



## On-site spectrophotometric determination of antimony in water, soil and dust samples of Central India

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### Abstract

A new, selective and sensitive on-site spectrophotometric method for the determination of antimony at trace level in water, soil and dust samples of Central India has been demonstrated. It is based on the color reaction of Sb(III) with  $I^-$  ions in the presence of a cationic surfactant cetylpyridinium chloride (CPC) in acidic media, and subsequent extraction of the complex with *N*-phenylbenzimidoylthiourea (PBITU) into chloroform to give a yellow colored complex. The value of apparent molar absorptivity of the complex in the terms of Sb is  $(7.84) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 440 nm. The detection limit of the method is  $5 \text{ ng ml}^{-1}$ . In addition, the present method is free from interferences of all metal ions that are associated during the determination of antimony in environmental samples.

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**Keywords:** Spectrophotometer; Antimony; Water; Soil; Dust

### 1. Introduction

Antimony is ubiquitously present in the environment as a result of natural processes and anthropogenic activities. Antimony is emitted mostly as the trioxide in the dust from metallurgical factories, coal-fired power plants and it may be present in gases, vapor and particulate forms in the atmosphere. Antimony is usually mixed with other metals such as lead and zinc to form mixtures of metals called alloys. These alloys are used in lead storage batteries, solder, type metal, ammunition, and pewter [1–4]. Antimony does harm to human health seriously; micro amounts of antimony will stimulate respiratory tract, mucous membrane of alimentary canal and skin, even lead to pulmonary edema. The Environmental Protection Agency of the United States (USEPA) and the Council of the European Communities consider antimony and its compounds as pollutants of priority interest [5,6]. The toxicological and physiological behavior of this element is dependent on its oxidation state. Antimony exists in the aquatic environment in two oxida-

tion states, III and V. It was reported that antimony(III) is more toxic and mobile than antimony(V) [7,8]. The antimony content in drinking water is regulated to be less than  $10 \text{ ng ml}^{-1}$  in the European Community,  $5.0 \text{ ng ml}^{-1}$  in USA and  $2.0 \text{ ng ml}^{-1}$  in Japan [9–11]. The determination of trace amount of antimony has received increasing attention in the environmental pollution studies. Hence, in order to achieve accurate, reliable and sensitive results, separation and preconcentration steps are often necessary prior to analysis. Various procedures have been demonstrated for the separation/preconcentration of trace-levels of antimony in environmental and biological samples [12–15]. All these methods are time consuming and required complex procedures for the separation of metals prior to instrumental analysis. In the present investigation, PBITU in chloroform with liquid–liquid extraction is applied for the determination of antimony from different environmental samples of Central India.

Many sophisticated analytical techniques, hydride generation-atomic absorption spectrometry (HG-AAS) [16,17], inductively coupled plasma-mass spectrometry (ICP-MS) [18,19], hydride generation-atomic fluorescence spectrometry (HG-AFS) [20–22], high performance liquid chromatography-atomic fluorescence spectrometry (HPLC-AFS) [23] and differential pulse anodic stripping voltammetry [24,25] are used for

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the determination of antimony in environmental and biological samples. These techniques are quite expensive and require costly maintenance and skilled hands for operation. Moreover, these instruments cannot be applied at the contaminated sites for the determination of antimony. Several chemical reagents are also reported for the spectrophotometric determination of antimony in environmental and biological samples, i.e. pyrogallol [26], sodium dodecylsulfate/nonylphenoxy polyethoxyethanol [27], brilliant green + hexachloroantimonate(V) + microcrystalline 1,4-dichlorobenzene [28], vanillylfluorone + poly(vinyl alcohol) [29], dibromodiethylbarbituric acid [30] and  $I_2$  + dithiozone [31]. Among these, some of the methods lack selectivity, sensitivity and matrix interfere during analysis. The intention of the present study is to develop new and selective method for on-site determination of antimony in environmental samples including, rain water, industrial wastewater, river water, soil and dust. The chemical variables like, acids, KI, ascorbic acid, surfactants, PBITU and solvents are investigated. The reaction mechanism involved in the formation of a colored  $\{[SbI_3-CP]PBITU\}$  complex is discussed. Application of the present method has been further extended for the investigation of antimony loading to environmental samples of Bhilai, Raipur, Korba and Bilaspur city.

