated as follows:

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

Here, $\varepsilon_{ML_\gamma}^{\lambda_1}$, $\varepsilon_{ML_\gamma}^{\lambda_2}$, $\varepsilon_L^{\lambda_1}$ ard $\varepsilon_L^{\lambda_2}$ are the molar absorptivities of ML_γ and L at wavelengths λ_1 and λ_2, respectively, whose ratio may be computed after the direct determination of L and ML_γ solutions.

The real (not apparent) molar absorptivity ($\varepsilon_{ML_\gamma}^{\lambda_2}$) and the molar ratio (γ) of effective L to M in reaction may be expressed as follows.

$$\varepsilon_{ML_\gamma}^{\lambda_2} = \frac{A_c}{\delta C_M}; \quad \eta = \frac{A_c - \Delta A}{A_0} \quad \text{and} \quad \gamma = \eta \times \frac{C_L}{C_M}$$

Here, the symbol η indicates the effective fraction of L, C_M is the molar concentration (mol/L) of M at the beginning and δ is the thickness of the cell. The term C_L is the molar concentration (mol/L) of L in the beginning solution and A_0 is the absorbance of the blank reagent (only L) measured at wavelength λ_2 against water reference. If γ' reaches maximum and remains constant, $\gamma = \gamma'$ where γ is a natural number. In fact, it is just the composition ratio of complex. In addition, the stepwise stability constant (K_n) of complex ML_γ may be computed according to the following equation. The molar ratio γ' of effective L to M in solution should be near to n–0.5 so as to give the minimum error.

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma' C_M)}$$

From all K_n, we can further calculate the cumulative constant (K) of complex ML_γ by the following expression:

$$K = K_1 \times K_2 \times \ldots \times K_n \times \ldots \times K_\gamma$$

EXPERIMENTAL

Absorption spectra were recorded on a Shimadzu UV/VIS 265 spectrophotometer with 1.0 cm cells.

Standard Cd(II) stock solution, 1000 mg/L was prepared by dissolving 1.000 g of high-purity metal cadmium (content > 99.9%) in 20 mL of 2 mol/L hydrochloric acid and diluted to 1000 mL.

Standard Cd(II), work solution, 1.00 mg/L was prepared daily by diluting the above standard Cd(II) stock solution.

The ligand solution, 0.500 mmol/L *p*-ABAA was prepared by dissolving 0.1715 g of *p*-acetyl-benzenediazoamino-azobenzene (*p*-ABAA) in 100 mL of acetone (A.R. grade, Shanghai Chemical Reagents) then diluting to 1000 mL with acetone. It is stored in a dark bottle and kept at less than 5°C.

KOH solution, 1.00 mol/L was used to adjust pH of solution.

The masking reagent was prepared by mixing 0.002 mol/L triethanolamine (A.R., Shanghai Solvant) and 0.02 mol/L sodium citrate (A.R., Shanghai Reagent) in equal volume. Adjusted the solution to pH 12.5 with 0.2 mol/L sodium hydroxide.

The anion surfactant, sodium dodecyl benzene sulfonate (SDBS, Shanghai Reagents), non-ionic surfactant, OP (Beijing Chemicals) and cationic surfactant, cetyl trimethylammonium bromide (CTMAB, Shanghai Reagents) solutions all 2% were prepared for increasing the solubility of complex and the reaction sensitivity.

Recommended procedures

A known volume of a wastewater sample containing less than 15 μg of cadmium was taken in a 25 mL volumetric flask and diluted to about 12.5 mL with water. Added 1 mL of OP solution, 0.5 mL of masking solution and 1 mL of 0.500 mmol/L *p*-ABAA. After mixed, added 1 mL of KOH solution. Diluted to 25 mL and mixed well. After 10 min, measured absorbances at 475 and 565 nm against a reagent blank, respectively.

