



## Development of surfactant assisted kinetic method for trace determination of thallium in environmental samples



Garima Pravin Pandey<sup>a</sup>, Ajaya K. Singh<sup>b,\*</sup>, Surendra Prasad<sup>c,\*\*</sup>, Lata Deshmukh<sup>a</sup>, Anupama Asthana<sup>b</sup>

<sup>a</sup> Dr. Ira Nimdeokar Postgraduate and Research Centre for Chemistry, Hislop College, Nagpur, Maharashtra 440002, India

<sup>b</sup> Department of Chemistry, Government V.Y.T. Postgraduate Autonomous College, Durg, Chhattisgarh 491001, India

<sup>c</sup> School of Biological and Chemical Sciences, Faculty of Science, Technology and Environment, The University of the South Pacific, Private Mail Bag, Suva, Fiji

### ARTICLE INFO

#### Article history:

Received 3 July 2014

Received in revised form 27 August 2014

Accepted 28 August 2014

Available online 6 September 2014

#### Keywords:

Thallium

Thallium kinetic determination

Surfactant assisted

Cetylpyridinium ion

Thallium determination

### ABSTRACT

A simple and highly selective surfactant assisted kinetic spectrophotometric method for the determination of thallium has been developed. The method is based on the quantitative oxidation of Tl(I) to Tl(III) using bromine water where the resulting Tl(III) liberated iodine from potassium iodide in acidic medium. The liberated iodine was subsequently reacted with  $I^-$  ion to form tri-iodide ions ( $I_3^-$ ). The tri-iodide ions formed were further reacted with cetylpyridinium cation ( $CP^+$ ) which produced a violet ion associate species having a  $\lambda_{max}$  of 512 nm at which reaction was monitored. The reaction variables such as time, temperature, reagent concentration and acidity were optimized for the indicator reaction to achieve maximum sensitivity. The linear regression calibration concentration range of  $0.007$ – $0.1 \mu\text{g mL}^{-1}$  Tl(I) was established as the Beer's law was obeyed in this range. Sandell's sensitivity and molar absorptivity of the ion associate species in terms of thallium were determined to be  $0.000133 \mu\text{g cm}^{-2}$  and  $1.99 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$  respectively. The limit of detection was determined as  $0.0029 \mu\text{g mL}^{-1}$ . The developed method has successfully been applied for the determination of thallium in different environmental samples with satisfactory results.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

In the past few decades there has been great emphasis especially on the determination of toxic trace metals [1–5]. The determination of toxic metals in agricultural and environmental samples has become increasingly important. This has led to major developments in the field of toxic trace metal analysis, with emphasis on the development and validation of analytical methods. As a result there has been considerable growth in the analytical procedure for the determination of various toxic metals [2]. Thallium is no exception to this [1,3–5]. A rare element in the earth's crust, thallium is found either as a native metal or in the most common ores. Both, the element and its compounds, are highly toxic [3,4,6]. It is a heavy metal which endures in the environment in combined state mainly with other elements like oxygen, sulfur and halogens in the form of inorganic compounds. It exists in nature as Tl(I) and Tl(III) ions but its monovalent state has higher stability, whereas trivalent state forms complexes of greater stability [5]. Each oxidation state of thallium exhibits different properties towards bioavailability and toxicity [6]. Therefore, the determination of thallium is of significance due to its wide range in application as a catalyst, in making alloys,

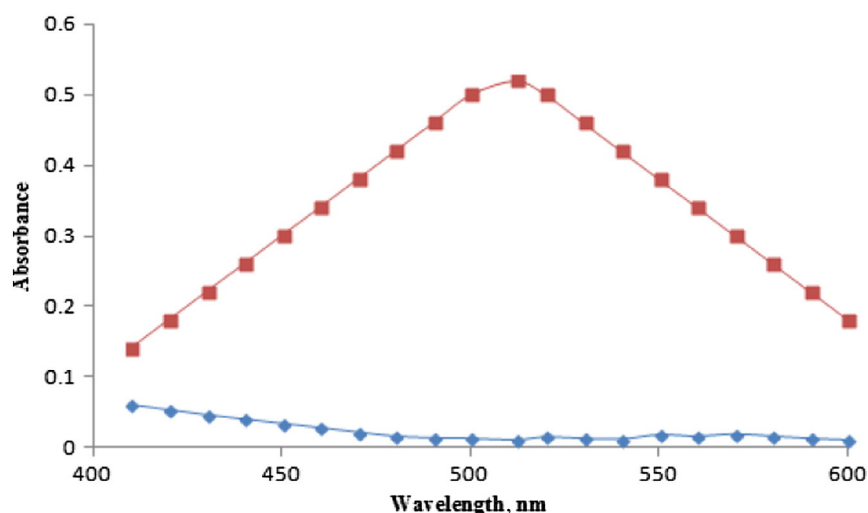
optical lenses, jewelry, low temperature thermometers, semiconductors, in dyes and pigments and in scintillation counters [7]. Thallium compounds have also been used as medicines, rodenticides and insecticides [8]. However, the US Environment Protection Agency has declared Tl in the list of priority pollutants in drinking water defining  $0.5 \mu\text{g L}^{-1}$  Tl as maximum permissible concentration. Thus thallium has regularly been determined in the environmental waters due to its risks on human being [5,7,9,10]. The concentration of thallium in environmental samples is quite low such as in surface water  $10$  to  $100 \text{ ng L}^{-1}$  [10], whereas in non-polluted soils lies between  $0.3$  and  $0.55 \text{ mg kg}^{-1}$  [11]. Because of very low concentration of Tl in the environmental samples its accurate assessment with low limit of detection has stimulated many researchers to develop sensitive and inexpensive analytical methods [3,5,7–10,12–18].

Therefore in the last few years many methods have been developed for the determination of thallium in different samples [1,3,5,7–29]. The most widely used techniques for its detection and determination are: extraction [23–25], single drop extraction [17], flotation and solid phase extraction [7,14,15]. However, many of these methods are laborious and carry a risk of contamination [12–17,19–22]. A variety of methods have also been proposed for the determination of thallium using inductively coupled plasma atomic emission spectroscopy (ICPAES) [18], electrothermal or flame atomic absorption spectroscopy [17,25], inductively coupled plasma-mass spectroscopy (ICPMS) [5,19,20,24], graphite furnace atomic absorption spectroscopy (GFAAS) [16,21],

\* Corresponding author. Tel.: +91 9406207572; fax: +91 788 2211688.

