Primary-Secondary Wavelength Spectrophotometric Determination of Trace Amounts of Silver in Wastewater with 2,4-Dibromo-6-Carboxy-Benzenediazoaminoazobenzene

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Summary: In the presence of Triton X 100 at pH 13 the reaction between silver (Ag^+) and chromogenic reagent, 2,4-dibromo-6-carboxy-benzenediazoaminoazo-benzene (DBCBAA) was developed to form a red complex. This reaction was highly selective in the presence of disodium ethylene diamine tetracetate (Na_2EDTA). Because of the interference of excess of DBCBAA the new method named as primary-secondary wavelength spectrophotometry (PSWS) was applied instead of the ordinary spectrophotometry for the determination of trace amounts of silver in wastewater. Results showed that such a method gave out the better precision and higher accuracy than the ordinary method. By analyzing several wastewater samples, the relative standard deviations were less than 3.69% and the recovery rate of Ag between 93.5 and 104%.

Introduction

Silver is one of precious metal elements. Many color reactions happen between Ag(I) and a lot of chromogenic agents, such as with azo compound [1], thio-ligand [2], acidic and basic dye [3], porphyrin compounds [4] and so on. The synthesis of chromogenic reagent, 2,4-dibromo-6-carboxy-benzenediazo-aminoazobenzene (DBCBAA) was made [5] with o-aminobenzoic acid and its structure as follows:
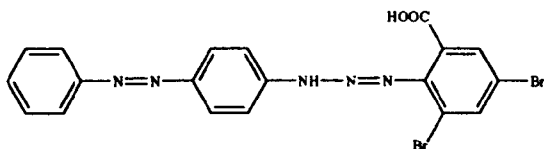
In this report, such a ligand was first to be applied for the determination of trace amounts of Ag in wastewater at pH 13 and in the presence of non-ionic surfactant, Triton-X 100 by primary-secondary wavelength spectrophotometry (PSWS). The recommended method was ever used for the determination of trace amounts of some pollutants [6-8]. It has been proved to bring out the better precision, higher sensitivity and simpler operation than the single wavelength spectrophotometry. The reaction above was one of new metal-ligand complex reactions and here it was used to study the updated determination of trace amounts of silver. Results showed that such as reaction was very selective in the presence of masking reagent, disodium ethylene

diamine tetracetate (Na$_2$EDTA) which may eliminate the interference of the co-existing metal ions, for example, cadmium (II), mercury(II) and so on. In this report, Lambert-Beer Law was not applied. The detection limit of silver was 0.02 mg/l and its recovery rate between 93.5 and 104% accompanying with the relative standard deviations (RSDs) less than 3.69%.

Principle

From absorption spectra (Fig. 1), moved curve 2 (colorimetric solution spectra) 1 absorbance unit up to curve 3 and it crossed curve 1 (a suspension liquid spectra, absorption A = $k\lambda^{k}$) [9]. Both P and S cross-points gave the following relationship [10].

$$\frac{AP+1}{As+1} = (\frac{\lambda p}{\lambda s})^{-k\,'}$$

To see Figure 1, the term, λp ws named Primary Wavelength and it was usually selected at peak absorption of the colorimetric solution. The term, λs was named Secondary Wavelength and it was usually selected at valley absorption. The following formula was found.

$$y = \lg(\frac{Ap+1}{As+1}) = \alpha\chi^{\beta}$$

Both α and β were constants and χ indicated the concentration (mg/l) of the clorimetric component. This equation was stable because of the use of (Ap=1)/(As+1). The effect of work environment on both α and β were little. Therefore, this method provided a simple operation and increased the precision and accuracy of trace analysis because it utilized the peak absorption and valley absorption of a colorimetric solution at the same time. In fact, this new method named as primary-secondary wavelength spectrophotometry (PSWS) was also one of dual-wavelength spectrophotometric methods but different from the others [11-13] in theory and operation.

Results and Discussion

Absorption spectra

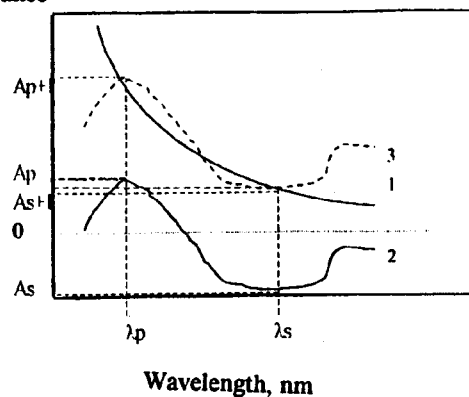Fig. 2 showed the absorption spectra of Ag-DBCBAA complex solution. The peak absorption

