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Primary-Secondary Wavelengths Spectrophotometric Determination of Trace Amounts of Cadmium in Wastewater with New Chromogenic Agent *m*-Nitrobenzenediazoaminoazobenzene

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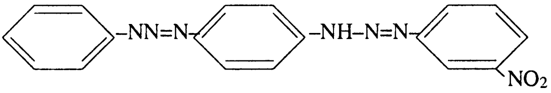
In basic solution and in the presence of non-ionic surfactant emulsifier OP, cadmium (Cd^{2+}) reacts with new chromogenic agent, *m*-nitrobenzenediazoaminoazobenzene (*m*-NBDA) to form yellow complex. This paper describes the determination of trace amounts of cadmium in wastewater by the updated method named primary-secondary wavelengths spectrophotometry (PSWS). The results showed that the working wavelengths should be selected at 460 and 550 nm and such a method gives higher precision, accuracy and sensitivity than that of ordinary spectrophotometry. By testing several wastewater samples, the relative standard deviations were less than 9% and the recovery rate of Cd between 91.8 and 110%.

INTRODUCTION

Cadmium (Cd) is one of most poisonous pollutants for body and other biological systems. It often exists in water polluted by metallurgical, chemical, electrolytic and other industries. At present trace amount of Cd is usually determined by cadions[1, 2], 4-hydroxy-benzoylhydrazone[3], di-2-pyridyl-methanone-2-(5-nitropyridyl) hydrazone[4], etc. The synthesis of a new chromogenic reagent, *m*-nitrobenzenediazoaminoazobenzene (*m*-NBDA), is carried out and its structure is as follows:



In this report, such a new ligand is applied for the determination of trace amounts of Cd in wastewater at pH 12.5 and in the presence of a non-ionic surfactant, emulsifier OP by primary-secondary wavelength spectrophotometry (PSWS) which is a new spectrophotometric method. Because PSWS can give higher

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precision and sensitivity than conventional spectrophotometry, the results have shown that the detection limit of cadmium is only 0.008 mg/L; its recovery rate between 91.8% and 110% and the relative standard deviations (RSDs) less than 9%.

Principle

From absorption spectra (Fig. 1) moved curve 2 (color solution) 1 unit absorbance up to curve 3 and it crossed curve 1 (absorption spectra[5] of suspension liquid, absorption equation: $A = k\lambda^{-y}$). Both B and C are crosspoints and they satisfy the above equation and the following relationship is further obtained.

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

where λ_p, the primary wavelength, is often selected at peak absorption of color solution and λ_s, the secondary wavelength, at valley absorption. They are shown in Fig. 1. If both λ_p and λ_s are selected, $y = k' \lg [(A_p + 1)/(A_s + 1)]$ (k' is a constant) and the following relationship formula is established[6]:

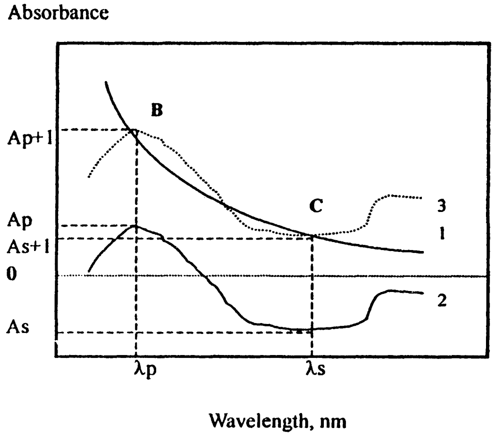

Fig. 1. Absorption spectra sketch: 1, suspension liquid against water; 2, complexation solution against ligand solution, 3, same as 2 but the absorbances translation up 1. λ_p: positive aborption (B peak) or primary wavelength; λ_s: negative absorption (C valley) or secondary wavelength

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

where both α and β are constant and the main variable X indicates 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 anaylsis. In fact, this method, named as primary-secondary spectrophotometry (PSWS), is also one of the dual-wavelength methods but different from the others[7, 8].

