

A Novel Method for the Spectrophotometric Determination of Thallium Using Methiomeprazine Hydrochloride

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A new, simple, sensitive, and rapid spectrophotometric method is proposed for the determination of trace amounts of thallium(III). The method is based on the oxidation of methiomeprazine hydrochloride by thallium(III) in phosphoric acid medium to give a blue radical cation, having a maximum absorption at 645 nm. Beer's law is valid over the concentration range 0.5–4.0 $\mu\text{g mL}^{-1}$, with molar absorptivity and Sandell's sensitivity of $3.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0064 \mu\text{g cm}^{-2}$, respectively. The detection limit of thallium determination is $0.01 \mu\text{g mL}^{-1}$. The tolerance limits for interfering ions are discussed. All variables were studied in order to optimize the reaction conditions. The efficacy of the proposed method is shown by the successful determination of traces of thallium in alloys, minerals, standard reference materials, water, and urine samples.

Key Words: Methiomeprazine hydrochloride (MMH), thallium(III) determination, spectrophotometry.

Introduction

Thallium is commonly found with lead, zinc, iron, tellurium and the alkalis¹. It is normally present only at trace level ($>10 \mu\text{g L}^{-1}$) in natural waters. It is toxic and is on several regulatory lists². Determination of trace amounts of thallium is of great importance because of its toxic nature and also because of its increasing industrial applications³. The main sources of thallium pollution at present are cement production and fossil fuel combustion. Owing to its increasing use in the semiconductor and electrical engineering industries, leading to increasing emissions into the environment, thallium has acquired growing importance as a pollutant. Both Tl^+ and Tl^{3+} are biologically active⁴. Recently, Hoffman⁵ has reported a case study and a comprehensive literature review on thallium poisoning during pregnancy. Numerous methods have been proposed for the spectrophotometric determination of thallium^{6–9}, most of which are based on extraction of ion-associates formed by basic dyes and thallium. These methods, however, are time consuming,

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have poor selectivity and also have the disadvantage of high blank values. Some of the other chromogenic reagents proposed for the determination of thallium are iodoacetic acid and hexamethylenetetramine¹⁰, pyronine G¹¹, brilliant green^{12,13}, mepazine hydrochloride¹⁴, bromopyrogallol red¹⁵, the azo compounds of benzimidazole¹⁶, alizarin violet¹⁷, and phenosafranine¹⁸. Although the methods involving these reagents are sensitive, they lack selectivity and suffer from serious interference of foreign ions normally occurring in the determination of thallium(III). Other notable methods used for the determination of thallium include ICP-MS^{19,20}, AAS^{21,22}, potentiometry²³, and voltammetry²⁴. Most of these methods are disadvantageous in terms of cost and the instruments used in routine analysis. AAS is often lacking in sensitivity and is affected by the matrix conditions of samples such as salinity. Hence, accurate determination of thallium at trace levels using a simple and rapid method is of paramount importance. Spectrophotometric methods can be used for the determination of trace amounts of thallium occurring in many samples. The availability of the spectrophotometric apparatus and the simplicity of analytical procedures make the technique very attractive for a wide range of applications. Spectrophotometric determination of thallium(III) based on starch-iodine and dithizone methods is considered the most sensitive⁶, but these methods suffers from various interfering ions and also from the instability of the reactants used. A recent literature survey also revealed that there is no report of effective and sensitive spectrophotometric methods for Tl(III). These deficiencies encouraged the authors to develop a simple, rapid, inexpensive and reliable method for the determination of trace amounts of thallium(III) in various samples.

Investigations on phenothiazines have yielded methiomeprazine hydrochloride [MMH], chemically, 10-[3-(NN-dimethylamine)-2-methylpropyl]-2-methylthio-phenothiazine hydrochloride as a sensitive reagent for the rapid spectrophotometric determination of thallium(III). This reagent has also been used for the spectrophotometric determination of palladium(II) and gold(III)²⁵, and selenium²⁶ in different samples. The proposed method is based on the oxidation of MMH by thallium(III) in phosphoric acid medium to give a blue species. The method has been successfully applied to the determination of thallium in various synthetic, environmental, and biological samples. The proposed method is simple, selective, rapid, cost-effective, free from various common interfering ions, and does not require extraction, close control of pH or heating steps.

Experimental

Apparatus

Jasco (model UVIDE C-610) and Elico (model SL-171) spectrophotometers with 1 cm matched glass cells were used for all absorbance measurements.

Reagents

All the chemicals used were of analytical-reagent grade and distilled water was used for dilution of reagents and samples.