## 2. Experimental

### 2.1. Reagents

All chemicals used were of analytical grade reagents obtained from E. Merck (Darmstadt, Germany). A standard solution of antimony(III) was prepared by dissolving appropriate amount of potassium antimony tartrate in 80 ml of concentrated  $H_2SO_4$  and diluted to 500 ml of distilled water. The fresh solution of KI (4.5 M, 75%, w/v) containing ascorbic acid (1.1 M, 20%, w/v) was used for the complex formation. A cationic surfactant cetylpyridinium chloride ( $5.6 \times 10^{-2}$  M, 0.02%, w/v) was prepared for color enhancement of the complex. A 5.0 M HCl solution was used for adjusting the acidity of aqueous solution. A PBITU ( $10.4 \times 10^{-3}$  M, 0.02%, w/v) was employed for extraction of antimony that was synthesized by condensation of *N*-phenylbenzimidoyl chloride with thiourea in equimolar ratio as described in literature [32].

### 2.2. Sample collection and preparation

Water, dust and soil samples were collected from contaminated sites of Bhilai (one biggest steel plant of India), Raipur (many industries like, metallurgy, alloys, sponge iron, etc.), Korba (open coal mines), and Bilaspur (industrial area). Rain-water samples were collected during the month of June–July, 2006 using automatic rain Collector (Dynamab, Pune, India). Coal mine and industrial wastewater samples were collected in polyethylene bottle. All water samples obtained were filtered with Whatman 42 filter paper. An aliquot of this sample was used for the determination of antimony according to described procedure.

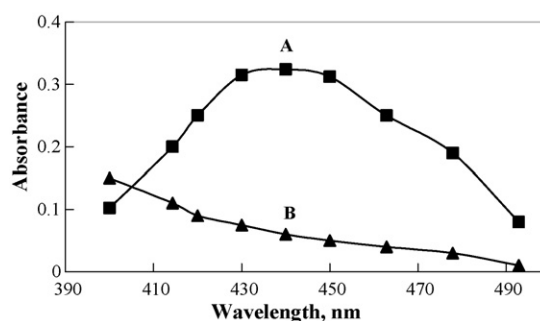


Fig. 1. Absorption spectra of the  $[SbI_3-CP]PBITU$  complex (A); and reagent blank (B) with other relevant reference.  $[Sb] = (4.1) \times 10^{-6}$  M,  $[HCl] = 3.0$  M,  $[KI] = 0.45$  M,  $[CPC] = 5.6 \times 10^{-2}$  M and  $[PBITU] = 8.0 \times 10^{-3}$  M.

Dust and soil samples were collected from Bhilai, Raipur, Korba and Bilaspur region during March–April, 2006. A 5.0 g of each sample was taken in a 250 ml beaker separately and digested with 10 ml of aqua-regia (3:1,  $HCl:HNO_3$ ) to dryness. This procedure was repeated thrice to remove excess of nitric acid by heating to dryness with the addition of 5 ml concentrated HCl. Then, the dried residue was dissolved in distilled water according to concentration of antimony present in dust and soil samples. Further analysis was carried out using described procedure.

### 2.3. Apparatus

UV–vis spectrophotometer (Systronic, type-106), matched with 1 cm quartz cell was used for absorbance measurement. A hydride generation atomic absorption spectrophotometer (GBC-932, Australia) equipped with lamp current 10 mA; slit width 0.2 nm and wavelength 217.6 nm used for the validity of the method.

### 2.4. Procedure for liquid–liquid extraction of antimony followed by spectrophotometric determination

A calibration curve was prepared by taking an aliquot of standard solution containing 0.10–15  $\mu g$  of Sb(III) in a 125 ml separatory funnel. To this, add 5 ml of HCl, 1 ml of KI and CPC solution and final volume was diluted with 10 ml distilled water. The aqueous phase was equilibrated with 10 ml of chloroform solution containing PBITU for 5 min of extraction time. Then, the organic extract was separated out over anhydrous sodium sulfate (2.0 g) in a 10 ml volumetric flask. The absorbance of the extract was measured against the reagent blank at 440 nm.

## 3. Results and discussion

### 3.1. Optimization of the method

#### 3.1.1. Absorption spectra

The absorption spectra of the  $\{[SbI_3-CP]PBITU\}$  complex in the chloroform against the reagent blank are shown in Fig. 1. Other metals like As(III), Sn(IV), Bi(III) and Fe(III) did not interfere during the extraction of antimony complex due to the

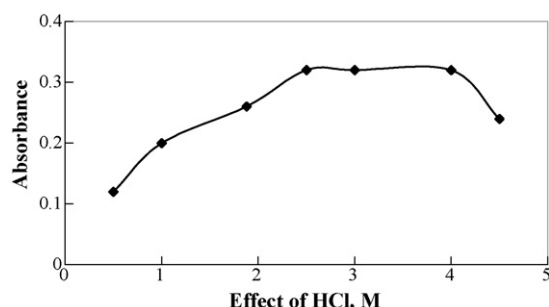


Fig. 2. Effect of acids on absorptivity of the complex with other relevant reference.  $[Sb] = (4.1) \times 10^{-6}$  M,  $[KI] = 0.45$  M,  $[CPC] = 5.6 \times 10^{-2}$  M and  $[PBITU] = 8.0 \times 10^{-3}$  M.

formation of lower oxidation state or formation of higher iodo-complex in acidic media.

