Determination of Trace Amounts of Arsenic in Waste Water by Primary-Secondary Wavelengths Spectrophotometry

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In sulfuric acid solution the conventional reaction of arsenic (As) with tin dichloride can form hydrogen arsenide in the presence of iodide and the product so formed reacts with diethyldithiocarbamate in chloroform medium to produce red silver colloid. The improvement for arsenic determination in waste water is the first to be made by primary-secondary wavelengths spectrophotometry (PSWS) using the above reaction. The result shows that both the analytical precision and accuracy are increased and gave out the higher sensitivity than the ordinary spectrophotometry.

INTRODUCTION

Arsenic is one of harmful elements for human body and in other biological systems. It exists widely in water polluted by chemical, metallurgical and other industries. At present arsenic is usually determined by colorimetry with diethyldithiocarbamate[1, 2]. It can give the high sensitivity and accurate determination, so it remains to be used now, especially in the trace determination of arsenic in environmental samples. In this paper the updated method named primary-secondary wavelengths spectrophotometry (PSWS) is applied for the determination of trace amounts of arsenic in water using the above reaction. The PSWS can give the higher precision and sensitivity than the conventional spectrophotometry and bring out the stable calibration graph. The results are all satisfactory. The recovery is between 94.0 and 102%, the relative standard deviation less than 2.9% and the detection limit is only 0.005 mg/L.

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[3]:

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

Curve **b** in Fig. 1., gives the absorption of a color solution. To move curve **b** for 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.

$$\begin{cases} A_1 + k_1 = k_2\lambda_1^{-y} & \ldots (2) \\ A_2 + k_1 = k_2\lambda_2^{-y} & \ldots (3) \end{cases}$$

Both k_1 and k_2 are the calculation factors. A lot of experiments have shown that factor Y is exponent to the determined component concentration (X mg/1 or μg) when $k_1 = 1$.

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

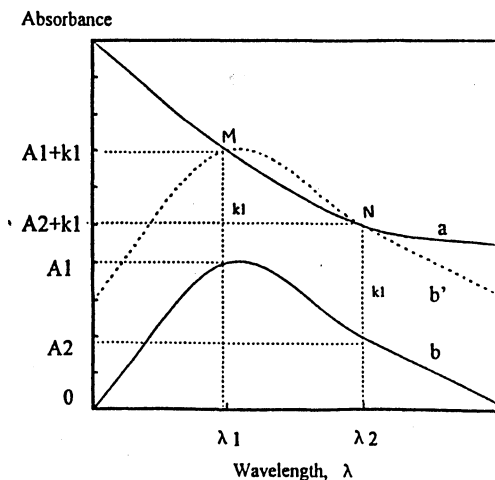Both α and β are constants when two wavelengths λ_1 and λ_2 are selected. In

Absorbance

Fig. 1.   Principle draft: **a,** suspending particle liquid against water; **b,** absorption spectrum sketch of a color solution; **b′,** obtained curve from moving curve **b** up k1 distance.

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 wrongly, 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 is termed as secondary wavelength (λ_s). 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 formula (5), the value of Y may be obtained, then to calculate X value from expression 4. Both Ap and As happen change with the variation of the operation conditions, *e.g.*, at room temperature. It is found that $\dfrac{(A_p + 1)}{(A_s + 1)}$ value changes little. Therefore, α and β are almost constant, which will happen little change with the variation of the operation conditions.

From the above principle the theory of PSWS is clear, which is different from other dual-wavelengths methods[4,5].

EXPERIMENTAL

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

Standard arsenic solution, 1.00 mg/mL: dissolving 0.1320 g of dry arsenious anhydride (As_2O_3, A.R., Shanghai Chemical) in 2 mL of 20% sodium hydroxide then adding 10 mL of 1 mol/L sulfuric acid and transmitting to 100 mL volumetric flask and diluting to 100 mL.

Standard arsenic use solution, 1.00 mg/L: preparing with the above standard arsenic solution.