\*\* Corresponding author. Tel.: +679 3232416; fax: +679 2321512.

E-mail addresses: [ajayaksingh\\_au@yahoo.co.in](mailto:ajayaksingh_au@yahoo.co.in) (A.K. Singh), [prasad\\_su@usp.ac.fj](mailto:prasad_su@usp.ac.fj) (S. Prasad).



**Fig. 1.** Absorption spectrum of reagent blank (no peak) and spectrum of the reaction system containing potassium iodide ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ), HCl ( $2 \text{ mol L}^{-1}$ ), ascorbic acid ( $2 \times 10^{-4} \text{ mol L}^{-1}$ ), CPC ( $1.6 \times 10^{-5} \text{ mol L}^{-1}$ ), and thallium ( $0.1 \mu\text{g mL}^{-1}$ ) at  $25^\circ\text{C}$ .

X-ray fluorescence spectroscopy [22], and electro-analytical techniques [1,10,26–29]. Most of these methods are disadvantageous in terms of cost and instruments used in analysis [19,20,30]. These methods are accurate and selective but they require relatively expensive instrumentation and highly skilled manpower [18–22,26–29]. Therefore, the development of inexpensive and sensitive method for the determination of thallium is still desirable.

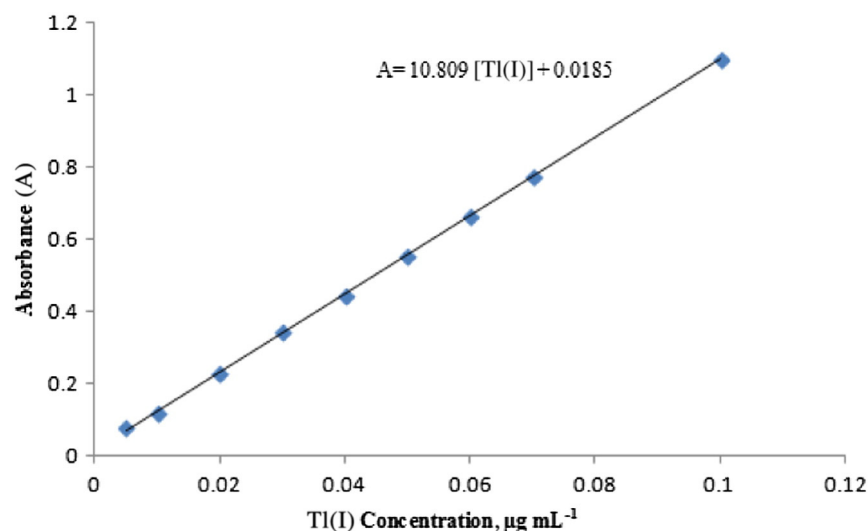
An easy availability of spectrophotometric apparatus and related simple reagents makes the technique quite useful for a wide range of detection and determinations of various analytes. At the same time kinetic methods of analysis have many advantages such as high sensitivity, good selectivity and rapidity, needing only expediency operation and simple equipments and have made kinetic methods an attractive analytical tool for the determination of various analytes [8,31–40]. In our continued efforts in developing various analytical methods [31–41], the mechanism of the formation of ion associate species ( $\text{I}_3\text{-CP}$ ) has been used to develop an analytical method for the determination of thallium. The factors affecting the formation of ion-associate species have been optimized. Therefore the present work reports a simple, accurate and cost effective kinetic method for the determination of thallium in environmental samples based on the quantitative

oxidation of thallium(I) to thallium(III) which liberated iodine from potassium iodide in acidic medium and liberated iodine was reacted with cetylpyridinium cation ( $\text{CP}^+$ ). The developed method was also applied for the determination of thallium in waste water and soil samples. The proposed method has also been compared with some existing methods for the determination of thallium.

## 2. Experimental

### 2.1. Reagents

All reagents used were of analytical grade and all the solutions were prepared in distilled deionized water. The stock solution of thallium was prepared by dissolving 100 mg of  $\text{TlNO}_3$  (Northern Minerals Ltd., India) in water containing 1–2 drops of concentrated  $\text{HNO}_3$  and diluted to 100 mL with water. The working standards were prepared by diluting the stock solution. A saturated solution of bromine in water was prepared daily. Potassium iodide (E. Merck, Mumbai, India)  $1 \times 10^{-2} \text{ mol L}^{-1}$ , hydrochloric acid (E. Merck, Mumbai, India)  $2 \text{ mol L}^{-1}$ , ascorbic acid (E. Merck, Mumbai, India)  $2 \times 10^{-4} \text{ mol L}^{-1}$  and cetylpyridinium chloride (CPC) (E. Merck, Mumbai, India)  $1.6 \times 10^{-5} \text{ mol L}^{-1}$  were also



**Fig. 2.** Calibration data for the determination of thallium, under the conditions: potassium iodide ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ), HCl ( $2 \text{ mol L}^{-1}$ ), ascorbic acid ( $2 \times 10^{-4} \text{ mol L}^{-1}$ ) and CPC ( $1.6 \times 10^{-5} \text{ mol L}^{-1}$ ) at  $25^\circ\text{C}$ .

**Table 1**

Spectral characteristics and other analytical figures of merit of the proposed method under the conditions: potassium iodide ( $1 \times 10^{-2}$  mol L<sup>-1</sup>), HCl (2 mol L<sup>-1</sup>), ascorbic acid ( $2 \times 10^{-4}$  mol L<sup>-1</sup>), CPC ( $1.6 \times 10^{-5}$  mol L<sup>-1</sup>) and thallium ( $0.1 \mu\text{g mL}^{-1}$ ) at pH 3 and temperature of 25 °C.

Parameters	Results
$\lambda_{\text{max}}$ (nm)	512
Range of Beer's law ( $\mu\text{g mL}^{-1}$ )	0.007–0.10
Molar absorptivity ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	$1.99 \times 10^6$
Sandell's sensitivity ( $\mu\text{g cm}^{-2}$ )	0.000133
RDS intraday precision (%)	0.61–1.20
RDS inter day precision (%)	0.46–1.30
Limit of detection ( $\mu\text{g mL}^{-1}$ )	0.0029
Limit of quantification ( $\mu\text{g mL}^{-1}$ )	0.0087

RSD Relative standard deviation.

prepared in distilled deionized water. Sodium acetate trihydrate (Merck, Mumbai, India) solution 2 mol L<sup>-1</sup> was used as acetate buffer to maintain pH of the reaction mixture. Formic acid 50% aqueous solution was prepared for use in this experiment.

