

## Improvement of Primary—Secondary Wavelengths Spectrophotometric Determination of Trace Amounts of Sulfide in Water

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In acidic solution and in presence of ferric ions the conventional reaction of sulfide ( $S^{2-}$ ) with *p*-aminodimethylaniline to form methylene blue dye has been applied for the improvement of the sulfide determination in natural water and waste water by the updated method named primary—secondary wavelengths spectrophotometry (PSWS). The results show that the analytical precision and accuracy were increased and given the higher determination sensitivity than the ordinary spectrophotometry.

### INTRODUCTION

Hydrogen sulfide is a poisonous and foul gas. It can affected the oxidation of biological cell by reacting cell colorant, oxidizing enzyme and so on, to make cell organism oxygen deficiency. Hydrogen sulfide is often produced from sulfide ( $S^{2-}$ ) under acidic environment. Sulfide usually exists in waste water polluted by, for example chemical, paper mill, mine—selecting, printing and dyeing, leather—making and other industries. In addition, sulfate ( $SO_4^{2-}$ ) may be reduced by anaerobic bacteria to form sulfide ( $S^{2-}$ ). Trace amounts of  $S^{2-}$  is often determined by spectrophotometry with *p*-aminodimethylaniline (PADA)<sup>1</sup>, ethyl violet<sup>2</sup>, molybdenum blue<sup>6</sup>, etc. But the reaction of  $S^{2-}$  with PADA is sensitive and selective in the presence of ferric ions. In this paper the updated method, primary—secondary wavelengths spectrophotometry has been applied for the determination of trace amounts of  $S^{2-}$  in waste water, which is more accurate and precise than the ordinary spectrophotometry using the above reaction. In addition, this new method may give the stable calibration graph to be affected hardly by the operation conditions. The results were all satisfactory. The sulfide recovery rate was between 94 and 110%, the relative standard deviation (RSD) less than 7.8 and the detection limit only 0.01 mg/L that was half of the conventional value.

For a colloid or suspension liquid the absorbance ( $A$ ) at wavelength  $\lambda$  is relative with the particle's property factor, particle property factor, particle diameter parameter  $\phi$  and amounts parameter  $\epsilon$ , their relation curve a shown in Fig. 1 and their expression is followed by<sup>4</sup>:

$$A = \phi \epsilon^{-2} \lambda^{-\epsilon} \quad \dots (1)$$

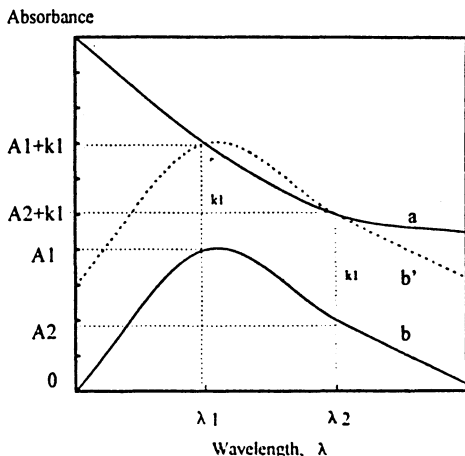


Fig. 1 Principle draft: a, a suspension liquid against water; b, absorption spectrum sketch of a ligand complex solution; b', obtained curve for moving curve b up  $k_1$  distance.

The absorption spectrum sketch curve b of a colored solution is shown in Fig. 1, too. We can see if curve b moves up  $k_1$  distance to  $b'$  position, both M and N are two intersect points that pass through curves  $b'$  and a. The absorbances at M and N should satisfy formula 1. Therefore,

$$A_1 + k_1 = k_2 \lambda_1^{-y} \quad \dots (2)$$

$$A_2 + k_1 = k_2 \lambda_2^{-y} \quad \dots (3)$$

Both  $k_1$  and  $k_2$  are optical parameters. Our experiments show that factor y is an exponent function with ligand amounts, that is with the determined component concentration (x mg/L) when  $k_1 = 1$ .

$$y = \alpha x^\beta \quad \dots (4)$$

where  $\alpha$  and  $\beta$  are constants with two wavelengths  $\lambda_1$  and  $\lambda_2$  respectively. In order to get maximum sensitivity the wavelength  $\lambda_1$  is necessary to be selected at the point of the maximum absorption and it is named as primary wavelength ( $\lambda_p$ ):  $\lambda_p = \lambda_{\max}$ , also  $A_p = A_1 = A_{\max}$ . The other wavelength  $\lambda_2$  may be selected but different  $\lambda_2$  will give the different  $\alpha$  and  $\beta$  values. We think that  $\lambda_2$  may be selected at the corresponding wavelength nearby of  $0.5A_{\max}$  and it be named as secondary wavelength ( $\lambda_s$ ). So we can obtain the following expression from the above equation group.

$$\left( \frac{A_p + 1}{A_s + 1} \right) = \left( \frac{\lambda_p}{\lambda_s} \right)^{-y} \quad \dots (5)$$

From equation (5) we may calculate y value, then to further give x value from equation 4. We see both  $A_p$  and  $A_s$  will change at the same step when the operation conditions, for example room temperature was varied. It is found  $(A_p + 1)/(A_s + 1)$  value varied little. So equation (5) has the corrected function

to operation conditions so that both  $\alpha$  and  $\beta$  are kept basically stable in  $y(x)$  model above.

