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## DETERMINATION OF THALLIUM IN SOIL

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A new spectrophotometric method is described for the determination of thallium in soil by extraction of Tl(III) with a toluene solution of N,N'-diphenylbenzamidine after acidification with 0.2–4.0 M HCl, and reaction of the extract with Crystal violet in the presence of 0.01–0.8 M HCl. The value of molar absorptivity of Tl(III)-X-CV complex (where X = Cl or Br; CV = Crystal violet) in toluene is  $7.00 \times 10^4$  l mole<sup>-1</sup> cm<sup>-1</sup> at the absorption maximum of 610 nm. The detection limit of the method is 20 ng ml<sup>-1</sup>. The present method is free from interference of almost metal ions commonly associated with Tl. The method has been applied for analysis of the metal to soils.

**KEY WORDS:** Spectrophotometry, extraction, thallium(III), soils.

### INTRODUCTION

Thallium is a metal as toxic as cadmium and nearly twice as mercury.<sup>1</sup> Primary sources of Tl in the environment are ferrous and non-ferrous mines, metal refineries, cement plants, coal burning, power plants, etc.<sup>2</sup>

Many dyes i.e. Crystal violet, Brilliant green, Rhodamine-B, cyanine dyes, Astrazone red 6B, Astrazone red violet-3R, etc. were reported for spectrophotometric determination of Tl in various complex materials but they involved many inter-elemental interferences.<sup>3–8</sup> Chlorpromazine has also been reported for spectrophotometric determination of Tl(III) but it is less sensitive and involves the interference of Au(III), Bi(III).<sup>9</sup> Therefore, in the present investigation, Tl(III) is prior extracted with a toluene solution of N,N'-diphenylbenzamidine, and then the extract is allowed to react with Crystal violet in order to overcome these interferences.

### EXPERIMENTAL

#### *Apparatus*

A Carl Zeiss Spekol equipped with 1-cm quartz cells was used for the absorbance measurements.

#### *Chemicals*

1.303 g TlNO<sub>3</sub> were dissolved in distilled water containing 2 ml of concentrated nitric acid and diluted to 1 litre. N,N'-Diphenylbenzamidine was synthesized as described

in the literature.<sup>10</sup> Solutions of 0.2%, w/v amidine in toluene, 0.04%, w/v Crystal violet in 0.1 M HCl, and 1%, w/v bromine water were used. All solutions used were presaturated with toluene.

### *Procedure*

An aliquot of Tl(I) solution containing up to 15  $\mu\text{g}$  of the metal is oxidised with 2 ml bromine water by heating in a boiling water bath till the solution becomes colourless.<sup>11</sup> The cold solution is transferred to a 100 ml separatory funnel with subsequent addition of 1 ml HCl (5M) in a final 10 ml aqueous solution. The aqueous solution is shaken with 5 ml toluene solution of amidine for 2 min. The aqueous phase is rejected and the extract is further washed with  $1 \times 2$  ml of diluted HCl (0.5M).

The extract is shaken with 3 ml dye solution for 2 min, and the extract is dried over anhydrous sodium sulphate (1 g). The absorbance of the extract is measured at 610 nm against the reagent blank.

## RESULTS AND DISCUSSION

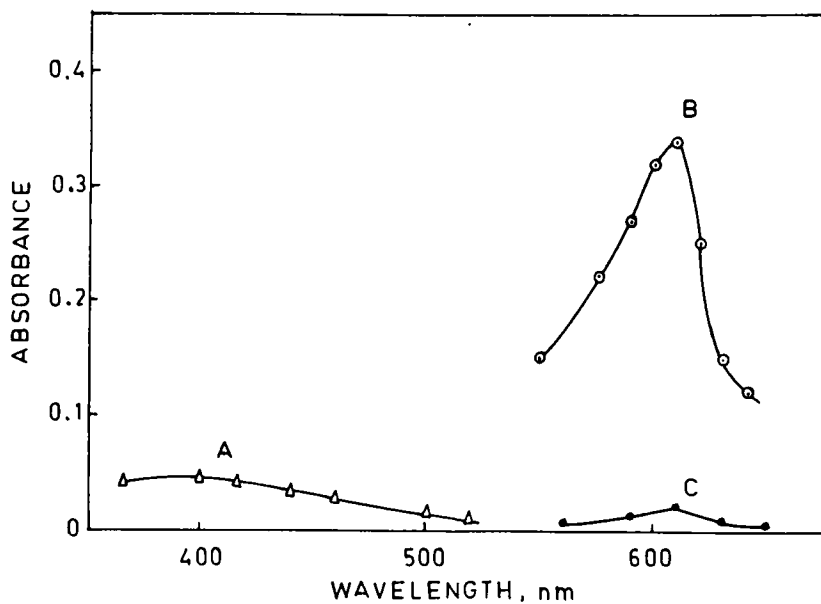
### *Absorption spectra of the complexes and the reagent blank*