## 2.2. Apparatus

A Systronics spectrophotometer 166 with 1 cm quartz cuvette was used for the absorbance and spectral measurements. A thermostatic water bath model MSW-273 (MAC Macro Scientific Works Pvt. Ltd., India) was used to control the temperature of the reaction system. A Systronics digital pH meter model 335 was used for the pH measurements.

## 2.3. General procedure

All the working solutions of the reagents were kept at 25 °C in the thermostatic water bath for 30 min to attain proper temperature. The aliquot of different standard solutions containing 0.007–0.1  $\mu\text{g mL}^{-1}$  thallium(I) was transferred into different 10 mL calibrated flasks. Saturated bromine water (0.5 mL) was added to each flask and shaken gently. Aqueous solution of formic acid (50%, 0.2 mL) was added to each flask to remove the excess of bromine from the reaction mixture. This was followed by the addition of 1.0 mL, of each, of ascorbic acid, HCl and KI solutions to each flask. The reaction mixture was shaken well until yellow color appeared due to liberation of iodine. To each reaction mixture 1.0 mL CPC solution was added while maintaining pH 3 with acetate buffer. The reaction mixture was diluted to 10 mL with the

distilled deionized water. Finally, the absorbance of the ion-associate species was measured after 1 min of dilution at 512 nm against the reagent blank. This general procedure was followed in the optimization of all reaction variables shown in the following sections.

## 3. Results and discussion

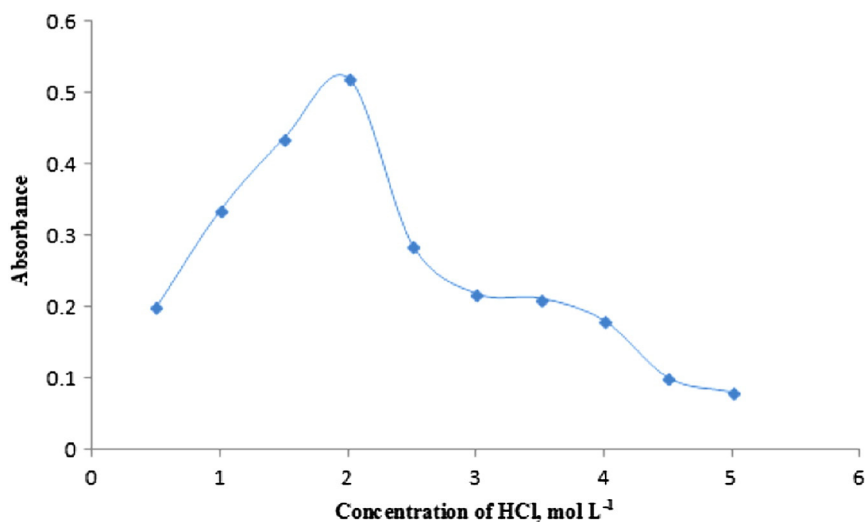
The indicator reaction used in the development of the proposed kinetic method for the determination of thallium involves three steps. The oxidation of TI(I) to TI(III) was carried out by bromine water. Then the liberated iodine due to TI(III) and potassium iodide reaction in acidic medium was subsequently reacted with iodide to form triiodide ion ( $\text{I}_3^-$ ). The tri-iodide ion was reacted with CPC which formed  $\text{I}_3\text{-CP}$  ion associate as a colored species having a  $\lambda_{\text{max}}$  at 512 nm at which the reaction was monitored.

### 3.1. Spectral characteristics and method validation

The absorption spectra of the ion associate species ( $\text{I}_3\text{-CP}$ ) obtained in the indicator reaction showed the maximum absorbance  $\lambda_{\text{max}}$  at 512 nm in aqueous medium while the reagent blank showed negligible absorbance at this wavelength as shown in Fig. 1. Beer's law is obeyed over the concentration range of 0.007–0.1  $\mu\text{g mL}^{-1}$  TI(I) shown in Fig. 2. The calculated molar absorptivity and the Sandell's sensitivity and other analytical figures of merit for the determination of thallium are given in Table 1. The detection limits ( $\text{DL} = 3.3 \text{ r/S}$ ) and quantitation limits ( $\text{QL} = 10 \text{ r/S}$ ), where S is the slope of the calibration curve and r is the standard deviation of blank ( $n=7$ ), were calculated as 0.0029 and 0.0087  $\mu\text{g mL}^{-1}$  respectively (Table 1). To check the precision of the method, three different concentrations of thallium (within the calibration range) were analyzed in five replicates in a single day i.e. intraday precision and also for five consecutive days i.e. inter-day precision. The relative standard deviations (%) of intra-day and inter-day studies given in Table 1 showed excellent precision of the proposed method.

### 3.2. Effect of acid concentration

The effects of various acids such as hydrochloric acid, sulfuric acid, perchloric acid, and acetic acid were studied in the oxidation of  $\text{I}^-$  with TI(III) under the conditions shown in Fig. 3. In the presence of  $\text{H}_2\text{SO}_4$ , the absorptivity of the ion-associate species was suppressed due to slow reaction. However in the presence of HCl, the oxidation of  $\text{I}^-$  was much faster, and the maximum absorbance of



**Fig. 3.** Effect of HCl concentration under the conditions: potassium iodide ( $1 \times 10^{-2}$  mol L<sup>-1</sup>), ascorbic acid ( $2 \times 10^{-4}$  mol L<sup>-1</sup>), CPC ( $1.6 \times 10^{-5}$  mol L<sup>-1</sup>), and thallium ( $0.1 \mu\text{g mL}^{-1}$ ) at 25 °C.

