Primary-Secondary Wavelengths Spectrophotometry for Improving the Determination of Nitrobenzene Compounds in Wastewater

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In acidic solution the conventional reaction of nitrobenzene with N-(1-naphthyl)-ethylendiamine-dihydrochloride (NEDA) in the presence of hydrazine sulfate and nitrite to form a red azo compound has been applied for the improvement of the determination of nitrobenzene compounds in water and wastewater by primary-secondary wavelengths spectrophotometry (PSWS). The updated method can bring out the higher precision and sensitivity than the ordinary spectrophotometry, but also the calculation model is stable. The result shows that the relative standard deviations were less than 2.1% and the recovery rate of nitrobenzene between 96 and 104%. The detection limit of nitrobenzene was equal to 0.008 mg/L.

INTRODUCTION

Nitrobenzene compound is harmful for any biological body. It exists in wastewater polluted by, for example, chemical, printing and dyeing, paint, leather and other industries. It is often determined by spectrophotometry[1, 2] and gas chromatography. The former includes the sensitive azo reaction. It is often applied because of the simple operation and good selectivity. At first nitrobenzene compound is changed into phenylamine, then diazotization with nitrite in acidic solution and diazo coupling with N-(1-naphthyl)-ethylendiamine-dihydrochloride (NEDA) is carried out to form red azo-dye. In this paper, this reaction was applied for improvement of determination of nitrobenzene in water and wastewater using the updated method, primary-secondary wavelengths spectrophotometry (PSWS). It may give high analytical sensitivity and precision to the calibration graph. The recovery rate of nitrobenzene was between 96 and 104%, the relative standard deviations (RSDs) less than 2.1% and the detection limit was only 0.008 mg/L.

The main formulas of PSWS[3] were given as follows:

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

$$Y = \alpha X^{\beta} \quad (2)$$

where λ_p is primary wavelength which is necessary to be selected at the maximal absorption and λ_s named as secondary wavelength often selected at the corresponding wavelength of about half of maximal absorption. Both α and β are constants.

From the formula given above because both A_p and A_s change meanwhile with the variation of the operation conditions, for example, room temperature, it is

found that $(A_p + 1)/(A_s + 1)$ value changes little. From the above principle PSWS is understood to be also one of the dual-wavelength spectrophotometric methods, which is different from the other dual-wavelength methods[4-6].

EXPERIMENTAL

Visible spectra were recorded with a Model 721 spectrophotometer (Shanghai, China), in a 2 cm glass cell.

Hydrazine sulfate (Shanghai Reagent), 2.5%; N-(1-naphthyl)-ethylendiamine-dihydrochloride (NEDA) solution, 1%; dissolved 1 g of NEDA (Shanghai Reagent) in 10 mL of distilled water and stored in a dark bottle at less than 5°C. Sodium nitrite (A.R., Shanghai Chemical) solution, 1%; Hydrochloric acid solution, 6 mol/l and zinc dust.

Standard nitrobenzene solution: Added 10 mL of absolute alcohol in a 25 mL volumetric flask and weighed. Then added 1–2 drops of nitrobenzene (Shanghai Organic Chemical) and weighed it again. Diluted to volume with distilled water and calculated nitrobenzene concentration. This standard solution should be stored at less than 5°C.

Standard nitrobenzene use solution, 10.0 mg/L: prepared by the above standard solution.

Recommended Procedure: A known volume of water sample after filtration containing less than 40 μg of nitrobenzene compound was taken in a 50 mL colorimetric tube. Then, diluted to required volume. Added 1.5 mL of 6 mol/l hydrochloric acid, 0.1 mL of copper sulfate solution and 0.5 g of zinc dust and mixed well. After 30 min, filtration was carried out and 0.5 mL of sodium nitrite solution was added to the filtrate. After 5 min, 0.5 mL of hydrazine sulfate solution and 1.5 mL of NEDA solution were added and mixed well. After 30 min, measured the absorbance at 550 and 580 nm, respectively, against a reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 1 gives the absorption spectra of nitrobenzene-NEDA solution in the presence of a nitrite. This solution's absorption reached

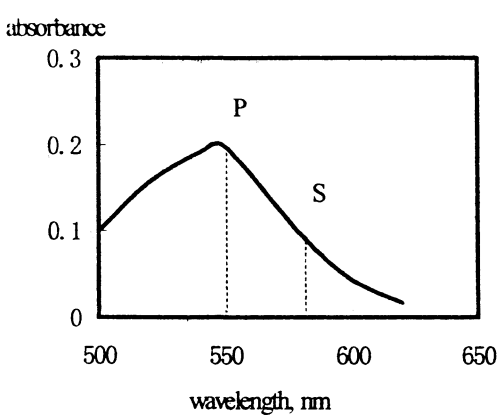

Fig. 1. Absorption spectrum of nitrobenzene-NEDA solution. P-550 and S-580 nm

maximal at 550 nm. From the above content the primary wavelength should be selected at 550 nm. The secondary wavelength was arranged at 580 nm here, that is $\lambda_p = 550$ nm and $\lambda_s = 580$ nm.