From above principle we has kown that PSWS is realy a dual—wavelength spectrophotometry but it has the different source and basis to compare with the other dual—wavelength method<sup>5-7</sup>.

## EXPERIMENTAL

Visible spectra were recorded with a Model 7230 spectrophotometer (Shanghai, China), in a 1 cm glass cell.

0.1 mol/L sodium thiosulfate by preparing with  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (A.R., Shanghai Chemical) then standardizing it with 0.050 mol/L standard potassium Dichromate and storing in a dark flask.

*Sulfide solution* Weighing 7.5 g of sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , A.R., Shanghai Chemical) to be dissolved in 100 mL of ion exchange water then diluting to 1000 mL. The standardization of this solution was carried out immediately with 0.1 mol/L standard iodine and the above standard sodium thiosulfate solution.

*Standard  $\text{S}^{2-}$  liquid, 5 mg/L:* Using the above  $\text{S}^{2-}$  solution containing 5 mg of  $\text{S}^{2-}$  to a 1000 mL volumetric flask and diluting to 800 mL with ion exchange water, adding 2 mL of 2 mol/L zinc acetate for forming  $\text{ZnS}$  suspension liquid. As so sulfide value remains stable for 2–3 weeks.

*Ferric ammonium sulfate solution:* Dissolving 25 g of ferric ammonium sulfate A.R., Shanghai Chemical) in 200 mL of ion exchange, water then adding 5 mL of concentrated sulfuric acid.

0.20% (m/V) *p*<sup>-</sup> aminodimethyl aniline (PADA): Dissolving 2 g of PADA (Shanghai Reagent) in 700 mL of ion exchange water and adding into 200 mL of concentrated sulfuric acid then diluting to 1000 mL after cool.

*Recommended Procedures:* The pretreatment of waste water sample should be carried out. Here nitrogen gas blow method was recommended.

It changes  $\text{S}^{2-}$  into  $\text{H}_2\text{S}$  by acidifying sample solution then  $\text{H}_2\text{S}$  was carried out by nitrogen gas from mother solution to absorption tube.

Added 30 mL of ion exchange water and 5 mL of PADA solution. After mixed, added 1 mL of ferric ammonium sulfate solution. Covered and mixed well. After 10 min, diluted to 50 mL and mixed. Measured that absorbances at wavelengths 665 nm and 700 nm, respectively, against a reagent blank.

## RESULT AND DISCUSSION

*Absorption Spectra:* Figure 2 gave the absorption spectra of  $\text{S}^{2-}$ -PADA-Fe(III) solution. This solutions absorption reached maximum at 665 nm. According to the relative content in principle the primary wavelength should be selected at 665 nm. The secondary wavelength was arranged at 700 nm here. That was  $\lambda_p = 665$  nm and  $\lambda_s = 700$  nm.

*Effect of PADA Concentration:* Figure 3 show the effect of the addition of PADA solution on factor  $y$  calculated from equation (5). We found the addition of PADA solution was more than 4 mL  $y$  remained almost constant and reached maximum. In this study, 5 mL of 0.20% PADA was selected.

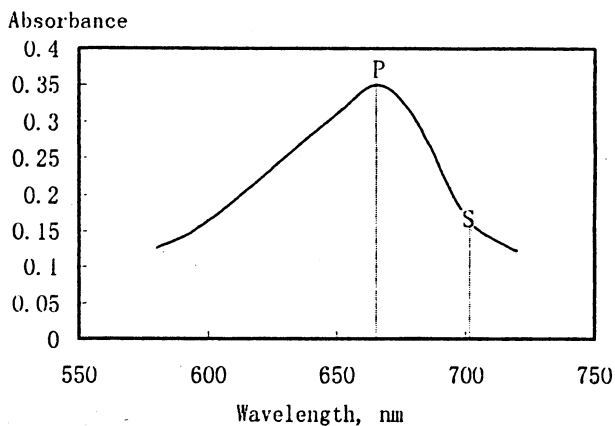


Fig. 2 Absorption spectrum of surfide solution in the presence of ferric and acidic solution against reagent blank: P point: 665 nm and S point: 700 nm

