

## Determination of thallium in environmental samples by surfactant assisted dispersive liquid-liquid microextraction combined with first order derivative spectrophotometry

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### ARTICLE INFORMATION



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### ABSTRACT

A surfactant assisted dispersive liquid-liquid microextraction (SA-DLLME) combined with derivative spectrophotometric method has been proposed for the determination of thallium(III) using a chelating agent diacetylmonoxime-*p*-hydroxybenzoylhydrazone. Disperser solvent was substituted by surfactant, which made the emulsification more effective and extraction, quite environment friendly. Carbon tetrachloride was employed as the extractant. The developed SA-DLLME technique was coupled with first order derivative spectrophotometric method to improve the analytical performance. Optimum conditions relevant to SA-DLLME and instrumental parameters were studied in detail. The enrichment factor of the method was found to be 23. The limit of detection and quantitation limit of first order derivative spectrophotometric method were found to be 0.22 and 0.67 µg/L, respectively. The relative standard deviation (RSD) for five replicates of 50.0 µg/L of thallium(III) was found to be 1.12%. The applicability of the method was evaluated by the trace level determination of thallium in different environmental samples.

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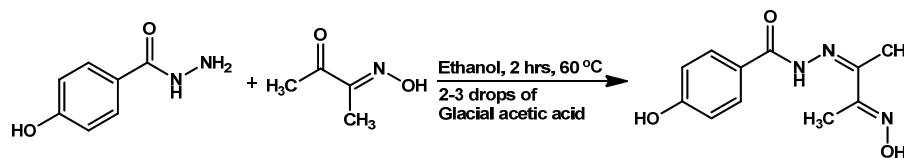
### 1. Introduction

Thallium and its compounds are highly toxic [1-3]. But they are commonly used in medicines for dermatological disorders, dyes, pigments, fungicides, insecticides, rodenticides and as reagents in chemical research [4]. They are also used in the manufacture of corrosion-resistant alloys, scintillation counters and low-melting special glass for highly reflective lenses [5-8]. The increasing applications of thallium compounds can cause human exposure to thallium substances. Therefore the development of sensitive and selective analytical procedures for trace level determination of thallium is of great importance.

Graphite furnace atomic absorption spectrometry [9,10] flow injection-differential pulse-anodic stripping voltammetry [11] cathodic and anodic stripping voltammetry [12-14], electrothermal atomic absorption spectrophotometry [15,16] inductively coupled plasma mass spectrometry [17-20] and thermal neutron activation analysis [21] are the most popular analytical techniques used for the determination of thallium at trace levels. However, these techniques are disadvantaged by the long duration, matrix effects, expensive facilities and their maintenance.

Various chromogenic agents are reported for the spectrophotometric determination of thallium such as 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, 3-methyl-2-benzothiazolinone hydrazone hydrochloride, imipramine hydrochloride, rhodamine B hydrazide, semimethylthymol blue, methiomeprazine hydrochloride, brilliant green, iodoacetic acid, hexamethylenetetramine, pyronin G, trifluoperazine hydrochloride and 9,10-phenanthraquinone monoethylthio semicarbazone [22-32]. Most of these methods are based on extraction using toxic organic solvents and also have the disadvantage of high blank values [25-29]. Most of the reported methods suffer interferences from various associated metal ions. Pre-concentration technique or masking agents have to be used to improve the selectivity of these methods [30-32].

In recent years the use of Dispersive Liquid-Liquid Microextraction (DLLME) techniques is of great interest since it is an environmentally benign, simple and fast, based on ternary component solvent system. In this method a suitable mixture of extraction solvent and disperser solvent is quickly injected into the aqueous sample containing analytes by a syringe.



Scheme 1

A cloudy solution is formed [33] and the analytes in the sample is extracted into the fine droplets of extraction solvent, sedimented at the bottom of the conical test tube after centrifugation. The amount of analytes in the sedimented phase can be determined by instrumental analysis.

Only a limited number of reports are found in the literature for surfactant assisted dispersive liquid liquid microextraction that uses surfactant as an emulsifier agent [34-37]. Cetyl trimethylammonium bromide, Tween 80, Tween 20, Triton X-100, Triton X-114 and sodium lauryl sulphate are the commonly used surfactants as disperser agents. Literature survey reveals that trace level determination of metal ions was seldom carried out using surfactant assisted dispersive liquid liquid microextraction [37,38]. Considering the analytical instruments coupled with DLLME, many advanced instruments used in previous studies are expensive and energy intensive. In comparison, spectrophotometer is a simple instrument but very cost-effective and widely used for analysis of different metal ions in several matrices such as water, food samples and pharmaceutical samples [39].