Effect of NEDA Addition: Fig. 2 shows the effect of the addition of 1% NEDA on factor Y calculated from formula 2. We found that when the addition of NEDA solution was more than 1.5 mL, Y value remained almost constant and reached maximal. In this work, 1.5 mL of NEDA solution was selected.

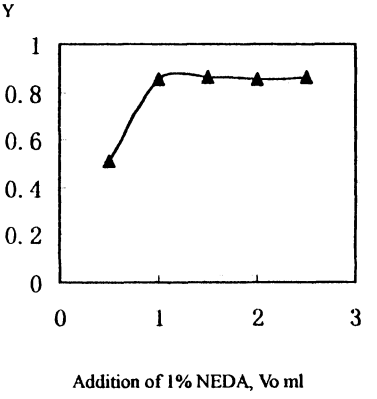

Fig. 2. Effect of NEDA on factor Y

Calibration Graph: A series of standard nitrobenzene solutions were prepared and the absorbances measured and plotted. From the measurement results curve lg Y *vs.* the logarithmic value of nitrobenzene amount (X μg), lg X is shown in Fig. 3.

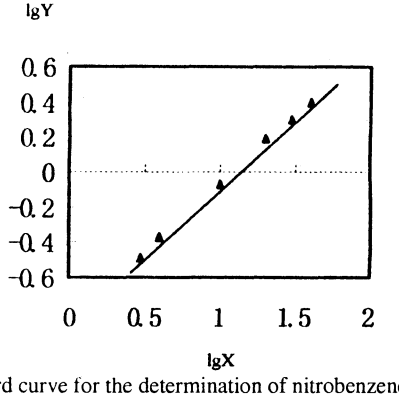

Fig. 3. Standard curve for the determination of nitrobenzene compounds

We found that the curve linearity is better. The cut distance lg α was calculated to be 0.845 and the oblique rate β to be 0.781 from the straight line in Fig. 3. The relation of Y with X was therefore obtained by the following expression:

$$Y = 0.143X^{0.781} \quad (3)$$

Effect of Foreign Ions: The recommended procedure was carried out; none of the following ions affected the determination of 0.10 mg/L nitrobenzene: 1000

mg/L Cl^-: Mg(II), SO_4^{2-}, NH_4^+, Ca(II), F^-, 100 mg/L: Al(III), Mn(II), Pb(II), Cu(II), Zn(II), Fe(II); 10 mg/L PO_4^{3-}: Cr(VI), Ni(II), Sn(II), Co(II), Fe(III), Ag(I), Au(III), Cr(IV).

Precision and Detection Limit: Six replicate determinations of 0.200 mg/L standard nitrobenzene were carried out, the relative standard deviation (RSD) being 0.9%. However, the RSD with the single wavelength method was 2.8%. The precision for PSWS was therefore better than that for the ordinary spectrophotometric method.

We used $L_{min} = S_d/S$ to calculate the detection limit of PSWS, where $k = 3$, S_d is standard deviation and S is sensitivity. Replicate determination of twenty reagent blanks gave S_d of Y value computed from $(A_p + 1)/(A_s + 1)$ to be equal to 0.02. The analyical sensitivity S was equal to the above α value, 0.143. Therefore, the detection limit concentration of nitrobenzene reached only 0.008 mg/L which was less than the ordinary value, 0.02 mg/L.

Samples Analysed: As a test of the method nitrobenzene compound was determined in, for example, sewage and wastewater. The results have been listed in Table-1. We found, the results by the recommended method tallied with those by the conventional method. The recovery rate of nitrobenzene was between 96 and 104% and the RSDs less than 2.1%.

TABLE-1
DETERMINATION OF NITROBENZENE COMPOUND IN WATER SAMPLES

Sample	By conventional method	By PSWS			
		Added	Found		Recovery, %
Sewage	1.16	0	1.20	1.17 1.15	
			1.20	1.21 1.16	
		1.0	2.18	2.09 2.18	97
Wastewater 1#	8.27	0	8.66	8.31 8.38	
		10.0	19.1	18.8 18.7	104
Wastewater 2#	28.9	0	30.6	29.3 29.9	
		10.0	41.1	38.4 38.5	96

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