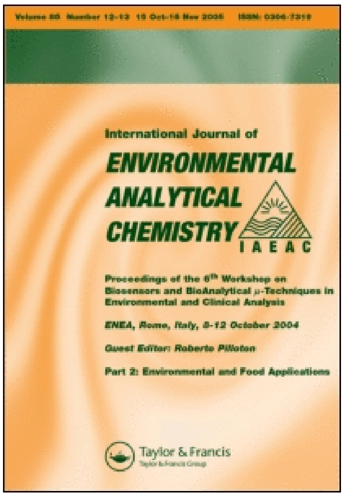

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DETERMINATION AND SPECIATION OF ANTIMONY IN WATERS

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A new spectrophotometric method for the determination and the speciation of inorganic antimony in waters is described. Antimony(V) is quantitatively extracted ($\geq$ 98.5%) with N,N'-diphenylbenzamidine (DPBA) into toluene, and the extract is reacted with the aqueous solution of brilliant green (BG). The value of molar absorptivity of the complex is $(1.54) \times 10^5$ l mole^{-1} cm^{-1} at absorption maximum 640 nm. The detection limit of the method is 10 ng ml^{-1}. Of various tested ions, only Tl (III) caused serious interference in the determination of the analyte that was overcame by masking with EDTA. The present method has been applied for the analysis of inorganic Sb(III), Sb(V) and total Sb at lower µg l^{-1} levels in waters.

KEY WORDS: Spectrophotometry, extraction, speciation, antimony, waters.

INTRODUCTION

Antimony is a toxic element which exists in the aquatic environment in two different valencies, +3 and +5. Antimony(III) is more toxic and mobile than antimony(V) [1]. Hydride generation AAS technique was used for monitoring antimony in waters[2-5]. Many spectrophotometric methods have also been reported for the determination of antimony in waters [6-11]. Dyes i.e. brilliant green, rhodamine-B, etc. are commonly employed for the routine analysis of antimony [11]. The quantitative determination of antimony(V) with brilliant green in toluene requires a double extraction [12]. In the present investigation, N,N'-diphenylbenzamidine (DPBA), and brilliant green (BG) in sequence have been used for the extraction and spectrophotometric determination of antimony(V) at µg l^{-1} levels in waters. DPBA is a strong base exists in two Forms I-II (Free base, I and Hydrochloric salt, II) and remarkably enhances the sensitivity of the classical brilliant green method [13].

EXPERIMENTAL

Apparatus

A Carl Zeiss "Spekol" Spectrophotometer matched with 1-cm quartz cuvettes was employed for absorbance measurements.

Chemicals

0.1 g antimony metal (99.9%) were dissolved in 15 ml concentrated H_2SO_4 by heating over a hot water bath and the resulting solution diluted to 1 liter with 1 M HCl containing 0.1% (w/v) tartaric acid. Working solution was prepared by further dilution of the stock solution with distilled water. N,N'-Diphenylbenzamidine (DPBA) was synthesized as described in the literature (13). 0.15% (w/v) DPBA in toluene, 0.5% (w/v) EDTA in water, 0.04% (w/v) brilliant green in water, 6.4% (w/v) cerric ammonium sulphate in 1 M H_2SO_4 and 1% (w/v) hydroxylammonium chloride in water were employed. All solutions used were presaturated with toluene.

Procedure for determination of antimony(V)

10–20 ml of water sample was taken in a 50-ml beaker, evaporated to 3 ml, and transferred to 100-ml separatory funnel. Into this 6 ml concentrated HCl and 0.5 ml EDTA were added and extracted with 7 ml toluene solution of DPBA for 2 min. The extract was transferred into another 100-ml separatory funnel containing 5 ml brilliant green solution and again equilibrated for 2 min. The extract was dried over anhydrous sodium sulphate (2 g) in a 25-ml volumetric flask. The absorbance of the extract was measured at 640 nm against the reagent blank. Sb(V) content present in the given water sample was computed from the calibration curve prepared.

