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Spectrophotometric Study of the Antimony(III)-2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol (3,5-Br₂-PADAP) Complex Formed in the Presence of Emulsifier OP

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A sensitive and selective method for the spectrophotometric determination of micro amount of antimony in surface water with 3,5-Br₂-PADAP and nonionic surfactant emulsifier OP is proposed. In 0.12~0.25 M HCl medium, Sb(III) forms blue-green trinary complexes with 3,5-Br₂-PADAP and OP. The complex exhibits maximum absorption at 630 nm, and the apparent molar absorptivity at this wavelength is $5.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Beer's law is obeyed for 0-25 μg of Sb(III) in 10 ml of solution. The colour is stable for 7 days. Antimony can be determined directly in aqueous solution without separation. The proposed method has been used for the determination of micro amounts of Sb(III) in surface water with satisfactory results.

KEY WORDS: Antimony determination, spectrophotometry, 3,5-Br₂-PADAP, emulsifier OP, surface water.

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INTRODUCTION

The determination of micro amounts of antimony has received considerable attention owing to concern with environmental protection. At present, the most commonly used reagent for spectrophotometric determination of antimony are basic dyes.¹⁻⁷ Recently there have been proposed some halogen derivatives of pyridylazo reagents.⁸⁻¹⁰ However, some of these methods require close control of conditions, some use toxic solvents, and some, which are too complex and time-consuming, are unsatisfactory for routine application. Therefore, any new procedure for the rapid and accurate determination of micro levels of antimony in environmental samples is of interest.

We have discovered that some nonionic surfactant such as emulsifier OP† may be used as solubilizing agent for the Sb(III)-3,5-Br₂-PADAP binary complex. This paper reports an investigation of the conditions for formation of the Sb(III)-3,5-Br₂-PADAP-OP complex in aqueous solution and the application of the system to determination of micro amounts of antimony in surface waters.

Experimental results show this method is simple, and better reproducibility and shorter analysis time are achieved. The extraction may also be avoided.

EXPERIMENTAL

Reagents

Unless stated otherwise, the reagents were of analytical-reagent grade or better. De-ionised water was used for dilution as this was found to be sufficiently pure for research purposes.

Standard antimony solution, 1.00 mg ml⁻¹

A stock solution of Sb(III) ion was obtained by the dissolution of 119.7 mg of GR grade Sb₂O₃ in 10 ml of 6 M HCl by heating and was diluted to 100 ml with 6 M HCl.

More dilute solutions (10 ug ml⁻¹) were prepared by diluting the standard solution with 0.5 M HCl. The solution was stable for 2 days.

3,5-Br₂-PADAP solution

Dissolve 100 mg of the reagent in 250 ml of emulsifier OP.

Absorption solution

Prepared by dissolving 150 mg of KMnO₄ in 500 ml of 0.015 M H₂SO₄.

Apparatus

In our experiments, two spectrophotometers were used.

Absorption spectra were recorded with a Model 751 spectrophotometer (made in Shanghai Analytical Instrument Factory, Shanghai, PR China).

Absorbance measurements were made with a Model 721 spectrophotometer. (3rd Analytical Instruments Factory, Shanghai, PR China.)

Operating procedure

1. Procedure A Transfer an aqueous sample solution containing not more than 25 μg of Sb(III) into a 10 ml standard flask, add enough 2 M hydrochloric acid to give a final acid concentration of 0.15 M.

Then add 0.5 ml of 20% KI, 1.5 ml of 3,5-Br₂-PADAP solution, and dilute to the mark with water. Mix well.

Measure the absorbance at 630 nm in a 1 cm cell against a reagent blank prepared in the same manner but containing no antimony.

2. Procedure B Separation apparatus see Figure 1. Place a volume of water sample, containing not more 20 μg of antimony (III), in a 100 ml distillation flask. Add the following reagents in the order given, mixing between additions: 4 ml of 20% tartaric acid, 8 ml of 6 M HCl, and 4 ml of 5% thiourea. Dilute the solution to about 25 ml with water and mix well. Place 5 ml of absorption solution in an absorption flask and then add two potassium borate tablets. Connect up the soft tube of emulsion and clog with a silicone rubber plug.

