

Spectrophotometric Determination of the Trace Amount of Thallium in Water and Urine Samples by Novel Oxidative Coupling Reaction

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Abstract: A novel, simple, rapid, sensitive and selective method has been proposed for the trace determination of thallium by spectrophotometric detection. This method is based on the oxidation of MBTH (3-methyl-2-benzothiazolinone hydrazone hydrochloride) by thallium(III) to form diazonium cation, which couples with IPH (Imipramine hydrochloride) in phosphoric acid medium at room temperature giving a blue colored species having a maximum absorption at 635 nm. The reagents and manifold variables influences on the sensitivity were investigated and the optimum reaction conditions have been established. The calibration curve was found to be linear over the range 0.1-5 $\mu\text{g mL}^{-1}$ with the molar absorptivity and Sandell's sensitivity of $2.9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $0.0071 \mu\text{g cm}^{-2}$ respectively. The tolerance limit of the method towards various ions usually associated with thallium has been detected. The relative standard deviation for five replicate determination of $2 \mu\text{g mL}^{-1}$ thallium was 0.47%. The method has been successfully applied for the determination of thallium(III) and thallium(I) in synthetic, standard reference materials, water and urine samples with satisfactory results. The performance of the proposed method was evaluated in terms of student's t-test and variance ratio F-test, to find out the significance of proposed method over the reported methods.

Keywords: Spectrophotometry, MBTH, Imipramine hydrochloride, Thallium, Water and Urine samples.

Introduction

Thallium is introduced into the environment by the combustion of coal and as a waste product from the production of zinc, lead and cadmium. The main source of thallium pollution at present is cement production. Despite high chronic and cumulative toxic effects

compared with that of lead, mercury and cadmium¹, its compounds are commonly used in medicines for dermatological disorders, dye pigments, photo chromic glasses, fungicides, insecticides and rodenticides, it is also included as a component of corrosion-resistance alloys^{2,3}. Thallium is a well-known neurotoxicant⁴ and has become a very important pollutant of the environment and was included in the list of 129 so-called “priority pollutants” by the US Environmental Protection Agency. It is regarded as one of the most toxic of the heavy metals, causing both chronic and acute poisoning⁵. Both oxidation states Tl(I) and Tl(III) exhibit biological and toxic activation⁶, but Tl(I) is more toxic and reactive form of thallium(III). It has been found that Tl(I) can be replaced with potassium ions in the activation of enzymes⁷. Thallium and its compounds are extremely toxic; skin-contact, ingestion and inhalation are all dangerous. Thallium causes gastrointestinal irritation and disorders of the nervous system after exposure for relatively short times. In the long term, this has the potential to cause effects such as changes in blood chemistry, damage to liver, kidney, intestinal, testicular tissue, and hair loss⁸, also it causes abdominal pain, diarrhea and tingling in the four extremities⁹. The highest concentration of thallium after poisoning is in the kidney and urine¹⁰ and can be identified in urine within a few hours¹¹. The increasing environmental and biological importance of thallium and its acute toxicity have made it necessary to develop sensitive and selective methods to determine its presence in diverse samples, in trace amounts. Various analytical techniques developed so far as cathodic and anodic stripping voltammetry (ASV)¹²⁻¹⁶, inductively coupled plasma mass spectrometry (ICP-MS)¹⁷, atomic absorption spectrometry (AAS)¹⁸⁻²⁰, thermal neutron activation analysis²¹ and electrothermal atomic absorption spectrometry²²⁻²⁴ have been used for trace determination of thallium(III). But its determination in real sample is complicated by interferences from coexisting metal ions (50% in the case of Cd)²⁵ and organic residues in the sample matrixes²⁶. This necessitates pretreatment of the sample^{27, 28}. Some of these methods have disadvantages in terms of cost and instruments used in routine analysis.

