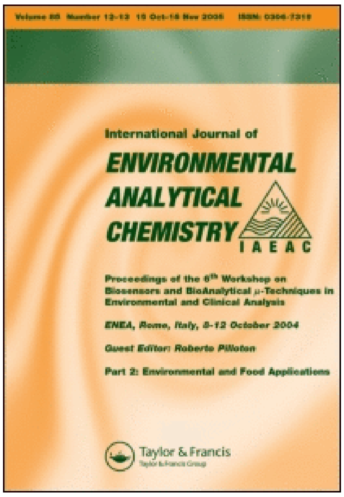

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Spectrophotometric Determination of Antimony in Industrial Waste Waters with Iodide and Amidines

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A new method has been developed for determination of trace amounts of antimony in industrial waste waters. It is based on the reaction of antimony(III) with iodide over 1.0–4.0 M H_2SO_4, and extraction of the iodo complex with amidine(HA) into chloroform as a $[Sb_2I_6HA]$ complex. The molar absorptivity of the complexes with 9 various amidines are found to be in the range of $(4.1\text{–}6.8) \times 10^3$ l mol^{-1} cm^{-1} at λ_{max}. Of these, the simplest compound, N,N'-diphenylbenzamidine(DPBA) was chosen for detailed studies, and detection limit of the method with this compound is 0.2 μg Sb/ml. The effect of diverse ions, solvents and acids was examined. Of various diverse ions tested, only Bi(III) causes serious interference in the determination of the metal. The method has been applied for the recovery of the metal to water samples containing up to 0.05 ppm Sb with relative standard deviation less than ±1.5%.

KEY WORDS: Antimony determination, iodide, N,N'-diphenylbenzamidine and N,N'-diarylbenz/substituted benzamidines, spectrophotometry, industrial waste waters.

INTRODUCTION

Antimony and its compounds are listed as priority pollutants by the U.S. Environmental protection agency, and water soluble antimony compounds cause nausea, vomiting and diarrhoea in human beings.[1–3]

Many spectrophotometric methods for determination of trace amounts of antimony in various water samples and other complex materials were reported.[4–9] The classical iodide method is applicable for the spectrophotometric determination of the metal over 1.2–1.9 M H_2SO_4, however, it suffers from interference of other elements which give coloured complex with iodide.[4] Various dyes such as rhodamine-B, brilliant green, crystal violet, etc. were reported for the micro determination of antimony(V) in a variety of complex materials.[5–7] These dyes are sensitive reagents but they are not selective, the reproducibility is also generally poor and most of the dyes form several cations in hydrochloric acid solution, each of which can form insoluble extractable products. Triphenyl tetrazolium chloride was used as a sensitive reagent for the spectrophotometric determination of Sb(V) in ultraviolet region ($\lambda_{max} = 265$ nm) by Aleksandov *et al.* but it suffers from interference of Fe, Au, Tl, Ba.[8] An indirect spectrophotometric determination of traces of Sb(III) by Cr(VI) with diphenylcarbazide in marine sediments and geothermal waters was proposed by Jonehara *et al.*,[9] but it also suffers from interference of oxidizing agents e.g. Fe(III), Mo(VI), W(VI), etc. Smith and Griffiths developed a method for determination of Sb(III) and Sb(V) in urine by solvent extraction procedure using IBMK as an extractant followed by electrothermal atomisation.[10] However, in this method the optimum pH-range is very narrow 4.5, and the distribution ratio of the metal varies with respect to hydrogen ion concentration.

This paper describes the spectrophotometric determination of antimony in industrial waste waters. It involves the separation of antimony(III) from most of matrix elements by chloroform extraction of $[SbI_3]$ with recently explored organic bases, amidines,[11–12] and spectrophotometric measurement of colour of $[Sb_2I_6HA]$ complex at λ_{max}. In this work, the sensitivity of the classical iodide method increases about one and a half fold by chloroform extraction of $[SbI_3]$ with amidine base. Moreover, this method removes most of the interferences of above well established methods.