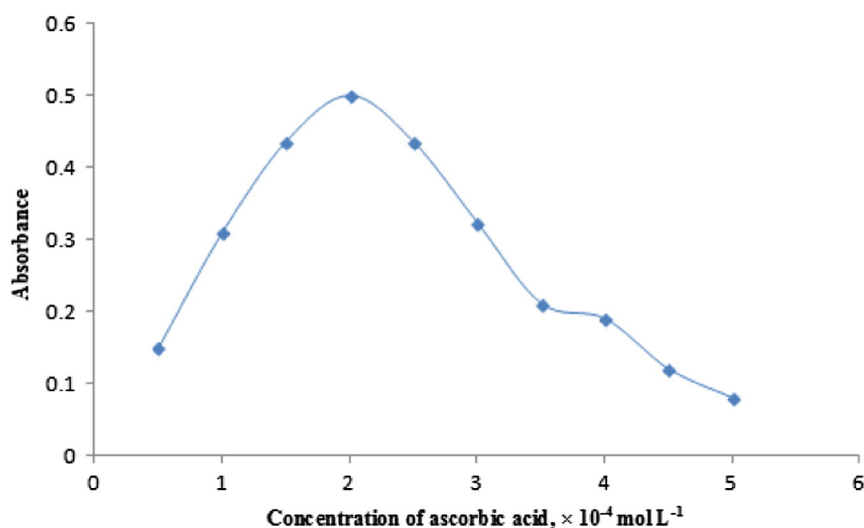


Fig. 4. Effect of ascorbic acid under the conditions: potassium iodide ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ), HCl ( $2 \text{ mol L}^{-1}$ ), CPC ( $1.6 \times 10^{-5} \text{ mol L}^{-1}$ ), and thallium ( $0.1 \mu\text{g mL}^{-1}$ ) at  $25^\circ\text{C}$ .

the ion-associate species was attained just within 1 min. Thus the effect of HCl concentration in obtaining maximum acidity range, to achieve the highest sensitivity, was investigated in the presence of  $1 \times 10^{-2} \text{ mol L}^{-1}$  KI,  $2 \times 10^{-4} \text{ mol L}^{-1}$  ascorbic acid, and  $1.6 \times 10^{-5} \text{ mol L}^{-1}$  CPC in the reaction mixture at  $25^\circ\text{C}$  and the plot of initial rate as absorbance against [HCl] is shown in Fig. 3. The highest reaction rate was found at [HCl]  $2 \text{ mol L}^{-1}$ . The results in Fig. 3 show that 1 mL of  $2 \text{ mol L}^{-1}$  hydrochloric acid gave the highest rate of reaction and thus selected for further study.

### 3.3. Effect of ascorbic acid

In the proposed indicator reaction, the ascorbic acid was used to prevent the oxidation of  $\text{I}^-$  ions by the third species i.e. foreign species present in the reaction system. Thus the effect of the concentration of the ascorbic acid on the reaction rate was investigated in the presence of  $1 \times 10^{-2} \text{ mol L}^{-1}$  KI,  $2 \text{ mol L}^{-1}$  HCl and  $1.6 \times 10^{-5} \text{ mol L}^{-1}$  CPC in the reaction mixture at  $25^\circ\text{C}$ . The plot of ascorbic acid concentration against absorbance as a measure of the initial rate is shown in Fig. 4. It was observed that  $2 \times 10^{-4} \text{ mol L}^{-1}$  ascorbic acid was required for the quantitative oxidation of  $\text{I}^-$  and thus selected for further study.

### 3.4. Effect of iodide ions and surfactants

The effect of KI concentration on the initial rate of the indicator reaction was investigated in the range of  $0.5 \times 10^{-2}$  to  $3.0 \times 10^{-2} \text{ mol L}^{-1}$ , in the presence of  $2 \times 10^{-4} \text{ mol L}^{-1}$  ascorbic acid,  $2 \text{ mol L}^{-1}$  HCl and  $1.6 \times 10^{-5} \text{ mol L}^{-1}$  CPC solution in the reaction mixture at  $25^\circ\text{C}$  and the result obtained is shown in Fig. 5. It is clear from Fig. 5 that  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  KI was required for the quantitative formation of  $\text{I}_3\text{-CP}$  ion associate species and thus  $1 \times 10^{-2} \text{ mol L}^{-1}$  was selected for KI concentration for further study.

The effects of various surfactants like sodium laurylsulfate (SLS), titronX-100, cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide (CTAB), tetradecyltri-methylammonium bromide (TDTMB) were studied towards their reaction with  $\text{I}_3^-$ . Among them, only the cationic surfactant CPC formed a stable violet colored species with  $\text{I}_3^-$ . Thus the effect of CPC concentration on the reaction was investigated in the range of  $0.2 \times 10^{-5}$  to  $2 \times 10^{-5} \text{ mol L}^{-1}$  in the presence of  $1 \times 10^{-2} \text{ mol L}^{-1}$  KI,  $2 \text{ mol L}^{-1}$  HCl, and  $2 \times 10^{-4}$  ascorbic acid in the reaction mixture at  $25^\circ\text{C}$ . A plot of the initial rate in terms of absorbance against CPC concentration is shown in Fig. 6. The optimum concentration of CPC was found to be  $1.6 \times 10^{-5} \text{ mol L}^{-1}$ . Beyond this concentration the absorptivity

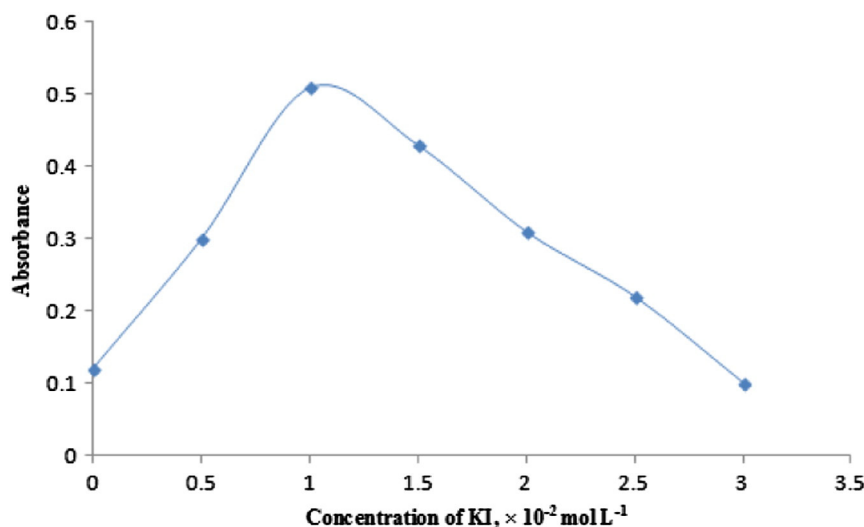
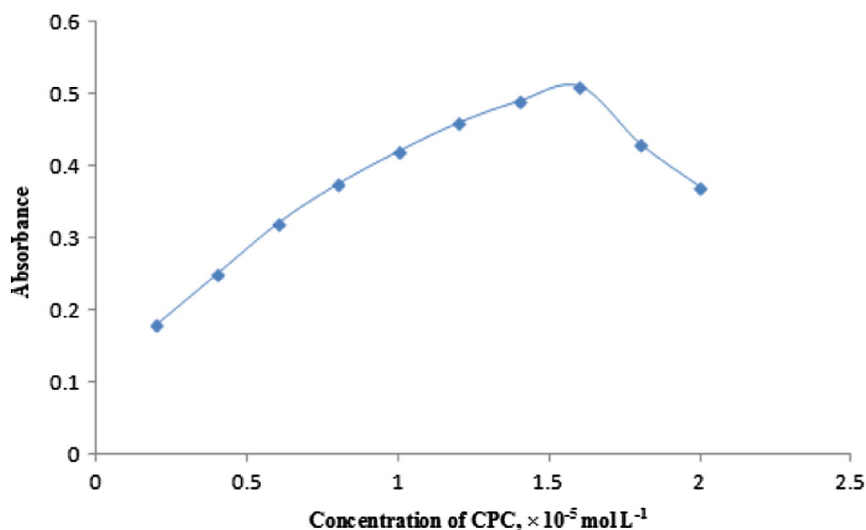


