Determination of Antimony in Environmental Water by Primary-Secondary Wavelengths New Spectrophotometry

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An acidic solution of antimony (Sb) may react with malachite green to form a blue coloured compound that can be extracted by benzene. In this paper with the absorption property of a suspended particle liquid against light, new analytical method as primary-secondary wavelengths spectrophotometry (P.S.W.S.) was studied to determine trace amounts of Sb in environmental water sample. It is recommended in both precision and sensitivity than the traditional single colorimetry method. Experiments for practical water samples have shown that the detection limit was 0.002 μg/mL Sb, the relative standard deviation is less than 8% and the recovery rate varies between 92.3 to 105%.

INTRODUCTION

The antimony (Sb) found in environmental water stems from industrial waste water of storage battery, typecasting, medical synthetic rubber and dyestuff etc., In acidic solution Sb may react with malachite green to form a blue compound that can be extracted by benzene. In this paper with the absorption property of a suspended particle liquid against light a new analytical method as primary secondary wavelengths spectrophotometry (P.S.W.S.) was applied for determination of trace amounts of Sb in waster water. The results show that both the precision and sensitivity of this method were increased to compare with the traditional single wavelength colorimetry. Again, the calculation model and curve gave only a little change with the operation conditions. The detection limit of Sb was 0.002 mg/L, RSD less than 8% and the recovery rate between 92.3 and 105%.

EXPERIMENTAL

For a colloid or suspended particle liquid the absorbance (A) at wavelength λ is relative to the particle's property parameters (diameter factor ε and amounts factor φ); their relation curve (a) is shown in Fig. 1 and their expression[1]

$$A = \phi\, \varepsilon^{-2}\, \lambda^{-\varepsilon} \tag{1}$$

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that can be extracted by benzene[2]. The sketch spectrum of such a colored solution is shown in Fig. 1 curve (b).
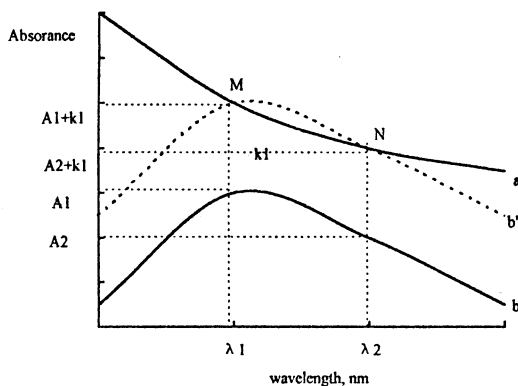

Fig. 1.   Sketch spectrun curve. a: colloidal solution absorption, b: b + k_1 subjunctive spectrum,
λ_1: primary wavelength, λ_2: secondary wavelength

Curve b was moved up k_1 distance to b′ position and to make b′ ∥ b was acrossed at M and N points with curve (a). At the corresponding wavelengths λ_1 and λ_2 the absorption of Sb(V) coloured solution can be regarded as the absorption of colloid solution of curve (a). From formula 1 we get:

$$\begin{cases} A_1 + k_1 = k_2\lambda_1^{-y} \\ A_2 + k_1 = k_2\lambda_2^{-y} \end{cases} \tag{2}$$

k_1, k_2 are all optical parameters. Experiments have shown $k_1 = 1$, y value is an exponent of Sb(V) concentration (x):

$$y = \alpha x^\beta \tag{3}$$

α, β are both constants from Sb(V) standard solution β, log α is respectively cut distance and oblique rate of the straight line of log y with log x. From formula 2, we obtain

$$\left(\frac{A_1 + 1}{A_2 + 1}\right) = \left(\frac{\lambda_1}{\lambda_2}\right)^{-y} \tag{4}$$

In order to get maximum sensitivity the wavelength λ_1 is necessary to be selected at the point of maximal absorption and named as primary wavelength $(\lambda_p) : \lambda_p = \lambda_{max}$; also $A_1 = A_p = A_{max}$. The wavelength λ_2 may be chosen wantonly but corresponds to different α and β values. It is selected at corresponding wavelengths near to $\frac{1}{2}A_{max}$ ($A_2 = A_s \approx 0.5A_{max}$) and it is named as secondary wavelength (λ_s). So formula (4) was changed into

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

We find when the operation conditions such as room temperature change, A_p

and A_s change at the same step but experimental results showed $(A_p + 1)/(A_s + 1)$ value varied hardly. So both α and β are very stable in the above model.

Instruments and Reagents

722 Type Spectrophotometer; 25 mL Colorimetric Analysis Tube; 250 mL Separatory Funnel.

10% tin protochloride solution; 20% sodium nitrite solution, 5% urea solution; 0.2% (W/V) malachite green solution; benzene, phosphorice (1 : 1); Sb(V) standard solution of 10 μg/mL concentration (the compound method: see References).

Above reagents are G.R. or A.R. and water in experiment is double distilled water.

Determination Process

At first acidify 100 mL water sample with 0.5 mL hydrochloric acid in 250 mL tapered flask; then heat it to be reduced to about 1 mL. Then add 5 drops of 10% tin protochloride solution and 5.5 mL of concentrated hydrochloric acid and heat to boiling; after cooling, add 5.0 mL 20% sodium nitrite solution. After 10 min, add 2.0 mL of 5% urea solution; then shake it to volatilize off CO_2. Then remove into 250 mL separatory funnel, to add 5 mL of phosphoric acid (1:1) and 10 mL water, and 0.5 mL of 0.2% malachite green solution and 10 mL of benzene; extract for 1 min. The organic phase is analysed at 640 nm and 660 nm wavelengths against the blank reagent with 1 cm absorption pool to get absorbance (A).

