Asian Journal of Chemistry Vol. 11, No. 4 (1999), 1225–1230

Primary-Secondary Wavelengths Spectrophotometric Determination of Trace Amounts of Cyanide in Waste Water

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In neutral solution and in the presence of isonicotinide the reaction of cyanide (CN—) with barbiturate has been applied for the improvement of cyanide determination in waste water by the updated method named primary-secondary wavelengths spectrophotometry (PSWS). The results show that the analytical precision and accuracy were increased and gave the higher determination sensitivity than the ordinary spectrophotometry.

INTRODUCTION

Cyanide is one of poisonous matters. It can connect the oxidation enzyme of the biological ferric cell to cause the organism oxygen deficiency. Cyanide often exists in waste water polluted by electrodeposit, mine-selecting and other chemical industries. Trace amounts of CN^- is often determined by spectrophotometry with barbiturate[1] and pyrazolone[2] in the presence of isonicotinide. But the former reaction is very sensitive and selective. Here the updated method, primary-secondary wavelengths spectrophotometry (PSWS) has been applied for the determination of trace amounts of CN^- in waste water, which is more accurate and precise than the ordinary spectrophotometric method. In addition, this new method may give the stable calibration graph to be affected hardly be the operation conditions. The results are all satisfactory. The cyanide recovery rate was between 90 and 106%, the relative standard deviations (RSDs) less than 7.2% and the detection limit only 0.002 mg/L that was half of the conventional value.

From the theory[3] of spectrophotometric absorption of a colloid solution or a suspension liquid. The following expression[4] is established for determination of trace amounts of pollutants in a formed color solution.

$$\left(\frac{Ap+1}{As+1}\right)=\left(\frac{\lambda p}{\lambda s}\right)^{-Y} \quad \ldots(1)$$

Where λp named as primary wavelength which is selected at the maximum abosrption point and λs as secondary one which is often chosen at half-peak absorption point. Ap and As are the corresponding absorbance at λp and λs, respectively. The factor y is exponent to the analytical component concentration (X mg/l or μg), as follows.

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

where both α and β are constants.

From the above y value may be obtained, then to give X value from expression 2. Both Ap and As happen change with the variation of the operation conditions for example room temperature. It is found that (Ap + 1)/(As + 1) value changes little. Therefore, both α and β are almost constant, which will happen little change with the variation of the operation conditions.

From the above principle PSWS is easy to understand to be also one of dualwavelengths spectrophotometries, which is different from the other dual-wavelengths methods[5–7].

EXPERIMENTAL

Visible spectra were recorded with a Model-721 spectrophotometer (Shanghai, China), in a 3 cm glass cell.

0.1 mol/L sodium thiosulfate by preparing with $Na_2S_2O_3 \cdot 5H_2O$ (A.R., Shanghai Chemical) then standardizing it with 0.50 mol/L standard potassium dichromate and storing in a dark flask.

Standard cyanide solution: weighing 0.25 g of sodium cyanide (A.R., Shanghai Chemical) to be dissolved in 100 mL of 0.1% sodium hydroxide and storing in a polyethylene bottle. The standardization of this solution was carried out immediately with standard silver nitrate solution in the presence of *p*-dimethylaminebenzenalrhodanine indicator.

Standard CN^- use solution, 1.00 mg/L: preparing with the abovestandard cyanide solution.

Tartaric acid (A.R, Shanghai Reagent) solution, 15%.

Sodium hydroxide solutions, 1% and 0.1%.

Methyl orange (Shanghai Reagent) solution, 0.05%.

Zinc nitrate (A.R., Shanghai Chemical), 10%.

Acetic acid (A.R., Beijing Chemical) solution, 1 mol/1.

Buffer solution, pH 5.8: mixing and dissolving 68.0 g of primary potassium phosphate (A.R., Shanghai Chemical) and 7.6 g of sodium hydrogenphosphate ($Na_2HPO_4 \cdot 12H_2O$, A.R., Shanghai Chemical) in 1000 mL of ion exchange water.

Chloramine T solution, 1%: dissolving 0.5 g of chloramine T (Shanghai reagent) in 50 mL of ion exchange water and storing in a dark bottle.