Procedure for determination of total antimony

The water sample was evaporated and transferred to a separatory funnel as above. It was oxidized by addition of 1 ml cerric ammonium sulphate and its excess reduced by adding dropwise hydroxylammonium chloride till the solution became colourless. 1 ml EDTA solution was added and diluted to 10 ml with distilled water. The aqueous solution was extracted with toluene solution of DPBA, and the extract reacted with brilliant green solution as above. The absorbance of the extract was measured at 640 nm against the blank. Total Sb present in the sample was evaluated from the calibration curve.

RESULTS AND DISCUSSION

Extraction of antimony(V) with DPBA

Antimony(V) as $SbCl_6^-$ is quantitatively extractable with toluene solution of DPBA (0.15% w/v) from a strong HCl solution. The absorption spectra of the complex against the reagent blank in toluene is shown in Figure 1. The complex shows a practically negligible absorption between 500–700 nm.

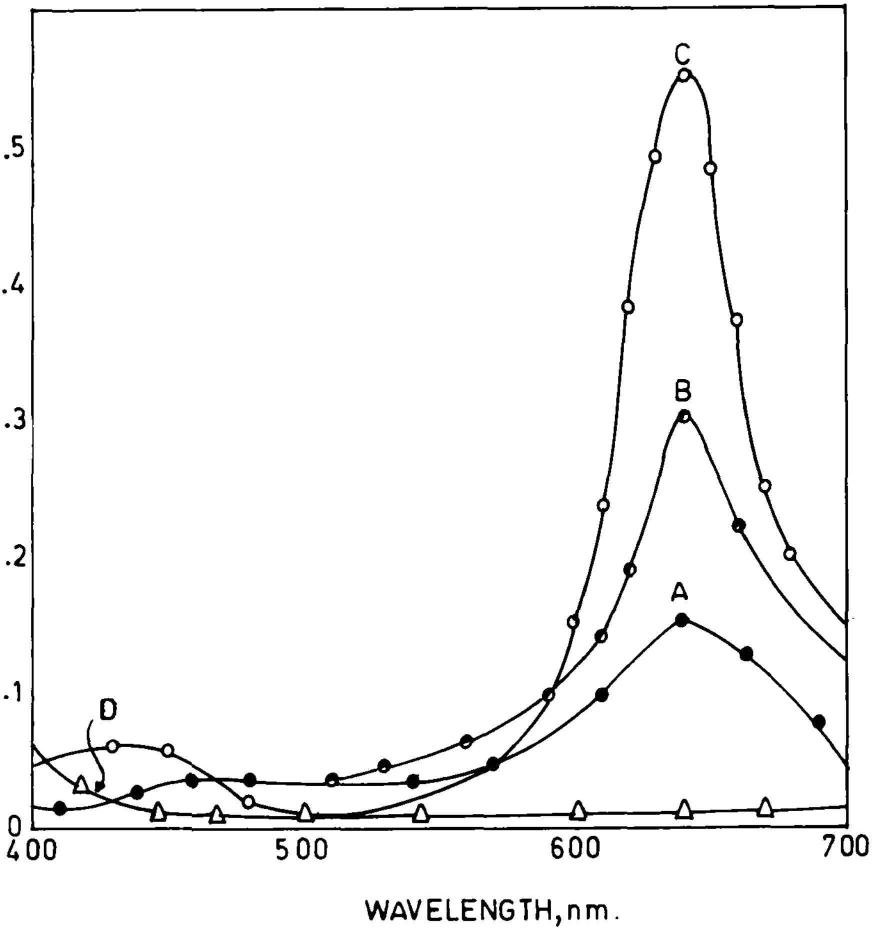

Figure 1 Absorption spectra of Sb (V) complexes and the reagent blank in toluence.

(A) [Sb Cl_6]BG complex (4.5 ug Sb (V) was extracted with equal volume of toluene from 6 M HCl solution).