Fig. 5. Effect of potassium iodide under the conditions: HCl ( $2 \text{ mol L}^{-1}$ ), ascorbic acid ( $2 \times 10^{-4} \text{ mol L}^{-1}$ ), CPC ( $1.6 \times 10^{-5} \text{ mol L}^{-1}$ ), and thallium ( $0.1 \mu\text{g mL}^{-1}$ ) at  $25^\circ\text{C}$ .



**Fig. 6.** Effect of CPC on the initial rate of the reaction under the conditions: potassium iodide ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ), HCl ( $2 \text{ mol L}^{-1}$ ), ascorbic acid ( $2 \times 10^{-4} \text{ mol L}^{-1}$ ), and thallium ( $1 \mu\text{g mL}^{-1}$ ) at  $25^\circ\text{C}$ .

i.e. the initial rate of formation of the ion associate species  $\text{I}_3\text{-CP}$  was found to decrease due to their co-precipitation. This study led to the optimization of CPC as  $1.6 \times 10^{-5} \text{ mol L}^{-1}$ .

### 3.5. Effect of pH and temperature

The effect of pH on the formation of ion-associate species ( $\text{I}_3\text{-CP}$ ) was studied up to pH 5 using acetate buffer and the reaction rate data obtained is plotted against pH as shown in Fig. 7. In the acidic solution at  $\text{pH} < 2.0$ , the reaction rate was found to be slow. However above pH 2.0, the reaction became dramatically fast and the maximum absorptivity of the  $\text{I}_3\text{-CP}$  species was obtained within 1 min. The highest absorbance i.e. initial rate due to the formation of  $\text{I}_3\text{-CP}$  species was found at pH 3 as shown in Fig. 7 and thus pH 3 was selected for further study.

The effects of temperature on the formation of  $\text{I}_3\text{-CP}$  ion associate species were studied in the range of  $15\text{--}40^\circ\text{C}$ . Beyond  $40^\circ\text{C}$ , some of the  $\text{I}_2$  formed was lost due to evaporation which was observed as the decrease in the absorptivity of the  $\text{I}_3\text{-CP}$  ion associate (Fig. 8). As shown in Fig. 8, above  $30^\circ\text{C}$ , the absorbance of the ion-associate species was decreased due to their thermal instability. It was also found that the

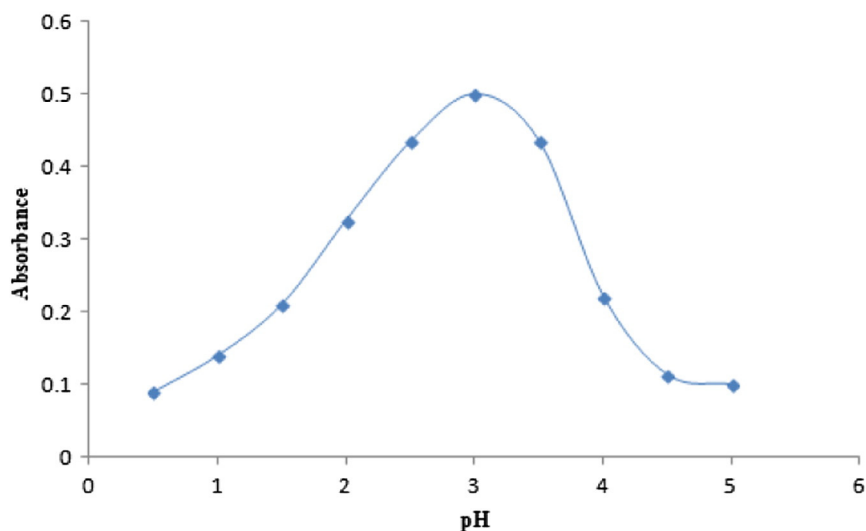
absorbance of the ion-associate species was stable for 12 h at  $25^\circ\text{C}$ . Hence the reaction was studied at  $25^\circ\text{C}$  for the optimization of all the reaction variables.

### 3.6. Determination of thallium

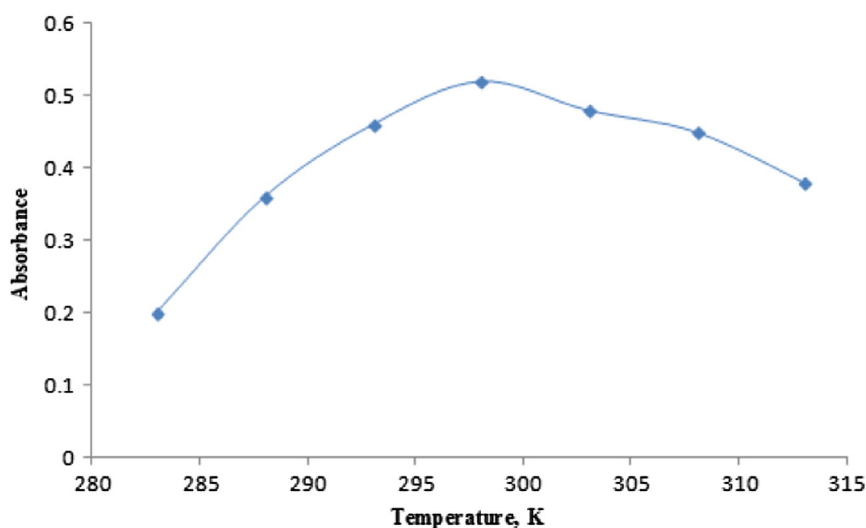
Following the general procedure reported in Section 2.3, the linear regression equation was obtained from the calibration curve by plotting the decrease in the absorbance of violet colored species against concentration of the thallium. For the determination of thallium in natural water and soil samples, 5 mL of thallium free water or extract from soil samples was taken and known amount of thallium was added and analyzed by following the general procedure. The recoveries of thallium have been tabulated in Table 2.