The absorption spectra of the Tl(III)- $\bar{X}$ -A ( $\bar{X}$  = Cl or Br; A = amidine) and Tl(III)- $\bar{X}$ -CV (CV = Crystal violet) complexes against the respective reagents blanks, and the reagent blank in toluene are plotted in Figure 1. The Tl(III)- $\bar{X}$ -A complex exhibits a practically negligible absorption over 500–700 nm. The complex is a deep coloured species, showing a sharp absorption maximum around 610 nm. The reagent blank has some absorption at this region, hence it was used as reference for all measurements.

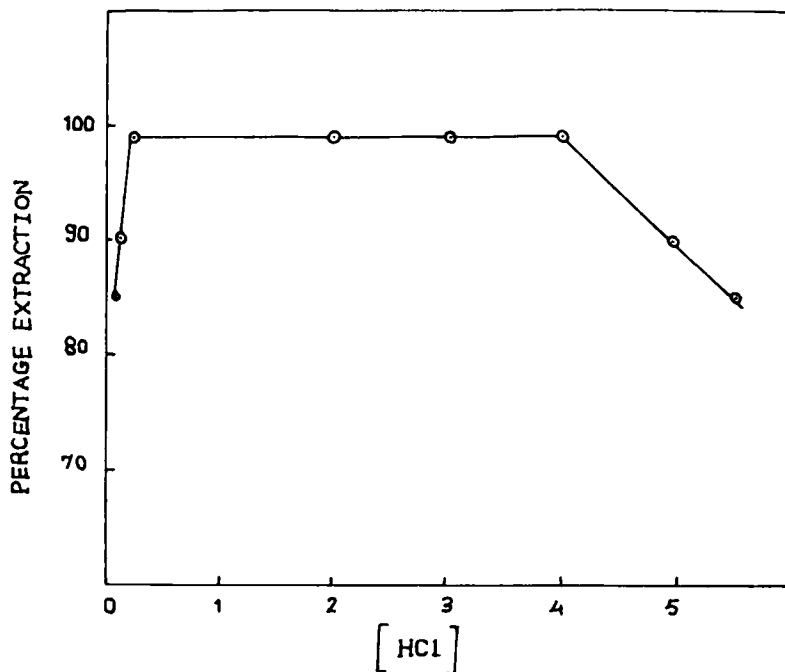
### *Amidine extraction*

Tl(III) is quantitatively extracted (99.0–99.5% in a single extraction, as determined by AAS after destroying the extract with acid treatments) with N,N'-diphenylbenzamidine in various organic solvents: benzene, toluene, chloroform, *n*-pentanol, MIBK and ethyl acetate. In *n*-pentanol, MIBK, ethyl acetate, other metal ion complexes i.e. Sb(V), Sn(IV), Fe(III), Ga(III), In(III), Au(III) were also extracted and interfered in the determination of the metal. In chloroform, the dye is extractable and the reagent blank has a very deep colour. Toluene is relatively less toxic than benzene, hence it was preferred as solvent for the extractive-spectrophotometric determination of the metal.

Two acids, HCl and H<sub>2</sub>SO<sub>4</sub>, were tested for the extraction of the metal. In H<sub>2</sub>SO<sub>4</sub>, the extraction of the metal was suppressed probably due to the formation of the unextractable sulphate complex. The complete extraction of the metal was obtained with HCl and the maximum recovery in a single extraction was  $99.0 \pm 0.2\%$ . The optimum acidity range was 0.2–4.0 M HCl (Figure 2). At least 0.1%, w/v amidine



**Figure 1** Absorption spectra of the complexes, and the reagent blank in toluene. (A), Tl(III)-X-A complex (X = Cl or Br; A = amidine):  $C_{\text{Tl(III)}} = 4.89 \times 10^{-6}$  M (in toluene),  $C_{\text{HCl}} = 0.5$  M,  $C_A = 7.35 \times 10^{-3}$  M in toluene. (B), Tl(III)-X-CV complex:  $C_{\text{Tl(III)}} = 4.89 \times 10^{-6}$  M,  $C_{\text{HCl}} = 0.1$  M,  $C_{\text{CV}} = 9.80 \times 10^{-4}$ . (C), The reagent blank.