Standard thallium(I) solution (1 mg mL⁻¹). Prepared by dissolving 0.1235 g of Tl₂SO₄ (BDH Chemicals Ltd., Poole, England) in water containing 2 mL of concentrated sulfuric acid and diluting to 100 mL in a calibrated flask with water. The stock solution was standardized titrimetrically²⁷, and solutions of lower concentrations were prepared by diluting the standard solution as and when required.

Methiomeprazine hydrochloride (MMH). A 1% (w/v) aqueous solution of MMH (Rhône-Poulenc, Paris) was prepared and stored in an amber glass bottle in a refrigerator at 0–10 °C. Under these conditions the reagent is stable for 2 months.

Others. The following reagents were prepared by dissolving required amounts of reagents in distilled water: orthophosphoric acid (10 M), bromine water (saturated), hydrochloric acid (10 M), formic acid, sulfuric acid (5 M), and citrate solution (5%).

Solutions of foreign ions. Solutions containing suitable concentrations of potentially interfering ions were prepared in water or in very dilute hydrochloric or sulfuric acid.

Procedure

Determination of thallium(III)

An aliquot of the sample solution containing 5–40 µg of thallium(I) was transferred into a series of 10 mL calibrated flasks. A volume of 0.5 mL of 10 M hydrochloric acid and 5 drops of saturated bromine water were added. After 2 min, 5 drops of formic acid were added and mixed well. One minute later, 5 mL of 10 M orthophosphoric acid and 1.0 mL of 1% MMH solution were added. The contents were diluted to the mark with distilled water, mixed well, and after 1 min the absorbance was measured at 645 nm against a reagent blank. The measurement should be performed within 2 h of color formation. The thallium(III) content was determined from the standard calibration graph prepared by the above procedure.

Results and Discussion

Thallium(III) instantaneously oxidizes methiomeprazine hydrochloride at room temperature (27±2 °C) in sulfuric, hydrochloric, phosphoric or acetic acid medium to give a blue species that is thought to be a radical cation²⁸. The blue radical cation exhibits maximum absorbance at 645 nm. The reagent blank had negligible absorbance at this wavelength. The formation of radical cation was also confirmed by passing an aliquot of the solution through cation and anion exchange resins. Only the cation exchange resin retained the blue species, indicating the cationic nature of this species.

The intensity and stability of the colored species depend on the nature and concentration of the acid employed. The blue species is not stable in either hydrochloric or sulfuric acid medium, and does not give maximum color intensity in acetic acid medium. Moreover, the absorbance of the colored radical cation formed in sulfuric, hydrochloric or acetic acid medium is lower than that for reaction in phosphoric acid. Phosphoric acid has therefore been selected for further studies. The rate of color development and the sensitivity of the reaction increased with increasing phosphoric acid concentration up to 3 M and remained constant over the range 3–7 M. Full color development occurred instantaneously over this concentration range at room temperature (27±2 °C); although this figure is normally high, the procedure is also valid for other temperatures in the range 10–50 °C. Although the color formation is instantaneous, it is recommended to take the absorbance readings after 1 min. Above the acid concentration of 7 M the reagent blank is a very light blue. Hence, an acid strength of 5 M was selected for all subsequent studies. The absorbance values remained constant for 2 h in the temperature range 10–50 °C. Above or below this range the absorbance values decreased gradually. Similar studies revealed that 1 mL of 1% MMH in a total volume of 10 mL was sufficient to provide a constant and maximum absorbance. It was also observed that there was no appreciable change in the absorbance if the order of addition of reagents was varied.

Choice of oxidizing agent

Thallium(III) can be determined after the oxidation of thallium(I) by bromine water or ceric sulfate solution in an acidic medium. For these methods, excess oxidizing agent must be removed prior to the determination of thallium(III), to avoid interference in the determination. Usually excess bromine was destroyed by adding phenol or formic acid and Ce(IV) was reduced by hydroxylamine⁶. In the present study, bromine water was used to oxidize Tl(I) to Tl(III), and the excess oxidizer was destroyed by the addition of formic acid. Some 0.5 mL of 10 M H₂SO₄ and 5 drops each of the bromine water and formic acid with a time gap of 2 min were sufficient for the oxidation of Tl(I) to Tl(III). The oxidation of thallium(I) with bromine occurs quantitatively in the cold, and this was confirmed by analyzing a known amount of Tl(I) solution after converting it into Tl(III), and subsequent determination of thallium(III) as described under the determination of thallium(III). The results obtained are presented in Table 1, and show that the oxidation of Tl(I) to Tl(III) is quantitative.

Table 1. Determination of thallium(I) as thallium(III).

