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

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In acidic solution and in the 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 analytical precision and accuracy were both increased and gave the higher determination sensitivity than the ordinary spectrophotometry.

INTRODUCTION

Hydrogen sulfide is a poisonous and foul gas. It can affect the oxidation of biological cells by reacting with cell colorants and oxidizing enzymes etc. to create 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)[1], ethyl voilet[2], molybdenum blue[3], 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 (PSWS) 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 deviations (RSDs) less than 7.8% and the detection limit only 0.01 mg/L that was half of the conventional value.

In a colloid solution or a suspension liquid the absorbance (A) is relative to the particle's diameter parameter ϕ and the particle amounts parameter ε at wavelength λ. Curve **a** is shown in the absorption spectrum sketch (Fig. 1). The expression is followed by[4].

$$A = \phi\varepsilon^{-2}\lambda^{-\varepsilon} \qquad \ldots(1)$$

Curve **b** in Fig. 1 gives the absorption of a color solution. To move curve **b** for $\mathbf{k}_1$ distance up to **b′** position, the intersect points, both M and N are formed in curve **a**. The absorbances at M and N points should satisfy formula above.

$$\begin{cases} A_1 + k_1 = k_2 \lambda_1^{-Y} & \ldots(1) \\ A_2 + k_1 = K_2 \lambda_2^{-Y} & \ldots(2) \end{cases}$$

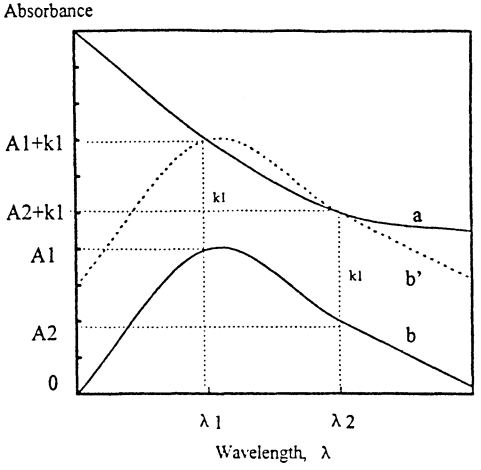

Fig. 1. Principle draft: a, a suspension liquid against water; b, absorption spectrum sketch of a ligand complex solution; b′, obtained curve for moving curve b up k_1 distance.

Both $\mathbf{k}_1$ and $\mathbf{k}_2$ are named the calculation factors. A lot of experiments have shown that factor y is exponent to the determined component concentration (X mg/l or μg) when $\mathbf{k}_1 = 1$.

$$y = \alpha X^{\beta} \qquad \ldots(4)$$

Both α and β are constants when two wavelengths λ_1 and λ_2 are selected. In order to get maximum sensitivity the wavelength λ_1 is necessary to be selected at the maximum absorption and it is named as primary wavelength (λp): $\lambda_p = \lambda_{max}$, also $A_p = A_1 = A_{max}$. The other wavelength λ_2 may be selected according to experimental conditions, which affects directly on both α and β values. λ_2 is often selected at the corresponding wavelength of about 0.5 A_{max} and it named as secondary wavelength (λs). The following expression is given out.

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

From this expression y value may be obtained, then to give X value from expression 4. Both A_p and A_s happen change with the variation of the operation conditions for example room temperature. It is found that $(A_p + 1)/(A_s + 1)$ 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 understood to be also one of dual-wavelengths spectrophotometries, which is different with the other dual-wavelengths methods[5-7].

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 $Na_2S_2O_3 \cdot 5H_2O$ (A.R., Shanghai Chemical) then standardizing it with 0.050 mol/L standard potassium dichromate and storing in a dark flask.

Standard 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 ZnS suspension liquid. 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-aminodimethylaniline (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 N_2 blow method was recommended and its installation was showed in Fig. 2. It changed S^{2-} into H_2S by acidifying sample solution then H_2S was carried out by nitrogen gas from mother solution to absorption tube. A known volume of a sample containing less than 40 μg of S^{2-} is adding into flask 1 then diluting to about 200 mL with ion exchange water. 10 mL of 2 mol/L zinc acetate was putting in

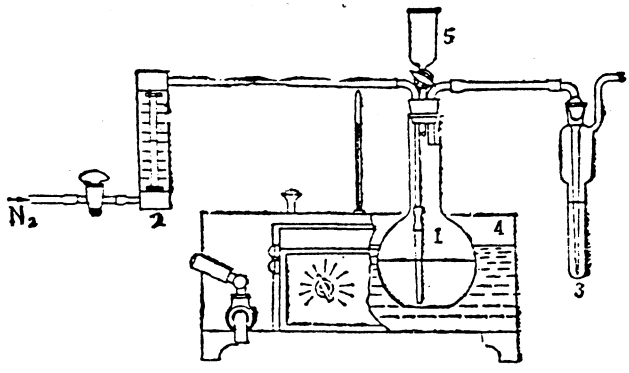

Fig. 2. Pretreatment installation for extracting hydrogen sulfide: (i) 500 mL level bottomed flask, (ii) gas flow counter, (iii) absorption tube, (iv) constant temperature water bath, (v) dropping funnel.

