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Primary-Secondary Wavelengths Spectrophotometric Determination of Trace Amounts of Cadmium with 2,4-Dibromo-6-Carboxy-Benzenediazoaminoazobenzene

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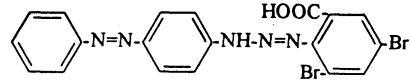
In basic solution and in the presence of non-ionic surfactant, emulsifier OP, the reaction of cadmium (Cd^{2+}) with new chromogenic agent, 2,4-dibromo-6-carboxy-benzenediazoaminoazobenzene (DBCBAA) forms red complex. It is one of most sensitive determinations of trace cadmium in environment. Because of the interference of excess of DBCBAA on complex absorbance the new method, primary-secondary wavelengths spectrophotometry (PSWS), was applied for the determination of trace amounts of cadmium in wastewater. The results showed that the working wavelengths should be selected at 520 and 610 nm and such a method gives out the higher precision, accuracy and lower detection limit than by ordinary spectrophotometry. By testing several wastewater samples, the relative standard deviations were less than 7.2% and the recovery rate of Cd is between 90 and 108%.

INTRODUCTION

Cadmium is one of the poisonous pollutants for human body and other organism. It often exists in water polluted by, for example, metallurgical, chemical, electrolytic and other industries. At present trace amounts of cadmium is usually determined by cadions[1,2], 4-hydroxy-benzoylhydrazone[3], di-2-pyridylmethanone-2-(5-nitropyridyl) hydrazone[4] we have synthesize the new chromogenic reagent, 2,4-dibromo-6-carboxy-benzenediazoaminoazo-benzene (DBCBAA) and its structure is given below:



In this report, the new ligand was applied for the determination of trace amounts of cadmium in wastewater at pH between 12 and 13 and in the presence of non-ionic surfactant, emulsifier OP by primary-secondary wavelength spectro-

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photometry (PSWS) which is the new spectrophotometric method. Because PSWS can give higher precision and sensitivity than conventional spectrophotometry the results have shown that the detection limit of cadmium was only 0.008 mg/L, its recovery rate is between 90.0% and 108% and the relative standard deviations (RSDs) is less than 7.2%.

Principle

From absorption spectra (Fig. 1) the curve 2 (color solution) 1 unit absorbance up to curve 2′ and it crossed curve 1 (absorption spectra of suspension liquid, absorption formula: $A = k\lambda^{-y}$). Both B and C were crosspoints and they meet the above equation and the following relationship[5] was further obtained:

$$\frac{A_p + 1}{A_s + 1} = \left(\frac{\lambda_p}{\lambda_s}\right)^{-y}$$

where λ_p is primary wavelength was often selected at peak absorption of colour solution and λ_s is secondary wavelength at valley absorption. They are shown in Fig. 1. If both λ_p and λ_s were selected, $y = k'\log\left(\frac{A_p + 1}{A_s + 1}\right)$ (k′ is a constant) and the following relationship formula was established:

$$\log\left(\frac{A_p + 1}{A_s + 1}\right) = \alpha X^{\beta}$$

where both α and β are constant and the main variable X is to indicate the colour-developed substance concentration (mg/L or μg). Because of the buffer function of $(A_p + 1)/(A_s + 1)$ the above equation is considered to stabilize the effect of variable work environment on both α and β and to improve the precision and accuracy of trace analysis. In fact, this method named as primary-secondary spectrophotometry (PSWS) is also one of the dual-wavelength methods but different from the others[6-8].

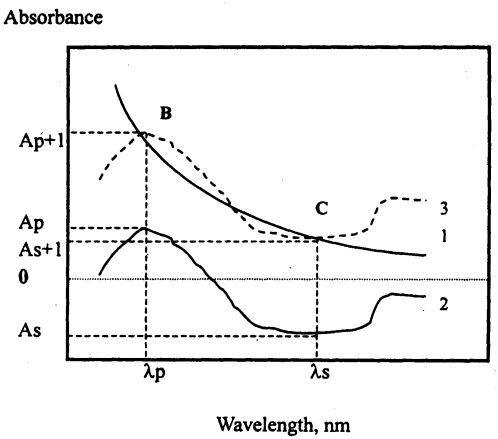

Fig. 1. Absorption spectra curves: 1. suspension liquid against water; 2. complex solution against ligand solution, 3. same as 2. but the absorbances translation up 1. λ_p = positive aborption (B peak) or primary wavelength; λs = negative absorption (C valley) or secondary wavelength.