EXPERIMENTAL

Apparatus

A Carl Zeiss Jena "SPEKOL" and an ECIL-UV-VIS spectrophotometer GS-865 with matched quartz cuvettes(1-cm) were used for absorbance measurements.

Reagents

A standard solution of antimony(III) was prepared by dissolving 0.2668 gm antimonyl potassium tartrate in 160 ml concentrated sulphuric acid and diluted to 1 liter with distilled water. The freshly prepared potassium iodide (30%, W/V) and ascorbic acid (10%, W/V) solutions were prepared. A 10 M H_2SO_4 was used for the extraction work. Amidines were synthesized as described in literature,[13] and their 0.35%(W/V) solutions in chloroform were employed.

Procedure

An aliquot of the solution containing not more than 400 μg of Sb(III) is taken in a 50-ml beaker and treated with 1.3 ml sulphuric acid. The cold solution is transferred to a 150-ml separatory funnel and treated with 1.0 ml ascorbic acid and 1.5 ml potassium iodide solutions. Finally the volume of the solution is diluted to 10 ml with distilled water, and extracted with 10 ml chloroform solution of amidine for 2 min. The aqueous solution is washed with 3×2 ml fresh portion of chloroform. All extracts, after drying over anhydrous sodium sulphate(2 gm) in a 25-ml beaker, are transferred to a 25-ml volumetric flask. The flask is filled up to the mark with chloroform and absorbance of the complex is measured against the reagent blank at λ_{max}.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra obtained for $[SbI_3]_2$ with DPBA in chloroform along with the reagent blank shows that the absorption maximum occurs at 400 nm (see Figure 1). The position of λ_{max} of the complex does not change with respect to concentration of the metal as well as sulphuric acid. The reagent blank exhibits a significant absorbance at λ_{max} of the complex, hence it was used as a reference for all further experiments.

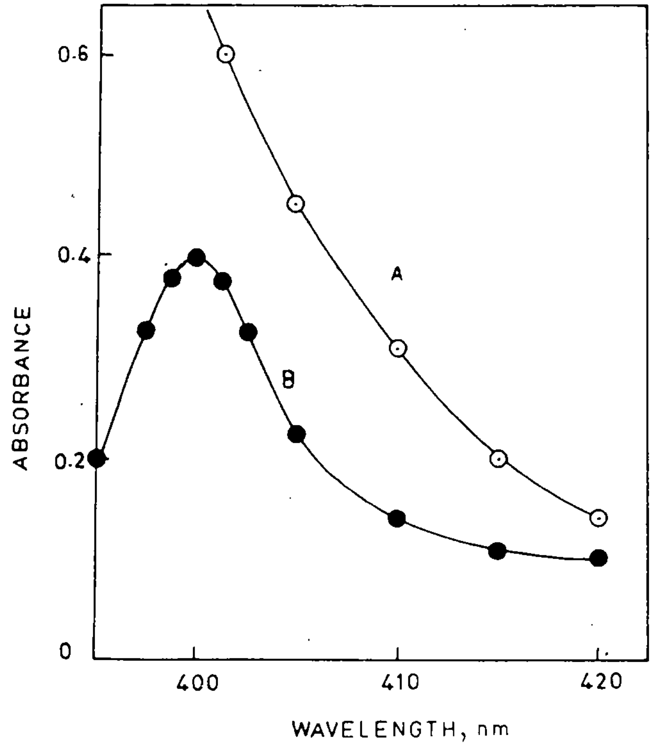

Figure 1 Absorption spectra of the reagent blank and the complex in chloroform: $[H_2SO_4]$, 1.3 M; [KI], 0.27 M; [DPBA], 0.013 M. (A): Reagent blank against chloroform; (B): The complex (formed with 8 ppm Sb(III) with I^- and DPBA) against reagent blank.