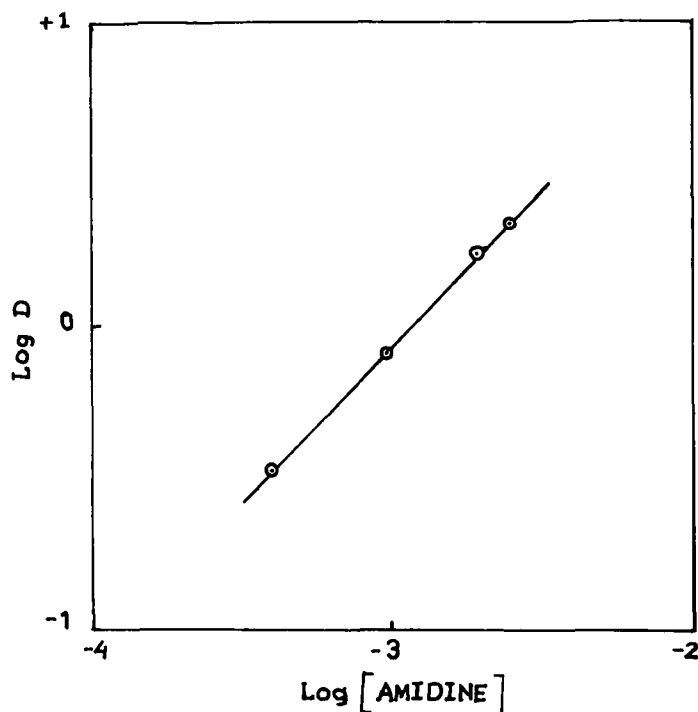


**Figure 2** Effect of HCl concentration on percentage extraction of the metal as halo complex in toluene:  $C_{\text{Tl(III)}} = 4.89 \times 10^{-6}$  M,  $C_A = 7.35 \times 10^{-3}$  M.

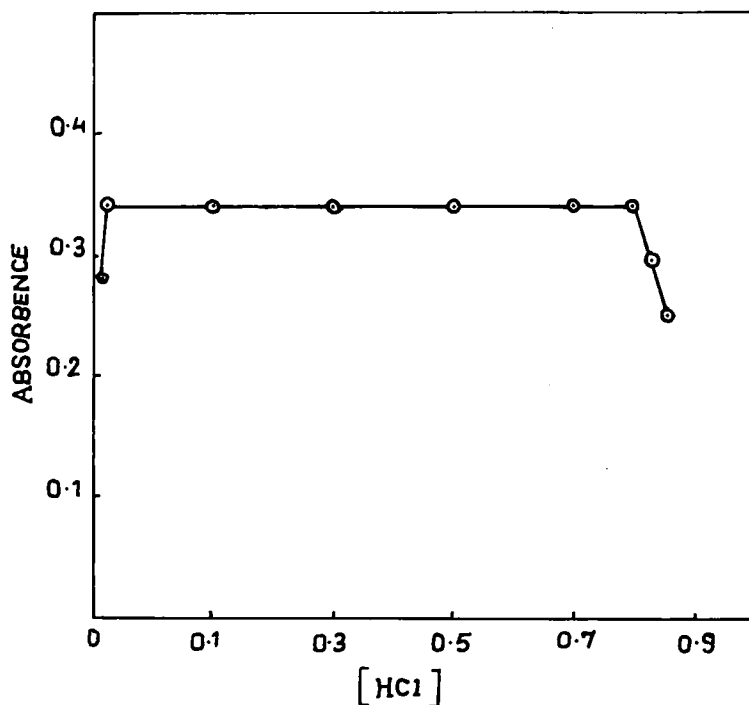
was needed for the complete extraction of the metal and addition of more reagent up to 0.3% had no adverse effect. The order of addition of reagents, prolonged extraction of the complex up to 20 min, standing time of the extract up to 2 hr, variation in temperature of the aqueous phase from 15 to 40°C, and variation in volume ratio of the organic to the aqueous phase from 4:1 to 1:2 were not found to be critical. Tl(III) in halide solution exists as  $[TlX_4]^-$ , and the ratio of the metal to amidine (A) in the extracted complex was determined by plotting the log distribution ratio of the metal to log molar amidine concentration in toluene. The results obtained showed a 1:1 Tl:A ratio in toluene (Figure 3).