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai, China), in a 10 mm glass cell.

Standard Cd(II) (1000 mg/L) solution: Prepared from 1 g high-purity cadmium dissolved in 20 mL of 2 mol/L hydrochloric acid and diluted to 1000 mL.

Standard Cd(II) (1 mg/L) working solution must be prepared daily with the above standard Cd solution.

Chromogenic agent solution, 0.20 mmol/L DBCBAA: dissolving 101 mg of 2,4-dibromo-6-carboxy-benzenediazoaminoazobenzene (purified DBCBAA) in 50 mL of acetone (A.R., Shanghai Reagent), then diluting to 1000 mL with acetone. It should be stored in a dark bottle.

KOH solution, 5% (m/v)

Masking reagent solution: mixed 0.002 mol/L triethanolamine (A.R. Shanghai Solvent) and 0.02 mol/L sodium citrate (A.R., Shanghai Reagent) and adjusted to pH 12 with 0.2 mol/L sodium hydroxide.

Emulsifier OP (Shanghai Organic) solution, 5%.

Recommended Procedures: A known volume of a sample containing less than 10 μg of Cd was taken in a 25 mL volumetric flask and add ion exchange water to about 10 mL. After that the we have added 0.5 mL of masking solution and 3 mL of chromogenic agent solution. After mixing well add 2 mL of KOH solution. Diluted to volume and mixed well. After 10 min, measured absorbances at 520 and 610 nm, respectively, against a reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 2 gives the absorption spectra of Cd-DBCBAA complex solution. From this spectra the peak absorption appears at 520 nm and

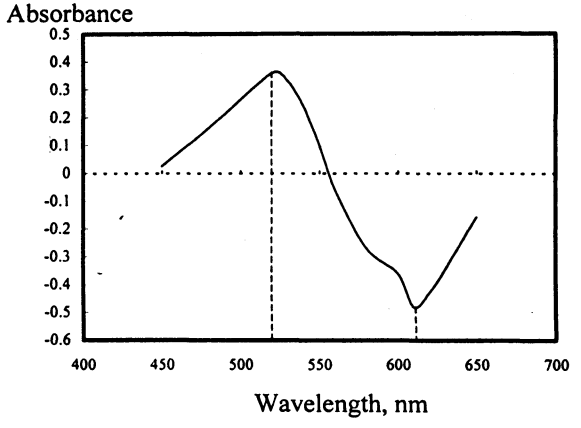

Fig. 2. Absorption spectra of Cd-DBCBAA complex solution containing 10 μg Cd at pH 12.5 and in the presence of OP, at 520 nm against reagent blank.

the valley at 610 nm. Therefore, the primary wavelength should be selected at 520 nm and the secondary wavelength at 610 nm. $\lambda p = 520$ nm and $\lambda s = 610$ nm.

Effect of DBCBAA Solution Addition: Fig. 3 showed the effect of the various addition of chromogenic reagent solution on absorbance of Cd complex solution and its Y calculated from equation above. It was found that the addition of reagent solution was more than 2.5 mL Y and absorbance remained maximal. In this work, 3 mL of 0.20 mmol/L DBCBAA was used.

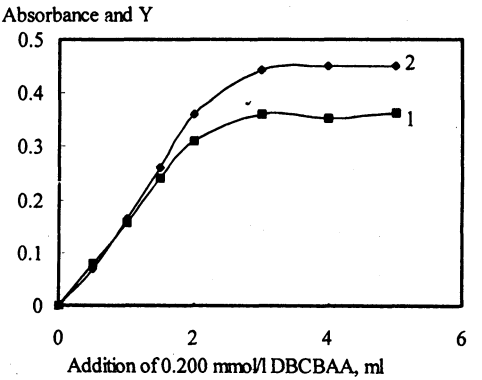

Fig. 3. Effect of 0.20 mmol/L DBCBAA addition on absorbance (curve 1) and Y (curve 2) of Cd (10 μg) complex solution in the presence of OP, at 520 nm.