### 3.1.2. Effect of acid

HCl and  $H_2SO_4$  were tested for the extraction of  $SbI_3$ -CP with PBITU into chloroform. A lower absorptivity of the complex was observed when the extraction was carried out with sulfuric acid solution. Hence, hydrochloric acid was selected for performing detailed studies. All most complete extraction of Sb complex was achieved at 2.5–4.0 M of HCl, shown in Fig. 2. Thereafter, the extraction was found to be decreased possibly due to the formation of non-extractable chloro-complex. For present investigation, 3.0 M of HCl was used for the extraction of antimony from sample solution.

### 3.1.3. Effect of potassium iodide and reducing agent

The effect of quantity of potassium iodide on the extraction of the metal with PBITU has been examined. The optimum concentration range of potassium iodide for maximum and constant extraction of the metal was found to be 0.30–0.70 M, shown in Fig. 3. Beyond these limits, the extraction of metal was suppressed. It may be due to incomplete complexation with iodide ion. In the present investigation, a 0.45 M KI was used for the extraction of metal. Ascorbic acid was used to reduce Sb(V) to Sb(III) and also prevent the liberation of iodine by any oxidizing species present in the analyte. A 0.11 M of ascorbic acid was found sufficient for reduction of metal ion and optimum color enhancement of the complex.

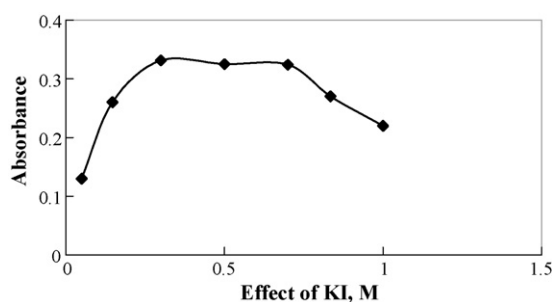


Fig. 3. Effect of KI on absorptivity of the complex with other relevant reference.  $[Sb] = (4.1) \times 10^{-6}$  M,  $[HCl] = 3.0$  M,  $[CPC] = 5.6 \times 10^{-2}$  M and  $[PBITU] = 8.0 \times 10^{-3}$  M.

Table 1

The value of apparent molar absorptivity of the complex with various surfactants

Surfactants	Structure	$\epsilon$ , $l\ mol^{-1}\ cm^{-1}$
Dodecyltrimethylammonium bromide (DTAB)	$CH_3(CH_2)_{11}\ N(CH_3)_3Br$	$5.66 \times 10^4$
Tetradecyltrimethylammonium bromide (TDTAB)	$CH_3(CH_2)_{13}\ N(CH_3)_3Br$	$6.02 \times 10^4$
Cetyltrimethylammonium bromide (CTAB)	$CH_3(CH_2)_{15}\ N(CH_3)_3Br$	$7.24 \times 10^4$
Cetylpyridinium chloride (CPC)	$CH_3(CH_2)_{15}\ N(C_5H_5)Cl$	$7.84 \times 10^4$

### 3.1.4. Effect of cationic surfactants

Antimony(III) reacts with  $I^-$  ions in strong acidic medium to give a yellow colored complex. In presence of cationic surfactants (CS), cetylpyridinium chloride (CPC), cetyltrimethyl ammonium bromide (CTAB), tetradecyltrimethyl ammonium bromide (TDTAB) and dodecyltrimethyl ammonium bromide (DTAB), the absorptivity of the complex was remarkably enhanced. This is possibly due to the formation of an ion associate complex. Among them, CPC was showed higher value of molar absorptivity possibly due to longer alkyl chain of surfactant molecule, shown in Table 1. A  $5.6 \times 10^{-2}$  M (0.02%) of CPC solution was needed for complete color development of the complex.

