Dispersive Liquid-Liquid Microextraction Based on Solidification of Floating Organic Drop Combined with Flame Atomic Absorption Spectrometry for Preconcentration and Determination of Thallium(III) in Water Samples

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ABSTRACT: *Dispersive Liquid-Liquid MicroExtraction technique based on Solidification of a Floating Organic drop (DLLME-SFO) combined with flame atomic absorption spectrometry was developed for determination of thallium in water sample. An appropriate mixture of acetone and 1-undecanol was rapidly injected into an aqueous sample containing $TlCl_4^-$ which forms an ion pair with brilliant green reagent and as a result a cloudy mixture was formed. After centrifugation, the test tube was cooled for 5 min and the solidified 1-undecanol drop formed on the top of the solution was transferred into a suitable vial and it was dissolved in 300μL of acetone and finally introduced into the flame atomic absorption spectrometer. Several factors affecting the extraction process, such as the volume of the extractant and disperser solvents, centrifugation time, concentration of brilliant green, concentration of HCl, ionic strength, volume of diluting solvent and interferences were studied. Under the optimum operating conditions, the calibration graph was linear in the range of 240-6000ng/mL with a limit of detection of 90 ng/mL and preconcentration factor was 17. The Relative Standard Deviation (RSD) for five replicate measurements of thallium was 3.6%. The accuracy of the method was assessed using a certified reference material (unalloyed zinc) and spiked tap water. The results demonstrated high accuracy, recovery and applicability of the presented method.*

KEY WORDS: *Thallium(III), Dispersive Liquid-Liquid Microextraction Technique Based on Solidification of a Floating Organic Drop(DLLME-SFO), Flame atomic absorption spectrometry, Brilliant green.*
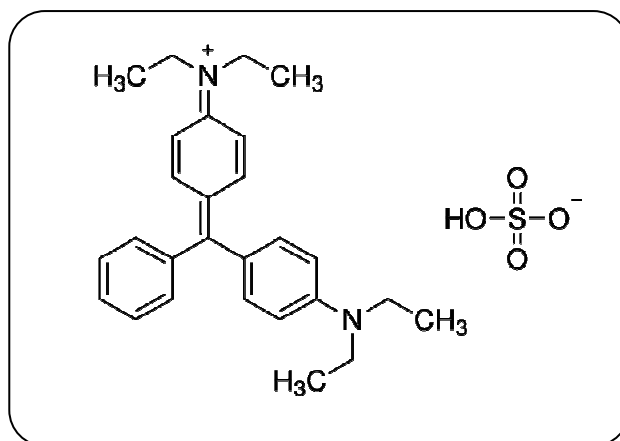
INTRODUCTION

Thallium is a heavy metal element and exists in environment with other elements (primarily oxygen, sulfur and halogens) in inorganic compounds. Thallium can be found in nature as Tl(I) and Tl(III) ions but its monovalent state has higher stability, whereas its trivalent state forms complexes of greater stability [1]. Its concentration in surface water usually is in the range [2] of 10–100 ng / L whereas in non-polluted soils [3] lies typically between 0.3 and 0.55 mg / kg.

However as the concentration of thallium in aquatic environment is very low, an analytical technique featuring high sensitivity and low detection limit is required. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [4-6], Laser-Excited Atomic Florescence Spectrometry (LEAFS) [7], and Electrothermal Atomic Absorption Spectrometry (ETAAS) [9-14] has been used for determination of thallium, but ICP-MS is an expensive analytical method and incurs high running cost, LEAFS is less frequently used technique and direct analysis with ETAAS involves many difficulties because of spectral and non-spectral interferences [13].

Flame Atomic Absorption Spectrometry (FAAS) is a simple and available technique for determination of thallium in real samples. However its main problem is the lack of sensitivity for trace analysis at μg / L level. This limitation can be overcome by the use of a preconcentration procedure. For this purpose various preconcentration/separation methods including single drop microextraction [14], hydride generation [15], solid phase extraction [16-19] have been used. However, these procedures are labor, time and reagent consuming, and require large volumes of sample. In 2008, Leong and Huang [20] reported a novel method called DLLME-SFO; this method is based on the principle of DLLME [21] and SFODME [22]. In this method, an appropriate mixture of 1-undecanol (as extractant solvent) and disperser solvent is rapidly injected into an aqueous sample by a syringe, and thereby, a cloudy solution is formed. The extraction solvent collected on the top of the test tube was cooled in an ice bath and the solidified 1-undecanol was then transferred into a suitable vial whereby immediately melted; and finally determined by a flame atomic absorption spectrometer. The vast contact area between the extraction solvent and the sample resulted in a faster mass transfer and shorter extraction time.