Fig. 1:   Absorption spectra sketch: 1, suspension liquid (colloidal system) against water, 2, colorimetric solution against reagent solution; 3, sam as 2 but the absorbance was moved up 1 unit. λp - peak absorption (P point) or primary wavelength, λs - valley absorption (S point) or secondary wavelength.
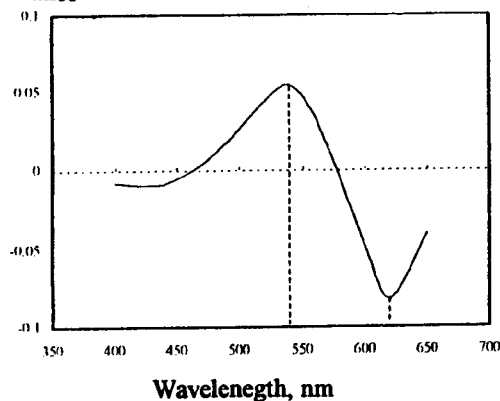

Fig. 2:   Absorption spectra of Ag- DBCBAA complex solution containing 5 μg Ag at pH 13 and in the presence of Triton-X 100, at 540 nm against reagent blank.

appeared at 540 nm and the valley at 620 nm. Therefore, 540 nm should be selected as primary wavelength and 620 nm as secondary wavelength. That was said that λp = 540 nm and λs = 620 nm.

Effect of DBCBAA concentration

The effect of the various addition of DBCBAA solution on absorbance of Ag complex

solution and y value was shown in Figure 3. It was found that the addition of 0.50 mmol/1 DBCBAA was more than 1.5 ml y remained maximal. In this work, 2 ml of DBCBAA solution was used.
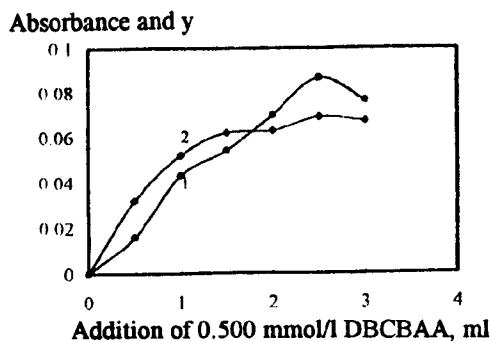
Absorbance and y

Fig. 3: Effect of 0.50 mmol/1 DBCBAA addition on absorbance (curve 1) and y (curve 2) of Ag (5 μg) complex solution in the presence of Triton X 100, at 540 nm.

The complex ratio of Ag(I) to DBCBAA is determined to be 1:5 by using the continuous variation method [14] and beta-corection spectrophotometry [15].

Effect of pH

The effect of pH on y values was shown in Figure 4. While pH was more than 12.5, y reached a maximal value and remained almost constant 2.5 ml of 1.0 mol/1 KOH was added, which may give the complexed solution pH 13.

Effect of surfactants

In the presence of different surfactant (OP, Trition-X 100, CTMAB and SDBS) and in no surfactant solution the measurement data were all shown in Fig. 5. It was found that the use of Triton-X 100 gave the maximal y among 4 surfactants. Therefore, Triton-X 100 was selected for use because of the maximal sensitivity. Varying the addition of 2% Triton-X 100, the effect curve was shown in Figure 6. While the addition of Triton-X 100 solution was more than 0.5 ml, y reached a maximal value. Therefore, 1 ml of Triton-X 100 solution was added.
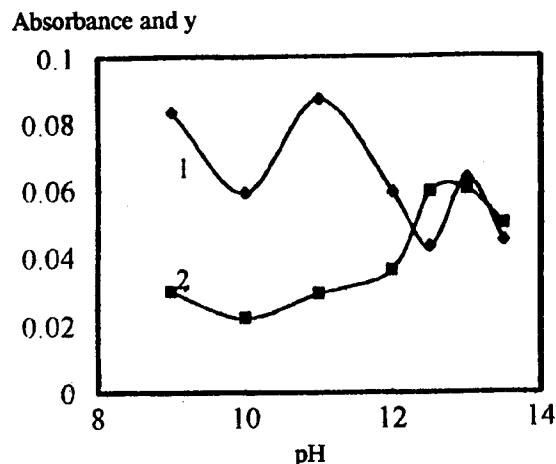
Absorbance and y

Fig. 4: Effect of pH on absorbance (curve 1) and y (curve 2) of Ag(5 μg)-DBCBAA complex solution in the presence of Triton X 100, at 540 nm.
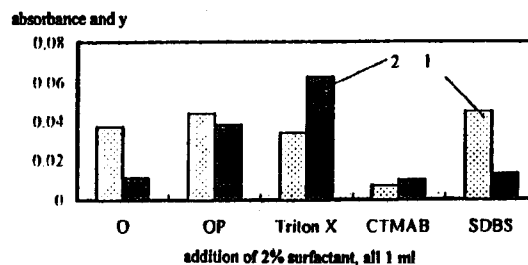

