

ARTICLES

Determination of Trace Amounts of Cadmium with *p*-Acetyl-Benzenediazoaminoazobenzene by Primary–Secondary Wavelength Spectrophotometry

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Abstract—The reaction between Cd^{2+} and a chromogenic agent, *p*-acetylbenzenediazoaminoazobenzene (*p*-ABAA) at pH 12.5 is sensitive and selective in the presence of triethanolamine and citrate. The solubilization and sensitization of the OP emulsifier (nonionic surfactant) was observed in the above reaction. Because the absorption of excess *p*-ABAA interferes with the absorption of the complex, primary–secondary wavelength spectrophotometry (PSWS) was used instead of the single-wavelength method in the determination of trace amounts of cadmium. Results showed that this method gave out a higher precision and better accuracy than the single-wavelength method, because two wavelengths that are located at the peak absorption and the valley absorption of the reaction solution were used simultaneously. By analyzing samples, the relative standard deviations were less than 8% and the recovery between 96.5 and 111%.

INTRODUCTION

Cadmium is one of the most poisonous pollutants of the biosphere, especially for the body and other organisms. It often exists in water polluted by, for example, metallurgical, chemical, electrolytic, and other industries. It can accumulate in the human body to result in the variation of kidney function and urological system. Cadmium can still check the self-cleaning role of surface water when its concentration is over 0.1 mg/L. It will still pollute rice and soil when irrigating with surface water containing Cd. Trace amounts of Cd is usually determined by AAS and spectrophotometry with cation [1], 4-hydroxy-benzoylhydrazone [2], di-2-pyridyl-methanone-2-(5-nitropyridyl) hydrazone [3] and so on. The synthesis of *p*-acetyl-benzenediazoaminoazobenzene (*p*-ABAA) was earlier reported [4] and its structure is given below.

The reagent was earlier applied in the determination of silver [5]. In this report, it was applied in the determination of trace amounts of Cd in wastewater. The reaction between Cd(II) and *p*-ABAA is sensitive at pH 12.5 and in the presence of nonionic surfactants. Primary–secondary wavelength spectrophotometry (PSWS) was utilized instead of the ordinary method (single wavelength spectrophotometry) because of the simultaneous use of both the peak absorption (A_p) and valley (A_s) absorption of the reaction solution. Its good precision and high accuracy are confirmed in the determination of some components [6–8]. It never uses the classical Lambert–Beer Law and its final expression is $\log B = \alpha x \beta$, where $B = [(A_p + 1)/(A_s + 1)]$ and

x indicates the concentration of the analyzed component. Both α and β are regression coefficients calculated from standard series of the determined component. They are often constant when both the primary wavelength λ_p and secondary wavelength λ_s are selected. They change little even if the change of operation environment happens, for example, at room temperature. This is because the measured absorbances A_p and A_s will change in step with and simultaneously with the environment. Therefore, the above expression remains basically stable [8]. This will decrease the operation procedure in the daily application of determination of a component. In fact, PSWS is one of the dual-wavelength methods but it is different from the others [9–11] in principle and operation. It may increase the precision and accuracy in analysis of trace amounts of a component by utilizing both the valley absorption and peak absorption of the color solution. Most metal ions will not interfere with the direct determination of trace cadmium in the presence of triethanolamine and citrate. For the analysis of samples, the results are all satisfactory.

EXPERIMENTAL

Apparatus and Reagents. Absorption spectra were recorded on a UV-VIS 265 spectrophotometer (Shimadzu, Japan) in 1.0-cm cells. The content of Cd in the samples was examined with an WFX-1F2 atomic absorption spectrophotometer (AAS, Beijing Sec. Opt. Instrument Works, China) at wavelength 228.8 nm.

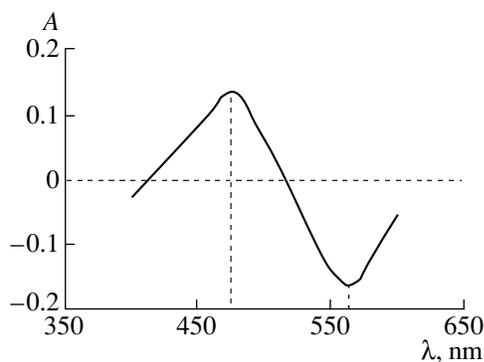


Fig. 1. Absorption spectra of Cd-*p*-ABAA solution at 475 nm containing 10 µg Cd at pH 12.5 and in the presence of OP against a reagent blank.