Spectrophotometric methods have been used for the determination of thallium occurring in many samples. Several reagents such as brilliant green²⁹, alizarin violet³⁰, pyronin G³¹, 9,10-phenanthraquinone monoethylthiosemicarbazone³², methemebrazine hydrochloride³³, *N,N*-diphenyl benzaamide³⁴, iodide and rhodamine B³⁵ and 4-(4-*N,N*-Dimethyl amino phenyl) urazol³⁶, have been employed for the spectrophotometric determination of thallium. Some of these methods are unsatisfactory and impractical for routine analysis because of either poor selectivity or need preconcentration and prior extraction. Some of these analytical methods use reagents or generate chemical wastes, which are more toxic than thallium. As a consequence, the analytical methods with high performance but which are not environmentally friendly are not acceptable. Hence, there is a great need to develop methods which are less harmful to human and to the environment as one of the basic principles of Green Chemistry³⁷. The availability of the spectrophotometric apparatus and the simplicity of the analytical procedures make the technique very attractive for a wide range of applications. This case has encouraged the investigators to develop a simple, rapid, sensitive, selective and reliable spectrophotometric method for the determination of thallium (III) in various samples. The recommended method is based on the oxidation of MBTH by thallium(III) to form diazonium cation, which gets couple with imipramine hydrochloride in phosphoric acid medium to give a blue colored species. The method has been successfully applied in the determination of thallium in synthetic, water and human urine samples. The proposed method is sensitive, selective, inexpensive, rapid, and free from various interfering ions and doesn't need extraction and close control of pH or heating step.

Experimental

A JASCO Model UVIDEK-610 UV/VIS spectrophotometer with 1cm-matched cells was used for all the spectral measurements. A pH-meter, EQUIP-TRONICS Model EQ-614 was employed for measuring pH values.

Reagents and solutions

All the chemicals used were of analytical reagent grade or the highest purity available. Doubly distilled water was used throughout the experiments for dilution of the reagents and samples. Glass vessels were cleaned by soaking in acidified solution of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$, followed by washing with concentrated HNO_3 and rinsing several times with distilled water.

Standard thallium(III) solution ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving 0.112 g of Tl_2O_3 (Fluka, Switzerland) in 50 mL of 2 N sulphuric acid and kept aside for over night, followed by diluting to 100 mL in a calibrated flask with distilled water. The stock solution was standardized titrimetrically³⁸, and solutions of lower concentrations were prepared by diluting the standard solution as and whenever required.

A stock solution of standard thallium(I) solution ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving 0.117 g of TlCl (Fluka, Switzerland) in 100 mL of distilled water, and solutions of lower concentrations were prepared by diluting the stock solution as and whenever required.

A 0.01% (w/v) aqueous solution of 3-methyl-2-benzothiazolinonehydrazone hydrochloride (MBTH) was freshly prepared by dissolving the requisite amount of MBTH (Merck, Germany) in distilled water and stored in dark colored bottle in a refrigerator maintaining temperature of 0-10 °C. This solution thus stored was stable for 10 days.

A 0.2%(w/v) solution of imipramine hydrochloride (IPH) was prepared by dissolving the requisite amount of IPH (BDH, England) in water and stored in dark colored bottle in refrigerator maintaining temperature between 0-10 °C, the solution thus stored was stable for one month.

A 5 M Orthophosphoric acid was prepared by suitable dilution of concentrated orthophosphoric acid (Ranbaxy, India) in doubly distilled water. Solutions containing suitable concentrations of potentially interfering ions were prepared in doubly distilled water or appropriate solvent, whenever required.

All the other solutions used through the experiments like sulphuric acid, bromine water, sulphamic acid and sodium fluoride were prepared by dissolving requisite amounts of the reagents in doubly distilled water.

Recommended procedure

Determination of thallium(III)

An aliquot of a sample solution containing 1-50 μg of thallium(III) was transferred into a series of 10 mL calibrated flasks, to which 1 mL of 0.01% of MBTH, 1 mL of 0.2% IPH and 1 mL of 3 M orthophosphoric acid were added. Then diluted to the mark with distilled water and mixed thoroughly. The blue color, which developed within 10 minutes at room temperature, was stable for 36 hours. The absorbance was measured at 635 nm against the corresponding reagent blank, and the calibration graph was constructed.

Determination of thallium(I)

An aliquot of a sample solution containing 1-50 μg of thallium(I) was transferred into a series of 10 mL calibrated flasks, 0.1 mL (1%) bromine water was added to oxidize Thallium(I) to thallium(III) and heated to near dryness. Then 0.2 mL phenol was added to remove any excess of bromine water and the above procedure for the determination of thallium(III) was followed.

