

## Synthesis of *p*-Nitrobenzenediazoamido Black 10B and Its Application to Spectrophotometric Determination of Micro Amounts of Cadmium

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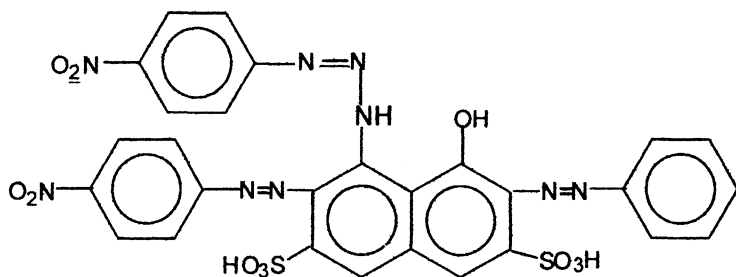
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A new azoamino reagent *p*-nitrobenzenediazoamido black 10B (*p*-NDABB) has been synthesized, and found to be a good chromogenic reagent for cadmium. In pH 9.8 Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-NaOH buffer solution cadmium reacts with *p*-NDABB to form green chelate (1 : 3), exhibiting an absorptivity  $1.81 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Beer's law is obeyed in the range 0–9 µg/25 mL Cd(II). The method is simple and rapid, with high sensitivity and good selectivity and it is applied to the determination of trace amounts of cadmium in waste water and industrial materials with satisfactory results.

### INTRODUCTION

Azoamino reagent is a good chromogenic reagent for spectrophotometric determination of cadmium<sup>1–5</sup>. In this paper, the preparation of *p*-nitrobenzenediazoamido black 10B (*p*-NDABB), and the chromogenic reaction of this reagent with cadmium in aqueous solution are reported. Its structure is:



It reacted with cadmium in pH 9.8 Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> NaOH buffer solution to form green chelate (1 : 3). The absorption maximum is at 600 nm and the molar absorptivity is  $1.81 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Beer's law was obeyed in the range 0–9 µg/25 mL Cd(II). The method is simple and rapid for determination of cadmium. In addition, this method has high sensitivity in the presence of both sulfocarbamide and sodium citrate. It was used to determine trace amounts of cadmium in wastewater and industrial samples with the following results: the recovery between 98–103% and the relative standard deviation is less than 2.8%.

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## EXPERIMENTAL

The following reagents were used:

1. Cd(II) standard solution: 1.0000 g of pure cadmium (99.99%) was dissolved in 30 mL of hydrochloric acid. It was transferred to a 1000 mL volumetric flask and diluted to volume with water. The concentration of this solution was  $1.000 \text{ mg mL}^{-1}$ , and it was diluted with water to contain  $5.0 \text{ } \mu\text{g mL}^{-1}$  Cd as required.
2. *p*-NDABB solution, 0.3% in water.
3. pH 9.8  $\text{Na}_2\text{B}_4\text{O}_7\text{-NaOH}$  buffer solution.
4. 1% Triton x-100 solution.
5. The masking reagent: sodium fluorinate (1%) plus sulfocarbamide (1%) plus sodium citrate (1%).

All chemicals above used were of analytical-reagent grade, and all solutions were prepared with redistilled water.

Absorbances and absorption spectra were recorded with a model 723G (Shanghai Instrument Factory) with 1 cm cells respectively. The pH measurements were made with a model PHS-3D pH meter (Chengdu Electroanalytical Instrument Factory). Elemental analyses were done with a CE model CE-1106 analyzer. A model PE-683 infrared spectrophotometer was used for recording IR spectra.