Brilliant green

The advantages of DLLME-SFO are, simplicity, high efficiency, rapidity, high recovery and higher extraction efficiency for heavy metal ions. Other advantages are low cost, simple extraction apparatus and consumption of very small amounts of less-toxic organic solvents. In addition, the extraction time is even shorter than SFODME. In this method there is no need to use a conical bottom glass tubes, which are easily damaged and difficulty cleaned. The floated extractant is solidified and easily collected for analysis.

The present work describes a simple method for extraction, preconcentration and determination of thallium(III) with brilliant green reagent based on DLLME-SFO complemented by a flame atomic absorption spectrometer. The results indicate that DLLME-SFO possesses a relatively high preconcentration factor, high sensitivity, and low detection limit; therefore it could be considered as an efficient technique for analysis of thallium (III) in real samples such as tap water.

EXPERIMENTAL SECTION
Reagents and standards

All reagents were of analytical reagent grade and deionized water was used throughout. A stock solution of 1000 mg / L thallium(III) ion was prepared by dissolving an appropriate amounts of $Tl(NO_3)_3 \cdot 3H_2O$ (Fluka) in 1% HNO_3. Working standard solutions were prepared freshly at various concentrations by appropriate dilutions of the stock standard solution with distilled water. A 0.015% (w/v) brilliant green (Merck) solution was prepared as the counter ion. The following reagents were employed for studying the interference effects:

KNO_3,$NaNO_3$,$Ca(NO_3)_2 \cdot 4H_2O$,$Zn(NO_3)_2 \cdot 6H_2O$,$Fe(NO_3)_3$,$Pb(NO_3)_2$,$Cd(NO_3)_2 \cdot 4H_2O$,$Cu(NO_3)_2 \cdot 3H_2O$,$Na_2CO_3.$ H_2O, CH_3COONa, $Co(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, $TlNO_3$ and $SnCl_2.2H_2O$ all from Merck.

Instrumentation

A shimadzu AA-670 atomic absorption spectrometer with a D2 lamp for background correction was used for determination of thallium. A thallium hollow cathode lamp (Shimadzu AA-670), adjusted at 5mA, was used as the radiation source. Measurements were carried out in peak height mode at 276.8 nm, using a spectral band width of 0.5 nm. Phase separation by centrifugation was assisted using Centurion Scientific Centrifuge (Model Andreas HettichD72, Tuttlingen, Germany).

Dispersive liquid-liquid microextraction based on solidification of floating organic drop (DLLME–SFO)

For DLLME-SFO, a mixed solution of 300 µL / L undecanol(extractant solvent) and 2mL acetone (disperser solvent) was rapidly injected into 10mL of aqueous solution. Then, 1.5 mL of brilliant green solution (0.015%) and 2 mL of HCl 2M was added (pH<2), and the vial was sealed. Upon the injection of organic solvent into water solution, a cloudy solution, consisting of many dispersed fine droplets of 1-undecanol, would be formed and the ion pair is back extracted into the fine droplets of 1-undecanol. After centrifuging at 4000 rpm for 4 min, the organic solvent droplets was floated on the surface of the aqueous solution due to its lower density with respect to water. The sample vial was placed in ice bath and the floated solvent became solidified as a result of its low melting point (11 °C). The solidified solvent containing the ion pair was transferred into a 1.5 mL by a spatula. The solidified organic solvent was melted quickly at room temperature. The extractant was then dissolved in 300µL of acetone to prior analysis by FAAS.