Determination of thallium(I) and thallium(III) in the mixture

For the determination of thallium(I) in a composite mixture containing both oxidation states of thallium, samples containing equal quantity of spiked thallium(I) and thallium(III) was taken in two 10 mL standard flasks. Recommended procedure for the determination of thallium(III) carried out for one standard flask, and thallium(III) was determined from Beer's law graph. For the second standard flask, the procedure for the determination of thallium(I) was carried out. So thallium(I) was determined by the difference in obtained in the oxidized [representing both Tl(I) and Tl(III)] and the unoxidised [representing Tl(III) samples].

Determination of thallium in water samples

Determination of thallium was carried out in environmental samples that were previously tested negative for thallium. Then river, lake and tap water samples spiked with thallium at a concentration within Beer's law limit were applied for the analysis. The spectrophotometric determination for the thallium analysis was carried out as per the procedure outlined above.

Determination of thallium in urine samples

Thallium may enter human body either deliberately as a component of drug or through contamination in water or food *etc.* Thus, its quantification in biological fluid is anticipated. A known amount of thallium(III) was added to 30 mL of healthy human urine that was previously tested negative for thallium, which was taken in a 100 mL micro-Kjeldahl flask, a glass bead and 5 mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed and cooled. Then 1 mL of concentrated sulphuric acid was added carefully followed by the addition of 1 mL of 70% perchloric acid and heating was continued to dense white fumes, repeating nitric acid addition if necessary. Further, heating was carried out for at least 30 min, followed by cooling. The contents of the flask were filtered and diluted up to the mark with distilled water in 100 mL calibrated flask. A suitable aliquot of urine sample was taken and analyzed by using the procedure outlined earlier.

Determination of thallium in synthetic mixtures

Certified samples of thallium were not available, therefore, composition of spiked synthetic mixtures of common metal ions that usually accompany thallium in natural samples were prepared in concentrations below the tolerance limit¹⁵, and analyzed directly by proposed method without any prior separation of thallium.

Results and Discussion

MBTH gets oxidized by thallium(III) in an aqueous medium at room temperature to form diazonium cation, which instantaneously gets coupled with IPH in orthophosphoric acid medium, resulting in the formation of a blue colored species.

Spectral characteristics

In proposed method a blue colored product was formed and to have minimum interference, it was necessary to found out the optimum wavelength for thallium determination. This wavelength must be specific for the quantitative and specific monitoring of Thallium-MBTH-IPH. The wavelength of maximum absorbance was identified by scanning the blue colored product over the range 400-750 nm with different concentrations of thallium(III). The optimum wavelength for getting the best results was found to be 635 nm and the reagent blanks had negligible absorption at this wavelength. The absorption spectra of the product are shown in Figure 1.

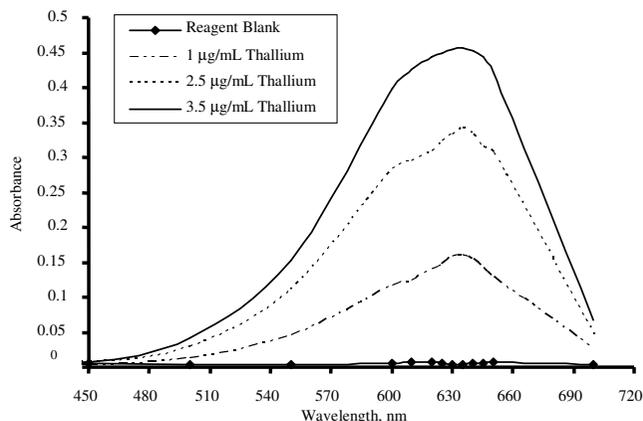


Figure 1. Absorption spectra of thallium(III) with MBTH & IPH.