Standard Cd(II) stock solution, 1.000 g/L was prepared by dissolving 1.000 g of high-purity cadmium (over 99.9%, Shanghai Reagents) in 20 mL of 2 M 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 solution.

Chromogenic agent solution, 0.50 mM *p*-ABAA, was prepared by dissolving 0.1715 g of *p*-acetyl-benzenediazoaminoazobenzene (content >98%, Shanghai Changke Reagents Institute, China) in 100 mL of acetone (A. R., Shanghai Reagents) then diluting to 1000 mL. It should be stored in a dark bottle.

A solution of 1.0 M KOH was used to adjust the acidity of the solution.

Masking reagent solution was prepared by mixing the same volume of 0.002 M triethanolamine (A. R., Shanghai Reagents) and 0.02 M sodium citrate (A. R., Shanghai Reagents), and it was adjusted to pH 12 with 0.2 M sodium hydroxide.

The following surfactant solutions, all 2%, were prepared so as to select a proper reagent for increasing sensitivity: alkylphenol ethoxylates (emulsifier OP, Shanghai Reagents) solution, SDBS (Shanghai

Reagents) solution, and cetyltrimethylammonium bromide (CTMAB) solution.

Recommended procedure. A known volume of a standard solution or a sample containing less than 20.0 µg of Cd(II) was taken in a 25-mL volumetric flask. Add 0.5 mL of masking reagent solution, 1 mL of OP solution, and 1.0 mL of *p*-ABAA solution. After mixing, add 1 mL of KOH solution. Dilute to volume and mix well. After 10 min, measure absorbances at 475 nm (A_p) and 565 nm (A_s), respectively, against a reagent blank. Calculate the term $\log B$.

RESULTS AND DISCUSSION

Absorption spectra. Figure 1 shows the absorption spectra of Cd-*p*-ABAA complex solution against a reagent blank. The peak absorption appeared at 475 nm, and the valley absorption at 565 nm. The analytical sensitivity will reach a maximum if two such wavelengths are selected as the measurement wavelengths. In this study, $\lambda_p = 475$ nm and $\lambda_s = 565$ nm.

Effect of the *p*-ABAA concentration. Figure 2 shows the effect of the various addition of chromogenic reagent solution on the term $\log B$. The term $\log B$ reached a maximum and remained almost constant when the addition of *p*-ABAA solution was more than 0.3 mL. In this work, 1.0 mL of 0.50 mM *p*-ABAA was used so as to obtain the maximum sensitivity and stable β value.

The complex ratio of Cd(II) to *p*-ABAA is determined to be 1 : 3 by using the continuous variation method [12] and beta-correction spectrophotometry [13].

Effect of pH. Figure 3 gives the effect of pH on $\log B$ values. We find that the calculation parameter values are very small at pH of the solution less than 12. The $\log B$ values approach the maximum and remain constant when pH is more than 12.5. In this study, 1 mL of 1.0 M KOH was added to give the solution a pH of about 12.5.

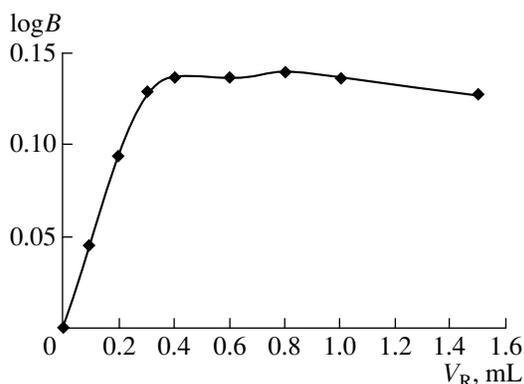


Fig. 2. Effect of addition of 0.50 mM *p*-ABAA on $\log B$ values.

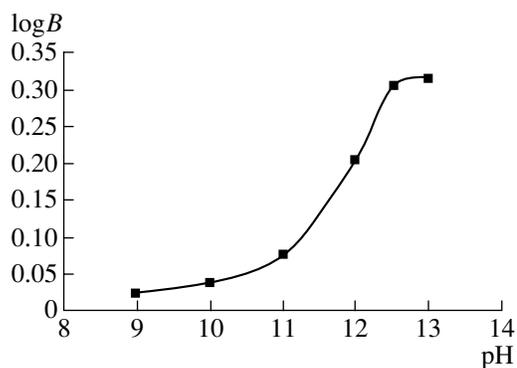


Fig. 3. Effect of pH on $\log B$ values.