Preparation of real samples and Standard reference material

Tap water was collected from local source.Standard reference material was used for validation of the method. The European Reference Material ERM®-EB325 was purchased and analyzed (IRMM).0.6520 g of the certified reference material was digested with 0.8 M HCl, on a hot
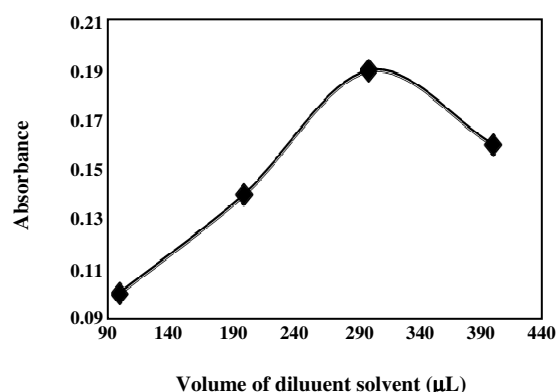

Fig. 1: Effect of diluent solvent volume on the absorbance of 2 mg / L of Tl^{3+}, 2 mL of HCl 2 M, 1 mL of brilliant green (0.015%),1mL of acetone, 300 µL of 1-undecanol and 2 min centrifuging time.

plate followed by addition of, 0.5 mL of 30% H_2O_2. After complete dissolution of the solid material, the solution was heated at 70 °C up to a volume of approximately 10 mL and; then diluted with HCl (0.8 M) to 25 mL. Appropriate dilutions were made prior to the analysis depending on the extent of thallium.

RESULTS AND DISCUSSION

Different parameters affecting the extraction efficiency such as type and volume of the extraction and disperser solvents, centrifuging time, brilliant green concentration, ionic strength, concentration of HCl and diluents solvent volume were optimized.

Influence of the diluent solvent volume

To examine the effect of diluents volume of acetone, solutions containing different volumes of acetone were used and the DLLME-SFO procedures was employed. When the diluent solvent was added in the various compositions, λ_{max} of complex was slightly shifted due to changes of polarity. 10 mL of an aqueous solution containing 20 µg Tl^{3+}, 1 mL brilliant green 0.015% and 2 mL of 2 M HCl was taken in each test tube and, then 1mL acetone and 300 µL 1-undecunol was added as disperser and extractant solvent, respectively. The extractant was mixed with different volumes of acetone (100, 200, 300 and 400 µL) prior to determination of thallium by FAAS shown in Fig. 1. The maximum absorbance was obtained using 300 µL of the diluent solvent.

Selection of disperser solvent

Miscibility of the disperser solvent with extraction solvent and sample solution is the most important criteria for selection of a disperser solvent. Acetone, acetonitrile and ethanol were selected as candidates of disperser solvents. A series of sample solutions containing Tl^{+3} were extracted using 1.0 mL of each disperser solvent containing 300µL of 1-undecanol. The results are shown in Fig. 2. According to the obtained results, similar signals were obtained using acetone and acetonitrile. Acetone was soluble in 1-undecanol and was miscible with water. Acetone enabled to disperse 1-undecanol as fine particles in aqueous phase and forms a cloudy solution (water/ acetone / 1-undecanol) and had higher absorbance. Finally, acetone was selected as the disperser solvent due to its low toxicity and low cost.

Optimization of extractant solvent volume

Selecting a suitable extraction solvent is a crucial parameter in this method. It should have low solubility in water, low melting point below room temperature, lower density than water, and good spectrophotometric behavior. By the increasing the extraction solvent volume, the final organic phase obtained by centrifugation is increased, resulting in a decrease of the concentration of the target analyte in organic phase. Although the extraction recovery keeps almost constant, the enrichment factor will be decreased, leading to a decrease of the sensitivity of the determination for the target compounds. Solutions containing different volumes of 1-undecanol(100, 200, 300, 400, 500 µL) and 1mL of disperser solvent were used. Based on obtained results (Fig. 3), the maximum absorbance was obtained using 300 µL of the extraction solvent. Therefore, 1-undecanol (melting point: 11 ^{0}C) was selected as the extractant solvent for this study.