Ag-DDC solution, 0.25%: dissolving 0.25 g of diethyldithiocarbamate (Ag-DDC, Shanghai Reagent) in 5 mL of chloroform and mixing well, then adding about 2 mL of triethanolamine (Shanghai Chemical) and diluting to 100 mL with chloroform.

Potassium iodide solution, 15%.

Tin dichloride solution: dissolving 40 g of tin dichloride ($SnCl_2 \cdot 2H_2O$, A.R., Beijing Chemical) in 40 mL of concentrated hydrochloric acid and diluting to 100 mL with deionised water then adding several tin particles to sotre for a long time.

De-arsenic zinc particles (A.R., Shanghai Chemical).

Lead acetate cotton: soaking 10 g of de-fat cotton in 100 mL of 8% lead acetate (A.R., Shanghai Chemical) then drying by wind.

Sulfuric acid solution, 50%.

Recommended Procedures

At first 50 mL of a waste water sample containing less than 25 μg of arsenic is taken in a triangular bottle. Put any lead acetate cotton in gas tube and 5.0 mL of Ag-DDC solution in absorption tube. Add 4 mL of 15% potassium iodide and 2 mL of tin dichloride solution into waste water and mix well. After 15 min, add quickly 4 g of zinc particle and connect immediately tube between bottle and tube. After diluting the absorption solution in the triangular bottle to 5.0 mL with chloroform, measure the transmittancy (T%) at 530 and 590 nm, respectively, against a reagent blank.

RESULT AND DISCUSSION

Absorption spectra: Fig. 2 gives the absorption spectra of the absorption solution of arsenic with Ag-DDC. The solution's absorption reaches maximum at
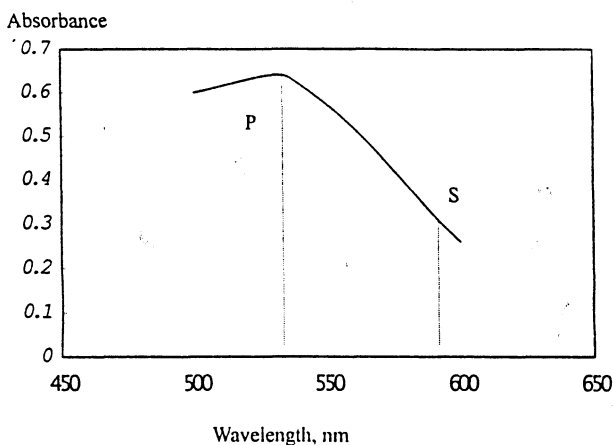

Fig. 2.   Absorption spectrum of As-Ag-DDC solution (0.4 mg/1 As) against reagent blank: P point 530 nm and S point 590 nm.

530 nm. According to the relative content above the primary wavelength should be selected at 530 nm. The secondary wavelength is arranged at 590 nm here. Thus in this case, $\lambda p = 530$ nm and $\lambda s = 590$ nm for calculation.

Effect of Ag-DDC: Fig. 3 shows the effect of Ag-DDC concentration on factor Y calculated from formula 5. We find that Y remains almost constant and reaches maximum while Ag-DDC concentration is more than 0.2%. In this work, 0.25% Ag-DDC is perpared.
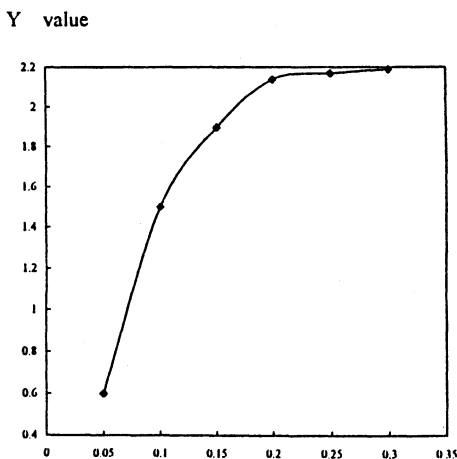
Y   value

Fig. 3.   Effect of Ag-DDC concentration on factor Y of 0.4 mg/l As.