The complex ratio of Cd(II) to DBCBAA is determined to be 1 : 4 by using the continuous variation method[9] and β-correction spectrophotometry[10].

Effect of pH: Fig. 4 gives the effect of the various pH. With pH more than 12 Y the absorbance reached maximal and remained almost constant. In this study, 2 mL of 5% KOH was selected.

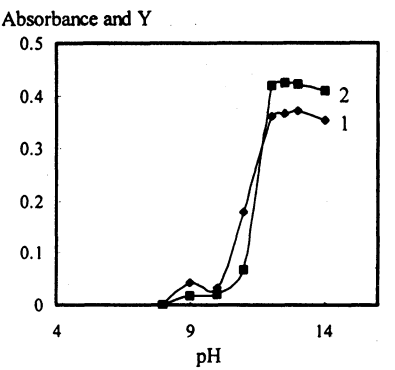

Fig. 4. Effect of pH on absorbance (curve 1) and Y (curve 2) of Cd (10 μg)-DBCBAA complex solution in the presence of OP, at 520 nm.

Effect of Surfactant Selection and Addition: In the presence of different surfactant, we have added 1 mL of 5% OP, CTMAB and SDBS solution respectively and in the absence of surfactant the results are shown in Fig. 5. It

was found that the use of OP gave the maximal Y so as to bring high sensitivity. On Varying the addition of 5% OP, the resulting curve is shown in Fig. 6. While the addition of OP solution was more than 0.5 mL, Y and absorbance reached maximal. Therefore, 1 mL of OP solution was selected.

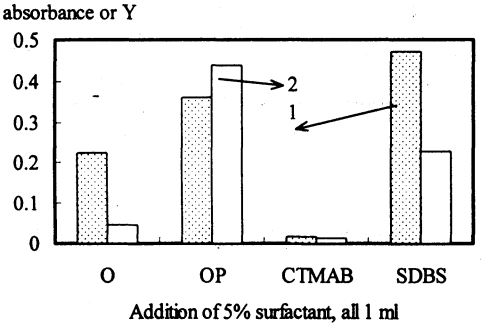

Fig. 5. Effect of different surfactants (all 1 mL of 5%) on absorbance (curve 1) and Y (curve 2) of Cd (10 μg)-DBCBAA complex solution, at 520 nm.

Effect of Time: For a Cd (10 μg) complex solution, the effect of reaction time on absorbance and Y is shown in Fig. 7. It was found that when the time was more than 5 min, Y reached maximal from curve 1. However, the raction between Cd(II) and DBCBAA was complete and Y reached maximal from curve 2 after 90 min in the case of the first addition of 5% KOH solution. Therefore, KOH was added finally and the measurement of absorbance was carried out after 5 min.

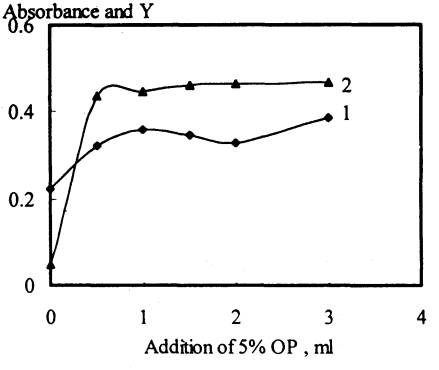

Fig. 6. Effect of the addition of 5% OP on absorbance (curve 1) and Y (curve 2) of Cd (10 μg)-DBCBAA complex solution, at 520 nm.