(B) [Sb Cl_6]BG complex (4.5 ug Sb (V) was extracted with equal volume of toluence solution of DPBA from 6M HCl solution).

(C) [Sb Cl_6] BG complex [4.5 ug Sb (V) was extracted with equal volume of toluene solution of DPBA from 6 M HCl solution].

(D) The reagent blank of the sequence procedure.

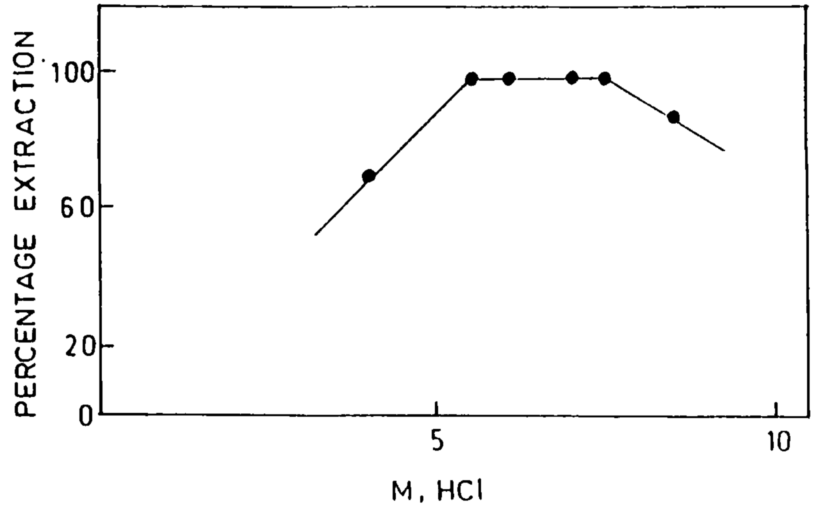

Figure 2 Effect of hydrochloric acid on the extraction of Sb (V) with DPBA.

The extraction efficiency was evaluated by extracting a solution containing 20 μg Sb(V) with DPBA at different acidity conditions. The extract was collected in a 50-ml beaker by washing the separatory funnel with 2×3 ml fresh toluene and evaporated on a hot water bath (≈ 60°C). The complex was reacted with bromopyrogallolred (BPR) as in the literature [14] and the percentage of extraction in a single extraction found to be 98.7 ± 0.2%, over 5.5–7.5 M HCl (Figure 2). Beyond these limits, the percentage extraction decreased. At least 1.0×10^{-3} M DPBA in toluene was required for the complete extraction of the metal and no adverse effect was seen up to 9.0×10^{-3}M. The extraction of the metal was not affected when the volume ratio of the organic to the aqueous phase was varied from 2:1 to 4:7. The molar ratio of the metal to DPBA in the extracted complex was determined by plotting log D versus log molar concentration of taken DPBA (Figure 3). The result obtained showed the co-ordination of $SbCl_6^-$ to DPBA in 1:1 molar ratio as an ion-pair complex.

Extraction of antimony(V) with brilliant green

Antimony(V) was extracted with BG in toluene as ion-pair complex with the lower colour intensity (Figure 1). In a double toluene extraction, the value of molar absorptivity of the complex was 0.98×10^5 l mole^{-1} cm^{-1} [12].

Extraction of antimony(V) with brilliant green and DPBA together

Antimony(V) was extracted with BG and DPBA together in toluene from 6 M HCl solution. In a single extraction the value of molar absorptivity of the complex was found to be 8.5×10^4 l mole^{-1} cm^{-1} at 640 nm (Figure 1).

