

Determination of Thallium by Starch Iodide Method and Its Applications in Environmental Samples

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The present method for determination of thallium involves the oxidation of Tl(I) to Tl(III), with bromine water and liberation of iodine by Tl(III) from potassium iodide in acidic medium. The liberated iodine is reacted with starch to form a blue coloured complex having $\lambda_{\max}$ 575 nm. The system obeys Beer's law in the range of 1-10 μg per 25 mL. The molar absorptivity and Sandell's sensitivity were found to be $1.98 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.00098 \mu\text{g cm}^{-2}$, respectively. The method has been successfully applied for the determination of thallium in water, industrial effluent, flue dust and biological samples.

Keywords: Thallium; Spectrophotometrically; Starch iodide; Environment.

INTRODUCTION

Thallium and its compounds are used in the manufacture of optical lenses, low temperature thermometers, semiconductors, luminescent tubes, dyes and pigments, photometric cells and scintillation counters.^{1,2} It forms a stainless alloy with silver, a corrosion resistant alloy with lead. Thallium sulphate has been widely employed as a rodenticide and as an ant killer. Its use has been prohibited in the U.S. since 1975 as a household insecticide and rodenticide^{2,3} Thallium liberated into the environment is accumulated in the soil by the biogeochemical reaction leading to the formation of organometallic compounds and also various industrial and metallurgical operations.^{4,5} Thallium is highly toxic. It can enter the body through the respiratory tract, gastrointestinal tract or skin; it enters the cell exchanging for intracellular potassium.³ Minute amounts tend to accumulate in body tissue over time and ultimately cause organ damage that can be irreversible and fatal. Systemic and chronic effects include damage to the liver, kidneys and central nervous system as well as cancer. Its TLV should not exceed 0.1 mg/m^3 .^{1,6}

Various analytical methods using AAS,⁷ GC,⁸ HPLC,⁹ pulse voltammetry,^{10,11} TLC,¹² laser induced fluorescence,¹³ fluorimetry,¹⁴ titrimetry,¹⁵ ion pair chromatography,¹⁶ and cation chromatography,¹⁷ have been reported for the direct determination of thallium. Although these instrumental methods are highly sensitive, these methods are costly and require trained staff for operation. Hence spectrophotometric methods are used. Thallium (I) is more toxic than thallium (III).

Several basic dyes and reagents have been reported for the determination of thallium (III) such as methylene blue, malachite green, brilliant green, crystal violet, p-aminophenol, phloroglucinol, leucocrystal violet^{18,19} and rhodamine B.²⁰

* The method using rhodamine B for determination of thallium involves acidifying the sample solution with hydrochloric acid, adding saturated bromine water, followed by addition of 0.2% rhodamine B after removing excess bromine, extracting the colour in benzene and measuring the absorbance at 560 nm. Here a simple and sensitive method for the determination of Tl(I) is described. The method involves the oxidation of thallium (I) to thallium (III) which liberates iodine from potassium iodide and liberated iodine is reacted with starch. The resultant coloured complex is measured at 575 nm. The method has been applied for the determination of thallium in biological and complex materials.

EXPERIMENTAL

Apparatus

A Systronics 106 digital spectrophotometer was used for spectral measurements, and a Systronics 335 digital pH meter was used for pH measurements.

Reagents

All chemicals used were of A.R. grade and double distilled deionised water was used throughout.

Standard thallium solution (BDH) - 100 mg of thallium

* Standard method

nitrate was dissolved in water containing 1-2 drops of concentrated nitric acid and diluted to 100 mL with water. Working standards were prepared by dilution of stock.

Bromine water - A saturated solution of bromine in water was prepared freshly; 5 mL bromine was dissolved in water and volume was made up to 100 mL.

Formic acid - 50% aqueous solution was prepared.

Potassium iodide (E Merck) - 0.1% aqueous solution was used.

Starch - 1% starch solution was prepared in water.

