Improvement of Determination of Trace Amounts of Nitrite in Water by Primary-Secondary Wavelengths Spectrophotometry

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In acidic solution and in the presence of *p*-aminobenzenesulfonic acid, the reaction between nitrite (NO_2^-) and α-naphthylamine was applied for the improvement in determination of NO_2^- in water by primary-secondary wavelengths spectrophotometry (PSWS) which was a new analytical method to give higher precision and sensitivity than ordinary spectrophotometry. The detection limit of NO_2^--N was equal to 0.002 mg/L. Results showed that for the analysis of practical samples the relative standard deviations are less than 8% and the recovery rate of NO_2^- is between 95.0 and 107%.

INTRODUCTION

Nitrite (NO_2^-) is harmful to any biological system. It often exists in wastewater polluted by, for example, chemical and food-making industries, and life sewage. In acidic solution the diazotization between NO_2^- and *p*-aminobenzenesulfonic acid can happen and then the azocoupling reaction was made with α-naphthylamine to produce a red azo dye. This reaction is sensitive and it is often used for the determination of NO_2^--N by spectrophotometry[1, 2]. In this paper, a new analytical method named primary-secondary wavelengths spectrophotometry (PSWS)[3, 4] was applied for improvement of determination of NO_2^--N in water using the above reaction. This method may give high analytical sensitivity and precision; the calibration graph can keep stable to be affected hardly by various operation conditions. All the experimental results were satisfactory. The recovery rate of NO_2^--N was between 95% and 107%, the relative standard deviation (RSD) less than 8% and the detection limit only 0.002 mg/L, that was only 2/5 of the conventional value.

Principle

From Ref. 3 the main equation of PSWS was expressed as follows:

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

where λ_p is the primary wavelength often selected at peak absorption of colour solution and λ_s named as secondary wavelength often selected at valley absorption or half-peak absorption. Both α and β are constant and the main variable X

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indicates the color-developed substance concentration (mg/L or µg). Because of the buffer function of $(A_p + 1)/(A_s + 1)$ the abve 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[5–7].

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai, China) in a 1-cm glass cell.

0.6% *p*-aminobenzenesulfonic acid was prepared by dissolving 0.6 g of *p*-aminobenzenesulfonic acid (AR, Shanghai Reagent) in 80 mL of warm water. Added 20 mL of concentrated hydrogen chloride after cooling.

0.6% α-naphthylamine was prepared by dissolving 0.6 g of α-naphthylamine (Shanghai Reagent) in 10 mL of 0.3% hydrogen chloride. Diluted to 100 mL. After filteration this solution was stored in a dark bottle at temperature 5°C. Sodium acetate solution was prepared by dissolving 16.4 g of sodium acetate (AR, Shanghai Chemical) in 1 litre of ion exchange water.

$Al(OH)_3$ suspension liquid was prepared by dissolving 125 g of potassium aluminium sulfate (AR, Shanghai Chemical) in 1000 mL of water. Heated it to 60°C and added slowly 55 mL of concentrated ammonia water. After 1 h, cleaned the suspension solid. Finally added 100 mL of ion exchange water to the concentrated suspension liquid.

Standard nitrite solution was prepared by dissolving 1.232 g of sodium nitrite (AR, Shanghai Chemical) in 100 mL of ion exchange water and diluting to 1000 mL. Added 1 mL of chloroform to the above solution. This solution must be standardized with 0.050 mol/L standard potassium permanganate and 0.0500 mol/L standard sodium oxalate.

Standard nitrite use solution, 0.500 mg/L NO_2^--N, was prepared by diluting the above solution.

Recommended Procedure: A known volume of a sample containing less than 5 µg of NO_2^--N was taken in a 50-mL colorimetric tube. After neutralization, diluted to 50 mL and added 1 mL of *p*-aminobenzenesulfonic acid solution. After 5 min, added 1 mL of sodium acetate solution and 1 mL of 0.6% α-naphthylamine. Mixed well and after 30 min, measured the absorbance at 520 and 560 nm, respectively, against a reagent blank.

Because of the possible interference of some oxidants, for example, chlorite, chloramine, thiosulfate, Fe(III) and so on, the pretreatment of a wastewater sample should be carried out. The procedure is as follows: At first adjust the pH of the sample to about 11 with 1% NaOH. Add one drop phenolphthalein solution and drop 10% phosphoric acid till the red colour just disappears. If the sample contains the suspended solid, flocculent precipitation with 2 mL of $Al(OH)_3$ suspension liquid and filtration should be carried out first.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 1 shows the absorption spectrum of $NO_2^--\alpha$-naph-

thylamine solution in the presence of p-aminobenzenesulfonic acid. The peak absorption was at 520 nm. Therefore, such a wavelength was selected as primary wavelength. The secondary wavelength was arranged at 560 nm which was near the half-peak absorption.
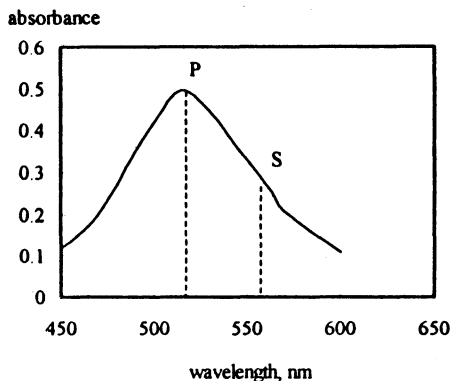