### Synthesis of *p*-NDABB

Dissolve 0.22 g (1.6 mmol) of *p*-nitroaniline in 20 mL of hydrochloric acid solution (1 : 1), and cool the solution to  $0^\circ\text{C}$ , add 0.24 g sodium nitrite with vigorous stirring for 20 min; the diazotate salt of *p*-nitroaniline was obtained. Dissolve 1.00 g (1.6 mmol) of amino black 10B in 10 mL ethanol solution (95%), and add 5 mL of 10% sodium carbonate solution. Add diazoate solution of *p*-nitroaniline dropwise to this solution with vigorous stirring, stir for 30 min and regulate solution pH to 3–5 with 10% sodium carbonate solution. Stir for 2 h at room temperature, and regulate solution to neutral with 10% sodium carbonate solution, and then let the mixture stand overnight. Filter off the precipitate. Wash with ethanol and recrystallize from saturated sodium carbonate solution and concentrated hydrochloric acid. Black-blue flakes were obtained (m.pt.  $154\text{--}156^\circ\text{C}$ ), and the yield was about 68%. The structure has been verified by thin-layer chromatography, elemental analysis, and IR. TLC (silica gel GF-254): a yellow spot is obtained in spreading agent (cyclohexane : ethyl acetate = 9 : 1),  $R_f = 0.47$ . Elemental analysis:  $\text{C}_{38}\text{H}_{19}\text{N}_9\text{O}_{11}\text{S}_2$  requires 54.22 C, 2.28 H, 14.97 N; found 53.79 C, 2.33 H, 15.11 N. IR ( $\text{cm}^{-1}$ ) (KBr):  $\nu(\text{OH})$  3459,  $\nu(\text{NH})$  3388,  $\nu(\text{ArH})$  3038,  $\nu(\text{C}=\text{C}, \text{N}=\text{N})$  1650–1450,  $\nu(\text{NO}_2)$  1350,  $\nu(\text{C}-\text{N})$  858.

### General procedure

Transfer 5  $\mu\text{g}$  of Cd(II) to a 25 mL volumetric flask. Add 5.0 mL of pH 9.8  $\text{Na}_2\text{B}_4\text{O}_7\text{-NaOH}$  buffer solution, 2.0 mL 1% Triton X-100 solution, 2.0 mL 0.3% *p*-NDABB solution and 1.0 mL of sodium fluoride-sulfocarbamide-sodium citrate solution. Dilute to volume with water and mix well. After 10 min record the absorbance at 450 nm in a 1 cm cell against a reagent blank.

## RESULTS AND DISCUSSION

### Properties of the reagent

The reagent was soluble in DMF (dark blue), acetone (grass green), dioxane (green-yellow), ethyl alcohol (pink), water (blue), acid solution (light blue) and basic solution (dark blue).

The composition of the chelate and complex constant was determined by the continuous variation method, the molar ratio method and  $\beta$ -correction spectrophotometric method<sup>6</sup>. All experiments indicated that a 1 : 3 cadmium chelate was formed, and the complex constant was  $K = 3.67 \times 10^5$ .

### Absorption spectra

The absorption spectra of *p*-NDABB and its cadmium chelate were recorded and are shown in Fig. 1. The absorption maximum of the reagent lies at 450 nm and that of the chelate at 600 nm. The 600 nm was chosen for measurements as its sensitivity is higher and the absorbance of the reagent itself is very small.

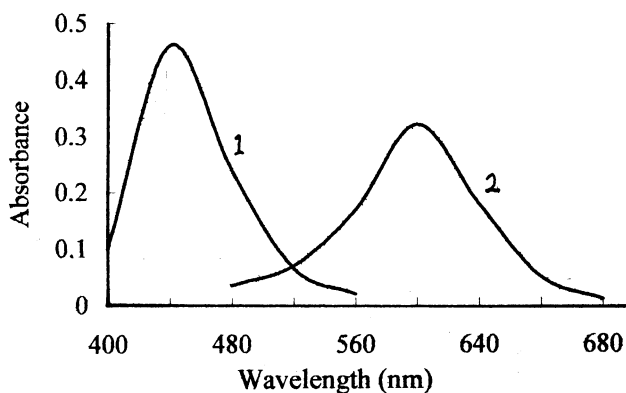


Fig. 1 Absorption spectra of *p*-NDABB and its cadmium chelate, 1 cm cell: (1) *p*-NDABB ( $3.56 \times 10^5$  M) vs. (2) Cd(II) chelate ( $1.78 \times 10^{-6}$  M) vs. reagent blank.