In the present investigation Surfactant Assisted Dispersive Liquid-Liquid Microextraction (SA-DLLME) coupled with first order derivative spectrophotometry was developed for the determination of thallium at ultra trace levels. The effectiveness of extraction was considerably enhanced in the established method due to the application of surfactant, which forms emulsified phase as well as helps in the formation of ion pair with ionic complex and making them extractable into organic phase. The use of surfactant as both emulsifier and ion pairing agent in the proposed method makes the extraction effective and greener. To the best of our knowledge there has been no report on application of SA-DLLME combined with derivative spectrophotometry for the determination of thallium. Derivatisation of the spectral profiles enhances the selectivity and sensitivity of the method [40,41]. A new chromogenic reagent diacetylmonoxime *p*-hydroxybenzoyl hydrazone (DMPHBH) was used as a chelating agent. In the present method, the metal ions those are usually associated with thallium could be tolerated in considerable excess. The influence of experimental parameters affecting the complex formation and extraction conditions were studied and optimized. The developed method has been successfully applied for the trace level determination of thallium in different samples.

## 2. Experimental

### 2.1. Instrumentation

All spectral measurements were done with a Shimadzu 1800 UV/VIS spectrophotometer equipped with 1.0 mL quartz cells and the instrumental parameters were optimised. pH Measurements were done using Elico LI 120 pH system. Phase separation of DLLME was achieved by means of Remi C-24 BL revolutionary table top high speed cooling centrifuge.

### 2.2. Reagents

All the chemicals used were of analytical reagent-grade. Doubly distilled water was used throughout the experiments

for dilution of the reagents and samples. An accurately weighed amount of  $Tl_2O_3$  (Johnson Mathey, Germany) was dissolved in 1 mL of concentrated nitric acid and made up to 100 mL in a volumetric flask to get 1000 mg/L stock solution of thallium(III). Working standard solutions were prepared by suitable dilution of standardized stock solution [42]. 0.2 M sodium acetate and 0.2 M acetic acid were used for the preparation of buffer solutions.

A solution of chelating agent DMPHBH (0.1%) was prepared in ethanol. Aqueous solution of 0.1% (*w:v*) sodium lauryl sulphate (CDH Pvt. Ltd. India) was prepared in distilled water. Analytical grade carbon tetrachloride was used as an extractant. Other chemical reagents including methanol, ethanol, chloroform and dichloromethane were all analytical grade. Solutions of the studied interfering ions of suitable concentrations were prepared using A. R. grade reagents.

### 2.3. Synthesis and characterisation of DMPHBH

An equimolar mixture of diacetylmonoxime and *p*-hydroxy benzoylhydrazide in ethanolic medium was refluxed for 2 hours in presence of two drops of glacial acetic acid. The resulting diacetylmonoxime-*p*-hydroxybenzoylhydrazone was recrystallized using ethanol (Scheme 1). Characterisation of ligand was done by IR,  $^1H$  NMR and mass spectroscopic methods spectral analysis. Colour: White. Yield: 78%. M.p.: 310-312 °C. FT-IR (KBr,  $\nu$ ,  $cm^{-1}$ ): 3300-3400 (NH, OH), 1647 (C=O), 1608, 1580 (C=N), 972 (N-O).  $^1H$  NMR (300 MHz,  $DMSO-d_6$ ,  $\delta$ , ppm): 11.34 (s, 1H, oxime-H), 10.48 (s, 1H, OH), 10.08 (s, 1H, NH), 6.82-6.85 (d, 2H,  $J = 9$  Hz, Ar-H), 7.74-7.77 (d, 2H,  $J = 9$  Hz, Ar-H), 2.49 (s, 3H, -CH<sub>3</sub>), 1.91 (s, 3H, -CH<sub>3</sub>). MS (EI,  $m/z$  (%)): 235.1 ( $M+1$ )<sup>+</sup> corresponding to the molecular formula  $C_{11}H_{13}N_3O_3$ .