Optimum reagents concentrations

The effect of MBTH, IPH were studied by using a fixed thallium(III) concentration in 10 mL standard flask. It was found that 0.01% MBTH in the range of 0.1-2 mL was necessary to get the blue color. Hence, 0.5 mL of 0.01% MBTH was selected to get the maximum color intensity and used for further studies. Also, a 0.2% of IPH in the range of 0.1-2 mL was necessary to get the blue color. Therefore, 1 mL of 0.2% IPH was selected to get the maximum color intensity. Excellent results were obtained using distilled water for dilution of the color product compare to the other solvents.

Effect of different acids

The effect of different acids on the stability and sensitivity of the colored species was studied with the optimum conditions. Various acids like hydrochloric acid, orthophosphoric acid, sulphuric acid and acetic acid were used at their optimum concentrations. The calibration graphs were plotted for the results obtained for the determination of different concentrations of thallium(III) within Beer's law range as shown in Figure 2, which indicated that hydrochloric acid has given color instantaneously with good sensitivity but blank color was increasing, whereas acetic acid gave less absorbance and had less sensitivity. Although sulphuric acid has given high absorbance but selectivity was less. Orthophosphoric acid showed highest sensitivity, selectivity, linearity and stability of blue colored product and the blank remained colorless. Hence, 1 mL of 5 M orthophosphoric acid was chosen as the optimal acidic medium for the determination of thallium(III) in total volume of 10 mL to give maximum color intensity as well as stability of the colored product.

Order of addition of the reactants

The effect of order of addition of the reactants was studied by using different orders of the optimized amounts of reactants following the proposed method. The results obtained have showed that, the order of reactants addition have no effect on the absorbance values as shown in Table 1, but for maintaining the uniformity of the order of reactants addition, series No.2 of Table 1 was followed throughout course of the determination of thallium(III).

Performance of the system for a thallium determination

In order to test the applicability of the proposed analytical technique, the absorbance of a series of solution, containing varying amounts of thallium within the Beer's law limit, were recorded against the corresponding reagent blank at 635 nm. The beer's law limits, molar

absorptivity, Sandell's sensitivity and optimum range by spectrophotometric determination are summarized in the Table 2. The slope, intercept and relative standard deviation were evaluated, which are included in the same table.

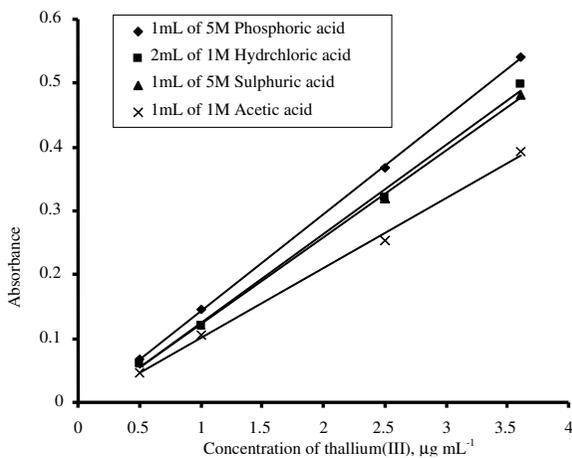


Figure 2. Effect of different acids.

Table 1. Effect of order of reactants addition.

S No.	Order of addition ^a	Absorbance for 2 $\mu\text{g mL}^{-1}$
1	A + B + C + D	0.398
2	A + B + D + C	0.399
3	A + D + C + B	0.397
4	B + C + A + D	0.397
5	B + D + A + C	0.397
6	B + D + C + A	0.397

^a A = MBTH, B = IPH, C = Thallium(III), D = H_3PO_4

Table 2. Optical parameters for the determination of Thallium(III).

Parameters	Characteristic
Colour	Blue
λ_{max} , nm	635
Stability, h	24
Beer's law range, $\mu\text{g mL}^{-1}$	0.1 - 5
Molar absorptivity, $\text{L mol}^{-1} \text{cm}^{-1}$	2.9×10^4
Sandell's sensitivity, $\mu\text{g cm}^{-2}$	0.0071
Optimum photometric range, $\mu\text{g mL}^{-1}$	0.2 - 4.5
Detection Limit, $\mu\text{g mL}^{-1}$.	0.011
Quantification Limit, $\mu\text{g mL}^{-1}$.	0.033
Regression Equation ^a	
Correlation coefficient	0.9998
Slope(a)	0.145
Intercept(b)	0.004
Standard deviation ^a	0.122
Relative standard deviation ^b · %	0.474
Reaction time, min	10

^a $\bar{Y} = ax + b$ where x is the concentration of Thallium(III) in $\mu\text{g mL}^{-1}$. ^b Ten replicates.