**Effect of the reagent concentration:** The absorbances of a series of solutions containing 5.0  $\mu$ g of cadmium and various amounts of 0.3% *p*-NDABB solution were measured. It was found that the addition of 1.5 to 3.5 mL of *p*-NDABB solution may bring out high absorbance. Therefore 2.0 mL of the ligand solution was chosen in all works. The time for the absorbance to reach a stable value was only 5 min at room temperature and the absorbance was stable for at least 24 h.

**Effect of buffer solution and surfactant concentration:** The absorbances of a series of solutions containing 5.0  $\mu$ g of cadmium and 2.0 mL of 0.3% *p*-NDABB, and various buffer solutions and surfactant concentrations were measured. Fig. 2 shows that cadmium reacts strongly with *p*-NDABB only at pH 9.2–10.0. Hence pH 9.8  $\text{Na}_2\text{B}_4\text{O}_7\text{-NaOH}$  is selected in the present work. To reach maximum sensitivity, 2.0 mL of 1% triton X-100 should be added.

**Calibration graph:** The calibration graph obtained by the general procedure

gives good linearity over the range 0–9  $\mu\text{g}/25$  mL cadmium. The linear regression equation was  $A = 0.0321x + 0.0039$  ( $x = \mu\text{g}/25$  mL Cd) and the correlation coefficient was 0.9987. The apparent molar absorptivity was  $1.81 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>, and the Sandell sensitivity was  $6.94 \times 10^{-4}$   $\mu\text{g cm}^{-2}$ .

*Effect of diverse ions:* Numerous cations and anions were examined by applying the method to a fixed amount of cadmium in the presence of increasing amount of the ion being studied. The tolerance limit was taken as the amount that caused an error of  $\pm 5\%$  of absorbance. For the determination of 5.0  $\mu\text{g}$  of cadmium by this method, the foreign ions can be tolerated at the levels given in Table-1. It was shown that cations and anions can be masked in the determination of cadmium by adding 1% sodium fluoride-sulfocarbamide-sodium citrite solution.

TABLE-1  
TOLERANCE LIMITS FOR THE DETERMINATION OF CADMIUM

Ion added	Amount tolerated ( $\mu\text{g}$ )	Ion added	Amount tolerated ( $\mu\text{g}$ )
Hydroxylamine hydrochloride	2000	Mn(II)	400
Citrate	2000	Mg(II)	400
CNS <sup>-</sup>	2000	Al(III)	100
Tartrate	1000	Ca(II)	250
Salicylic acid	1000	Zn(II)	125
Thiourea	1000	Bi(III)	50
F <sup>-</sup>	1000	Tl(III)	50
Cl <sup>-</sup>	1000	Hg(II)	5
Br <sup>-</sup>	1000	Zr(IV)	50
I <sup>-</sup>	1000	Ce(IV)	25
K(I)	1000	W(VI)	20
Na(I)	1000	U(VI)	15
Li(I)	1000	Pd(II)	12
NH <sub>4</sub> (I)	1000	Pb(II)	9
NO <sub>2</sub> <sup>-</sup>	1000	Ni(II)	7
Cr(III)	1000	Fe(III)	50
Ba(II)	1000	Co(II)	10
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	550	Ag(I)	5
SO <sub>4</sub> <sup>2-</sup>	800	Au(III)	5
V(V)	900	Cu(II)	20
Sr(II)	400		