Thallium(I) taken ($\mu\text{g mL}^{-1}$)	Thallium(I) found ($\mu\text{g mL}^{-1}$) ^a	Recovery (%)	RSD (%)
1.00	0.991 \pm 0.005	99.0	0.50
1.50	1.492 \pm 0.003	99.3	0.20
2.00	2.011 \pm 0.002	100.5	0.10
4.00	3.992 \pm 0.001	99.8	0.02

^aMean \pm standard deviation (n = 5).

Analytical features

A linear calibration graph was obtained for 5–40 μg of thallium(III) in a final volume of 10 mL. The calibration graph has a correlation coefficient of 0.999. The detection limit [DL = 3.3 σ /S] and quantitation limit [QL = 10 σ /S] (where, ' σ ' is the standard deviation of the reagent blank, n = 10 and 'S' is the slope of the calibration curve) of thallium(III) determination are 0.01 and 0.035 $\mu\text{g mL}^{-1}$, respectively. The molar absorptivity, specific absorptivity and Sandell's sensitivity of the color system were $3.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, 0.155 mL g⁻¹ cm⁻¹ and 0.0064 $\mu\text{g cm}^{-2}$, respectively. The precision and accuracy of the method were established by the analysis of 10, 15, and 20 μg of thallium(III) in a final volume of 10 mL, using the recommended procedure. Ten replicate determination of each concentration gave a relative standard deviation (RSD) of 0.04% , 0.02% and 0.01% , for 10, 15 and 20 μg of Tl(III), respectively.

Effect of diverse ions

The interference of a number of ions commonly associated with thallium was investigated by adding different amount of diverse ions to 2 $\mu\text{g mL}^{-1}$ of thallium(III) solution to evaluate the analytical utility of the method. An error of $\pm 2\%$ in the absorbance values was considered tolerable. The tolerance limits of the foreign ions tested are given in Table 1. The major advantage of the proposed method is that MMH can be used as a selective reagent for the determination of thallium(III) in the presence of large amounts of Fe(III) and In(III), which are usually associated with thallium-containing samples. Because the Tl-solution included a sulfuric acid, the ions like Ba²⁺, Pb²⁺ and Sr²⁺ normally precipitate as sulfates but can be dissolved in

acidic medium; therefore, these ions do not interfere in the Tl(III) determination as they are unstable in acid medium.

Table 2. Effect of interfering ions on the determination of thallium(III) [$2 \mu\text{g mL}^{-1}$].

Interfering ions	Tolerance limit ($\mu\text{g mL}^{-1}$)
Cu^{2+} , Ni^{2+} , Al^{3+} , Na^+ , K^+ , Mn^{2+} , Zn^{2+} , oxalate, Cl^- , Br^- , citrate, tartrate, NO_3^-	≥ 2500
Co^{2+} , WO_4^{2-} , NO_2^- , In^{3+} , MoO_4^{2-} , Fe^{3+}	≥ 600
I^- , IO_3^- , $\text{Cr}_2\text{O}_7^{2-}$, VO_3^- ,	≤ 1

Applications

The thallium contents of alloys, minerals, standard reference materials, water, and urine samples were determined by the proposed method, and the results are shown in Tables 3-6, respectively.

Determination of thallium in alloys

Certified samples of thallium alloys were not available. Therefore, synthetic mixtures containing some of the metal ions commonly found in thallium alloys were prepared and the thallium content was determined using the method described under the determination of thallium(III) (Table 3).

Table 3. Determination of thallium in synthetic mixtures corresponding to thallium alloys.

Alloy	Composition (%)	Thallium content of solution (μg)			
		Taken	Found ^a	RSD (%)	Recovery (%)
Alloy for bearing	Tl, 2; Cu, 98	8.0	7.99 ± 0.05	0.6	99.9
		10.0	10.0 ± 0.03	0.3	100.0
		12.0	11.98 ± 0.01	0.1	99.8
Low melting alloy	1) Tl, 7; Bi, 52; Pb, 34; Cd, 7	6.5	6.48 ± 0.06	0.9	99.7
		10.5	10.49 ± 0.04	0.4	99.9
		12.5	12.5 ± 0.02	0.1	100.0
	2) Tl, 8.9; Bi, 44.2; Pb, 35.8; Cd, 11.1	8.0	8.00 ± 0.07	0.9	100.0
		10.0	9.98 ± 0.05	0.5	99.8
		12.0	11.99 ± 0.03	0.3	99.8

^a Mean \pm standard deviation (n = 5).