EXPERIMENTAL

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

Standard Cd(II) solution, 1000 mg/L: prepared from 1.000 g high-purity cadmium dissolved in 20 mL of 2 mol/L hydrochloric acid and diluted to 1000 mL.

Standard Cd(II) working standard, 5.0 mg/L, must be prepared daily with the above standard Cd solution.

Chromogenic agent solution, 0.50 mmol/L *m*-NBDA: prepared by dissolving 173 mg of *m*-nitrobenzenediazoaminoazobenzene (*m*-NBDA) in 50 mL of acetone (AR, Shanghai Reagent) and then diluting to 1000 mL with acetone. It should be stored in a dark bottle.

KOH solution, 1.5% (w/v).

Masking reagent solution: Mixed 0.002 mol/L triethanolamine (AR, Shanghai Solvent) and 0.02 mol/L sodium citrate (AR, 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 25 μg of Cd was taken in a 25-mL volumetric flask and ion exchange water added to about 20 mL. Added 0.5 mL of masking solution, 1.5 mL of chromogenic agent solution and 1 mL of KOH solution. Diluted to volume and mixed well. After 10 min, measured absorbances at 460 and 550 nm, respectively, against reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 2 gives the absorption spectra of Cd-*m*-NBDA complexation solution. From this spectrum the peak absorption appears at 460 nm and the valley at 550 nm. Therefore, the primary wavelength should be selected at 460 nm and the secondary wavelength at 550 nm. That is, $\lambda_p = 460$ nm and $\lambda_s = 550$ nm.

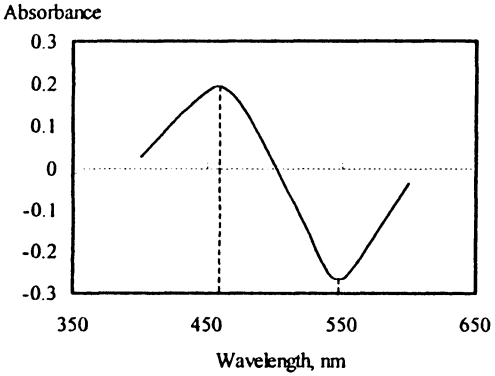

Fig. 2. Absorption spectra of Cd-*m*-NBDA complexation solution containing 10 μg Cd at pH 12.5 and in the presence of OP, at 460 nm against reagent blank

Effect of m-NBDA Solution Addition: Fig. 3 shows the effect of the various additions of chromogenic reagent solution on absorbance of Cd complexation

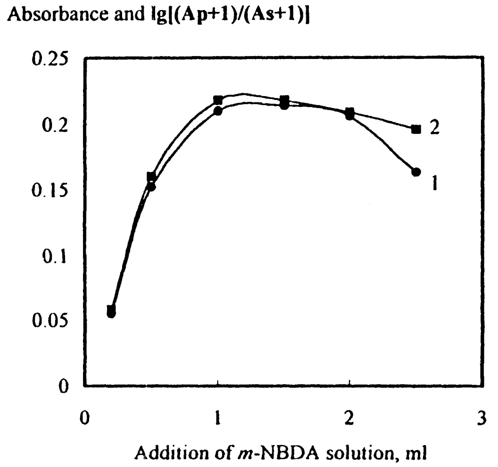

Fig. 3. Effect of 0.50 mmol/L m-NBDA addition on absorbance (curve 1) and lg $[A_p + 1)/(A_s + 1)]$ (curve 2) of Cd (10 μg) complexation solution in the presence of OP, at 460 nm

solution and its lg $[(A_p + 1)/(A_s + 1)]$ calculated from equation above. It was found that the addition of reagent solution was between 0.5 and 2.0 mL lg $[A_p + 1)/(A_s + 1)]$ and absorbance remained maximal. In this work, 1.5 mL of 0.50 mmol/L m-NBDA was used.