Calibration Graph: A series of standard Cd (0–10 μg/25 mL) solutions were prepared and the absorbance of each was measured and plotted and then Y of each solution was calculated. Two calibration graphs are shown in Fig. 8. It was found that all points around curve 2 (the relative coefficient of linearity, $R_2 = 0.9992$) was much more linear than those around curve 1 ($R_1 = 0.9745$). The

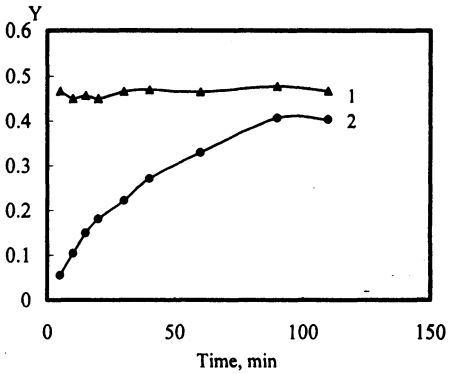

Fig. 7. Effect of color-developed time on Y of Cd (10 μg)-DBCBAA complex solution in the presence of OP, at 520 nm: 1. KOH solution was added finally; 2. KOH solution was added firstly.

accuracy of curve 1 is too bad to determine trace amounts of cadmium because of the dispersion of the standard points. Curve 2 is expressed by the following equation ($\alpha = 0.032$ and $\beta = 1.09$):

$$Y = 0.032X^{1.09}$$

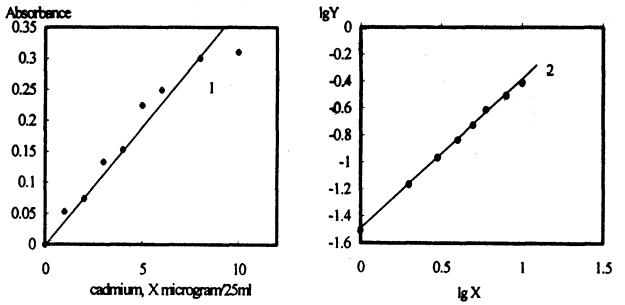

Fig. 8. Calibration graph for the determination of cadmium at 520 nm: 1. absorbance; 2. Y.

Precision, Accuracy and Detection Limit

Eight replicate determinations of standard solution containing 2 μg Cd were carried out; the results are listed in Table-1. The relative errors were between –7 and +14.5% and standard deviation (RSD) being 6.4% by PSWS. However, the relative errors were between –23 and +15% and the RSD being 11.4% by the single wavelength method. The accuracy and precision for PSWS was therefore higher than that for the ordinary spectrophotometric method.

TABLE-1
THE RESULT AND COMPARISON FOR REPLICATED DETERMINATIONS OF 2 μg Cd BY PSWS AND BY ORDINARY SPECTROPHOTOMETRY

Method	Found, μg		Average, μg	Relative error, (%)	Relative standard deviation, %
Ordinary spectrophotometry (in OP presence)	1.54	1.84	1.94	−23 ~ +15	11.4
	2.08	1.90			
	2.30	1.84			
	2.02	2.02			
PSWS (in OP presence)	2.10	2.29	2.10	−7.0 ~ +14.5	6.4
	2.13	2.05			
	1.86	2.02			
	2.21	2.16			

We used $L_{min} = kS_b/S$ to calculate the detection limit of Cd by PSWS, where $k = 3$, S_b named as standard deviation and S named as sensitivity. Replicate determination of twenty reagent blanks gave S_b of Y was equal to 0.002. The analytical sensitivity S was equal to the above α value, 0.032. Therefore the detection limit of Cd was $L_{min} = 0.2$ μg/25 mL (0.008 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), 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), Cr(IV); 50 μg of Co(II), Ni(II), Cu(II), Hg(II) and 10 μg of Ag(I).

Samples Analyzed: As a test of the method cadmium was determined in wastewater and surface water. The results were listed in Table-2. It was found that the result by the recommended method was corresponding to that with the conventional method. The RSDs were less than 7.2% and the recovery rate of cadmium between 90 and 108%.

TABLE-2
DETERMINATION OF CADMIUM IN WATER SAMPLES

Sample	Cd concentration, mg/L		RSD, %	Recovery, %
	Added	Found*		
Wastewater	0	0.585	2.1	
	1.00	1.66		101.5
Surfacewater	0	0.010	7.2	
	0.010	0.018		90.0
Sewage	0	0.045	4.3	
	0.050	0.099		108

*average of six determinations

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