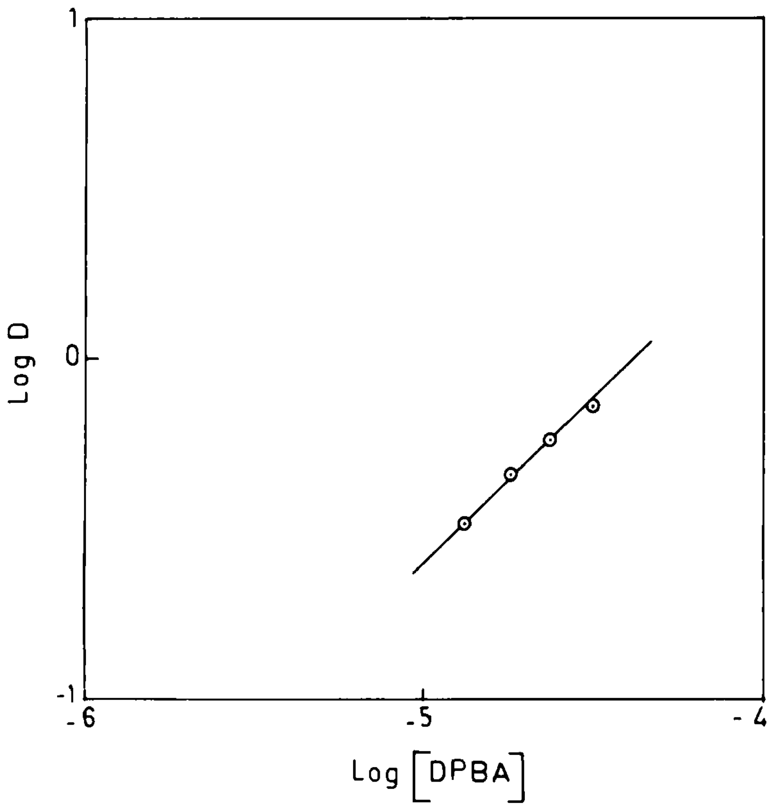

Figure 3 Determination of the molar ratio of Sb (V) to DPBA in the extracted complex.
$[Sb^V] = 2.5 \times 10^{-6}$ M, HCl = 6.0 M

Extraction of antimony(V) with DPBA, and brilliant green in sequence

Antimony(V) was extracted with toluene solution of DPBA, and BG in sequence with the highest colour intensity of the complex. The value of molar absorptivity of the complex in a single extraction was 1.54×10^5 l mole^{-1} cm^{-1} at 640 nm (Figure 1). The optimum pH range for full colour development for the extract was found to be 0.5–3.0 (Figure 4). At least 3×10^{-3}M BG in the solution was needed for the full colour development of the extract. BG concentration beyond 4×10^{-3}M increased the blank absorbance (Figure 5). The absorbance of the extract remained intact when the volume ratio of organic to the aqueous phase ranged from 4:1 to 4:3. The molar ratio of $SbCl_6^-$ to BG^+ in the extracted $[SbCl_6]H.DPBA$ complex was determined by plotting log A/A_{max} - A versus log molar concentration of BG taken (Figure 6). The result obtained showed that the exchange of DPBA with BG in the extracted complex was 1:2 molar ratio.

$$[SbCl_6]H.DPBA_o + 2\,BG^+\,Cl^- \rightleftharpoons ([SbCl_6]BG)BG.DPBA.Cl_o + H^+$$

the subscript o denotes the organic phase.