Determination of thallium in minerals

The minerals were dissolved in aqua regia and boiled to near dryness twice with distilled water to reduce the acidity. The residue was leached with distilled water, filtered through a Whatman No. 41 filter paper and the filtrate was diluted to a known volume with water. Suitable aliquots of the sample solutions were analyzed according to the proposed procedure for thallium(III). The reliability of the procedure was checked by the method of standard addition following the recommended procedure, and also by the starch-iodine method²⁹. The statistical analysis of the results by F- and t-tests showed no significant difference in accuracy or precision between the proposed and reference methods (Table 4).

Table 4. Determination of thallium in minerals.

Sample ^a (w/v)	Thallium spiked ($\mu\text{g g}^{-1}$)	Proposed method			Reference method ²⁹			F-test ^c	t-test ^d
		Thallium found ^b ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	Thallium found ^b ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)		
Sphalerite (2 g/50 mL)	- 50	74.9 \pm 0.3 124.8 \pm 0.2	0.4 0.2	- 99.9	74.7 \pm 0.5 124.5 \pm 0.4	0.7 0.3	- 99.8	2.8 4.0	0.8 1.5
Galena (1 g/100 mL)	- 100	315.6 \pm 0.4 415.5 \pm 0.3	0.1 0.1	- 100.0	315.3 \pm 0.6 415.1 \pm 0.4	0.2 0.1	- 99.9	2.2 1.8	0.9 1.8

^aVolume of sample taken, 3 mL.

^bMean \pm standard deviation (n = 5).

^cTabulated F-value for (4,4) degrees of freedom at P(0.95) is 6.39.

^dTabulated t-value for 8 degrees of freedom at P(0.95) is 2.306.

Determination of thallium in standard samples

Known amounts of finely ground standard samples (rock, granite) were opened out by repeatedly heating with concentrated nitric acid and hydrogen fluoride ^{11,30}. The mixture was heated with 2 mL of 5 M sulfuric acid and evaporated to fumes of sulfur trioxide. The residue was leached with water, filtered and diluted up to a known volume after heating it with 5% citrate solution. Suitable aliquots of this sample solution were analyzed for thallium(III) by following the proposed procedure. The reliability of the procedure was checked by the method of standard addition to the same samples and the data (Recovery, RSD, t-value) show that the method works satisfactorily (Table 5).

Table 5. Determination of thallium in standard reference materials.

Sample	Certified value of thallium ($\mu\text{g mL}^{-1}$)	Thallium ($\mu\text{g mL}^{-1}$)		Recovery (%)	RSD (%)	t-test ^b
		Added	Found ^a			
SY-2 ^c (rock)	1.5	-	1.49 \pm 0.03	99.3	2.0	0.7
		1.0	2.48 \pm 0.01	99.5	0.4	-
MA-N ^c (granite)	15.0	-	14.98 \pm 0.06	99.8	0.4	0.7
		1.5	16.47 \pm 0.04	99.9	0.2	-

^a Mean \pm standard deviation (n = 5).

^bTabulated t-value for 4 degrees of freedom at P(0.95) is 2.776.

^c USGS samples, collected from Atomic Mineral Division-Bangalore, India.

Determination of thallium in water

All filtered environmental water samples (100 mL) were analyzed for thallium. They tested negative. To these samples a known amount of thallium was added and analyzed for thallium by the proposed procedure for thallium(III) (Table 6). Accurate recoveries were achieved in all samples.

Determination of thallium in urine

A known amount of thallium was added to a urine sample (30 mL), taken in a 100 mL micro-Kjeldahl flask (which tested negative for thallium). 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. Sulfuric acid (1 mL of concentrated) 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. Heating was continued 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 a 100 mL calibrated flask. A suitable aliquot of urine sample was taken and analyzed using the procedure outlined earlier (Table 6). Excellent recoveries were obtained in all solutions,

Table 6. Determination of thallium in water and urine samples.

Sample	Thallium spiked (μg)	Thallium found ^a (μg)	RSD (%)	Recovery (%)
River water	6.0	5.98 ± 0.06	1.0	99.7
	8.0	7.99 ± 0.04	0.5	99.7
	10.0	10.00 ± 0.02	0.2	100.0
Lake water	6.0	5.97 ± 0.07	1.2	99.5
	8.0	7.98 ± 0.05	0.6	99.8
	10.0	9.99 ± 0.03	0.3	99.9
Urine	6.0	5.99 ± 0.06	1.0	99.8
	8.0	8.00 ± 0.03	0.4	100.0
	10.0	9.98 ± 0.01	0.1	99.8

^a Mean \pm standard deviation (n = 5).