Procedure

To an aliquot containing 1-10 µg of Thallium (I), 0.5 mL of bromine water was added and shaken gently. One or two drops of formic acid were added to remove excess of bromine. To it 1 mL of 0.1% potassium iodide and 1 mL of starch solution was added. The contents were shaken well; the solution was made up to the 25 mL mark. The blue coloured complex formed was measured at 575 nm, against a reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectrum of the colour system showed maximum absorbance at 575 nm; the reagent blank gave negligible absorbance at this wavelength.

Adherence to Beer's law, Molar absorptivity and Sandells sensitivity

The colour system obeyed Beer's law in the concentration range of 1-10 µg/25 mL (0.04-0.4 ppm). The molar absorptivity and Sandell's sensitivity were found to be $1.98 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.00098 \text{ µg cm}^{-2}$, respectively.

Effect of reagent concentration

Under the proposed reaction conditions 0.5 mL of bromine water, 1 mL of 0.1% potassium iodide and 1 mL of starch solution were required. For the removal of excess bromine 1-2 drops of formic acid was sufficient.

Conditions for colour development

The colour development requires hardly ~ 5 minutes; pH of the final solution was 3-4. The colour was stable for more than 24 hours under optimum conditions.

Reproducibility

The reproducibility of the method was checked by analysing 5 µg of Tl(I) per 25 mL of the final solution for a period

of seven days. The standard deviation and relative standard deviation were found to be ± 0.0087 and 1.87%, respectively.

The tolerance limit (in ppm) of various ions was studied. Most of the common ions do not interfere with the procedure. As^{+5} , Se^{+4} which also liberate iodine under similar conditions, interfere with this method. The cations and anions like Sn^{+2} , Hg^{+2} , Fe^{+3} , NO_3^- and citrate did not interfere with the proposed method. (Table 1).

Effect of various oxidants

The influence of different oxidants on the reaction was studied. Other oxidants used were ceric sulphate, sodium nitrite and hydrogen peroxide keeping the other conditions unchanged. The excess of ceric sulphate was removed by using hydroxyl ammonium chloride; sodium nitrite was removed by using sulphamic acid and hydrogen peroxide decomposed itself. The sensitivity of the reaction by using the above oxidants was found to be much less as compared with the present method. This suggests that the sensitivity of spectrophotometric determination of thallium depends on the oxidant used. Of the four oxidants tested, bromine water gave high sensitivity.

APPLICATIONS

(1) In biological samples

To assess the applicability of the method to biological samples, known amounts of thallium were added to urine and deproteinised blood samples.²¹ They were then analysed by present and reported methods.²⁰ In the reported method after addition of known amounts of thallium to urine and blood samples, the solution was acidified by 2.0 M hydrochloric acid, 0.5 mL of saturated bromine water was added and excess bromine was removed by heating, after cooling, diluted to 10 mL with 2.0 M hydrochloric acid; 1 mL of 0.2% rhodamine B was added and colour was extracted in benzene and the absorbance was measured at 560 nm. The recovery was

Table 1. Effect of Foreign Ions in the Determination of Thallium Concentration of Thallium 5 µg/25 mL

Foreign ions added	Tolerance limit (ppm)
La^{+3} , Zr^{+4}	8000
AsO_4^{-3} , Sn^{+4} , PO_4^{-3} , Cu^{+2} , NO_2^-	5500
Sb^{+3}	4100
CO^{+2} , Pb^{+2}	2700
Fe^{+3} , Zn^{+2}	1000
Citrate	200

Tolerance limit may vary the absorbance values by $\pm 2\%$.

Table 2. Determination of Thallium in Biological Samples

Samples	Thallium added μg	Thallium found*		% Recovery	
		Proposed method	Reported method ²⁰	Proposed method	Reported method ²⁰
(1) Blood	6	5.83	5.76	97.1	96
Serum	8	7.90	7.68	98.75	96
(2 mL)	10	9.78	9.55	97.8	95.58
(2) Urine	6	5.85	5.79	97.5	96.5
(2 mL)	8	7.89	7.72	98.62	96.5
	10	9.83	9.71	98.3	97.1

* Mean of three replicate analyses

found to be ~ 97-98% (Table 2).