### 2.4. Surfactant assisted dispersive liquid-liquid microextraction procedure

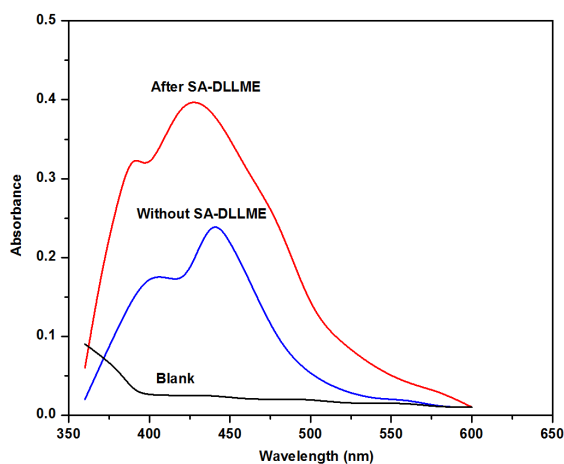
Suitable aliquots of thallium(III) [up to 100  $\mu g/L$ ] were transferred into a series of 15 mL calibrated conical centrifuge tubes. The optimum concentration of chelating agent (0.5 mL, 0.1% of DMPHBH) was added to metal solution. 1 mL of sodium acetate-acetic acid buffer solution of pH = 4.8 was added. Thallium ions react with DMPHBH to form a reddish yellow coloured species. The optimum amount of surfactant sodium lauryl sulphate (1 mL, 0.10% (*w:v*)) was added to the solution. The final volume was adjusted to 10.0 mL with doubly distilled water. 500  $\mu L$  of extractant ( $CCl_4$ ) was injected rapidly into the solution by using a syringe. After the injection the solution was shaken manually for 1 min. Cloudy solution was quickly formed, as the fine droplets of the immiscible extraction solvent were dispersed in the aqueous sample. After this stage, centrifugation (3 min at 4000 rpm) was used to settle these droplets to the bottom of the conical tube. After removing bulk aqueous solution by a syringe the extraction phase was diluted to 750  $\mu L$  with ethanol and transferred to 1 mL quartz microcell. The absorbance was measured at 425 nm against the reagent blank. The first order derivative amplitudes were measured at 390nm and 470 nm and calibration graphs were constructed by plotting the derivative amplitude against the concentration of  $Tl(III)$  ions.

## 2.5. Isolation and characterisation of coloured species

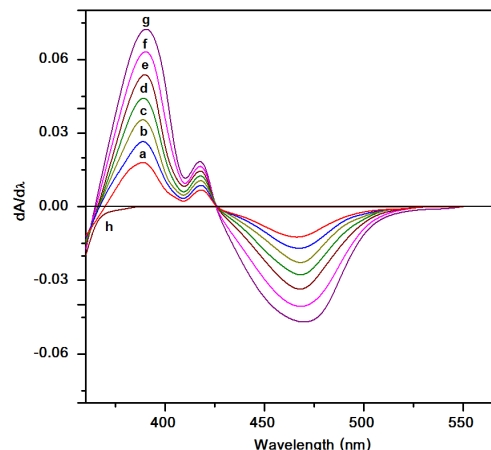
One equivalent of thallium(III) solution and two equivalents of DMPHBH solution were mixed to get Tl(III)-DMPHBH coloured complex which was isolated by using ethyl acetate as an extractant in the absence of SLS. The solid product was obtained by slow evaporation of the extract. IR and NMR spectroscopic methods were used to characterise of isolated species. The positions of signals due to oxime-OH, phenolic-OH and -NH protons ( $\delta$ , 11.41, 10.48 and 10.09 ppm, respectively) in the coloured species and free ligand are found to be almost same. This suggests absence of bonding of these groups to the central metal ion. In the complex  $\nu_{C=O}$  band remains in the original position suggests that carbonyl oxygen is not involved in bonding. The coordination through nitrogen atoms of C=N groups is indicated by the shifting of bands due to  $\nu_{C=N}$  (both azomethine and oxime) to lower frequencies. The  $\nu_{N-O}$  band shifts to higher frequency and appeared at  $1033\text{ cm}^{-1}$ . This suggests the coordination of the oxime group through N atom.