### 3.7. Effect of diverse ions

To evaluate the analytical applicability of the developed method, it was applied to determination of thallium in environmental samples in the presence of various other species. The influence of various ions,



**Fig. 7.** Effect of pH under the conditions: potassium iodide ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ), HCl ( $2 \text{ mol L}^{-1}$ ), ascorbic acid ( $2 \times 10^{-4} \text{ mol L}^{-1}$ ), CPC ( $1.6 \times 10^{-5} \text{ mol L}^{-1}$ ), and thallium ( $0.1 \mu\text{g mL}^{-1}$ ) at  $25^\circ\text{C}$ .



**Fig. 8.** Effect of temperature under the conditions: potassium iodide ( $1 \times 10^{-2}$  mol L $^{-1}$ ), HCl (2 mol L $^{-1}$ ), ascorbic acid ( $2 \times 10^{-4}$  mol L $^{-1}$ ), CPC ( $1.6 \times 10^{-5}$  mol L $^{-1}$ ), and thallium ( $0.1 \mu\text{g mL}^{-1}$ ).

several organic and inorganic pollutants and pesticides was examined under the optimum conditions following the general procedure of the method (cf. Section 2.3). The effect of possible interferences on the determination of  $0.01 \mu\text{g mL}^{-1}$  of thallium concentration was studied. A variation of  $\pm 2\%$  in the recovery of  $0.01 \mu\text{g mL}^{-1}$  thallium was considered tolerable. The results obtained on the tolerance limits of the foreign species are given in Table 3.

#### 4. Application

##### 4.1. Determination of thallium in waste water sample

The developed method was successfully applied for the determination of thallium in waste water samples that were collected from a nearby steel plant situated at Bhilai, Chhattisgarh (India) on 05 August 2013. The sample was filtered through Whatman filter paper no. 40 and the filter paper was washed repeatedly with deionized double distilled water collecting filtrate and noting the dilution factor. 5 mL of the aliquot of the filtrate was analyzed, by proposed procedure, diluting the sample aliquot by 100–500 times and multiplying by dilution factor. The concentration of thallium in water samples was calculated using linear regression equation. The results obtained are shown in Table 4.

##### 4.2. Determination of thallium in soil sample

The soil samples were also collected from a nearby steel industry situated at Bhilai, Chhattisgarh (India) on 5 August 2013. The samples were homogenized and sieved to  $5 \mu\text{m}$  size. 5 mg of the homogenized samples was digested with acid mixture (10 mL HCl:HNO $_3$  3:1; v/v)

**Table 2**

Determination of thallium in natural water samples and soil samples under the conditions: potassium iodide ( $1 \times 10^{-2}$  mol L $^{-1}$ ), HCl (2 mol L $^{-1}$ ), ascorbic acid ( $2 \times 10^{-4}$  mol L $^{-1}$ ), CPC ( $1.6 \times 10^{-5}$  mol L $^{-1}$ ) at pH 3 and temperature of 25 °C.

Samples	Tl added ( $\mu\text{g}$ )	Tl found ( $\mu\text{g}$ ) <sup>c</sup>	Recovery (%)	RSD (%)
<sup>a</sup> Water (a)	20.0	18.6	93.00	0.28
(b)	40.0	37.9	94.75	0.22
(c)	60.0	59.5	99.10	0.16
<sup>b</sup> Soil (a)	20.0	19.9	99.50	0.28
(b)	40.0	39.5	98.75	0.32
(c)	60.0	59.5	99.10	0.16

<sup>a</sup> Amount of water samples: 50 mL.

<sup>b</sup> Amount of soil sample: 25 g.

<sup>c</sup> Mean of three replicate analyses.

and evaporated under vacuum to 2 mL. Finally, the contents were diluted to 10 mL with water in a volumetric flask. The 5 mL aliquot was analyzed for thallium, by the developed method, diluting the sample aliquot by 100–500 times and multiplying by dilution factor. The concentration of thallium in soil was calculated using linear regression equation and the results obtained are shown in Table 4.

#### 5. Conclusion

The proposed method was also compared with other existing spectrophotometric methods shown in Table 5. The proposed method

**Table 3**

Effect of foreign species on the determination of thallium under the reaction conditions: potassium iodide ( $1 \times 10^{-2}$  mol L $^{-1}$ ), HCl (2 mol L $^{-1}$ ), ascorbic acid ( $2 \times 10^{-4}$  mol L $^{-1}$ ), CPC ( $1.6 \times 10^{-5}$  mol L $^{-1}$ ) and thallium ( $0.01 \mu\text{g mL}^{-1}$ ) at pH 3 and temperature of 25 °C.

Foreign species	Tolerance limit (ppm) <sup>a</sup>
SO $_4^{2-}$ , CO $_3^{2-}$ , CH $_3$ COO $^-$ , benzene, acetone	1000
Se $^{4+}$ , Fe $^{2+}$ , urea, thiourea, Sn $^{2+}$ , Fe $^{3+}$	600
Aniline, Al $^{3+}$	350
Cr $^{3+}$ , Cd $^{2+}$ , Mg $^{2+}$ , Na $^+$ , K $^+$ , Mn $^{2+}$ , NH $_4^+$ , NO $_3^-$ , F $^-$	200
Zn $^{2+}$ <sup>b</sup>	100
Dithiocarbamate pesticides, Hg $^{2+}$	40
Br $^-$ , I $^-$ <sup>c</sup>	20
Phenol	10
Mn $^{7+}$ , PO $_4^{3-}$	10

<sup>a</sup> Causing ( $\pm$ )2% variation.

<sup>b</sup> Masked with 0.1% EDTA solution.

<sup>c</sup> Removed by addition of nitric acid and boiling the solution.

**Table 4**

Application of the method for the determination of thallium in real samples under the reaction conditions given in Table 2.

Samples	Originally Tl found ( $\mu\text{g}$ )	Tl added ( $\mu\text{g}$ )	Total Tl found ( $\mu\text{g}$ )	Recovery <sup>c</sup> (%)
<i>Waste water samples<sup>a</sup></i>				
(A)	2.23	10.0	11.79	96.40
(B)	2.03	10.0	11.50	95.59
(C)	2.39	10.0	11.29	91.12
<i>Soil samples<sup>b</sup></i>				
(A)	1.23	10.0	11.10	98.84
(B)	1.02	10.0	10.99	99.72

<sup>a</sup> Amount of waste water sample: 5 mL.