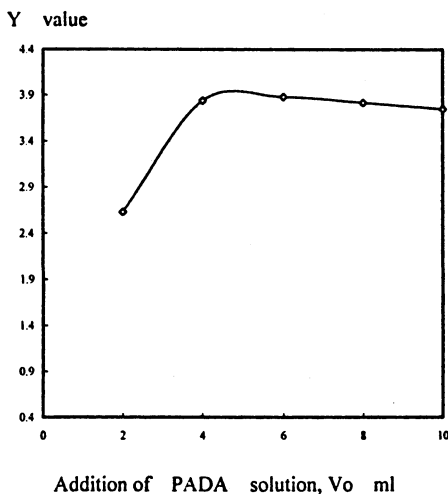


Fig. 3 Effect of PADA addition of factor y

TABLE-1  
DETERMINATION OF STANDARD SURFIDE SOLUTIONS

S <sup>2-</sup> amounts x, mg/L	Transmittancy* (%)		y value
	665 nm	700 nm	
0	100	100	
0.10	85.2	95.8	0.952
0.20	70.4	89.6	1.830
0.30	60.2	85.3	2.570
0.40	52.8	81.4	3.100
0.50	44.9	78.5	3.880

\*: Absorbance =  $\log(100/\text{transmittancy})$

**Calibration Graph:** A series of standard surfide solutions were prepared and the absorbance of each was measured and plotted. The measurement results and the exponent  $y$ 's calculation ones were all listed in Table-1. Curve  $\log Y$  with the logarithm value of  $S$  concentration ( $x$  mg/L),  $\log X$  was shown in Fig. 4.

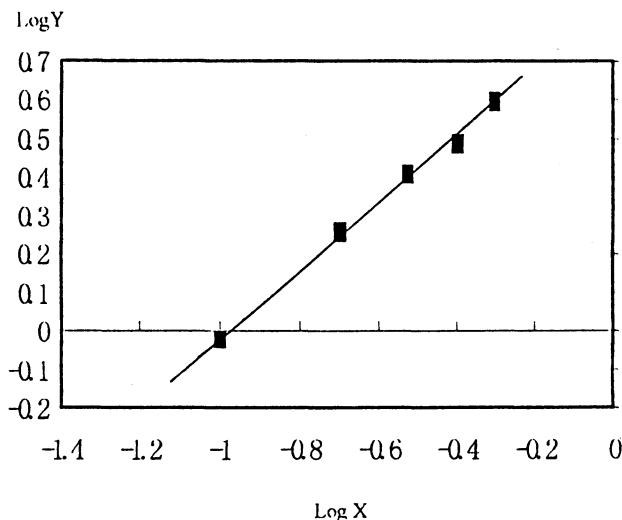


Fig. 4 Standard curves for the determination of surfide (the relative coefficient,  $r = 0.9991$ )

We found that the curve linearity was well. The cut distance  $\log \alpha$  was calculated to be 0.849 and the oblique rate  $\beta$  to be 0.860 from the straight line in Fig. 4. The relation of  $y$  with  $x$  was therefore obtained by the following expression.

$$y = 7.06x^{0.860} \quad \dots (6)$$

**Effect of Foreign Ions:** According to the recommended procedure, none of the following ions affected the direct determination of 0.10 mg/L  $S^{2-}$  (<20% error): 1000 mg/L  $Cl^-$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ti(IV)$ ,  $Al(III)$ ,  $Fe(III)$ ,  $Fe(II)$ ,  $Zn(II)$ ,  $Br^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ ; 100 mg/L  $Mn^{2+}$ ,  $Cu(II)$ ,  $Ni(II)$ ,  $Co(II)$ ,  $Cr(III)$ ,  $H(II)$ ; 10 mg/L  $Ag^+$ ,  $Sb(III)$ ,  $Sn(IV)$ . If some reductants, for example 1 mg/L  $SO_3^{2-}$  and  $S_2O_3^{2-}$  existed in sample. The stored sample by zinc acetate must be filtered before gas blow pretreatment.

**Precision and Detection Limit:** Six replicate determinations of 0.300 mg/L standard surfide were carried out, the relative standard deviation (RSD) being 4.0%. However, the RSD with the single wavelength method was 7.1%. The precision for PSWS was therefore better than that for the ordinary spectrophotometric method.

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 equal to 0.025. The analytical sensitivity ( $S$ ) was equal to the above  $\alpha$  value, 7.06. Therefore the detection limit ( $L_{\min}$ ) of  $S^{2-}$  was 0.01 mg/L.

*Sample Analysed:* As a test of the method sulfide was determined in sewage and waste water. The results had been listed in Table-2. We found the results by the recommended method is comparable with the conventional method. The RSDs were less than 7.8% and the recovery rate of  $S^{2-}$  between 94.0 and 110%.

TABLE-2  
DETERMINATION OF SULFIDE IN WATER SAMPLES

Sample name	By conventional method	By PSWS		
		Added	Found	Recovery %
Sewage 1#	0.078	0	0.076 0.078 0.067	110
		0.030	0.072 0.071 0.069	
			0.108 0.110	
Waste water 1#	1.01	0	1.01 1.02 10.9	102
			1.02 1.05 0.98	
		1.00	2.11 2.04 2.04	
Waste water 2#	0.300	0	0.309 0.304	94.0
		0.200	0.484 0.504	

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