## 3. Results and discussion

In this work, surfactant assisted dispersive liquid-liquid microextraction (SA-DLLME) coupled with first order derivative spectrophotometry has been used for the determination of trace amounts of thallium. Thallium(III) reacts with DMPHBH to form a reddish yellow colored species. Therefore DMPHBH was used as a chelating agent. During the experiment, the concentration of  $500\text{ }\mu\text{g/L}$  was used for the determination of thallium (III) without SA-DLLME (from 350 to  $600\text{ nm}$ ). The absorption spectrum of the colored complex under the optimum conditions shows absorbance maxima at  $440\text{ nm}$ . For SA-DLLME, only  $60\text{ }\mu\text{g/L}$  of thallium was used for the determination. The pre concentrated complex of Tl-DMPHBH shows absorption maximum at  $425\text{ nm}$ . The preliminary enhancement of sensitivity was noticeable and the maximum absorption wavelength after SA-DLLME was found to be moved slightly to the shorter wavelength compared to the value without SA-DLLME. During the experiment, the blank absorbance of all reagents was corrected (Figure 1). First order derivative spectrum shows a peak at  $390\text{ nm}$  and a trough at  $470\text{ nm}$ . Zero-crossing point at  $425\text{ nm}$  corresponds to the  $\lambda_{\text{max}}$  of the complex (Figure 2).



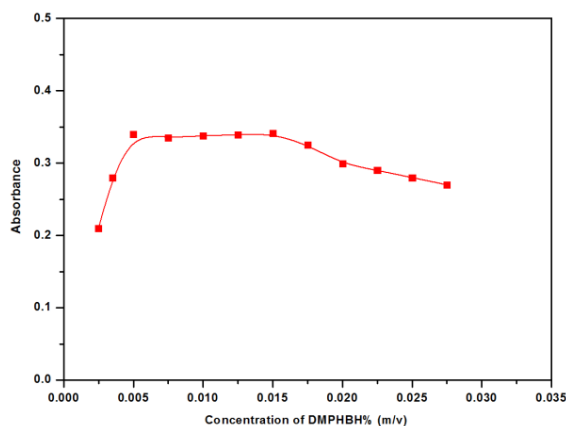
**Figure 1.** Absorption (zero order) spectra for the determination of thallium(III) with/without SA-DLLME. Without SA-DLLME conditions:  $500\text{ }\mu\text{g/L}$  of Tl(III);  $2.0\text{ mL}$  of  $0.1\%$  DMPHBH;  $2\text{ mL}$  buffer solution of  $\text{pH} = 4.8$  in a total volume of  $10\text{ mL}$ . SA-DLLME conditions:  $60\text{ }\mu\text{g/L}$  of Tl(III);  $0.5\text{ mL}$  of  $0.1\%$  DMPHBH;  $1\text{ mL}$  of  $0.1\%$  SLS;  $1\text{ mL}$  buffer solution of  $\text{pH} = 4.8$  in a total volume of  $10\text{ mL}$ .



**Figure 2.** First order derivative spectra of Tl(III)-DMPHBH system with SA-DLLME: (a-g)  $20, 30, 40, 50, 60, 70, 80\text{ }\mu\text{g/L}$  of Tl(III), (h) reagent blank.

### 3.1. Effect of concentration of chelating agent

The effect of concentration of the chromogenic reagent on the sensitivity and stability of the colored species has been investigated in detail, as shown in Figure 3. It was found that  $0.005\text{--}0.010\%$  (w:v) DMPHBH were required for the formation of colored species with maximum intensity. Below these concentrations, less intense colored species were formed, while the addition of excess of reagent could be co-extracted into organic phase results in decrease of extraction efficiency of target analytes. However,  $0.005\%$  DMPHBH in a total volume of  $10\text{ mL}$  was found to be optimum for SA-DLLME method.



**Figure 3.** The effect of DMPHBH concentration on the absorbance of Tl(III)[ $50\text{ }\mu\text{g/L}$ ]-DMPHBH coloured species.

### 3.2. Effect of sodium lauryl sulphate as disperser agent and ion pairing agent

In this method surfactant has two fundamental functions: 1) Disperser agent 2) The ion pair formation with positively charged colored species and making them extractable into organic phase. Cationic in nature of Tl(III)-DMPHBH colored species was established by ion exchange chromatographic studies. Sodium lauryl sulphate was found to be the most appropriate ion pairing agent making ionic species extractable via ion pair formation phenomenon. The effect of variable concentrations of sodium lauryl sulphate, SLS (anionic surfactant), on the absorption profiles of the colored species has been investigated (Figure 4).