Effect of solvents

The effect of various solvents such as 1-pentanol, methyl isobutyl ketone, ethyl acetate, diethyl ether, chloroform, carbon tetrachloride, benzene and cyclohexane on the extraction of $[SbI_3]$ with DPBA were studied. Of these, diethyl ether, carbon tetrachloride, benzene and cyclohexane are unable or could partially extract the complex. Other solvents extract the complex quantitatively, and their nature greatly affects the λ_{max} and absorptivity of the complex as: 1-pentanol (ε, 7600; λ_{max}, 420), ethyl acetate (ε, 1880; λ_{max}, 430), methyl isobutyl ketone (ε, 1220; λ_{max}, 460) and chloroform

(ε, 6100 $l\,mol^{-1}\,cm^{-1}$; λ_{max}, 400 nm). In the case of 1-pentanol, the extraction of the metal is not selective and the colour of the extract is unstable. Chloroform was preferred as an extraction solvent in the present investigation for detailed studies.

Effect of acids

Extraction of the metal with iodide and amidine was carried out in sulphuric acid medium. The absorbance of the complex in chloroform was found to be constant and maximum in an acid concentration range 1.0–4.0 M H_2SO_4 (see Figure 2). The full extraction of the metal also occurs at acidity higher than 4 M H_2SO_4 but colour of the reagent blank deepens as the acidity increases. Hydrochloric acid could not be used as it reduces the colour intensity of the complex and also liberates iodine from iodide.

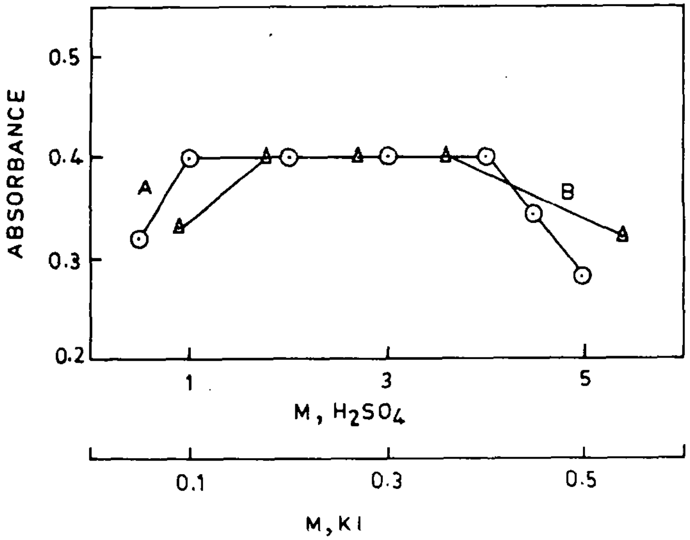

Figure 2 Effect of concentration of sulphuric acid and potassium iodide on the extraction of the metal: 1[Sb^{3+}], 1.62×10^{-4} M; [DPBA], 0.013 M. (A): Effect of molar concentration of sulphuric acid. (B): Effect of molar concentration of potassium iodide.

Effect of ascorbic acid and amount of reagents

In the present investigation, ascorbic acid was employed to destroy iodine liberated by air oxidation or by reaction of Sb(V) with iodide. At least 0.011 M DPBA in chloroform is required for colour development of the complex and no adverse effect was observed up to 0.014 M DPBA. The maximum and constant extraction of the metal is achieved over 0.18 to 0.30 M KI in the aqueous solution. Beyond these limits, incomplete extraction of the metal was observed. Thus in the present investigation, the extraction of the metal was performed with 0.013 M DPBA and 0.27 M KI. The sequence of order of addition of reagents was not critical.

Effect of dilution and salting out agent

The effect of dilution of the aqueous phase on the extraction of the metal was studied, and data obtained showed that the colour of the extract is unaffected over volume ratio of 1:2 to 3:2 (aqueous:organic). The effect of salting out agent e.g. K_2SO_4 on the extraction of the metal was examined, and no adverse effect was seen up to 0.25 M K_2SO_4.