Precision and accuracy of the proposed method

The precision and accuracy of the proposed method were studied by analyzing solutions containing of 1, 3 and 4 $\mu\text{g mL}^{-1}$ of thallium(III) using proposed method. Ten replicate determination of each concentration gave (RSD %) of 0.4, 0.6 and 0.5% respectively. The lower values of the relative standard deviation indicate high precision and accuracy of the method.

Effect of diverse species

In order to evaluate the suitability of the recommended method for the spectrophotometric determination of thallium(III), the effect of some foreign species commonly accompany thallium(III) were studied by adding known amounts of diverse ions to a standard thallium solution. The tolerance limit given in Table 3, was defined as the concentration of foreign species that caused an error of $\pm 3\%$ or less in the determination of 2 $\mu\text{g mL}^{-1}$ of thallium(III) by the recommended method. The analyses were shown that there was noninterference by most of the cations and anions, except for Cr^{6+} , which would be tolerated at low concentration level. The use of masking agents in the analytical procedure increases the tolerance limit of some of the ions, such as using sodium fluoride to mask Fe^{2+} , Fe^{3+} . As shown in Table 3.

Table 3. Effect of diverse ions on the spectrophotometric determination of Thallium(III) (2 $\mu\text{g mL}^{-1}$).

Diverse species	Tolerance limit $\mu\text{g mL}^{-1}$	Diverse species	Tolerance limit, $\mu\text{g mL}^{-1}$
Urea	100 000	Thallium(I)	700
Sulphamic acid	80 000	Cd^{2+} , $\text{NO}_2^{-\text{a}}$, Hg^{2+} ,	500
$\text{NO}_3^{-\text{(a)}}$, PO_4^{3-} , SO_4^{2-} ,	35 000	Mn^{2+} , Cl^-	
Mg^{2+}		Tartarate, Ni^{2+}	250
Al^{3+} , Ca^{2+}	15 000	$\text{Fe}^{3+\text{b}}$	150
Phenol	5 000	$\text{Ce}^{4+\text{c}}$	100
Zn^{2+} , SO_3^{2-} , Na^+ , K^+ ,	3 000	Ba^{2+} , Mo^{6+}	75
$\text{Fe}^{2+\text{b}}$, F^-		WO_4^- , Cu^{2+} , Pb^{2+}	50
Perchlorate, CH_3COO^-	2 000	$\text{Br}^{-\text{d}}$	25
Hydroxylamine	1 500	Dichromate	1

^a. Masking by the addition of 2 mL of 1M sulphamic acid,

^b. Masking by the addition of 4 mL 0.3M sodium fluoride,

^c. Masking by addition 2 mL 1M of hydroxylamine,

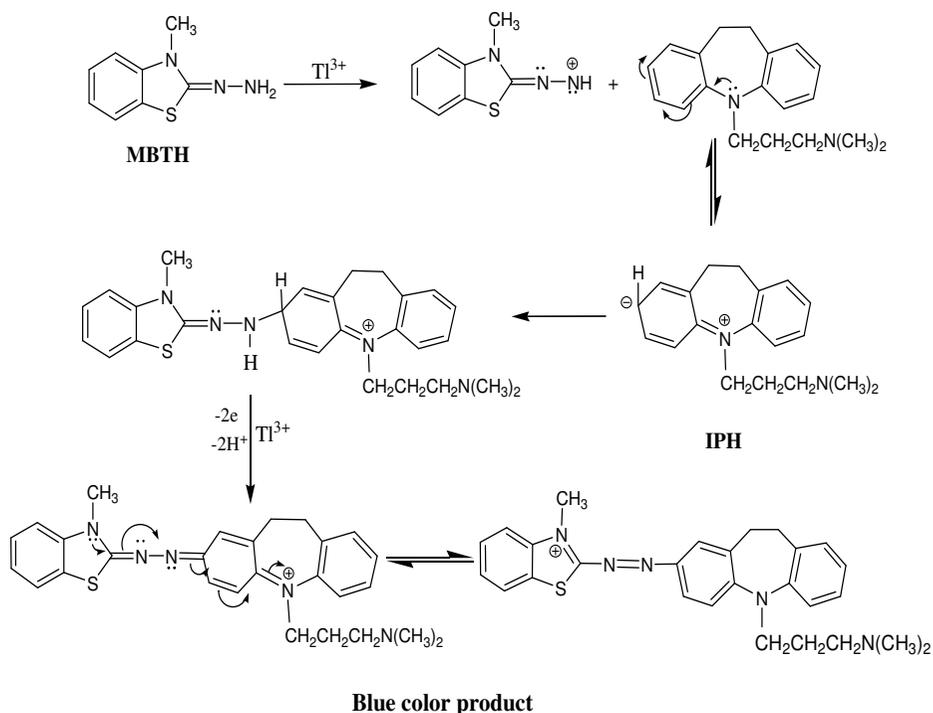
^d. Masking by the addition of 4 mL 10% of urea.