Fig. 5: Effect of different surfactant (all 1 ml of 2%) on absorbance (curve 1) and y (curve 2) of Ag(5 μg)-DBCBAA complex solution, at 540 nm.
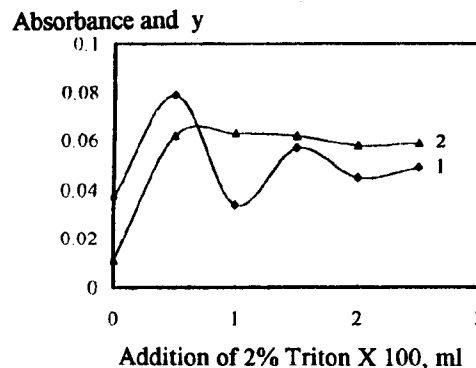
Absorbance and y

Fig. 6: Effect of the addition of 2% Triton-X 100 on absorbance (curve 1) and y (curve 2) of Ag(5 μg)-DBCBAA complex solution, at 540 nm.

Effect of time

The effect of the reaction time on y values was shown in Figure 7. When the time was between 5 and 30 min y reached maximum.
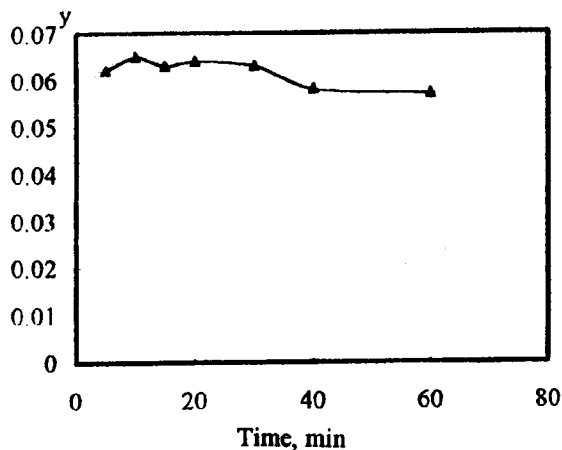

Fig. 7:   Effect of color-developed time on y Ag(5 μg)-DBCBAA complex solution in the presence of Triton-X 100.

Calibration graph

A series of standard Ag (0-10 μg/25 ml) solutions were prepared and the absorbance of each was measured and plotted. Each y was calculated. Two calibration graphs were shown in Figure 8. It was found that all points of around curve 2 (the relative coefficient of linearity, R2=0.9990) was much more linear then that around curve 1 (R1 = 0.983). It was found that from curve 1 the accuracy was too bad to determine trace amounts of silver because of the divergent points. However, all points around curve 2 approached the straight line (especially, y values between 0.05 and 0.07). It was expressed as follows (α=0.0094 and β=1.08): y = $0.0094X^{1.08}$

Precision, accuracy and detection limit

Eight replicate determinations of standard solution containing 2.00 μg Ag were carried out, the results were listed in Table-1. The relative errors (REs) were between -7 and +6% and standard deviation (RSD) 4.1% by PSWS. However, the REs were between -6 and +34.5% and the RSD 10.7% by the single wavelength method. The accuracy and
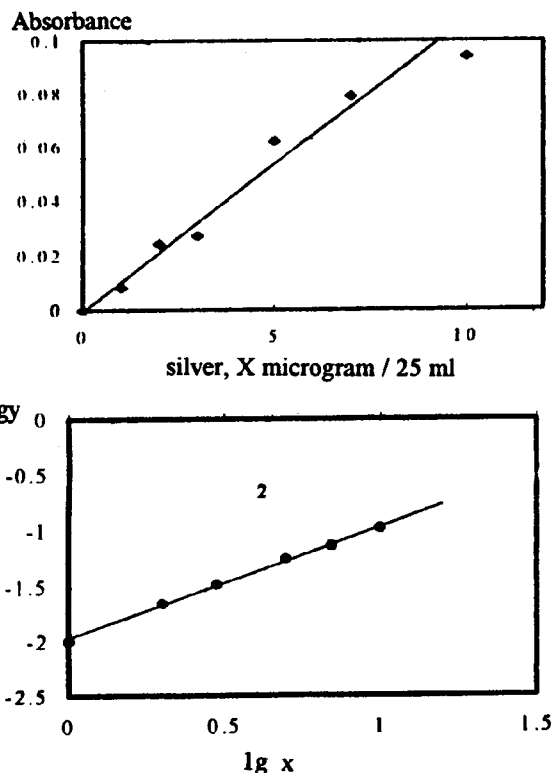

Fig. 8:   Calibration graph for the determination of water at 540 nm: 1, absorbance 2, y.