**Table 1.** Analytical figures of merit.

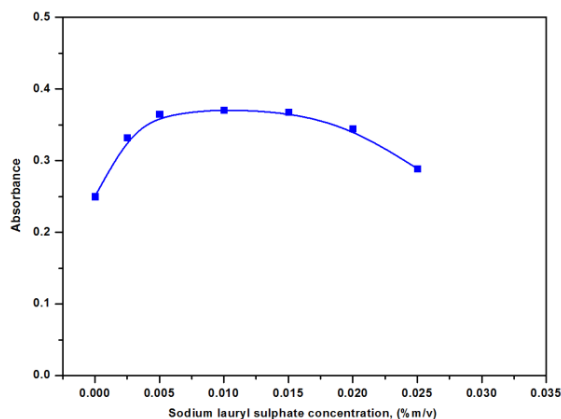
Parameters	Without SA-DLLME Zero order, 440 nm	With SA-DLLME Zero order, 425 nm	First order derivative	
			390 nm <sup>c</sup>	470 nm
Detection limit $C_L$ ( $k = 3$ ) ( $\mu\text{g/L}$ )	6.70	1.10	0.22	0.80
Quantitation limit $C_Q$ ( $k = 10$ ) ( $\mu\text{g/L}$ )	20.3	3.30	0.66	2.42
Upper Linear range ( $\mu\text{g/L}$ )	1450	95	100	100
Regression equation ( $y$ ) <sup>a</sup>				
Slope, $m$	0.0003	0.0067	0.0009	0.0005
Intercept, $c$	0.001	0.003	0.0005	0.0014
Correlation coefficient, $r$	0.9988	0.9997	0.9998	0.9982
Relative standard deviation (%) <sup>b</sup>	1.22	0.85	1.12	0.79
% Range of error <sup>b</sup> (95 % confidence limit)	1.55	1.15	0.86	1.08
Sensitivity enhancement factor <sup>d</sup>	23			

<sup>a</sup>  $y = mx + c$  where  $y$ , absorbance/derivative amplitudes;  $m$ , slope;  $x$ , concentration of thallium(III) in  $\mu\text{g/L}$ ;  $c$ , intercept.

<sup>b</sup> For five replicate analyses within Beer's law limits.

<sup>c</sup> Recommended for estimation.

<sup>d</sup> Sensitivity enhancement factor was calculated by the slope ratio of the calibration curves for thallium determination with and without SAE-DLLME.



**Figure 4.** The effect of SLS concentration on the absorbance of Tl(III) [60  $\mu\text{g/L}$ ]-DMPHBH colored species.

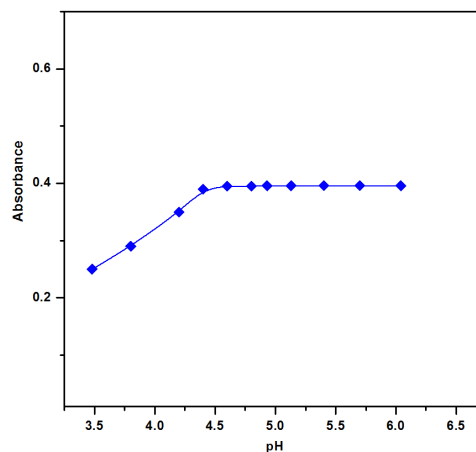
An overall SLS concentration of 0.01% (w:v) was maintained for further studies. An excess of surfactant could affect the extraction efficiency to some extent.

### 3.3. Effect of type and volume of extraction solvent

Extraction efficiency of the method primarily depends on the type of extractant and its volume used. This was studied using some conventional organic extractants such as dichloromethane, chloroform and carbon tetrachloride. The results showed that higher absorbance was obtained when carbon tetrachloride was used as an extractant and 500  $\mu\text{L}$  volume was found to be optimum for this experiment. After SA-DLLME, the enriched samples were diluted to 750  $\mu\text{L}$  by ethanol for the subsequent determination.