Optimization of disperser solvent volume

To examine the effect of disperser solvent volume, solutions containing different volumes of acetone(0.5, 1, 1.5 and 2mL) and 300µL volume of extraction solvent was used. The disperser solvent volume directly affects the formation of the cloudy solution (water/disperser solvent/extraction solvent), the degree of the dispersion of the extraction solvent in aqueous phase, and subsequently, the extraction efficiency. The results is shown in Fig. 4 which
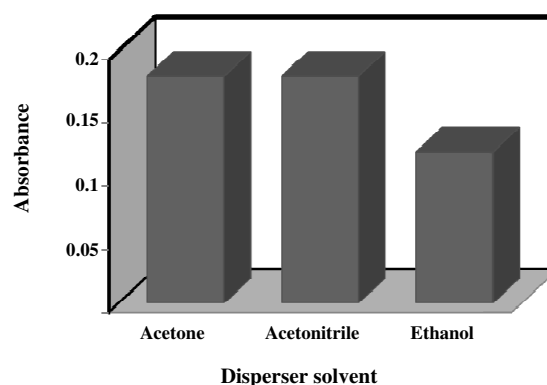

Fig. 2: Effect of disperser solvent on the absorbance of 2 mg / L of Tl^{3+}, 2 mL of HCl 2 M, 1 mL of brilliant green (0.015%), 1 mL of disperser solvent, 300 µL of 1-undecanol, 2 min centrifuging time and 300 µL of diluent solvent.
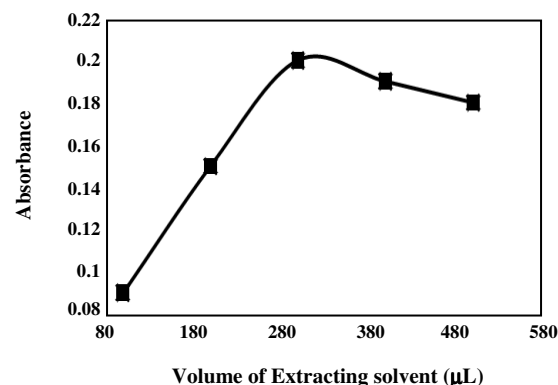

Fig. 3: Effect of extracting solvent volume on the absorbance of 2 mg L^{-1} of Tl^{3+}, 2 mL of HCl 2 M, 1 mL of brilliant green (0.015%), 1 mL of acetone, 2 min centrifuging time and 300 µL of diluent solvent.
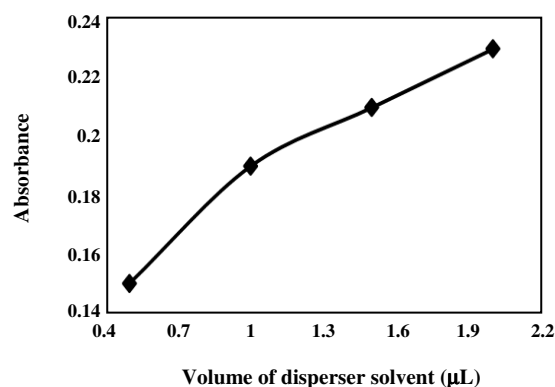

Fig. 4: Effect of disperser solvent volume on the absorbance of 2 mg / L of Tl^{3+}, 2 mL of HCl 2 M, 1 mL of brilliant green (0.015%), 300 µL of 1-undecanol, 2min centrifuging time and 300 µL of diluent solvent.

reveals 2mL of disperser solvent would give the maximum absorbance. The results show that by increasing the volume of disperser, the Tl signal would increase. However, volumes higher than 2mL was not employed due to the restricted volume of the test tube.

Effect of centrifuging time

If the centrifugation time is not enough, the organic phase cannot be completely collected on top of vial. The effect of centrifugation time on the extraction efficiency was performed using 2mL of acetone and 300µL volume of extraction solvent added to the aqueous solution. Different centrifugation times (2, 3, 4, 5 min) were used and the results (Fig. 5) show that the maximum absorbance was obtained for 4 min centrifugation time.

Influence of HCl concentration

To investigate the effect of HCl concentration on the complex formation, different volumes of 2 M HCl (0.5, 1, 1.5, 2, 2.5 mL) were added to the test tube while other operating conditions were kept constant. Based on the obtained results (Fig. 6), the maximum absorbance was obtained using 2 mL of 2 M HCl (pH<2).