Effect of time and temperature on color stability

Under the optimized conditions, although the color developed instantaneously, 10 min were allowed to obtain the maximum and constant absorbance. The colored product was stable for 24 hour. The absorbance varied by not more than 3% over a period of 36 hour and the color development was independent of temperature in the range of 10-90 °C. Hence, 10 min reaction at room temperature was sufficient for the routine analysis.

Reaction mechanism

Under the reaction conditions, MBTH loses $2e^-$ and a proton on oxidation with thallium(III) forming the electrophilic intermediate (active coupling species) which couples with IPH to give a blue colored product. The probable reaction pathway based on the reactivity of MBTH with aromatic amines³⁹⁻⁴¹ is shown in Scheme 1.



Scheme 1. Reaction pathway for the formation of colored product by MBTH and IPH

Performance of the proposed method and statistical comparison with reported methods

The proposed method was applied for the determination of thallium by spiked environmental and biological samples with known quantity of thallium(III) and carrying out recovery studies. The results obtained by the proposed method were confirmed by measurements of thallium contents using the reported methods^{32, 42}. The results were analyzed statistically by Student's t-test and the variance ratio F-test at 95% confidence level. The calculated t and F-values did not exceed those theoretical values. It is evident from Table 4, that there is no significant difference between the spiked amounts and those detected by proposed method and the reported methods, indicating that the proposed method is as accurate and precise as the reported methods. Comparative study between the proposed method and some reported methods has shown that, the proposed method is simple, rapid, and highly sensitive than these methods in literature as shown in Table 5.

Application of the method in synthetic mixtures

Certified samples of thallium were not available so the proposed method was applied to a variety of synthetic samples to evaluate its effectiveness. The composition of the synthetic mixtures was selected to contain the common metal ions that usually accompany thallium in natural samples¹⁵. The mixtures were analyzed by recommended procedure and the obtained results showed good recoveries for thallium(III) as shown in Table 6.

Table 4. Determination of Tl(III) in spiked different water and urine samples by a proposed method and reported methods.

Sample	Thallium added $\mu\text{g mL}^{-1}$	Proposed method		Reported method ^{32, 42}		t-test ^b	F-test ^c
		Thallium Found ^a $\mu\text{g mL}^{-1}$	Recovery %	Thallium Found ^a $\mu\text{g mL}^{-1}$	Recovery %		
River water ^{d, e}	0.5	0.496 \pm 2.3	99.2	0.502 \pm 1.66	100.4	0.95	1.86
	2.0	1.998 \pm 0.65	99.9	2.006 \pm 0.67	100.3	0.96	1.06
	4.0	4.002 \pm 0.41	100.05	4.006 \pm 0.52	100.15	0.34	1.59
Lake water ^{d, f}	0.5	0.494 \pm 2.31	98.8	0.502 \pm 1.67	100.4	1.26	1.85
	2.0	1.998 \pm 0.65	99.9	2.004 \pm 0.45	100.2	0.85	2.13
	4.0	3.986 \pm 0.38	99.65	3.996 \pm 0.29	99.9	1.17	1.77
Tap water ^d	0.5	0.494 \pm 2.31	98.8	0.502 \pm 1.97	100.4	1.27	1.86
	2.0	1.994 \pm 0.57	99.7	1.992 \pm 0.42	99.6	0.32	1.85
	4.0	3.990 \pm 0.40	99.75	3.998 \pm 0.48	99.95	0.72	1.48
Human urine ^d	0.5	0.484 \pm 2.36	96.8	0.486 \pm 1.84	97.02	0.37	1.86
	2.0	1.982 \pm 0.42	99.1	1.978 \pm 0.43	98.9	0.76	1
	4.0	3.978 \pm 0.21	99.45	3.984 \pm 0.29	99.6	0.95	1.85