Effect of temperature and stability of the colour of the extract

The effect of temperature and standing time on the colour intensity of the extract in the organic solution was examined (see Table 1). In

Table 1 Effect of temperature on extraction, and standing time on colour intensity of the complex in chloroform with 8 ppm of Sb(III)

Temperature °C	*Absorbance of the complex immediately after extraction at λ_{max} 400 nm*	*Absorbance of the complex after standing time of 30 min at λ_{max} 400 nm*
10	0.400	0.405
15	0.400	0.400
20	0.320	0.400
25	0.320	0.395
30	0.30	0.340

the present investigation, the working temperature was 22±2 °C, hence it is recommended that the colour of the extract is measured after a standing time of 30 min. The extract was stable for at least 2 hrs at room temperature. A shaking time of 1 min was sufficient for the full extraction of the complex in the organic solution and further extraction up to 10 min did not cause any adverse effect.

Optimum concentration range, sensitivity, effect of nature of amidines on colour reaction of the complex, and precision

The system obeys Beer's law over 0.8–16 μg Sb/ml with DPBA. The detection limit of the method is 0.2 μg Sb/ml. The extraction of Sb(III) with 9 various N,N'-diarylbenz/substituted benzamidines in chloroform was examined. The nature, degree and position of substituents in three phenyl rings of the compound affect the colour intensity of the complex in the organic solution. The +I (inductive) effect causing groups (e.g. CH_3) decreases the colour intensity of the complex while reverse effect is seen with −I causing groups (e.g. Cl). Maximum steric hindrance is observed when the substituents in all three rings are introduced in ortho or meta position (see Table 2). The molar absorptivity and Sandell's sensitivity of the complexes lie in the range of $(4.1–6.8) \times 10^3$ $l\,mol^{-1}\,cm^{-1}$ and $(2.96–1.77) \times 10^{-2}$ μg Sb cm^{-2} at λ_{max}, 390–400 nm, respectively. To check the precision of the method, 10 replicate measurements containing 200 μg Sb/25 ml were made and relative standard deviation was estimated to be ±1.2%.

Extraction mechanism

The ratio of variables in the complex was evaluated by plotting log distribution ratio of the metal versus log molar concentration of iodide or log molar concentration of amidine(HA) in the chloroform. The slopes 2.8 and 0.46 obtained (see Figure 3) show that three moles of iodide and a half mole of amidine are co-ordinated to each antimony ion in the extracted complex. It means that one molecule of amidine is shared by two $[SbI_3]$ species in the manner similar to various hydrocarbon complexes of trihalo antimony(III).[14] The

Table 2 Spectral data of iodoantimony(III) complex with various amidines in chloroform

Amidine	λ_{max}, *nm*	ε *l mol*$^{-1}$ *cm*$^{-1}$	*Sandell's sensitivity* μg *Sb cm*$^{-2}$
N,N'-Diphenylbenzamidine	400	6100	0.01995
N,N'-Di(4-chlorophenyl)-2-chlorobenzamidine	400	6100	0.01995
N-(3-Chlorophenyl)-N'-phenyl-2-chlorobenzamidine	395	6850	0.01777
N-(3-Methylphenyl)-N'-(2,3-dimethylphenyl)-2-chlorobenzamidine	390	4100	0.02969
N-(4-Chlorophenyl)-N'-(2,6-dimethylphenyl)-benzamidine	395	6100	0.01995
N-(4-Chlorophenyl)-N'-(2-chlorophenyl)-benzamidine	405	5300	0.02297
N-(2-Chlorophenyl)-N'-(2,3-dimethylphenyl)-benzamidine	395	6400	0.01902
N-Phenyl-N'-(2,3-dimethylphenyl)benzamidine	395	5300	0.02297
N-(4-Chlorophenyl)-N'-(2,3-dimethylphenyl)-2-chlorobenzamidine	397	4600	0.02646

extraction mechanism may be expressed as:

1) formation of triodoantimony(III) complex

$$Sb^{3+} + 3I^{-} \rightleftharpoons [SbI_3]$$

2) chloroform extraction of hexaiodoantimony(III) complex with amidine.

$$2[SbI_3] + HA_o \rightleftharpoons [Sb_2I_6HA]_o$$

subscript o denotes to the organic phase.