### 3.1.5. Effect of PBITU

The effect of concentration of PBITU on the extraction of the metal was observed. In order to obtain a complete extraction of the metal, at least  $4.0 \times 10^{-3}$  M (0.01%, w/v) of PBITU in chloroform solution was found to be necessary. Further more addition of PBITU up to  $10.4 \times 10^{-3}$  M (0.03%, w/v) had no adverse effect. The results are shown in Fig. 4. All extraction work was performed with  $8.0 \times 10^{-3}$  M (0.02%, w/v) of PBITU.

### 3.1.6. Effect of solvents

The selection of appropriate solvents with different characteristics is a key factor for the liquid–liquid extraction of analyte from aqueous phase to organic phase. Solvents should have the property of high vapor pressure, immiscibility with aqueous phase and high solubility with metal complex. On the basis of the above properties, several extraction solvents such as methyl isobutyl ketone, 1-pentanol, chloroform and toluene

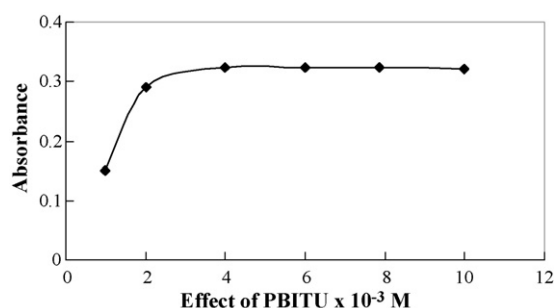


Fig. 4. Effect of PBITU on absorptivity of the complex with other relevant reference.  $[Sb] = (4.1) \times 10^{-6}$  M,  $[HCl] = 3.0$  M,  $[KI] = 0.45$  M and  $[CPC] = 5.6 \times 10^{-2}$  M.

were selected for the extraction metal complex for 5 min of extraction time. Among them, chloroform was chosen as best extracting solvent for the detailed study. The reason is due to higher value of molar absorptivity of the complex.

### 3.1.7. Percentage of extraction

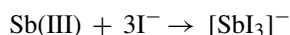
A  $0.5 \mu\text{g ml}^{-1}$  of antimony was extracted with  $\text{I}^-$ ,  $\text{CP}^+$  and PBITU as described in the procedure. Then extract was digested with acids and residue dissolved in deionized water. The metal content was determined by HG-AAS method. The percentage extraction was found to be  $(97.3 \pm 0.2\%)$  in single extraction.

### 3.2. Calibration curve and statistical data

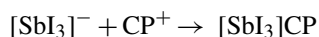
Five points calibration curve was prepared by plotting the absorbance of the complex versus concentration of antimony taken in the aqueous solution. The optimum concentration range on the basis of Beer's law was found to be  $0.01\text{--}1.5 \mu\text{g ml}^{-1}$  of antimony with correlation coefficient of 0.999. The slope and intercept of the calibration curve were 0.0635 and 0.016, respectively. The apparent value of molar absorptivity of the complex in terms of antimony was found to be  $(7.84) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 440 nm in chloroform solution. The detection limit (3 times of standard deviation) of the method was determined and found to be  $5 \text{ ng ml}^{-1}$  of Sb. The relative standard deviation of the method was found to be 1.3% at six replicates analysis.

### 3.3. Composition of the complex

The color complex of the antimony was determined by the curve fitting method [33]. The molar ratio of metal to  $\text{I}^-$ ,  $\text{CP}^+$  and PBITU were determined by logarithmic value of distribution ratio of metal  $[\log\{A_{\text{eq}}/(A_{\text{max}} - A_{\text{eq}})\}]$ . Where  $A_{\text{max}}$  is the maximum absorbance of the complex at  $\lambda_{\text{max}}$  under optimum reagent concentrations; and  $A_{\text{eq}}$  is the absorbance of  $\text{Sb(III)}$  complex at equilibrium concentration that obtained by equilibration with different known concentrations of reagents, viz.  $\text{I}^-:\text{CP}^+:\text{PBITU}$  versus log values of varied known concentrations of  $\text{I}^-:\text{CP}^+:\text{PBITU}$  in chloroform. The inclination of the curves for  $\text{Sb(II)}$   $\text{I}^-:\text{CP}^+:\text{PBITU}$  were found to be 1:3:1:1. The probable reaction mechanism can thus be expressed as: Formation of an iodo-complex



Formation of extractable ion-pair complex with CPC



Formation of extractable ion complex with PBITU



where o subscript denotes to the organic phase.