<sup>b</sup> Amount of soil samples: 5 mg.

<sup>c</sup> Mean of three replicate analyses.

**Table 5**  
Comparison of the developed method with other spectrophotometric methods for the determination of thallium where Beer's law range is given in  $\mu\text{g mL}^{-1}$ .

Reagents	$\lambda_{\text{max}}$ (nm)	Beer's law range (detection limit)	Remarks [Ref]
Starch iodide method	575	0.04–0.4	Less sensitive [42]
Leuco crystal violet	590	0.08–0.8	Less sensitive and use of costly reagents [43]
Rhodamine B	560	0.4–2.8	Less stability of the color system [44]
Brilliant green	640	0.2–2.0	$\text{Sn}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Fe}^{3+}$ , $\text{NO}_3^-$ , citrate interfere [45]
Rhodamine B hydrazide + SDS	565	0.005–6.4	Extractive procedure required more solvents [46]
Potassium iodide + CPC	512	0.007–0.1 (0.0029 $\mu\text{g mL}^{-1}$ )	Simple, fast, sensitive, more selective and less interference from cations and anions [present method]

SDS: Sodium dodecyl sulfate.

was found to be more sensitive, simple and selective as compared to other spectrophotometric methods for determination of thallium shown in Table 5 and has shown to have the lowest limit of detection. The less time consumption i.e. rapidity, stability and easy availability of the reagent and free from various interfering species is one advantage of the developed method. The present method was applied for the determination of thallium in industrial waste water and soil samples.