#### *Colour development of the dye extract*

The toluene extract of the halide complex is allowed to react with the aqueous solution of Crystal violet to get a dense coloured complex in toluene. The maximum and constant absorbance of the complex is obtained when the acidity of the aqueous solution (after equilibration) lies between pH 2.0 and 0.8 M HCl (Figure 4). At least 0.001%, w/v Crystal violet is sufficient for maximum colour development of the complex in toluene, and further addition up to 0.2% has no adverse effect. The colour of the extract is stable for at least 4 hr at room temperature ( $22 \pm 2^\circ\text{C}$ ). An



**Figure 3** Determination of molar ratio of the metal to amidine in the extracted complex:  $C_{Tl(III)} = 4.89 \times 10^{-6}$  M,  $C_{HCl} = 0.5$  M.

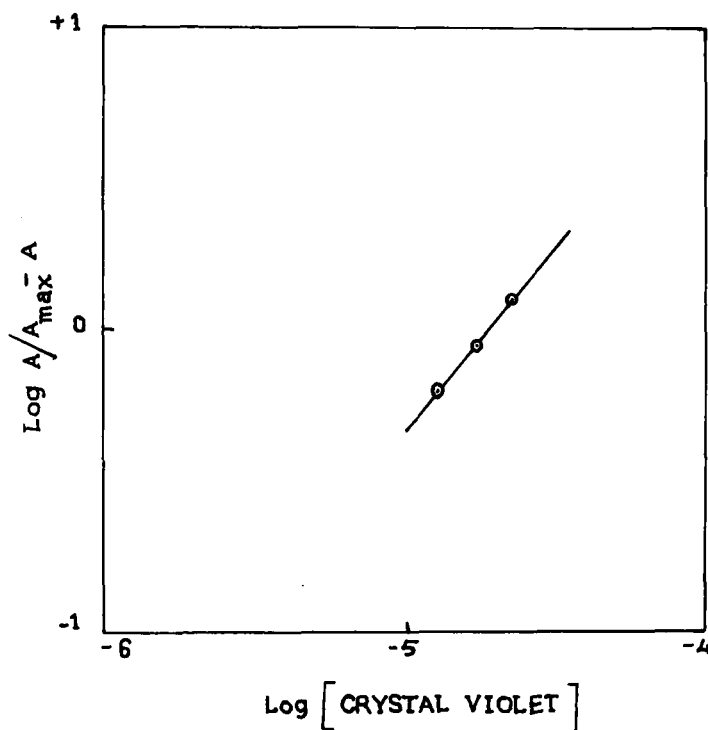


**Figure 4** Effect of HCl concentration on absorbance of the complex in toluene:  $C_{\text{Tl(III)}} = 4.89 \times 10^{-6}$  M in toluene,  $C_{\text{CV}} = 9.80 \times 10^{-4}$  M.

equilibration period of 1 min is sufficient for the maximum colour development of the extract. Variation in volume ratio of the organic phase to the aqueous phase from 4:1 to 1:5, and variation in temperature of the aqueous phase from 15 to 40°C do not change the absorbance of the extract. The ratio  $[\text{TlX}_4]^-$  to the dye in the toluene extract was determined by plotting  $\log [A/(A_{\text{max}}-A)]$  versus log molar concentration of crystal violet (CV) taken in the aqueous solution (Figure 5). The slope of the curve show the formation of 1:1 ion-pair complex ( $\text{TlX}_4^- : \text{CV}$ ) in toluene.