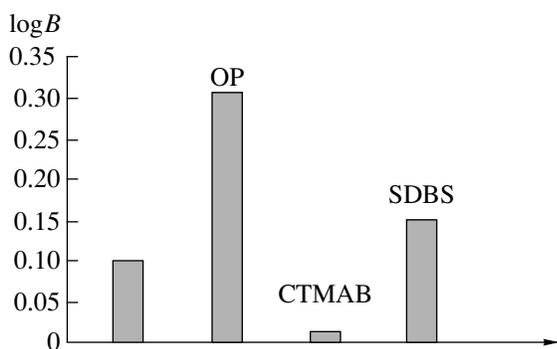


Fig. 4. Effect of various surfactants (all 1 mL of 2%) on $\log B$ values.

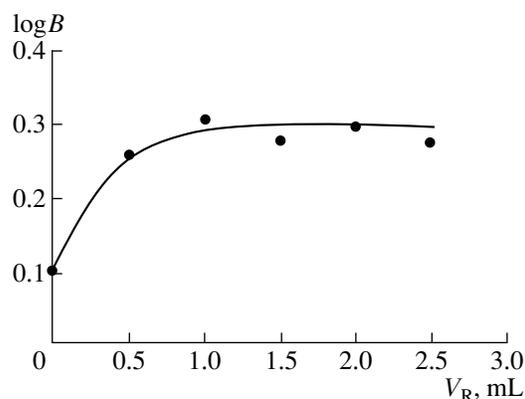


Fig. 5. Effect of addition of 2% OP on $\log B$ values.

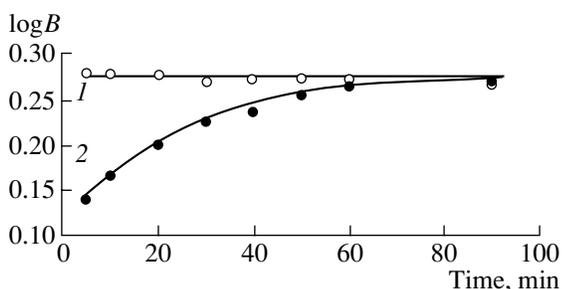


Fig. 6. Effect of time on $\log B$ values: 1, KOH solution was added after the addition of *p*-ABAA; 2, KOH solution was added in the beginning.

Effect of selection and addition of surfactant. In the presence of different surfactants, such as OP, CTMAB, and SDBS solution, the experimental results are shown in Fig. 4. We find that the use of OP gives the highest $\log B$ value: about 3 times that obtained in absence of any surfactant. In this work, OP was selected. By varying the addition of 2% OP, the change in $\log B$ values is shown in Fig. 5. The term $\log B$ approaches the maximum when the addition of OP solution is more than 0.5 mL.

Effect of time. The effect of the reaction time on $\log B$ is shown in Fig. 6. The reaction is complete in 5 min, because $\log B$ approaches a constant. However, from curve 2 we observe that the reaction between Cd(II) and *p*-ABAA ends after 60 min if KOH solution was added in the beginning. This is because Cd(II) will first form Cd(OH)₂ colloid particles, then its OH⁻ is replaced by *p*-ABAA to form the more stable complex Cd(*p*-ABAA)₃. The second step of the reaction is slow, and it affects the reaction speed of the whole reaction system. The alkaline KOH solution should be added after the addition of *p*-ABAA solution, and the measurement of absorbances is carried out after 10 min in this work.

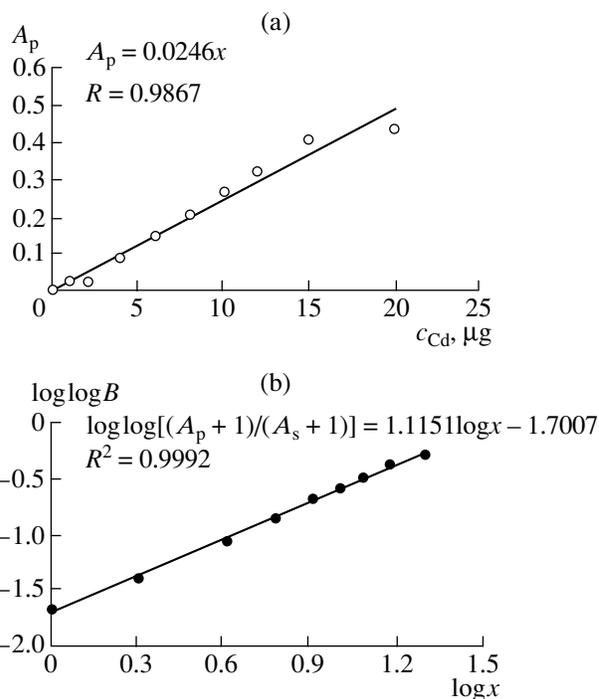


Fig. 7. Standard curves for the determination of cadmium: (a) conventional procedure (475 nm), (b) derivative spectrophotometry.