RESULTS AND DISCUSSION

Absorption spectra: Fig. 1 shows the absorption spectra of *p*-ABAA and Cd-*p*-ABAA solution in the presence of OP. From curve 3, two wavelengths

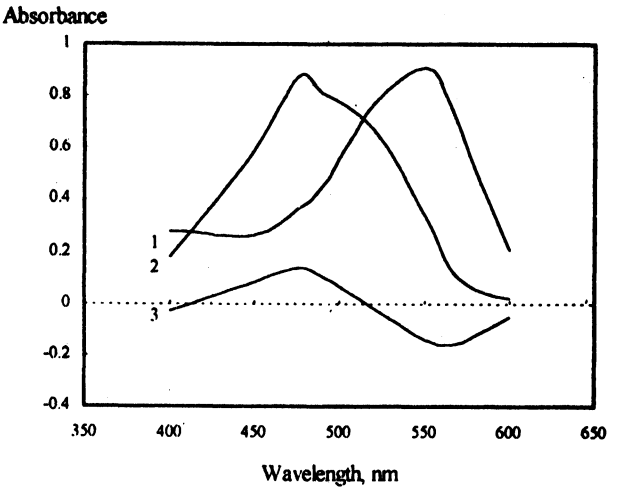


Fig. 1. Absorption spectra of *p*-ABAA and its Cd complex solution in the presence of OP at pH 12.5 : 1, 0.020 mmol/L *p*-ABAA against water; 2, Cd (more than 100 μg) complex solution with *p*-ABAA (0.020 mmol/L), against water; 3, Cd (5.00 μg) complex solution with 0.020 mmol/L *p*-ABAA against a reagent blank.

should be selected such that the difference in absorbances is a maximum: 475 and 565 nm. The β value of *p*-ABAA solution is 0.470 calculated from curve 1. At the same method, the α of Cd-*p*-ABAA complex is 0.195 calculated from curve 2. Therefore, $A_c = 1.08(\Delta A - 0.470\,\Delta A')$ at 475 nm.

Effect of addition of *p*-ABAA solution: Fig. 2 gives the effect of the addition of 0.500 mmol/L *p*-ABAA on the absorbance of the reagent blank and the complex solution. From curve 1, it is impossible for the composition ratio of

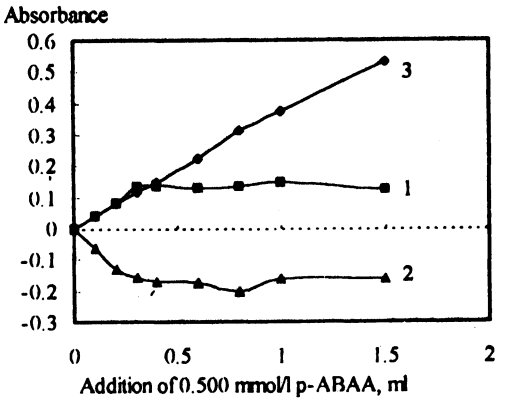


Fig. 2. Effect of *p*-ABAA addition on absorbance of the reagent blank and its Cd complex solution at pH 12.5 in presence of OP: 1, Cd (10 μg) complex solution against reagent blank at 475 nm; 2, same as 1 but at 565 nm; 3, the reagent blank against water at 475

p-ABAA to Cd to be calculated accurately with the conventional molar ratio method[18] by reason of non-sharpness of the inflexion point. The A_c and γ' of each solution were obtained and their curves are shown in Fig. 3. From curve 2, γ' remains constant 3 when the addition of *p*-ABAA solution is over 0.4 mL. Therefore, Cd(*p*-ABAA)$_3$ was formed here. From curve 1 in Fig. 3 we can

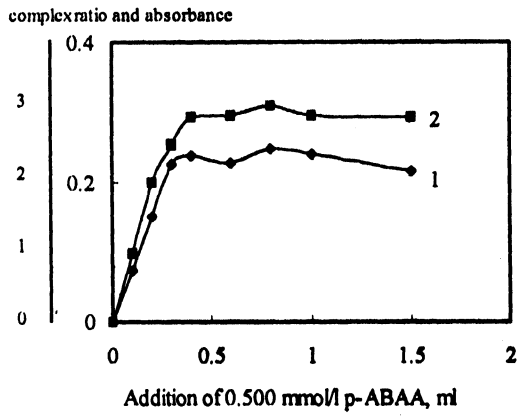


Fig. 3. Curves of A_c and γ' : 1, A_c at 475 nm; 2, γ'.