Ligand reagent: mixing 1.0 g of sodium isonicotinide (Shanghai reagnet) and 1 g of sodium barbiturate (Shanghai reagnet) and 100 mL of ion exchange water by heating.

Recommended procedures

The pretreatment of waste water sample should be carried out. According to Figure 1, at first 10 mL of 1% sodium hydroxide was taken in acceptor 2 and 200 mL of a sample containing less than 50 μg of CN^- in flask 1. Added 7 drops of methylene orange solution and 10 mL of zinc nitrate solution to flask 1 and connect each device as Fig. 1. Then added quickly 5 mL of 15% tartaric acid and turned on electric furnace and water for cooling. Kept solution red from beginning to end. Stopped the distillation till the accepted solution was near to 100 mL. 5.00 mL of this solution was taken in a 10 mL colorimetric tube and add 1.5 mL of pH 5.8 buffer solution and 0.2 mL of 1% chloramine T. After 3 min, add 2.5 mL of ligand reagnet and diluted to 10 mL Mixed well After 30 min, measured the transmittancy at wavelength 570 and 600 nm respectively against a reagent blank.

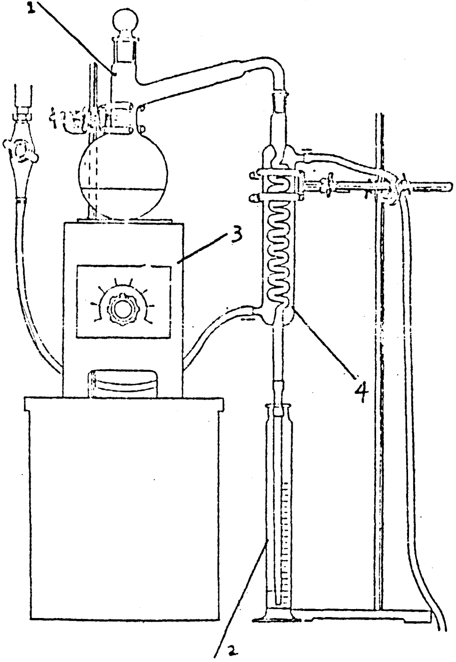

Fig. 1. Distillation installation for pretreating cyanide sample: (i) 500 mL distillation flask, (ii) 100 mL acceptor, (iii) electric furnace, (iv) condenser

RESULT AND DISCUSSION

Absorption spectra: Figure 2. gave the absorption spectra of CN^- colored

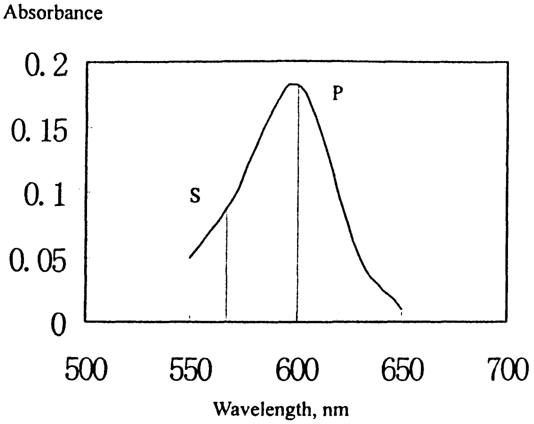

Fig. 2. Absorption spectrum of cyanide colored solution against reagent blank: P point 600 nm and S point 570 nm.

solution. This solution absorption reached maximum at 600 nm. According to the relative content in principle the primary wavelength (λ_p) should be selected at 600 nm. the secondary wavelength (λ_s) was arranged at 570 nm here.

Effect of ligand reagent: Figure 3 show the effect of the addition of ligand reagent solution on factor y calculated from expression (2). We found when the addition of ligand solution was more than 2 mL y remained almost constant and reached maximum. In this study, 2.5 mL of the ligand reagent was selected.