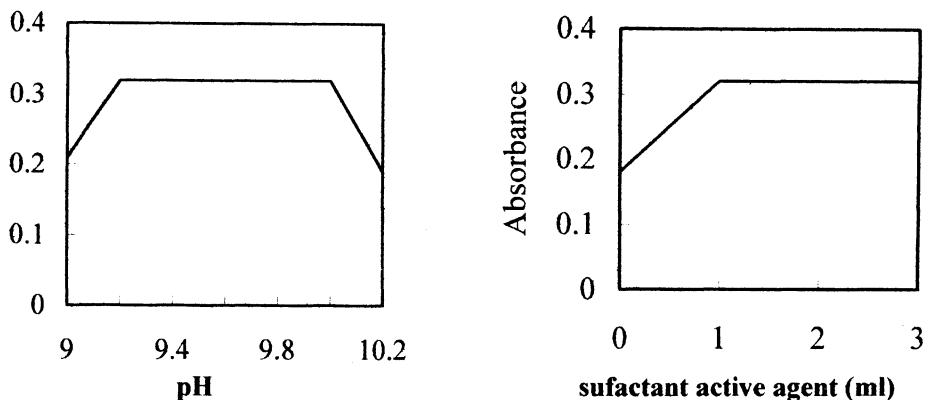


Fig. 2 Effect of pH and surfactant active agent.

### Samples analysed

As a test of the method, cadmium was determined in water and alloy. The results are listed in Table-2. The recovery of cadmium is between 98 and 103%. The relative standard deviation is less than 2.8%.

TABLE-2  
RESULTS OF CADMIUM DETERMINATION IN THE SAMPLE<sup>a</sup>

Sample	ABDAB method <sup>b</sup>		Standard method	RSD, %	Recovery, %
	Introduced	Found			
0113 water	0	0.1300	0.130	1.2	103
	0.1000	0.2330			
CW0104	0	0.0690	0.070	2.2	98
	0.0100	0.0788			
By02171-1	0	0.1950	0.200	0.8	103
Zinc sheet	0.1000	0.2990			
By0421-2	0	0.1120	0.105	2.3	103
Zinc alloy	0.1000	0.2150			

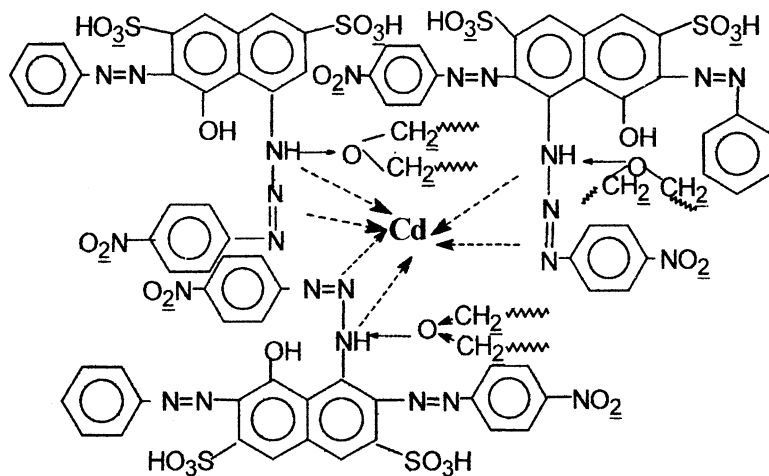
<sup>a</sup>A measuring unit of standard water and alloy is mg mL<sup>-1</sup> and % respectively.

<sup>b</sup>Average of six determinations.

### The probable mechanism of the reaction

The experiment shows that the absorption spectra were moved to red wavelength by adding basic solution and the infrared spectra of *p*-NDABB in 3388 cm<sup>-1</sup> ν(N—H) were weakened obviously in Cd(II) to form chelate. It was added at sensitivity by anion active agent and it moved to negative pole.

According to reference<sup>7,8</sup>, the probable structures of chelates are



### Conclusion

Relatively large conjugate system and polar-functional groups were led into azoamino molecule; the reagent property was improved in solubility of water solvent, sensitivity and selectivity in the determination of cadmium.

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