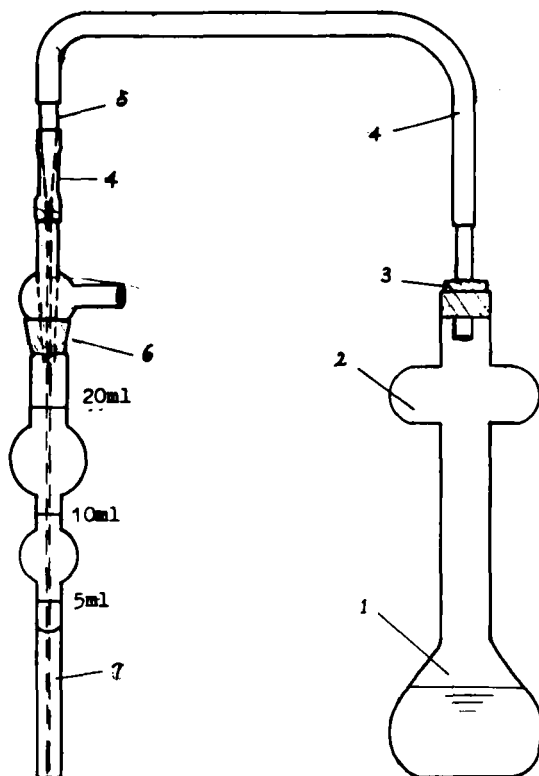


Figure 1 Separation apparatus of the Sb(III) by evolution as stibine: (1) distillation flask (100 ml); (2) putting place of potassium boranes; (3) silicon rubber plug; (4) soft tube of emulsion; (5) plastic tube (the tip of plastic tube was pulled to capillary shape, and its bore of gas outlet was below 1 mm); (6) stopper of frosted glass (14 mm); (7) absorption solution (its height is not below 50 mm).

Let tablet fall into the sample solution. When the reaction stops, wash the soft tube with small amount of water and collect the washing solution in an absorption flask. The purple of the solution can be faded by the addition of 2 drops of a 5% thiourea solution. Determine the antimony content in an aliquot according to the procedure A.

RESULTS AND DISCUSSION

The conditions given in the procedure are based on the results given

below. In the exploratory work the absorbance was measured in arbitrary units with fixed instrument settings but no standards.

Absorption spectra

The absorption spectra of Sb(III)-3,5-Br₂-PADAP-OP system and its reagent blank are shown in Figure 2.

This shows the maximum absorbance of the system to be at 630 nm. In the following experiments, the absorbances are measured at 630 nm against a reagent blank.

Effect of emulsifier OP

Our experimental results show that when used amount of OP was below 1 ml, coloured solutions appeared cloudy, but above 1 ml, the

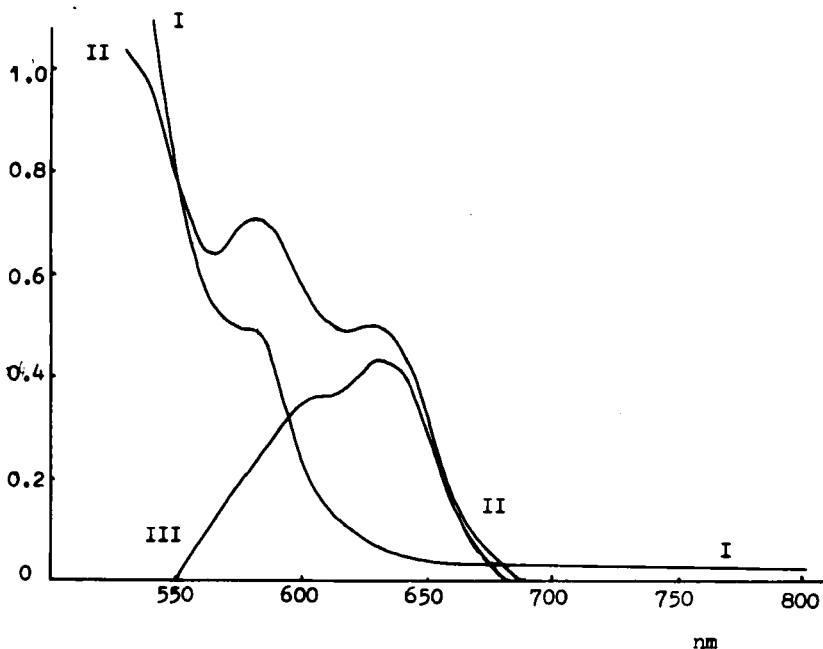


Figure 2 Absorption curves: Curve I; reagent blank vs. water; II: Sb(III)-3,5-Br₂-PADAP-OP system vs. water; III: the complex vs. reagent blank, [Sb] = 8.2×10^{-6} M; [3,5-Br₂-PADAP] = 4.6×10^{-5} M; [OP] = 0.24 M.

solution became clear and the absorbance obtained was maximum and constant. Therefore, 1.5 ml of OP were used.

Effect of 3,5-Br₂-PADAP

The absorbance of the coloured complex is constant and at its maximum when the volume of 0.1% 3,5-Br₂-PADAP used is varied between 0.2 and 1.5 ml. Hence, 1.5 ml of 0.04% 3,5-Br₂-PADAP solution was chosen for use

Effects of amounts of reagents

The effect of changing the amount of 2 M HCl and 20% KI is shown in Figure 3. Maximum and constant absorbance can be obtained with 1 ml of 2 M HCl, and 0.5 ml of 20% KI.