RESULTS AND DISCUSSION

Absorption Spectrum

The absorption spectrum curve of Sb(V)-Malachite Green colored benzene solution is drawn in Fig. 2.
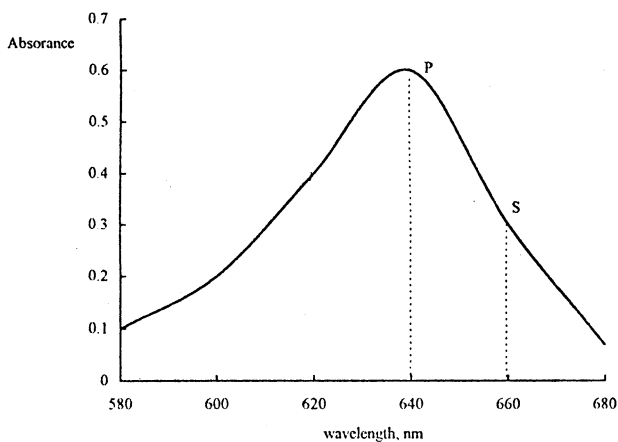

Fig. 2.   Sb(V) colored solution spectrum; P: primary wavelength point, S: secondary wavelength point

Hence the primary wavelength was chosen at 640 nm: $\lambda_p = 660$ nm; the secondary wavelength was chosen at 660 nm: $\lambda_s = 660$ nm.

y(x) Model

For the series between 0–2.0 mL of 10 µg/mL Sb(V) standard solution analytical results are put in Table-1.

TABLE-1
ANALYSED RESULTS OF Sb(V) STANDARD SOLUTION

Standard		Absorbance		Parameter
Added Volume (mL)	x (µ gSb)	640 nm	660 nm	y
0	0	0	0	0
0.2	2.0	0.113	0.059	1.615
0.5	5.0	0.298	0.147	4.032
1.0	10.0	0.582	0.290	6.631
1.5	15.0	0.788	0.386	8.269
2.0	20.0	1.149	0.561	10.392

log x-log y curve is given in Fig. 3. To get the function, log y = 0.794 log x + 0.00281. So $\alpha = 10^{0.00281} = 1.01$, $\beta = 0.794$. Hence
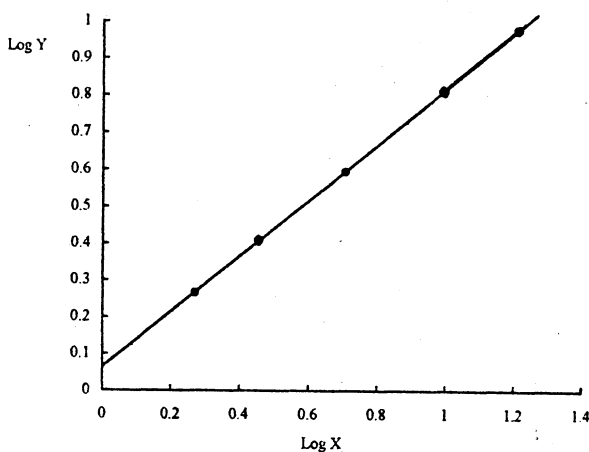
$$y(x) = 1.01x^{0.794} \tag{6}$$

Fig. 3.   log y-log x standard curve

Precision and Determination Limit

According to determination process to analyse 5.0 µg and 15.0 µg of Sb(V) standard the results of 7 parallel tests were repectively averaged 4.486 µg and 14.7 µg. The relative standard deviation (RSD) was separately 2.1% and 0.9%, but the traditional single wavelength colorimetry's RSD was separately 3.6% and 1.5%. So the new method is higher in precision than the single colorimetry.

Because Sb(V) was calculated from $(A_p + 1)/(A_s + 1)$ but not A, the rate value had cushioning effect for results to raise analytical precision. Experimenting 20 parallel blanks the standard deviation of y value was Sb = 0.07; the detection limit was calculated to be 0.21 µg Sb(V). If 100 mL water was determined the limit of concentration was 0.002 µg/mL.

Determination of Samples

The analytical results are given in Table 2 for determination of river water, ethyle works waste water, coking plant waste water and synthetic water. The RSD < 8.2% and the recovery rate was 92.3%–105%. The results by primary-secondary wavelengths spectrophotometry were basically the same as the traditional colorimetry ones.

TABLE-2
ANALYTICAL RESULTS OF Sb(V) IN SAMPLES

Sample	Single wavelength colorimetry (mg/L)	Sb(V), mg/L		Recovery rate, %
		Adding standard	Determined value	
Synthetic water	0.042	0	0.045, 0.041, 0.048, 0.039, 0.041, 0.046	105
		0.050	0.091, 0.099, 0.097	
River water	0.113	0	0.101, 0.106, 0.111	92.3
		0.100	0.2112, 0.206, 0.206	
Ethyle works waste water	0.784	0	0.779, 0.783, 0.780	98.4
		0.500	1.268, 1.271, 1.279	
Coking plant waste water	1.730	0	1.74, 1.68, 1.69	100
		1.00	2.71, 2.76, 2.74	

Conclusion

The principle and method are new and simple. The results are accurate and precise. The calculated curve is very stable not to be basically affected by environmental conditions. It is suited to analyse NH_3—N^4 and other trace components, too.

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