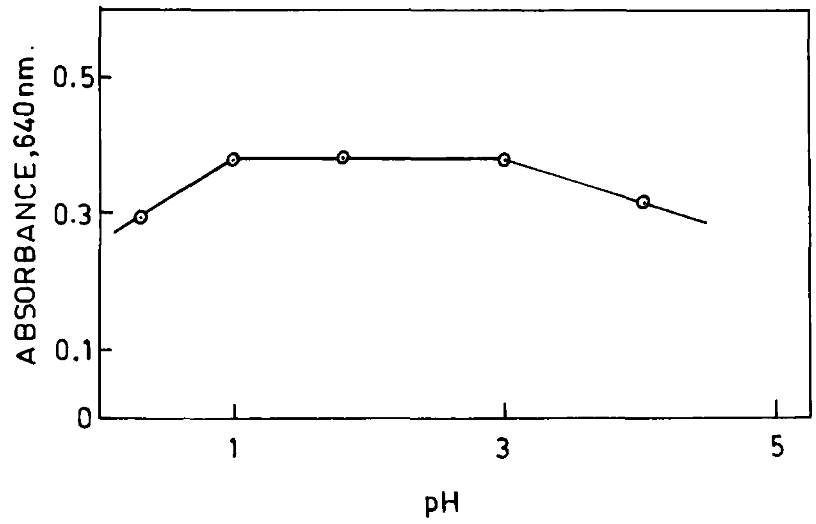

Figure 4 Effect of pH on the absorbance of the extract. [Sb^V]= 2.5 × 10^{-6} M in the organic solution.

One of the co-ordinated BG$^+$ may form a counter cation with $SbCl_6^-$ while the other with DPBA.Cl$^-$.

Calibration curve and statistical data

Ten solutions containing, respectively, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 μg Sb(V) were taken, oxidized with cerric ammonium sulphate, the excess reduced with

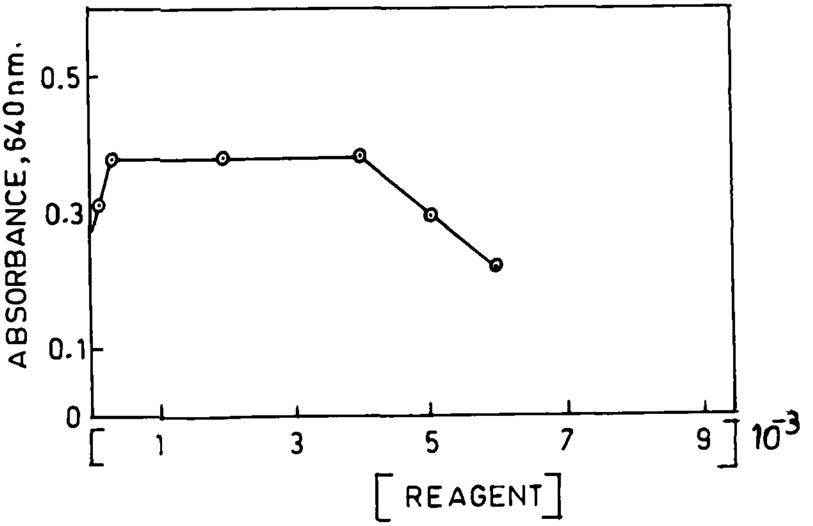

Figure 5 Effect of brilliant green concentration on the absorbance of the extract. [Sb^V] = 2.5× 10^{-6} M in the organic solution, pH = 2.0