Conclusions

In this paper, a new, simple, highly sensitive, selective and inexpensive method with methoimeprazine hydrochloride was developed for the determination of thallium in synthetic, environmental, and biological samples. Although many sophisticated techniques such as voltammetry, AAS, ICP-AES, and ICP-MS are available for the determination of thallium at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement of consumables, and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories in developing countries with limited budgets. The sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method are very reliable for the determination of thallium in different samples. Moreover, the proposed method does not involve any extraction steps and hence the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed procedure can serve as an alternative method for the determination of thallium(III) at trace levels.

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References

1. F.D. Snell and C.T. Snell, *Colorimetric Methods of Analysis*, D. Van Nostrand Company, New York, 3rd edn, vol. II, 1949, p.47.
2. *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 19th edn.,1995, p.3-100.
3. I.M. Korenman, *Analytical Chemistry of Thallium*, Ann Arbor-Humphrey, London, 1996, pp.2-3.
4. D.L. Tsalev and Z.K. Zaprianov, *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice*, vol. I, Analytical Aspects and Health Significance, CRC Press, Boca Raton, FL, 1983, pp196-199.
5. R.S. Hoffman, **J. Toxicology-Clinical Toxicology**, **38**, 767-775 (2000).
6. Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood Ltd., Chichester, London, 1986, p.569.
7. Z. Gregorowicz and J. Ciba, **Talanta** **28**, 805-808 (1981).
8. A.G. Fogg, C. Burgess and D.T. Burns, **Talanta** **18**, 1175-1196 (1971).
9. M.Sager and G.Tolg, **Mikrochim. Acta II**, 231-245 (1982).
10. D. Mihajlovic and T. Stafilov, **Fresenius J. Anal. Chem.**, **356**, 371-374 (1996).
11. K.K. Namboothiri, N. Balasubramanian and T.V. Ramakrishna, **Talanta**, **38**, 945-949 (1991).
12. N. Agarwal and K.S. Patel, **Analisis**, **19**, 134-135 (1991).
13. M.K. Deb, P.K. Agnihotri, M. Thakur and R.K. Mishra, **Chem. Speciation Bioavailabs**, **10**, 53-60 (1998).
14. H.S. Gowda and G.K. Rekha, **Indian J. Chem.**, **28**, 179-180 (1989).
15. H. Ladzinska-Kulinska, **Chem.Anal (Warsaw)**, **31**, 843-849 (1986).
16. M.S. Chernovyants, I.V. Evlashenkova, N.V. Kuplevatskaya, L.N. Divaeva, V.A. Anisimova and K.N. Bagadasarov, **Z. Anal. Khim.**, **51**, 931-934 (1996).
17. R. Zhang, H. Wang and J. Wen, **Fenxi-Huaxue**, **16**, 111-113 (1988) through *Anal. Abstr.*, 50, 8B89 (1988).
18. H. Zhov, W. Li, L.Guan and C. Liu, **Fenxi-Shiyanshi** **6**, 61(1987), through *Anal. Abstr.*, 49, 11B110 (1987).
19. P. Medek, J. Pavlickova, J. Zbiral, E. Cizmarova and V. Kuban, **Int. J. Environ. Anal. Chem.**, **81**, 207-219 (2001).
20. M.T. Wei and S.J. Jiang, **J. Anal. Atom. Spectrom.**, **14**,1177-1181 (1999).
21. D. Zendelovska and T. Stafilov, **Anal. Sci.**, **17**, 425-428 (2001).
22. O. Mestek, R. Koplík, H. Fingerova, M. Suchanek, **J. Anal. Atom. Spectrom.**, **15**, 403-407 (2000).
23. J.M. Zen, W.W. Wang and A.S. Kumar, **Electroanal.**, **13**, 321-324 (2001).
24. T.H. Lu and I.W. Sun, **Electroanal.**, **10**,1052-1056 (1998).
25. H.S. Gowda, K.A. Padmaji and K.N. Thimmaiah, **Analyst**, **106(1259)**, 198-205 (1981).
26. H.S. Gowda and B.N. Achar, **Indian J.Chem.**,**19(2) A**,178-179 (1980).
27. H.S. Gowda, R. Shakunthala and V. Subrahmanya, **Indian J .Chem.** **20A**, 68-71 (1975).
28. P.C.Dwivedi, K.G. Rao, S.N. Bhat and C.N.R. Rao, **Spectrochim. Acta** **31A**, 129-135 (1975).
29. C.W. Sill and H.E. Peterson, **Anal. Chem** **21**, 1268-1273 (1949).
30. F.D. Snell, *Photometric and Fluorimetric Methods of Analysis, Metals, Part I*, Wiley, New York, 1978, pp.50-52.