calculate the real absorptivity $\varepsilon^{475\ nm}_{Cd(p\text{-}ABAA)3} = 1.28 \times 10^5$ L mol^{-1} cm^{-1} in presence of OP, but from curve 1 in Fig. 2 it is apparent that $\varepsilon^{475\ nm}_{Cd(p\text{-}ABAA)3} = 7.70 \times 10^5$ L mol^{-1} cm^{-1} at pH 12.5. In the determination of trace amounts of cadmium, 1.0 mL of 0.500 mmol/L *p*-ABAA was selected because of the maximal A_c from curve 1 in Fig. 3.

Effect of pH: By varying pH of the solution, its effect on absorption of Cd-*p*-ABAA solution is shown in Fig. 4. We observe that the absorbances approach to maximum and remain almost constant when pH is more than 12. In this study, 1 mL of 1.0 mol/L KOH was selected.

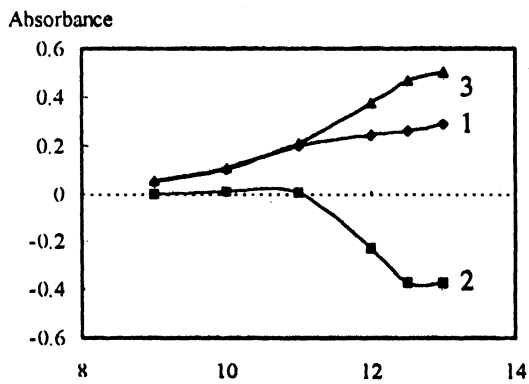


Fig. 4. Effect of pH on absorbance ΔA (at 475 nm curve 1), ΔA′ (at 565 nm curve 2) and A_c (at 475 nm curve 3) of Cd (10 μg)-*p*-ABAA complex solution *in the presence of OP.*

Effect of surfactant selection and addition: By using the different surfactant, OP, CTMAB and SDBS, their effect on absorption of Cd-ABAA solution are shown in Fig. 5. We observe that the use of OP gives the highest peak and

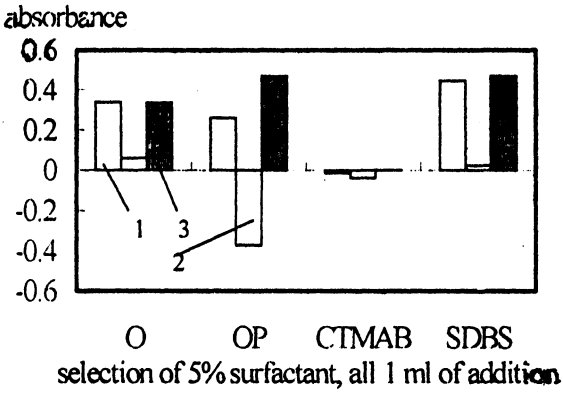


Fig. 5. Effect of surfactant selection on absorbance ΔA (curve 1 at 475 nm), ΔA′ (curve 2 at 565 nm) and A_c (curve 3 at 475 nm) of Cd (10 μg)-*p*-ABAA complex solution.

deepest valley absorption. By varying the addition of 2% OP, its effect is shown in Fig. 6. While the addition of OP solution is over 0.5 mL, The A_c reaches maximum. In this study, 1 mL of OP solution was used.