The complex ratio of Cd(II) to m-NBDA is determined to be 1 : 3 by using the continuous variation method[9] and β-correction spectrophotometry[10].

Effect of 5% OP Addition: On varying the addition of 5% OP, the resulting curve is shown in Fig. 4. While the addition of OP solution was more than 1 mL, lg $[(A_p + 1)/(A_s + 1)]$ and absorbance reached maximal. Here, 1 mL of OP solution was used.

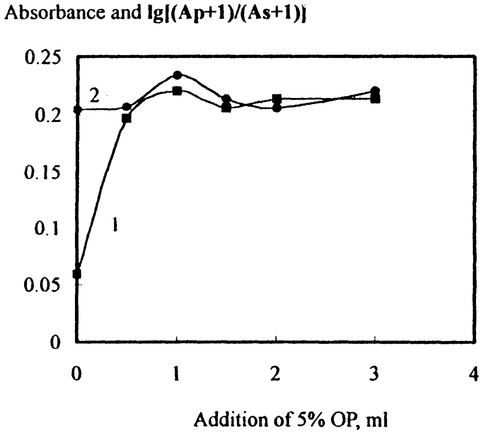

Fig. 4. Effect of the addition of 5% OP on absorbance (curve 1) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) of Cd (10 μg)-m-NBDA complexation solution, at 460 nm

Effect of 1.5% *KOH Addition:* Fig. 5 gives the effect of the varied addition of 1.5% KOH on absorbance of Cd complexation solution and its lg $[(A_p + 1)/(A_s + 1)]$. It was found that when the addition of reagent solution was more than 1 mL the maximal lg $[(A_p + 1)/(A_s + 1)]$ values and absorbances were obtained. In this study, 1 mL of 1.5% KOH was used.

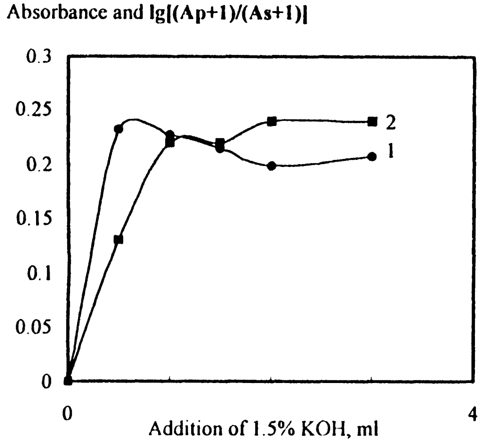

Fig. 5. Effect of the addition of 1.5% KOH on absorbance (curve 1) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) of Cd (10 μg)-*m*-NBDA complexation solution in the presence of OP, at 460 nm

Effect of Time: For a Cd (10 μg) complexation solution, the effect of reaction time on absorbance and lg $[(A_p + 1)/(A_s + 1)]$ is shown in Fig. 6. It was found that when the time was more than 10 min, lg $[(A_p + 1)/(A_s + 1)]$ and absorbance were maximal. In this work, the measurement was carried out waiting for 10 min after the final reagent solution was added and diluted to mark.

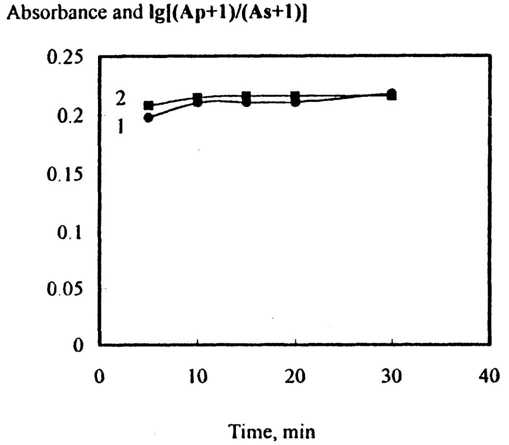

Fig. 6. Effect of colour-developed time on absorbance (curve 1) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) of Cd (10 μg)-*m*-NBDA complexation solution in the presence of OP, at 460 nm