### 3.4. Selection of pH

The quantitative formation of the colored species and the extraction efficiencies are found to depend on the kind of buffer or the strength of the acid used. Various acidic buffers and different acids (Sulphuric acid, hydrochloric acid, acetic acid, nitric acid and phosphoric acid) were used for the study. Intensity was found to be decreased for Tl(III)-DMPHBH colored species in various acid medium. Sodium acetate-acetic acid buffer was found to be optimum because of higher sensitivity and longer stability of the colored species. The maximum and constant absorbance of the colored species was obtained in the pH range 4.60-6.04. Hence 1 mL of sodium acetate-acetic acid buffer solution of pH = 4.8 was used in further analytical studies. The results are shown in Figure 5.



**Figure 5.** Effect of pH on the absorbance of Tl(III) [60  $\text{mg/L}$ ]-DMPHBH colored species.

### 3.5. Phase separation

Phase separation after SAE-DLLME was done by means of centrifugation. By this, the turbid solution became pellucid and the organic phase was settled to the bottom of the conical tube. The optimum centrifugation rate and time were found to be 4000 rpm and 3 min, respectively.

### 3.6. Analytical parameters

Calibration graphs were plotted by using absorbance (at  $\lambda_{\text{max}}$ , 425 nm) or derivative amplitudes (at 390 and 470 nm) against concentration of thallium(III). The optimum concentration range, slope, intercept and correlation coefficient values are recorded in Table 1. The linear regression analysis of calibration plot shows a good linear fit. The high value of correlation coefficient and nearness of the intercept to zero show that calibration graphs are linear. The low percentage relative standard deviation and percentage error values calculated from five replicate analyses reflected good precision and accuracy of the proposed method.

Limit of detection  $C_L$  ( $k = 3$ ) and limit of quantification  $C_Q$  ( $k = 10$ ) in normal and derivative modes are presented in Table 1. Lower limit of linear range is determined by the limit of quantification value [43,44]. Derivative mode at 390 nm was recommended for the determination of thallium(III) in various samples based on lower detection limit, better sensitivity and selectivity.

**Table 2.** Tolerance limit of coexisting ions for the determination of 50 µg/L thallium(III) ions.

Ion added	Tolerance limit (µg/L)
Chloride, Nitrate, Sulphate	3000
Tartrate, oxalate, Citrate	800
Mn(II), Zn(II), Al(III), Cd(II), Cr(III), Mo(VI), Fe(III)	750
Co(II), Pb(II), Ni(II), W(VI), Zr(IV)	400
Ce(IV), Hg(II), Cr(VI), V(V), Ti(IV)	200
Cu(II)	30(500) <sup>a</sup>

<sup>a</sup> Measurement in the derivative mode at 390 nm.**Table 3.** Determination of thallium in mineral samples.

Sample	Tl spiked (µg/g)	Thallium content (µg/g)				F-test	t-test
		Proposed method		Reference method			
		Found <sup>a</sup> (Recovery %)	RSD %	Found <sup>a</sup> (Recovery %)	RSD %		
Sphalerite (1.0 g/50 mL)	-	55.2	0.64	55.7	0.76	1.22	0.86
	20	75.3 (100.5)	0.56	75.6 (99.5)	0.49	1.16	1.04
Galena (0.5 g/100 mL)	-	164.3	0.74	164.5	0.32	0.93	0.73
	25	189.4 (100.4)	0.43	189.3 (99.2)	0.50	1.10	1.12

<sup>a</sup> Mean value of five determinations.**Table 4.** Determination of thallium in various samples.

Sample	Thallium added, µg/L	Thallium found <sup>a</sup> by reference method, µg/L, ± RSD %	Thallium found <sup>a</sup> By proposed method ± RSD %	F-test	t-test
Natural water	50.00	50.30±1.37	50.20±1.48	1.14	1.49
	60.00	60.50±1.09	60.44±1.05	1.08	1.78
	40.00	40.15±1.41	40.10±1.15	1.48	1.94

<sup>a</sup> Mean value of five determinations.