#### *Effect of oxidizing agent*

The effect of the oxidizing agents bromine water, ceric sulphate, hydrogen peroxide and sodium nitrite were tested towards the oxidation of Tl(I) into Tl(III). All of them quantitatively oxidise the metal (with the same spectral characteristics with CV) but with ceric sulphate and sodium nitrite, the reagent blank has relatively higher colour. In the present investigation, bromine water was used for further experimental work, and at least 0.2 ml (1% w/v) was needed for the maximum oxidation of the metal. Addition of more bromine water (5 ml saturated bromine water, 95.5%, w/v) had no adverse effect. The removal of the bromine excess by heating over boiling water was necessary, otherwise the reagent blank had high colour.



**Figure 5** Determination of molar ratio of the metal to CV in the extracted complex.  $C_{\text{Tl(III)}} = 4.89 \times 10^{-6}$  M in toluene,  $C_{\text{HCl}} = 0.1$  M.

#### *Optimum concentration range, sensitivity and precision*

The system obeyed the Beer's law up to  $3.0 \mu\text{g Tl}$  per ml of toluene with a correlation coefficient of 0.99. The value of molar absorptivity of the complex is  $7.00 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$  at the absorption maximum of 610 nm. The detection limit of the method is  $20 \text{ ng ml}^{-1}$  in the aqueous solution (amount causing more absorbance than blank absorbance + twice of std. dev. of 10 replicate blank measurements). The rel. std. dev. of the method is  $\pm 1.0\%$  (10 replicate measurements at the level of  $6.0 \mu\text{g Tl}/5 \text{ ml}$  toluene).

#### *Effect of diverse ions*

The effect of various ions on the determination of  $6.0 \mu\text{g Tl(III)}$  ( $60 \text{ ng ml}^{-1}$  in the aqueous solution) was examined separately as in the procedure. Of the various ions tested, only Au(III) caused serious positive interference in the determination of the metal. The tolerable amount of various diverse ions are summarized in Table 1.

**Table 1** Effect of diverse ions for the determination of  $0.6 \text{ ng ml}^{-1}$  Tl(III)

| <i>Ion</i>  | <i>Tolerable amount</i><br>$\mu\text{g ml}^{-1}$ |
|---|--|
| Mn(II), $\text{PO}_4^{3-}$  | 7,500  |
| Fe(III), EDTA   | 2,000  |
| Cu(II), Cd(II)  | 7,000  |
| Ni(II), $\text{AsO}_4^{3-}$   | 4,000  |
| Co(II), $\text{C}_2\text{O}_4^{2-}$                                 | 1,500  |
| Zn(II), U(VI)   | 2,500  |
| Al(III), Cr(III)  | 1,000  |
| Sb(V), Bi(III), V(V), Nb(V), Ta(V),<br>Sn(IV), Ge(IV), $\text{F}^-$ | 200  |
| Zr(IV), La(III)   | 3,000  |
| Ga(III)   | 500  |
| In(III)   | 1,500  |
| Mo(VI)  | 50   |
| W(VI)   | 100  |

### *Application of the method*

The application of the method was tested for analysis of thallium content in soil extracts. Soil samples were taken from four different sites of the mine area of Dalli-Rajhara, characterized by different degree of heavy metals. A weighed amount of the powdered sample (1.0 gm) was treated with hot water, filtered and the filtrate diluted to 100 ml. The metal content was then determined as the reported procedure. The results of Tl determination were compared with those obtained by AAS, (Table 2). The data obtained by the two methods were comparable.

### CONCLUSION

The present method remarkably enhances the selectivity and sensitivity of the classical dye methods previously used. The acidity range is widened. The method is also more reliable for the analysis of the metal in complex materials.

**Table 2** Thallium content in soil extract

| <i>Sampling location</i><br><i>Dalli-Rajhara</i><br><i>mines</i> | <i>Tl found by</i><br><i>the present method</i><br>$\mu\text{g g}^{-1}$ Tl | <i>Rel. Std. dev<sup>+</sup> of</i><br><i>the present method</i><br>$\pm \%$ | <i>Tl found by</i><br><i>AAS method</i><br>$\mu\text{g g}^{-1}$ Tl |
|--|--|--|--|
| Conde-A  | 105  | 1.2  | 103  |
| Conde-B  | 71   | 1.0  | 72   |
| Bharat-Dalli mine  | 93   | 1.2  | 92   |
| Mayur-Pani mine  | 100  | 1.3  | 99   |

+ = mean of five determination.



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