### 3.4. Effect of diverse ions

Effects of various diverse ions in the determination of antimony were examined as described procedure. Different solution

Table 2

Determination of antimony ( $\text{ng ml}^{-1}$ ) in rain, coalmine and industrial wastewater samples

Sample/site	Present method	RSD, % (n = 5)	HG-AAS	RSD, % (n = 5)
RW-1, Bhilai	13.4	1.2	13.1	3.2
RW-2, Korba	25.2	1.0	25.4	3.5
RW-3, Raipur	10.5	1.4	10.6	2.8
RW-4, Bilaspur	20.1	1.5	19.8	3.2
CMW-1, Korba	15.1	1.3	14.9	2.1
CMW-2, Korba	14.0	1.2	14.1	2.5
IWW-1, Bhilai	20.3	1.2	19.9	2.3
IWW-2, Raipur	16.5	1.4	16.8	3.4
IWW-3, Korba	33.0	1.5	32.8	3.1
IWW-4, Bilaspur	16.7	1.4	16.5	2.8

RW: rain water, CMW: coal mine water, IWW: industrial waste water.

of diverse ions containing  $0.5 \mu\text{g ml}^{-1}$  of antimony were investigated; none of the diverse ions ( $\mu\text{g ml}^{-1}$ ) tested interfered to any significant extent in the determination of antimony is summarized: Nb(V): 200; Cu(II), Se(IV), Mo(VI), Re(VII): 450; Cd(II), Hg(II), Al(III), Pb(II): 1200; Zr(IV), W(VI), As(V): 2000; nitrate, Ag(I), La(III), Ti(IV), V(V), Co(II), Zn(II), Be(II): 5000; Mn(II), Fe(III), Ni(III), U(VI), Cr(IV): 1500; and oxalate, EDTA, citrate, tartrate, fluoride: 2500.

### 3.5. Application of the method for determination of antimony in water, soil and dust samples of Central India

This method has been successfully applied for the determination of Sb in water, soil and dust samples of Central India. The result obtained by the present method was checked with HG-AAS and found to be compatible. The results obtained in water, dust and soil samples are shown in Tables 2 and 3. Higher concentration of antimony was found in the samples of Bhilai and Korba region may be due to more emission of antimony by steel, thermal power plants and coalmines.

### 3.6. Comparison of present method with other spectrophotometric methods

The potentiality of the present method was compared with the results of earlier spectrophotometric methods for the determination of antimony. Table 4 revealed that the suitability of the

Table 3

Determination of antimony ( $\mu\text{g g}^{-1}$ ) in dust and soil samples

Sample/Site	Present method	RSD, % (n = 5)	HG-AAS	RSD, % (n = 5)
D-1, Bhilai	1.3	1.5	1.5	2.4
D-2, Raipur	2.2	1.3	2.5	3.5
D-3, Korba	1.0	1.6	1.3	2.8
D-4, Bilaspur	1.2	1.5	1.4	1.9
S-1, Bhilai	4.1	1.4	4.1	2.0
S-2, Raipur	2.1	1.2	2.2	2.5
S-3, Korba	5.4	1.3	5.2	3.2
S-4, Bilaspur	1.3	1.5	1.0	3.0

D: dust, S: soil.



Table 4  
Comparison of spectrophotometric determination of antimony with other methods

Reagents	Solvents	$\lambda_{\max}$ , nm	$\epsilon$ , l mol <sup>-1</sup> cm <sup>-1</sup>	Remarks
Bromopyrogallol red + micelles [27]	Water	538	$4.80 \times 10^4$	Strong oxidizing or reducing agents causes interference
KI + Dithiozone [31]	Acetone	507	$2.56 \times 10^4$	Metals ion like Fe(III), Cu(II) interfere and less sensitive
Rhodamin-B [34]	Chlorobenzene + CCl <sub>4</sub>	565	–	Color system is unstable for long time
Bromopyrogallol red [35]	Water	560	$3.54 \times 10^4$	Poor sensitivity and selectivity
Present method	Chloroform	420	$7.84 \times 10^4$	Simple, highly sensitive and free from interferences of other ions present in environmental samples.

present work in the terms of molar absorptivity, matrix interference, linear dynamic range, etc. The present method overcomes all the drawbacks of other reported spectrophotometric methods.

#### 4. Conclusions

The feasibility of method has been successfully demonstrated for on-site spectrophotometric determination of antimony in water, soil and dust samples from contaminated sites. The extraction of yellow colored complex in chloroform with PBITU makes this method very sensitive and selective for separation and preconcentration of antimony. As compared with other spectrophotometric methods, this method has many advantages in terms of simplicity, rapidity and sensitivity and this can be applied at sample source.

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