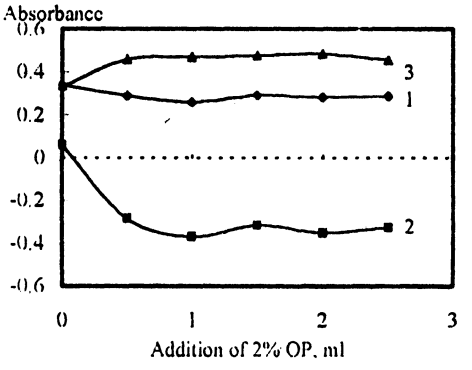


Fig. 6. Effect of addition of 2% OP on absorbance ΔA (curve 1), ΔA′ (curve 2) and A_c (curve 3) of Cd (10 μg)- *p*-ABAA complex solution in the presence of OP.

Effect of time: For Cd-*p*-ABAA complex solution, the effect of the reaction time on A_c is shown in Fig. 7. From curve 1, the reaction is completed in 5 min because of the reach of maximal A_c. The color absorption of solution remains almost constant for at least 4 h. In addition, Curve 2 showed absorption of the complex solution when KOH solution was added in the first of all. From it we find that the reaction is complete after 1 h. Therefore, the basic solution should be added finally.

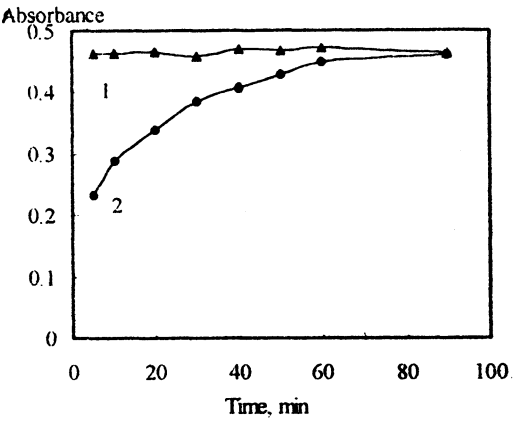


Fig. 7. Effect of color-developed time on absorbance A_c of Cd (10 μg)-*p*-ABAA complex solution : 1, KOH solution added finally; 2, KOH solution added in the first of all.

Determination of stability constant, K: The following solutions were prepared for the determination of stability constant of complex: 0.0178 μmol/25 mL Cd(II) with 0.025 μmol/25 mL *p*-ABAA and 0.0445 μmol/25 mL Cd(II) with 0.075 and 0.150 μmol/25 mL *p*-ABAA. The n^{th} step stability constant of Cd (*p*-ABA/A)$_3$ and its cumulative that K_n and K were all calculated and their data are listed in Table-1 at pH 12.5 and temperature 15°C and in ionic strength 0.1.

TABLE-1
DETERMINATION OF STABILITY CONSTANT OF Cd COMPLEX WITH *p*-ABAA AT pH 12.5 AND IN THE PRESENCE OF OP AT TEMPERATURE 15°C AND IN IONIC STRENGTH 0.1

Complex solution in presence of OP	Absorbance		Composition ratio, γ	Stability constant, K
	at 475 nm	565 nm		
0.713 μmol/L Cd(II) + 1.00 μmol/L *p*-ABAA	0.014	−0.022	0.748	$K_1 = 6.36 \times 10^6$
	0.020	−0.020	0.715	$K_1 = 5.12 \times 10^6$
1.78 μmol/L Cd(II) + 3.00 μmol/L *p*-ABAA	0.059	−0.091	1.320	$K_2 = 0.97 \times 10^6$
	0.047	−0.096	1.360	$K_2 = 1.42 \times 10^6$
1.78 μmol/L Cd(II) + 6.00 μmol/L *p*-ABAA	0.136	−0.156	2.560	$K_3 = 0.88 \times 10^6$
	0.131	−0.162	2.640	$K_3 = 1.37 \times 10^6$
				$K = 7.78 \times 10^{18}$

Calibration graph: A series of standard Cd (0–15 μg/25 mL) solutions were prepared and the absorbance of each was measured. A_c of each solution was obtained. Calibration curves are shown in Figure 8. We find that all points around curve 2 (linear correlation coefficient, $R_2 = 0.9992$) is more linear than that around curve 1 ($R_1 = 0.9976$). As a result, β-correction method gives higher accuracy than the single wavelength spectrophotometry. The following equations are established for determination of cadmium: $A_c = 0.0457X + 0.013$ but $\Delta A = 0.0275X - 0.011$.