Stability of the absorbance intensity

The stability of the absorbance value of the system was carefully studied. At room temperature, the blue-green Sb(III)-3,5-Br₂-PADAP complex developed instantaneously and the absorbance remains stable for 7 days.

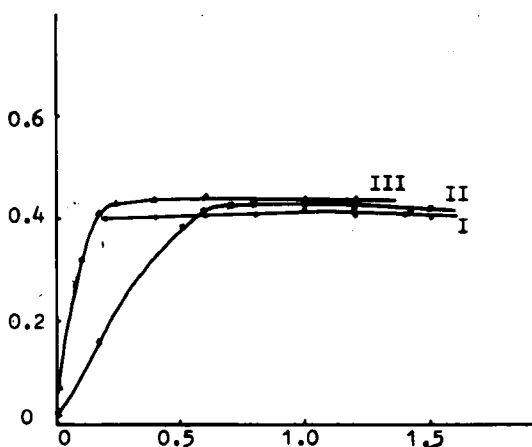


Figure 3 Effect of amounts of used reagents: Curve I: 0.1% 3,5-Br₂-PADAP solution; II: 2 M hydrochloric acid; III: 20% potassium iodide.

Effect of foreign ions

The effect of various amounts of 35 foreign ions was examined by determining $10\ \mu\text{g}$ of Sb(III). The results indicated that the following ions (amounts given in milligrams) do not interfere: Na^+ (100), K^+ (100), Ca^{2+} (20), Mg^{2+} (5), Zn^{2+} (10), Cd^{2+} (1), Mn^{2+} (29), Ni^{2+} (1), Mo(VI) (2), Y^{3+} (1), Be^{2+} (1), Al^{3+} (1), B(III) (1), La^{3+} (1), Ce^{3+} (1), As(III) (5), Ba^{2+} (10), NH_4^+ (5), Hg^{2+} (0.5), Fe^{3+} (0.5), V(v) (0.5), Cr(VI) (0.2), Co^{2+} (0.1), Ti(IV) (0.2), Ag^+ (0.25), Bi^{3+} (0.5), W(VI) (0.02), Sn^{2+} (0.05), Cu^{2+} (0.005), Cl^- (100), NO_3^- (20), NO_2^- (0.25), F^- (0.10), PO_4^{3-} (2), and SO_4^{2-} (15). From above results, we can see that the selectivity of the proposed method is better.

If the amount of foreign ions exceeds tolerance level, their interference can be eliminated by Procedure B. In these cases, following amounts of ions (given in μg) also do not interfere: W(VI) (1000), Sn^{2+} (1000), Co^{2+} (1000), Cu^{2+} (1000), F^- (1000) and NO_2^- (1000). Evidently, the separation of stibine from other ions is satisfactory.

Calibration and sensitivity

Beer's law was obeyed over the range $0\text{--}2.5\ \mu\text{g ml}^{-1}$ of Sb(III). The molar absorptivity, calculated from the slope of the graph, was $5.2 \times 10^4\ \text{l mol}^{-1}\ \text{cm}^{-1}$ at 630 nm. According to Sandell's expression, the sensitivity of the system was $2.2 \times 10^{-3}\ \mu\text{g cm}^{-2}$.

Application

The antimony contents of surface water samples are determined by the proposed method.

Determining procedure

Suitable amounts of surface water (below 10 ml) were pipetted into a 10 ml standard flask. The procedure A for antimony was then applied. When the amount of foreign ions in water samples exceeds tolerance level, we should use Procedure B.

Results obtained

To estimate the accuracy of the procedure, a recovery study was conducted, the results are shown in Table 1. As shown in Table 1, the accuracy is acceptable.

Table 2 gives the results obtained for antimony (III) in the surface water samples tested. The coefficients of variation found (6 replicates at each level) were 3.0, 2.8, 3.7 and 5.6% at the 0.3198, 0.2315, 0.2453 and 0.0922 mg L⁻¹ levels, respectively.

Table 1 Recovery study

Sample no.	Antimony amount, ug			Recovery %	Mean value of the recovery
	Original	Added	Found		
1	7.76	6.00	13.2	90.7	90.7
			13.2	90.7	
2	4.80	6.00	10.4	93.3	95.0
			10.6	96.7	
3	4.92	6.00	10.6	94.7	92.2
			10.3	89.7	
4	5.52	6.00	11.6	101.3	103.8
			11.9	106.3	

Table 2 Reproducibility

Samples no.	Results determined mg L ⁻¹			Average \bar{x}	Standard deviation	Coefficient of variation %
1	0.328	0.329	0.305	0.3198	0.0097	3.0
	0.312	0.319	0.326			
2	0.231	0.231	0.225	0.2315	0.0065	2.8
	0.229	0.229	0.244			
3	0.235	0.241	0.246	0.2453	0.0090	3.7
	0.256	0.256	0.238			
4	0.097	0.093	0.090	0.0922	0.0051	5.6
	0.088	0.086	0.099			

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