### 3.7. Effect of diverse ions

In order to evaluate the selectivity of the proposed method the effect of associated ions on the trace level determination of thallium(III) was studied in both the zero order and the derivative modes and the results are recorded in Table 2. A large number of anions and cations did not interfere even when present in excess amounts. Copper(II) interacts with DMPHBH forming a coloured species having  $\lambda_{\max}$  at 390 nm. Recording spectra in the derivative mode enhances the selectivity of the method. The derivative amplitudes measured at 390 nm (zero-crossing point of Cu(II)-DMPHBH complex) were found to be independent of concentration of copper(II). This was confirmed by the construction of calibration graphs for the standards containing thallium(III) alone and in the presence of copper(II) ions at 390 nm. The slopes of the calibration graphs had similar values implying that the interference of copper(II) is completely removed. The linear regression analysis of calibration graph gives the following equations. Correlation coefficient values are given in parenthesis.

$$[D]_{390 \text{ nm}} = 0.00092 [\text{Tl(III)}] + 0.0005 \quad (0.9998) \quad (1)$$

$$[D]_{390 \text{ nm}} = 0.00089 [\text{Tl(III)}] + 0.0003 \quad (0.9993) \quad (2)$$

Equation (2) represents linear regression analysis of calibration graph in presence of 500 µg/L copper(II). Thus, by measuring the derivative amplitudes at 390 nm the interference due to copper can be eliminated up to 10 fold excess. Thus the selectivity of the method is noticeably enhanced by recording spectra in the derivative mode.

### 3.8. Composition and stability constant

The composition of the complex was studied by Job's continuous variation method and mole ratio method and was found to be 1:2 (metal:ligand). Proposed structure of Tl(III)-DMPHBH complex is depicted in Figure 6. Limiting logarithmic method was used to determine the stability constant of complexes and was found to be  $1.1 \times 10^7$  for Tl(III)-DMPHBH complex [45].

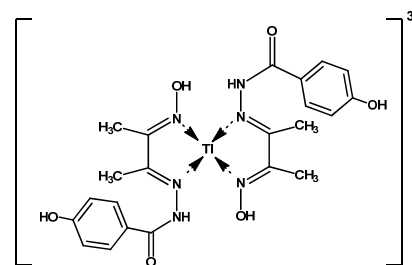


Figure 6. Proposed structure of Tl-DMPHBH complex.

## 4. Applicability of the proposed method

To ascertain the usefulness of the proposed reagent, the method has been tried for the determination of thallium(III) in minerals, soil and water samples.

### 4.1. Analysis of thallium in mineral samples

Minimum quantity of aqua regia was used to dissolve an accurately weighed sample of the powdered mineral. The solution was heated to dryness, treated with distilled water and filtered. The residue was dissolved in 10 M HCl and few drops of saturated bromine water was added which converted the Tl(I) ions present to Tl(III). The solution was heated on a steam bath for about 15 min to remove excess bromine. The solution was made up to a known volume using distilled water and analysed for thallium. The obtained results are in good agreement with the expected values. The method of standard addition and Rhodamine B method [46] were used to check the reliability of the procedure. The results are given in Table 3.

### 4.2. Determination of thallium in soil samples

The soil sample is powdered and air dried. A known weight the sample (about 1 g spiked with a known amount of thallium), was taken in a platinum crucible and heated with 5 g of anhydrous sodium carbonate. The dried material is extracted with distilled water and separated through a Whatman No. 40 filter paper. The filtrate is acidified with 10 M



HCl and saturated bromine water was added. The resulting solution was diluted to 25 mL with distilled water. The amount of thallium is estimated by following the proposed procedure (Table 4).

#### 4.3. Determination of thallium in water samples

The accuracy of the method was studied by the analysis of thallium in water samples spiked with different known amounts of thallium. The proposed procedure was used for the analysis of thallium(III) in each sample. The results are shown in Table 4. The Student's t-test and variance ratio F-test were used for the statistical comparison of the results of the proposed method with those of the reported Rhodamine B method [46]. The results show that the accuracy and precision of the proposed and reference methods were comparable.

#### 5. Conclusion

The proposed method offers advantages of simplicity, sensitivity and selectivity for the ultra-trace level determination thallium(III). The method is based on the surfactant assisted dispersive liquid-liquid microextraction coupled with derivative spectrophotometry. Sodium lauryl sulphate was used as surfactant to substitute traditional disperser solvent. Perhaps this is the first method reporting on the use of SADDLME for the determination of thallium in trace levels. The developed method was effectively applied for the determination of thallium in minerals, soil and water samples.

#### Acknowledgements

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