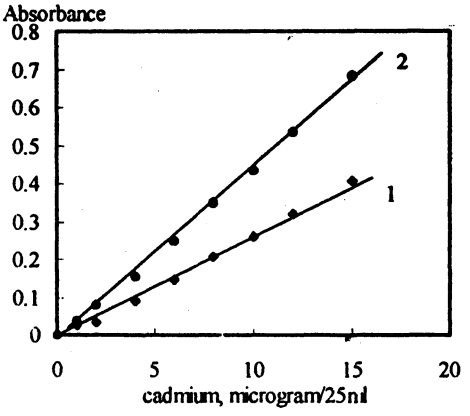


Fig. 8. Standard curves for the determination of cadmium using Cd-*p*-ABAA reaction at pH 12.5 at 475 nm : 1, ΔA; 2, A_c.

Precision, accuracy and detection limit: Eight replicated determinations of standard solution containing 1.00 μg Cd were carried out. The results are listed in Table-2. The relative errors (REs) are between −1.5% and +14.0% the relative standard deviation (RSD) 5.2% in OP presence by β-correction method, but REs between −1.8% and +38% and RSD 12.9% by single wavelength spectrophotometry. Therefore, both the precision and accuracy with β-correction method are higher than that with the single wavelength spectrophotometry.

TABLE-2
RESULTS AND COMPARISON OF REPLICATED DETERMINATION OF 1.00 μg CADMIUM BY β-CORRECTION METHOD WITH THAT BY THE SINGLE WAVELENGTH SPECTROPHOTOMETRY

Method	Found, μg		Average, μg	Relative error, %	Relative standard deviation (%)
Single wavelength spectrophotometry	1.35	1.13			
	1.09	0.98	1.19	−1.8~ + 38	12.9
	1.13	1.38			
	1.09	1.38			
β-correction method	1.14	1.01			
	1.07	1.03	1.05	−1.5~ + 14	5.2
	1.05	1.12			
	0.98	1.01			

We used $L_{min} = kS_b/S$ to calculate the detection limit of Cd, where k = 3, S_b named as standard deviation and S named as sensitivity. Replicate determination of twenty reagent blanks gave S_b of both A_c were equal to 0.0023. The analytical sensitivity S was equal to 0.0457. Therefore the detection limit of Cd is only 0.15 μg/25 mL (0.006 mg/l).

Effect of foreign ions: The recommended procedure was carried out, none

of the following ions will affect the direct determination of 5 μg of Cd (<10% error): 10 mg of Cl^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_3^-, I^-, F^-, PO_4^{3-}, NH_4^+, K(I), Na(I), Li(I), Ca(II), Mg(II), Zn(II), Be(II), Sb(III); 1 mg of Al(III), Sn(IV), Sn(II), W(VI), Ti(IV); 200 μg of Pb(II), Nd(III), Tl(I), Fe(II), Fe(III), Ga(III), Ge(IV), Mo(VI), La(III), Zr(IV), Se(IV), Sc(III), V(V), Cr(IV), Cu(II); 100 μg of Co(II), Ag(I), Ni(II) and 20 μg of Hg(II).

Sample analyzed

As a test of the method, cadmium was determined in several samples. The results are all listed in Table-3. The recovery rates of standard cadmium were between 98.5 and 110% and RSD 7.1 % by β-correction spectrophotometry

TABLE-3
DETERMINATION OF CADMIUM IN WATER SAMPLES USING Cd-*p*-ABAA REACTION AT pH 12.5

Sample	Cd concentration mg/l		Recovery (%)
	Added	Found*	
Wastewater	0	0.097 0.107	
		0.093 0.111	
		0.098 0.096	RSD 7.1%
		0.108	
		aver. 0.101	
	0.200	0.316	107
		0.322	110
		0.317	108
Huaibe River water	0	<0.006	
	0.200	0.216	108
		0.217	108
		0.197	98.5

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