Calibration graph. A series of standard Cd (0–20.0 μg) solutions were prepared and measured. Two curves are shown in Fig. 7. Curve 7a ($A_p \sim x$) was obtained by measuring absorption only at the single wavelength 475 nm, and curve 7b ($\log B \sim \log x$) was obtained by carrying out the recommended method. Their slope, intercept, and correlation coefficient are given in Fig. 7, too. We observe that all points of line b (linear correlation coefficient 0.9992) are much more linear than line a (linear correlation coefficient 0.9867). So the single wavelength method will bring poor accuracy and great deviation in the determination of trace amounts of cadmium with *p*-ABAA as a chromogenic

Table 1. Result of replicate determinations of 1.00 µg standard Cd(II) by PSWS and the single wavelength (only at 475 nm) method

Method	Found, µg	Average, µg	RSD, %
Single wavelength spectrophotometry	1.08 0.83	0.91	18.7
	0.79 0.67		
	0.83 1.13		
	0.79 1.13		
PSWS	1.04 0.96	0.98	7.4
	1.09 1.04		
	1.00 0.96		
	0.91 0.87		
	0.91 0.87		

Table 2. Determination of cadmium in two samples by the recommended method and AAS sample

Sample	Cd(II) amount, µg		Recovery, %
	added	found	
10.0 mL of wastewater sampled from chemical industry at Huaihe River basin	0	1.39 1.41	97.0–111
		1.29 1.18	
		Mean: 1.32 RSD: 8.0% 1.19*	
	2.00	3.26 3.55	
10.0 mL of lake water sampled from Huaihe River basin	0	<0.2 <0.2	96.5–110
		Mean: <0.2 <0.05*	
		2.00	

* Average of three determinations by AAS.

agent. We obtain the regression equation of line b as $\log B = 0.020x^{1.12}$ ($\alpha = 0.020$ and $\beta = 1.12$).

Precision, accuracy, and detection limit. Eight replicate determinations of a standard solution containing 1.00 µg Cd(II) were carried out; the results are listed in Table 1 ($n = 8$). The relative errors (REs) were between -13 and $+9.0\%$, and the standard deviation (RSD) was 7.4% by PSWS. However, the REs were between -33 and $+13\%$ and the RSD was 18.7% by the single wavelength method. Both the accuracy and precision by PSWS were therefore higher than that by the ordinary spectrophotometric method.

The detection limit calculated by the $3s$ -test ($n = 20$) was found to be 0.08 µg/mL.

Effect of foreign ions. When the recommended procedure is carried out, triethanolamine may mask Al(III), Ti(IV) and citrate may mask Cu(II), Ag(I), Hg(II) and other metal ions. None of the following ions will affect the direct determination of 5.0 µg of Cd

($<10\%$ error): 10 mg of Cl^- , SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, NO_3^- , I^- , F^- , PO_4^{3-} , NH_4^+ , K(I), Na(I), Ca(II), Mg(II), Zn(II), Be(II); 1 mg of Al(III), Sn(II), Ti(IV); 200 µg of Pb(II), Fe(II), Fe(III), Mo(VI), V(V), Cu(II), Cr(IV); 100 µg of Ag(I), Co(II), Ni(II); and 20 µg of Hg(II).

Samples analyzed. As a test of the method, Cd was determined in wastewater and surface water, both sampled from the Huaihe River basin of China. The results are listed in Table 2. We calculated the average concentration of cadmium in wastewater and lake water samples as 0.132 and <0.02 µg/mL, respectively. The recovery of added standard Cd (II) was between 96.5 and 111% , and the RSD was 8.0% . In addition, in order to confirm the data obtained by the recommended method, we determined the content of Cd in samples by AAS. The average of three replicate determinations is listed in Table 2. It is clear that, the data obtained by the two methods are identical. Therefore, the recommended method can give an accurate determination of microamounts of Cd in water.

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