## References

- C. Kokkinos, A. Economou, Tin film sensor with on-chip three electrode configuration for voltammetric determination of trace Tl(I) in strong acidic media, *Talanta* 125 (2014) 215–220.
- I. Algul, D. Kara, Determination and chemometric evaluation of total aflatoxin, aflatoxin B1, ochratoxin A and heavy metals content in corn flours from Turkey, *Food Chem.* 157 (2014) 70–76.
- J. Kucera, M.J. Vobecky, Low level determination of thallium in biological and environmental reference materials by RNAA using several counting methods, *J. Radioanal. Nucl. Chem.* 217 (1997) 131–137.
- R.S. Hoffman, Thallium poisoning during pregnancy: A case report and comprehensive literature review, *J. Toxicol. Clin. Toxicol.* 38 (2000) 767–775.
- B.K. Ostrega, M. Sadowska, K. Piotrowska, M. Wojda, Thallium(III) determination in the Baltic sea water samples by ICPMS after preconcentration on SGXC18 modified with DDTc, *Talanta* 112 (2013) 73–79.
- C.H. Lan, T.S. Lin, Acute toxicity of trivalent thallium compounds to *Daphnia magna*, *Ecotoxicol. Environ. Saf.* 61 (2005) 432–435.
- A.S. Amin, A.M. El-Sharjawi, M.A. Kassem, Determination of thallium at ultra trace levels in water and biological samples using solid phase spectrophotometry, *Spectrochim. Acta A* 110 (2013) 262–268.
- M. Tabatabaee, M.R. Shishehore, H. Bagheri, Z. Ebrahimifard, Thallium determination using catalytic redox reaction between methylene blue and ascorbic acid, *Int. J. Environ. Sci. Technol.* 7 (2010) 801–806.
- A.K. Das, M. Dutta, M.L. Cervera, M. Guardia, Determination of thallium in water samples, *Microchem. J.* 86 (2007) 2–8.
- Z. Lukaszewski, W. Zembrzanski, A. Piela, Direct determination of ultratrace of thallium in water by flow-injection–differential-pulse anodic stripping voltammetry, *Anal. Chim. Acta.* 318 (1996) 159–165.
- A. Tremel, P. Masson, H. Garraud, O.F. Donald, D. Baize, M. Mench, Thallium in French agrosystems-II. Concentration of thallium in field-grown rape and some other plant species, *Environ. Pollut.* 97 (1997) 161–168.
- X.J. Chang, Q.Q. Su, X.J. Wei, B.T. Wang, Determination of thallium in water samples, *Microchim. Acta* 137 (2001) 209–213.
- B. Rezaei, S. Meghdadi, N. Majidi, Preconcentration of thallium(III) with 2,6-bis(N-phenyl carbamoyl)pyridine on microcrystalline naphthalene prior to its trace determination in human serum spectrophotometrically, *Spectrochim. Acta A* 67 (2007) 92–97.
- K.S. Abou-El-Sherbini, G.A.E. Mostafa, M.M. Hassanien, A new selective chromogenic reagent for the spectrophotometric determination of thallium(I) and (III) and its separation using flotation and the solid-phase extraction on polyurethane foam, *Anal. Sci.* 19 (2003) 1269–1275.
- M.S. Hosseini, Y. Naseri, Determination of thallium(I) by flotation–spectrophotometric method using iodide and rhodamine B, *Anal. Sci.* 19 (2003) 1505–1508.
- H.R. Oliveira, M.F. Mesko, M.G.R. Vale, C.A.P. Silveira, R.S. Picoloto, E.M. Becker, Development of methods for the determination of cadmium and thallium in oil shale by-products with graphite furnace atomic absorption spectrometry using direct analysis, *Microchem. J.* 116 (2014) 55–61.
- M. Chamsaz, M.H. Arbab-Zavar, A. Darroudi, T. Salehi, Preconcentration of thallium(I) by single drop microextraction with electrothermal atomic absorption spectroscopy detection using dicyclohexano-18-crown-6 as extractant system, *J. Hazard. Mater.* 167 (2009) 597–601.
- R. Shekhar, K. Madhavi, N.N. Meeravali, S.J. Kumar, Determination of thallium at trace levels by electrolyte cathode discharge atomic emission spectrometry with improved sensitivity, *Anal. Methods* 6 (2014) 732–740.
- K. Takeda, S. Ikushima, J. Okuzaki, S. Watanabe, T. Fujimoto, T. Nakahara, Inductively coupled plasma mass spectrometric determination of ultra-trace elements in electronic-grade water and chemicals using dulcitol, *Anal. Chim. Acta.* 426 (2001) 105–109.
- S.F. Wolf, D.L. Unger, J.M. Friedrich, Determination of cosmochemically volatile trace elements in chondritic meteorites by inductively coupled plasma mass spectrometry, *Anal. Chim. Acta.* 528 (2005) 121–128.
- A.F. Silva, D.L.G. Borges, B. Welz, M.G.R. Vale, M.M. Silva, A. Klassen, U. Heitman, Method development for the determination of thallium in coal using solid sampling graphite furnace atomic absorption spectrometry with continuum source, high-resolution monochromator and CCD array detector, *Spectrochim. Acta B* 59 (2004) 841–850.
- D. Mihajlovic, T. Stafilov, Determination of thallium in geological samples by X-ray fluorescence spectrometry, *X-Ray Spectrom.* 27 (1998) 397–400.
- P.S. Patil, V.M. Shinde, Extraction and spectrophotometric determination of thallium(III) with thioethoxytrifluoroacetone, *Talanta* 24 (1977) 696–697.
- L.B. Escudero, R.G. Wuilloud, R.A. Olsina, Sensitive determination of thallium species in drinking and natural water by ionic liquid-assisted ion-pairing liquid–liquid microextraction and inductively coupled plasma mass spectrometry, *J. Hazard. Mater.* 244–245 (2013) 380–386.
- Y. Li, Y. Peng, Y. Ma, Q. Hu, G. Yang, Solid phase extraction and flame atomic absorption spectrometry for the determination of trace thallium, *Asian J. Chem.* 21 (2009) 4593–4598.
- E. Shams, M. Yekehtaz, Determination of trace amounts of thallium by adsorptive cathodic stripping voltammetry with xylenol orange, *Anal. Sci.* 18 (2002) 993–996.
- M.M. Hassanien, K.H.S. Abou-El-Sherbini, G.A.E. Mostafa, A novel tetrachlorothallate(III)-PVC membrane sensor for the potentiometric determination of thallium(III), *Talanta* 59 (2003) 383–392.
- H. Dong, H. Zheng, L. Lin, B. Ye, Determination of thallium and cadmium on a chemically modified electrode with Langmuir Blodgett film of p-allylcalixarene, *Sensors Actuators B* 115 (2006) 303–308.
- G.J. Lee, H.M. Lee, Y.R. Uhm, M.K. Lee, C.K. Rhee, Square-wave voltammetric determination of thallium using surface modified thick-film graphite electrode with Bi nanopowder, *Electrochem. Commun.* 10 (2008) 1920–1923.
- K. Urbánková, L. Sommer, The microdetermination of thallium by ICP-AES after previous preconcentration on modified silica. Comparison with integrated-platform graphite atomic absorption spectrometry, *Microchim. Acta* 162 (2008) 127–132.
- G.P. Pandey, A.K. Singh, L. Deshmukh, S. Prasad, L.J. Paliwal, A. Asthana, S.B. Mathew, A novel and sensitive kinetic method for the determination of malathion using chromogenic reagent, *Microchem. J.* 113 (2014) 83–89.
- R.M. Naik, S. Prasad, B. Kumar, S.B.S. Yadav, A. Asthana, M. Yoshida, Ligand substitution kinetic assay of antitubercular drug isoniazid in pure and pharmaceutical formulations, *Microchem. J.* 111 (2013) 108–115.
- R.M. Naik, S. Prasad, B. Kumar, V. Chand, Kinetic assay of D-penicillamine in pure and pharmaceutical formulations based on ligand substitution reaction, *Microchem. J.* 111 (2013) 97–102.
- R.M. Naik, A. Agarwal, S. Prasad, Determination of trace amounts of mercury(II) in water samples using a novel kinetic catalytic ligand substitution reaction of hexacyanoruthenate(II), *Spectrochim. Acta A* 74 (2009) 887–891.
- V. Chand, S. Prasad, Trace determination and chemical speciation of selenium in environmental water samples using catalytic kinetic spectrophotometric method, *J. Hazard. Mater.* 165 (2009) 780–788.
- S. Prasad, R.M. Naik, A. Srivastava, Application of ruthenium catalyzed oxidation of [tris(2-aminoethyl)amine] in trace determination of ruthenium in environmental water samples, *Spectrochim. Acta A* 70 (2008) 958–965.
- S. Prasad, Kinetic determination of organosulphur ligands by inhibition: Trace determination of cysteine and maleonitriledithiolate (MNMT), *Microchem. J.* 85 (2007) 214–221.
- S. Prasad, Kinetic method for determination of nanogram amounts of copper(II) by its catalytic effect on hexacyanoferrate(III)–citric acid indicator reaction, *Anal. Chim. Acta.* 540 (2005) 173–180.
- R. Prasad, R. Kumar, S. Prasad, A fluorescence quenching-based sensor using new metallo-tetraazaporphyrin dye as a recognition element for aniline assay in aqueous solutions, *Anal. Chim. Acta.* 646 (2009) 97–103.
- S. Prasad, T. Halafih, Development and validation of catalytic kinetic spectrophotometric method for determination of copper(II), *Microchim. Acta* 142 (2003) 237–244.
- S. Thatai, P. Khurana, S. Prasad, D. Kumar, A new way in nanosensors: gold nanorods for sensing of Fe(III) ions in aqueous media, *Microchem. J.* 113 (2014) 77–82.

- [42] A. Asthana, A. Pillai, V.K. Gupta, Determination of thallium by starch iodide method and its applications in environmental samples, *J. Chin. Chem. Soc.* 50 (2003) 399–402.
- [43] S.K. Chatterjee, A.K. Pillai, V.K. Gupta, Sub ppm determination of thallium(I) in biological and complex materials, *J. Indian Chem. Soc.* 79 (2002) 261–263.
- [44] P. Nagaraja, N.G.S. Al-Tayar, A. Shivakumar, A.K. Shresta, A.K. Gowda, Spectrophotometric determination of the trace amount of thallium in water and urine samples by novel oxidative coupling reaction, *E-J. Chem.* 6 (2009) 1153–1163.
- [45] M.K. Deb, P.K. Agnihotri, M. Thakur, R.K. Mishra, Fractionation and spectrophotometric determination of thallium with N, N'-diphenylbenzamidine, brilliant green and cetylpyridinium chloride, *Chem. Speciat. Bioavailab.* 10 (1998) 53–60.
- [46] A.S. Parakudyil, A.K. Pillai, S.B. Mathew, Sensitive spectrophotometric determination of thallium(I) using rhodamine B hydrazide in micellar medium, *Anal. Methods* 3 (2011) 1546–1551.