tube 3 and 10 mL of 50% phosphoric acid into the funnel 5. Turned on power and heated water bath to keep water temperature between 65–80°C. Turned on the cork of funnel 5 and phosphoric acid solution up to flask 1 and mixed with sample to form H_2S gas. Switched on N_2 source to carry H_2S from flask 1 to tube 3, where ZnS was formed. After 40 min, switch off power and N_2 source. The absorption suspension liquid was transmitted to 50 mL volumetric flask. Add 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 the absorbances at wavelengths 665 nm and 700 nm, respectively, against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra: Fig. 3 gave the absorption sepctra of S^{2-}-PADA-Fe(III)

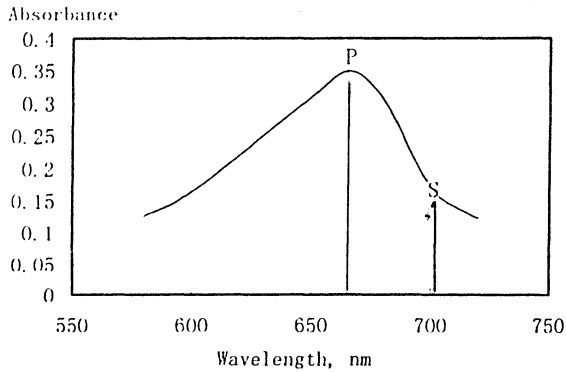

Fig. 3. Absorption spectrum of sulfide solution in the presence of ferric and acidic solution against reagent blank: P point 665 nm and S point 700 nm.

solution. This solution's absorption reached maximal at 665 nm. According to the relative content in principle the primary wavelength (λ_p) should be selected at 665 nm. The secondary wavelength (λ_s) was arranged at 700 nm here.

Effect of PADA concentration: Fig. 4 shows the effect of the addition of PADA solution on factor y calculated from formula 5. We found when the addition of PADA solution was more than 4 mL, y remained almost constant and reached maximum. In this study, 5 mL of 0.2% PADA was selected.

Calibration graph: A series of standard sulfide solution were prepared and the absorbance of each was measured and plotted. The measurement results and the exponent y values were all listed in Table-1. Curve log y with the logarithm value of S^{2-} concentration (X mg/L), lg X was shown in Fig. 5.

We found that the curve linearity was well. The cut distance lg α was calculated to be 0.849 and the oblique rate β to be 0. 860 from the straight line in Fig. 5. The relation of y with X was therefore obtained by the following expression.

$$y = 7.06X^{0.860} \quad \ldots(6)$$

TABLE-1
DETERMINATION OF STANDARD SULFIDE SOLUTIONS

S^{2-} concen. X, mg/L	Transmittancy *, %		y value
	665 nm	700 nm	
0	100	100	—
0.10	85.2	95.8	0.95
0.20	70.0	89.6	1.83
0.30	60.2	85.3	2.57
0.40	52.8	81.4	3.10
0.50	44.9	78.5	3.88

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

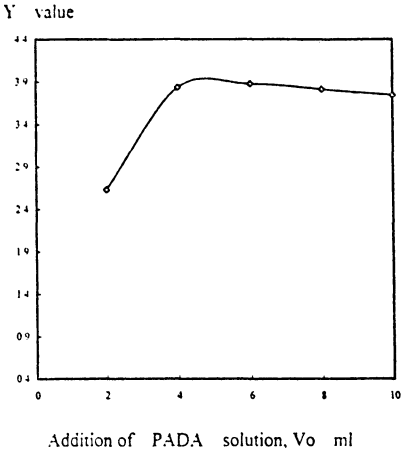

Fig. 4. Effect of PADA addition of factor y.

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), Hg(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 sulfide 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 higher than that for the ordinary spectrophotometric method.

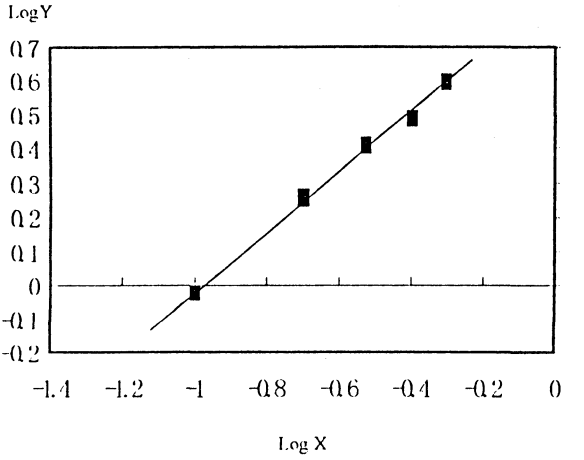

Fig. 5. Standard curves for the determination of sulfide (the relative coefficient = 0.9991).

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 compound from (Ap + 1)/(As + 1) was equal to 0.025. The analytical sensitivity (S) was equal to the above α value, 7.06. Therefore the detection limit (L_{min}) of S^{2-} was 0.01 mg/L.

Sample analyzed: 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 tallied 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, %
	0.076	0	0.076	0.078	
Sewage 1#			0.067	0.072	
			0.071	0.069	110
		0.030	0.108	0.110	
Waste water 1#	1.010	0	1.01	1.02	
			1.09	1.02	
			1.05	0.98	102
		1.000	2.11	2.04*	
Waste water 2#	0.300	0	0.309	0.304	
		0.200	0.484	0.504	94

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