^a Mean \pm Relative Standard Deviation ($n = 5$); ^b Tabulated t -value for eight degrees of freedom at P (0.95) is 2.78; ^c Tabulated F -value for (4,4) degrees of freedom at P (0.95) is 6.39; ^d Gave no test for thallium; ^e Kukkaraheli lake- Mysore, India; ^f Cauvery River- Mysore, India.

Table 5. Comparison of recommended method with reported methods.

Method	Beer's Law range $\mu\text{g mL}^{-1}$	Molar absorptivity, $\text{L mol}^{-1} \text{cm}^{-1}$	Remarks	References
9,10-Phenanthraquinone monoethylthiosemicarbazone	0.2-10	2.2×10^4	Separation by flotation and solid-phase extraction	32
Methiomeprazine hydrochloride	0.5-4	3.2×10^4	Color Stability less than 2hours	33
N,N' -diphenylbenz amidne	0.1-1.2	1.8×10^5	Based on the extraction	34
4-(4'-N,N-Dimethyl aminophenyl) urazol	0.016-6.13	—	Need extraction, control of pH, 30°C and high interfere with Fe^{3+}	36
Phenosafranine	—	6.65×10^4	Several ions interfere	43
Trifluperazine hydrochloride	0.5 - 6.5	2.14×10^4	Less sensitive	44
Bromopyrogallol red +CTAB	—	3.5×10^4	Several ions interfere	45
MBTH + IPH	0.1 - 5	2.9×10^4	Simple, rapid, sensitive, stable color, less interference and no need prior extraction, control of pH or temperature.	Proposed method

Table 6. Determination of Tl(III) in synthetic mixtures of common metal ions that usually accompany thallium in nature.

Mixture	Thallium(III) added, $\mu\text{g ml}^{-1}$	Thallium(III) found ^b $\mu\text{g mL}^{-1}$	Mean Recovery, %
$\text{Fe}^{3+(a)}$, Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+}	2	1.95 ± 0.59	97.5
$\text{Fe}^{3+(a)}$, Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+}	4	3.94 ± 0.38	98.5
Cu^{2+} , Zn^{2+} , $\text{Fe}^{3+(a)}$, Pb^{2+}	2	1.96 ± 0.81	98
Cu^{2+} , Zn^{2+} , $\text{Fe}^{3+(a)}$, Pb^{2+}	4	3.90 ± 0.34	97.5

^a. Masking by the addition of 4mL of 0.3M sodium fluoride.

^b. Mean \pm Relative Standard Deviation ($n = 5$)

Conclusion

The proposed method that involves coupling of MBTH with IPH as new reagents in the determination of thallium(III) has some advantages such as simplicity, selectivity, stability and sensitivity as compared to some reported methods as shown in Table 5. This method has applied for the determination of thallium in urine which is very important to determination of thallium in human body. The color development was maximum and involves less stringent control of experimental conditions including duration for time analysis and pH control, which make this method easy and more practical as far as the procedure is concerned. In addition, the proposed method neither involves solvent extraction nor employs sophisticated instruments. The method has high tolerance limit for interfering species that are commonly present with thallium which is another added advantage. Thus, it can be concluded that this proposed method can be applied for the determination of thallium in various analytical procedures.

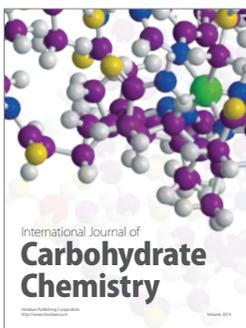
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