(2) In Industrial effluents

5 mL of effluent was taken from a nearby steel plant and filtered through Whatman filter paper No:40 and analysed for thallium by the present and reported methods.²⁰ The reported method is described above. The recovery range was found to be ~ 96-98% (Table 3).

(3) In natural water

5 mL of thallium free water sample was taken and a

known amount of thallium was added and analysed by the present and reported methods.²⁰ Recovery range ~ 98.6-98.7% (Table 3).

(4) In flue dust

The flue dust sample (5 mg) was taken from an acid plant of the steel industry. It was digested with acid mixture (10 mL HCl:HNO₃ 3:2 v/v)²² and evaporated under vacuum to 2 mL, and the contents were collected and diluted to 25 mL with water. The 5 mL aliquot was analysed for thallium by the present and reported methods.²⁰ The percentage of recovery

Table 3. Determination of Thallium in Complex Materials

Sample	Thallium originally found*, in μg	Thallium Added, in μg	Total Thallium, in μg		% of Recovery	
			Present method	Reported method ²⁰	Present method	Reported method ²⁰
Tap water	--	6	5.92	5.80	98.67	96.67
5 mL	--	8	7.89	7.74	98.62	96.75
	--	10	9.86	9.67	98.60	96.70
Industrial effluent	2.25	5	6.99	6.88	96.41	94.89
	2.01	5	6.86	6.80	98.0	97.14
5 mL	2.40	5	7.13	7.09	96.35	95.81
Flue dust	1.60	5	6.38	6.35	96.67	96.21
5 mg	1.57	5	6.29	6.18	95.73	94.06
	1.98	5	6.75	6.69	96.80	95.86

* Mean of three replicate analyses

Table 4. Comparison with other Spectrophotometric Methods

Reagent	Medium	λ_{Max} nm	Beer's law range ppm	Remarks
1. Brilliant green ¹⁸	4 M HCl	640	0.2-2.0	Sn ⁺² , Hg ⁺² , Fe ⁺³ , NO ₃ ⁻ , citrate interfere
2. Crystal violet ¹⁸	0.05 M HCl	595	0.4-2.4	Sn ⁺² , Fe ⁺³ , Sb ⁺³ , NO ₃ ⁻ , citrate interfere
3. Methyl violet ¹⁸	0.18-0.2 M HCl	605	0.4-2.8	Sb ⁺³ , Hb ⁺² , Fe ⁺³ , citrate interfere
4. Rhodamine B ²⁰	2 M HCl	560	0.4-2.8	Sn ⁺² , Sb ⁺³ , Fe ⁺³ , NO ₃ ⁻ , interfere
5. Methylene green ¹⁸ and blue	0.15-0.2 M HCl	650	0.4-2.8	Sb ⁺³ , Fe ⁺³ , Ag ⁺ NO ₃ ⁻ , interfere
6. Leuco crystal ¹⁹ violet	3.5-4.5 pH	590	0.08-0.8	Less sensitive, reagent is costly.
7. Iodine starch (Proposed method)	3-4 pH	575	0.04-0.4	very sensitive, free from interference from common cations and anions, simple.

was found to be ~ 95-96.5% (Table 3).

CONCLUSION

The present method for the determination of thallium is simple, sensitive, rapid and avoids the use of hazardous chemicals. This method can be compared favourably with most of the other reported methods (Table 4). The method has been successfully applied for the determination of thallium in biological and complex material (Tables 2 and 3).

ACKNOWLEDGEMENT

The authors are grateful to Pt. Ravishankar Shukla University Raipur (C. G.) and Department of Chemistry, Government Arts and Science College Durg (C. G) for providing lab facilities.

Received April 19, 2002.

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