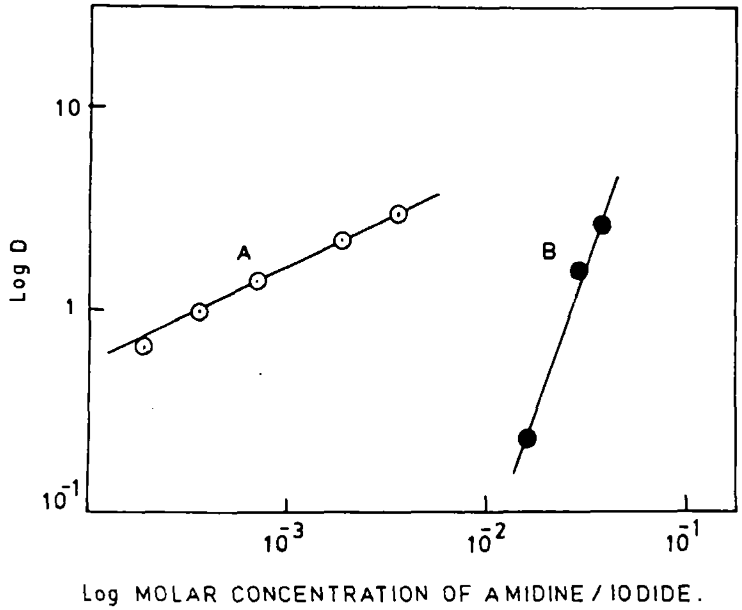

Figure 3 Curve-fitting method to determine the ratio of variables in the complex: $[Sb^{3+}]$, 1.62×10^{-4} M (in the aqueous phase); $[H_2SO_4]$, 1.3 M. (A): log*D* versus log molar concentration of DPBA in chloroform. (B): log*D* versus log molar concentration of potassium iodide in the aqueous solution.

It is assumed that amidine acts as a bidentate neutral chelating agent by donating the lone pair of electrons from both N-atoms or π-electrons from phenyl rings similar to aromatic hydrocarbons.

Effect of diverse ions

The effect of various diverse ions in the determination of 200 μg Sb(III) was studied as in the procedure. A large number of diverse ions (except Bi, Pd) do not interfere in the present method. The tolerance limit of the various diverse ions (in mg) causing error less than $\pm 2\%$ are shown in parenthesis as: Tl, Nb (0.2); Cu, Ag, Hg, Re, Mo (0.5); Cd, Pb, Al, Se, Zr (1); W, AsO_4^{3-} (2); Ti, Hf, V(4); Be, Ca, La, No_3^- (5); Mn, Ni, Fe(III), U, EDTA, $C_2O_4^{2-}$ (20); citrate (45); F^- (50).

Table 3 Results of analysis for antimony(III) in industrial waste water which volume is reduced to 30–90 folds

Sample	*Volume of the sample taken, ml*	*Sb added ppm*	*This method*		*The classical iodide method*		*Relative std. dev.** ±%
			Sb found ppm	*Sb content ppm*	*Sb found ppm*	*Sb content ppm*	
BFWW	300	5	5.098	0.098	5.092	0.092	1.4
BFWW	600	4	4.102	0.102	4.093	0.093	1.3
BFWW	900	3	3.103	0.103	3.096	0.096	1.2
TWW	300	6	6.050	0.050	6.048	0.048	1.5
TWW	600	5	5.051	0.051	5.049	0.049	1.3
TWW	900	4	4.051	0.051	5.050	0.050	1.5

BFWW = Blast furnace waste water; TWW = Total waste water; * = four measurements were made.

Application of the method

Two different waste water samples (blast furnace and total waste waters) from Bhilai Steel Plant were collected. A known volume of the water sample is taken and reduced to about 10 ml, and then the metal content of the sample is determined by standard addition method as in the proposed procedure. The results are listed (see Table 3) with standard deviation values of 4 replicate measurements. The results obtained with these samples by the present method are in good agreement with the results obtained by the classical iodide method.[4] The relative standard deviation for the determination of Sb(III) in these waste waters was estimated to be less than ±1.5%.

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