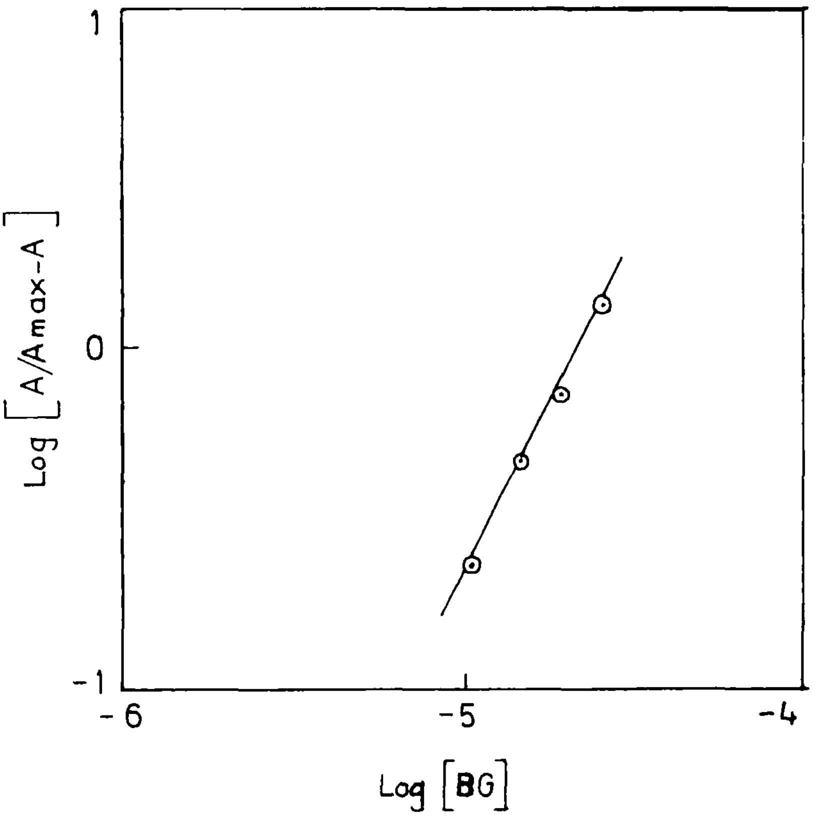

Figure 6 Determination of the molar ratio of Sb (V) to brilliant green (BG) in the extract.

hydroxylammonium chloride, extracted with toluene solution of DPBA, and the extract equilibrated with BG as in the procedure. The absorbance of the extract was measured at 640 nm against the blank. The system followed Beer's law up to 0.6 μg Sb ml^{-1} toluene with slope, intercept, and correlation coefficient of 0.97, 0.09, and +0.9, respectively. The relative standard deviation of the method for six replicate measurements at the level of 0.3 μg Sb ml^{-1} toluene was ±1.0%.

Detection limit, and molar absorptivity

The detection limit of the method was 10 ng ml^{-1}, the amount causing more absorbance than 0.012 (twice of the std. dev. of six measurements of the sample solution). The value of molar absorptivity of the complex in toluene was found to be 1.54×10^5 l $mole^{-1}$ cm^{-1} at absorption maximum at 640 nm.

Table 1 Effect of diverse ions on the determination of 0.2 μg Sb(V) ml^{-1}.

Ion added	*Tolerance limit*$^+$ μg ml^{-1}
Cu(II), Fe(III)	150
Mo(VI), Hg(II), Ag(I)	100
Nb(V), Sn(IV)	50
Mn(II)	1,000
Cr(III), U(VI)	4,500
Ni(II), Co(II), Zn(II), Al(III), EDTA, PO_4^{3-}	2,000
La(III), Ti(IV), V(V)	600
Pb(II), Cd(II), Zr(IV), Se(IV), W(VI)	200
Be(II), AsO_4^{3-}	400
F^-, NO_3^-, $C_2O_4^{2-}$	5,000
Tl(III)	10*

+ Causing error ≤ 2%

* In the presence of EDTA (1ml, 1%, w/v)

Effect of diverse ions

The effect of various ions in the determination of 2 μg Sb/10 ml of the aqueous solution was examined separately. Of various tested ions, Tl(III) caused serious interference in the determination of Sb and was removed by masking with EDTA. The tolerance limit of various ions are summarized in Table 1.

Application of the method

The waste waters of Bhilai Steel Plant (Bhilai, India) were tested for the analysis of Sb(V) and total Sb. Concentration of Sb(V) (without oxidising) and total Sb (with oxidising by cerric ammonium sulphate) were evaluated as recommended in the procedures. The Sb(III) concentrations were obtained by substracting Sb(V) concentration from

Table 2 Determination of antimony in waters (in μg l^{-1}).

Sample	*Rhodamine-B method*	*Present method*		
		Total Sb (rel. std. dev)$^+$ ±%	*Sb(V) (rel. std. dev)*$^+$ ±%	*Sb(III)*
S_1	74.3	75.2	64.1	11.1
		(1.0)	(1.1)	
S_2	117.2	118.0	55.8	62.2
		(1.2)	(1.0)	

S_1 & S_2 are waste water of Bhilai Steel Plant (Bhilai, India) collected at two different zones.

+ based on Six measurements.

the total Sb concentration. The total Sb concentration in water samples was determined by the classical rhodamine-B method using the standard spike method [11]. The analysis data obtained are shown in Table 2.

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