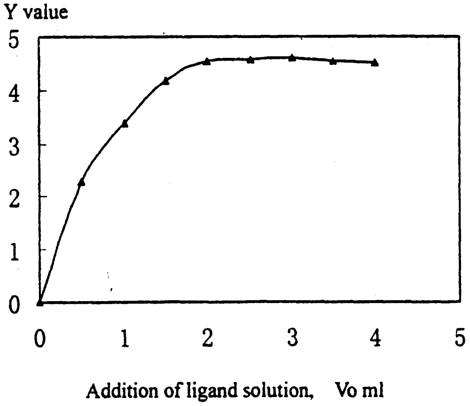

Fig. 3. Effect of ligand reagent addition on factor Y

Calibration graph: A series of standard cyanide solutions were prepared and the absorbance of each was measured and plotted. The measurement results and the exponent y was all listed in Table-1. Curve log y with the logarithm value of CN^- concentration (X μg), lg X was shown in Fig. 4.

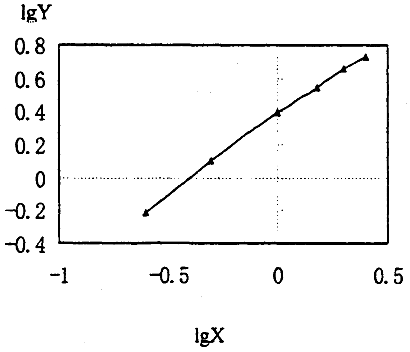

Fig. 4. Standard curves for the determination of cyanide.

We found that the curve linearity was well. The cut distance lg α was calculated to be 0.382 and the oblique rate β to be 0.942 from the straight line in Fig. 4. The following expression was obtained.

$$y = 2.41\ X^{0.942} \qquad \ldots(3)$$

TABLE-1
DETERMINATION OF STANDARD CYANIDE SOLUTIONS

CN^- amounts X, μg	Transmittancy*, %		y value
	600 nm	570 nm	
0	100	100	—
0.25	80.5	87.1	0.61
0.50	65.0	77.9	1.34
1.00	42.1	61.2	2.46
1.50	26.0	49.0	3.72
2.00	16.5	38.9	4.58
2.50	10.8	32.0	5.35

*: Absorbance = 1 g (100/transmittancy).

Effect of foreign ions: According to the distillation procedure[8], none of the following ions affected the direct determination of 0.10 mg/L CN^- (< 10% error): 1000 mg/L Cl^-, Mg^{2+}, Ca^{2+}, Al(III), SO_4^{2-}, NO_3^-, NH_4^+; 100 mg/L Fe(II), Mn^{2+}, Cu(II), Ni(II), Zn(II), Cr(III); 10 mg/L Cd(II), Hg(II), Sn(II), Fe(III), SCN^-.

Precision and detection limit: Six replicate determinations of 1.00 μg standard cyanide was carried out, the relative standard deviation (RSD) being 1.8%. However, the RSD with the single wavelength method was 2.5%.

We used $L_{min} = kSb/S$ to calculate the detection limit of PSWS, where k = 3, Sb named as standard deviation and S named as sensitivity. Replicate determination of twenty reagent blanks gave Sb of Y value computed from (Ap + 1)/(As + 1) was eaual to 0.01. The analytical sensitivity (S) was equal to the above α value, 2.41. Therefore the detection limit (L_{min}) of CN^- was 0.002 mg/L.

Sample analyzed: As a test of the method cyanide was determined in sewage and waste water. The results had been listed in Table-2. We found the results be the recommended method agreed with the conventional method. The RSDs were less than 7.2% and the recovery rate of CN^- between 90 and 106%.

TABLE-1
DETERMINATION OF CN^- IN WATER SAMPLES

Sample title	By conventional method	By PSWS			
		Added	Found		Recovery, %
Sewage 1#	0.026	0	0.022	0.023	
			0.024	0.025	
			0.025	0.027	90
		0.020	0.043	0.041	
Waste water 1#	0.221	0	0.224	0.234	
			0.219	0.231	
			0.224	0.228	99
		0.20	0.418	0.433	
Waste water 2#	0.102	0	0.097	0.104	
		0.100	0.219	0.194	106

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(*Received*: 20 February 1999; *Accepted*: 9 July 1999) AJC-1776