Calibration Graph: A series of standard Cd (0–25 μg/25 mL) solutions were prepared and the absorbance of each was measured and plotted. The $\lg[(A_p + 1)/(A_s + 1)]$ calculation of each solution was carried out. The two calibration graphs are shown in Fig. 7. It was found that all points around curve 2 (the relative coefficient of linearity, $r = 0.9995$) are much more linear than those around curve 1 ($r = 0.9859$). The accuracy of curve 2 is not proper to determine trace amounts of cadmium because of the dispersion of the standard points. Curve 2 is expressed by the following equation ($\alpha = 0.0167$ and $\beta = 1.12$).

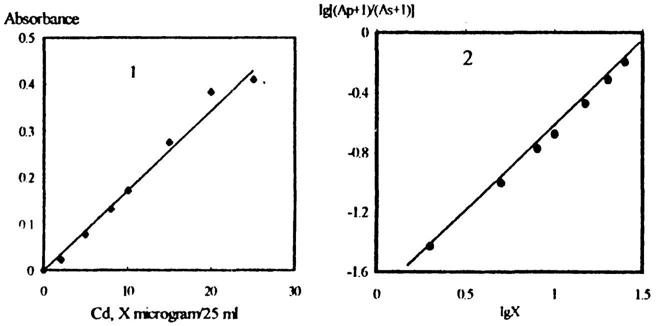

Fig. 7. Calibration graph for the determination of cadmium at 460 nm: 1, absorbance; 2, $\lg[A_p + 1)/(A_s + 1)]$

$$\lg[(A_p + 1)/(A_s + 1)] = 0.0167X^{1.12}$$

Precision and Detection Limit: Six experimental determinations of standard solutions containing 2.00 and 10.00 μg Cd were carried out. The relative standard deviations (RSDs) being 8% and 4% respectively. However, the RSDs by the single wavelength method were 16% and 5%. The precision for PSWS was therefore higher than that for the ordinary spectrophotometric method.

We used $L_{min} = kS_b/S$ to calculate the detection limit of Cd by PSWS, where $k = 3$, S_b is the standard deviation and S the sensitivity. Replicate determination of twenty reagent blanks gave S_b of $\lg[(A_p + 1)/(A_s + 1)]$ was equal to 0.004. The analytical sensitivity S was equal to the above α value, 0.0167. Therefore the detection limit of Cd was $L_{min} = 0.2$ μg/25 mL.

Effect of Foreign Ions: The pretreatment of sample was carried out according to the recommended procedure. None of the following ions will affect the direct determination of 10 μg of Cd (< 10% error): 1 mg of Cl^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_3^-, K(I), Ca(II), Mg(II), Na(I), Tl(I); 500 μg of Al(III), Sn(II), Zn(II), I^-, F^-, PO_4^{3-}, NH_4^+; 50 μg of Fe(II), Ni(II), Cr(III); 25 μg of Co(II), Cu(II), and 10 μg of Pb(II), Hg(II), Ag(I).

Samples Analyzed: As a test of the method Cd was determined in, for example, wastewater and surface water. The results are listed in Table-1. It was found that the result by the recommended method was corresponding to that with the conventional method. The RSDs were less than 9% and the recovery rate of Cd between 91.8 and 110%.

TABLE-1
DETERMINATION OF CADMIUM IN EXPERIMENTAL SAMPLES

Sample	Cd concentration, mg/L		RSD, %	Recovery, %
	Added	Found*		
Wastewater	0	0.652	2.6	
	1.00	1.570		91.8
Surface water	0	< 0.010	9.0	
	0.020	0.022		110.0
sewage	0	0.080	5.0	
	0.100	0.176		96.0

*Average of six determinations

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