Calibration Graph: A series of standard arsenic solutions are prepared and the absorbance of each is measured and plotted. The measurement results and the exponent Y values are all listed in Table-1. Curve lg Y against the logarithm of arsenic concentration (X µg), lg Y was shown in Fig. 4.
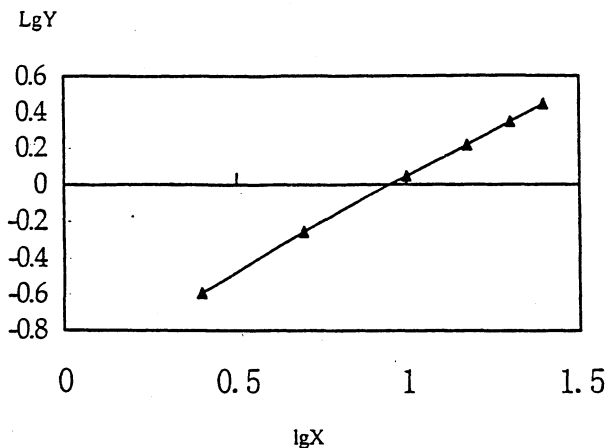
LgY

lgX

Fig. 4.   Standard curve for the determination of arsenic (the relative coefficient = 0.9996).

TABLE-1

DETERMINATION OF STANDARD ARSENIC SOLUTIONS

Arsenic amounts X, μg	Transmittancy*, %		Y value
	620 nm	650 nm	
0	100.0	100.0	—
2.5	88.0	94.0	0.256
5.0	71.0	84.0	0.614
10.0	48.0	68.4	1.16
15.0	34.0	58.8	1.65
20.0	25.0	54.1	2.19
25.0	16.2	46.9	2.78

*:   absorbance = lg (100/transmittancy).

We find that the linerarity of curve is very well. The cut distance lg α is calculated to be −0.959 and the oblique rate β to be 1.01. The expression of Y with X is therefore obtained.

$$Y = 0.11 X^{1.01} \qquad \qquad \dots (6)$$

Effect of foreign ions: None of the following ions affect the direct determination of 5 μg of arsenic (<10% error): 1 mg of Cl^-, Mg^{2+}, SO_4^{2-}, NO_3^-, NH_4^+; 0.1 mg of PO_4^{3-}, Pb^{2+}, Mn^{2+}, Cu^{2+}, Cr(VI), Zn^{2+}, Hg^{2+}, Fe^{2+}, Ag^+, Al^{3+}, Ni^{2+}, Co^{2+} and 50 μg of Sb(III).

Precision and detection limit: Six replicate determination of standard solution containing 5.0 μg of arsenic is carried out, the relative standard deviation (RSD) being 1.6%. However, the RSD with the single wavelength method is 3.0%. The precision for PSWS is therefore higher than that for the ordinary spectrophoto- metric method.

We use the formula $L_{min} = kS_b/S$ to calculate the detection limit of arsenic by PSWS, where k = 3, S_b named as standard deviation and S named as sensitivity. Replicate determination of twenty reagnet blanks gives S_b to be 0.01. The analytical sensitivity S is equal to α value, 0.11. Therefore, the detection limit of arsenic is $L_{min} = 0.27$ μg. If 50.0 mL of sample is analyzed, so the detection limit concentration reaches only 0.005 mg/1. This value is less than that of the conventional spectrophotometry.

Sample analyzed: As a test of the method arsenic is determined in waste water, sewage and surface water (Tuo river). The results are listed in Table-2. We find the results by the recommended method tally with the conventional method. The recoveries of arsenic are between 94.0 and 102% and the relative standard deviations less than 2.9%.

TABLE-2
DETERMINATION OF ARSENIC IN WATER SAMPLES IN mg/l

Sample	By conventional method	By PSWS			
		Added	Found		Recovery, %
Waste water	3.15	0	3.08		
		3.00	6.18	6.09	102
Sewage	0.062	0	0.061	0.058	
			0.057	0.060	
			0.061	0.058	
		0.050	0.110	0.102	94.0
River water	0.231	0	0.227	0.219	
			0.230	0.226	
			0.231	0.220	
		0.200	0.419	0.411	95.0

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