Fig. 1.   Absorption spectrum of NO_2^--α-naphthylamine solution in the presence of p-amino-benzenesulfonic acid against reagent blank: P point, 520 nm and S point, 560 nm

Effect of α-Naphthylamine Concentration: The effect of the addition of 0.6% α-naphthylamine is given in Fig. 2 While the addition of α-naphthylamine solution was more than 0.8 mL, $1 g [(A_p + 1)/(A_s + 1)]$ value reached maximum and remained almost constant. In this work, 1.0 mL of 0.6% α-naphthylamine was added.
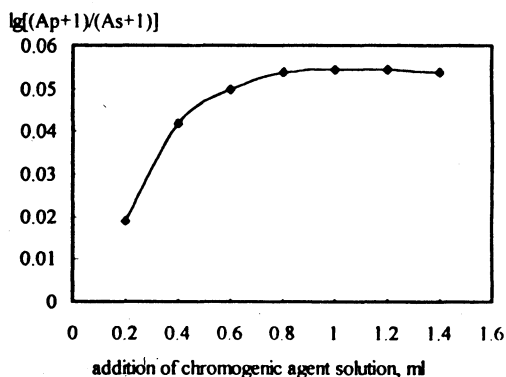

Fig. 2.   Effect of α-naphthylamine concentration

Calibration Graph: A series of standard NO_2^--N solutions were prepared and the absorbance of each was measured and plotted. Fig. 3 shows the work graph $1gY \sim 1gx$ (here $Y = 1g(Ap + 1)/(As + 1)$). It was found that this curve was quite linear. This relationship was therefore obtained as follows: $Y = 0.779X^{0.813}$
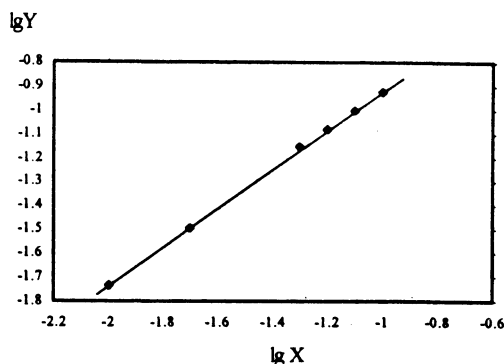
lgY

lg X

Fig. 3. Standard curve for the determination of NO_2^--N (the relative coefficient, r = 0.9998)

Effect of Foreign Ions: Because of the co-existence of chloramine, chlorite, thiosulfate, Fe(III), some samples should be pretreated before the measurement. Once the recommended procedure has been carried out, none of the following ions will affect the determination of 0.010 mg/L NO_2^--N: 1000 mg/L Cl^-, Mg^{2+}, SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, Br^-; 100 mg/L Al(III), Ti(IV), Sn(II), Mn(II), Pb(II), Cu(II), Zn(II), Fe(II), I^-, F^- and 10 mg/L PO_4^{3-}, Cr(VI) Ni(II), Sb(II), Co(II), Fe(III), Ag(I), Au(III), $S_2O_3^{2-}$, chlorite.

Precision and Detection Limit: Six replicate determinations of standard NO_2^--N solutions containing 1.00 μg were carried out, the relative standard deviation (RSD) being 2.5%. However, the RSD with the single wavelength method was 4.3%. The precision for PSWS was therefore better than that for the ordinary spectrophotometric method.

We used $L_{min} = kS_b/S$ to calculate the detection limit of PSWS, where k = 3, S_b is the standard deviation and S the sensitivity. Replicate determination of twenty blanks gave S_b of Y value equal to 0.0005. The analytical sensitivity S was equal to the above α value, 0.779. Therefore the detection limit concentration reached only 0.002 mg/L.

Samples Analyzed: As a test of the method are NO_2^--N was determined in, for example, sewage, wastewater and lake water. The results are listed in Table-1.

TABLE-1

DETERMINATION OF NO_2^--N IN WATER

Sample	Ordinary method, mg/L	Added, mg/L	Found mg/L (PSWS)	Aver. recovery (%)
Sewage	0.294	0	0.276 0.268 0.310 0.301 0.295 0.304	
		0.200	0.611 0.609	107
Wastewater	1.01	0	0.981 0.962 1.03 1.01 0.964 0.976	
		1.00	2.08 1.95	103
Lake water	0.023	0	0.022 0.025 0.026 0.024 0.020 0.025	
		0.020	0.045 0.041	95

We found that the averages by the recommended method were all similar to the ordinary method[2]. The recovery rate of NO_2^--N was between 95.0 and 107% and the RSDs less than 8%.

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