Table-1: The result and comparison for replicated determination of 2.00 μg Ag by PSWS and by ordinary spectrophotometry

Method	Found, μg	Average, μg	Relative error, %	Relative standard deviation, %
Ordinary spectrophotometry	2.14 2.19 2.31 2.69 2.36 2.10 1.88 2.14	221	-6 ~ + 34.5 aver. + 10.5	10.7
PSWS	1.95 2.12 2.07 2.03 1.94 1.99 1.86 1.97	1.99	-7 ~ +6 aver. -0.5	4.1

precision for PSWS was therefore higher than that for the ordinary spectrophotometric method.

We use L_{min} =kS_b/S to calculate the detection limit of such as method where k=3, S_b named as standard deviation and S named as sensitivity. Twenty replicate determinations of reagent blanks gave S_b of y values was equal to only 0.0015. The sensitivity S was equal to α value, 0.0094 above.

Therefore, the detection limit of Ag was L_{min} =0.5μg/25-ml (0.02 mg/l).

Effect of foreign ions

The recommended procedure was carried out, none of the following ions will affect the direct determination of 5 μg of Ag (<10% error): 10 mg of CL, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_3^-, CI', F', PO_4^{3-}, NH_4^+, K(I), Na(I), Ca(II), Mg(II), Zn(II), Be(II), 1 mg of Al(III), Sn(II), Ti(IV); 200μg of Pb(II), Fe(II), Fe(III), Mo(VI), V(V), Cr(IV); 50 μg of Co(II), Ni(II), Cu(II), Hg(II) and Cd(II).

Samples analyzed

As a test of the method Ag was determined in wastewater. The results were listed in Table-2. It was found that the results obtained by the recommended method was similar to that obtained by the conventional method (CM) with cadion as chromogenic reagent [16]. The RSDs were less than 3.69% and the recovery rate of Ag between 93.5 and 104% for the recommended method.

Table-2: Determination of silver in water samples

Sample	Added	Ag concentration, mg/l Found	With cadion agent	RSD, %	Reco-very, %
Wastewater 1#	0	0.326			
		0.339	0.329		
		0.347			
		0.342	0.333	2.25	
		0.344			
		0.334	0.345		
		aver. 0.339	aver. 0.336		
	0.200	0.531			960
		0.526			93.5
Wastewater 2#	0	0.542			
		0.545	0.522		
		0.526			
		0.533	0.519	1.91	
		0.528			
		0.518	0.534		
		aver. 0.532	aver.0.525		
	0.200	0.736			102
		0.734			101
Wastewater 3#	0	0.087			
		0.093	0.098		
		0.091			
		0.086	0.091	3.69	
		0.087			
		0.090	0.094		
		aver. 0.089	aver. 0.094		
	0.100	0.184			95.0
		01.94			104

Experimental

Apparatus and reagents

Visible spectra were recorded with a Lambda 19 (Perkin Elmer) double-beam recording spectrophotometer with 10 cm cells.

Standard Ag(I) solution, 100 mg/l: Prepared from 0.1573 g silver nitrate (A.R., Shanghai Reagent) to dissolve in 20 ml of distilled water and diluted to 1000 ml. It should be stored in dark bottle.

Standard Ag(I) working standard, 5.00 mg/l must be prepared daily by diluting standard Ag solution above.

Chromogenic agent solution, 0.50 mmol/l DBCBAA dissolving 125.2 mg of 2,4-dibromo-6-carboxy-benzenediazoaminoazobenzene (it was made and purified by Wang, etc. [5]) in 50 ml of acetone (A.R., Shanghai Reagent) then diluting 500 ml with acetone. It should be stored in a dark bottle.

KOH solution, 1.0 mol/l was prepared in distilled water and it ws used to adjust or control pH of the reaction solution.

Na_2-EDTA solution, 5% was prepared by dissolving 5 g of disodium ethylene diamine tetraacetate (A.R., Shanghai Reagents) in 100 ml of distilled water. It was used to mask the other metal ions beside Ag(I).

The anion surfactant, sodium dodecyl benzene sulfonate (SDBS, Shanghai Reagent), nonionic surfactant, OP (Beijing Chemical) and Triton X-100 (Shanghai Reagent), cationic surfactant, cetyl trimethylammonium bromide (CTMAB, Shanghai Reagent) solutions all 2% were prepared for trying to increase both the solubility of complex and sensitivity of this complex reaction.

Recommended procedures

A known volume of a sample containing less than 10 μg of Ag was taken in a 25-ml volumetric flask. Added ion distilled water to 10 ml mark. Added 0.5 ml of EDTA solution, 2.5 ml of KOH solution and 1 ml of Triton-X 100 solution. After mixing well, added 2 ml of DBCBAA solution.

Diluted to volume and mixed. Beetween 10 and 30 min, measured absorbances at 540 and 620 nm, respectively, against a reagent blank.

Acknowledgements

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