Influence of ion pair forming reagent concentration

The effect of the concentration of brilliant green reagent as an ion pairing reagent with $TlCl_4^-$, was studied. Different concentrations (0 – 0.03% w/v) of brilliant green were used. Under the optimum conditions, the effects of brilliant green concentration on the extraction efficiency is shown in Fig. 7. The efficiency of thallium (III) tetrachloride extraction increases with increasing the concentration brilliant green and its maximum value corresponds to 0.0225 % in the aqueous solution.

Effect of ionic strength

To investigate the influence of ionic strength on microextraction performance, various experiments were performed by adding different amounts of KCl (0 to 1 mol / L). Tow opposite effects were observed when the ionic strength of solution was increased. By increasing the amount of KCl, the volume of the sedimented phase increases, which decrease the enrichment factor. On the other hand, salting-out effect that increases the enrichment factor by increasing the extraction efficiency. According to the obtained results, the enrichment factor is nearly constant by increasing the amount of KCl.
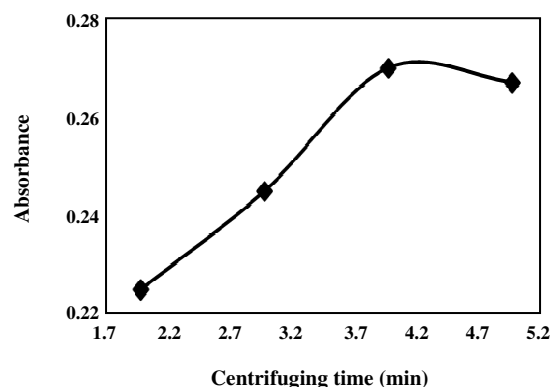

Fig. 5: Effect of centrifuging time on the absorbance of 2 mg / L of Tl^{3+}, 2 mL of HCl 2 M, 1 mL of brilliant green (0.015%), 2 mL of acetone, 300 µL of 1- undecanol and 300 µL of diluent solvent.
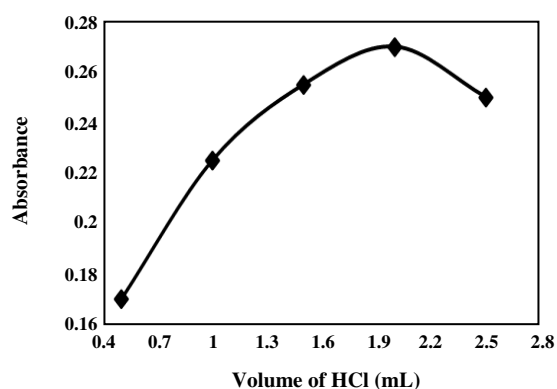

Fig. 6: Effect of concentration HCl for extraction of 2 mg / L of Tl^{3+}, 1 mL of brilliant green (0.015%), 2 mL of acetone, 300 µL of 1-undecanol, 4 min centrifuging time and 300 µL of diluent solvent.
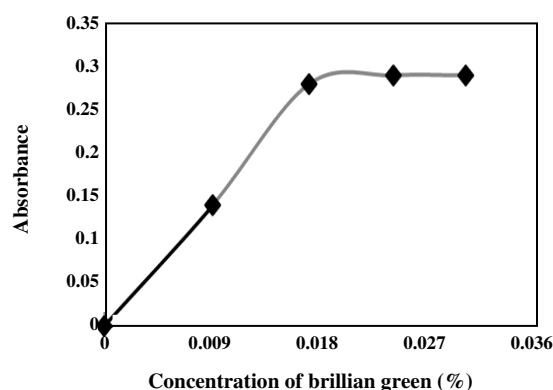

Fig. 7: Effect of brilliant green concentration on the absorbance of 2 mg / L of Tl^{3+}, 2 mL of HCl 2 M, 2 mL of acetone, 300 µL of 1-undecanol, 4min centrifuging time and 300 µL of diluent solvent.

Table 1: Effect of interfering ions on the recovery of Tl^{3+} ions.

Interfering ions	Recovery (%)
Sn^{2+}	99.3
Cd^{2+}	98.1
Cu^{2+}	98.6
Co^{2+}	99.5
Ca^{2+}	102.8
Pb^{2+}	99.1
Zn^{2+}	99.1
Na^+	100.9
K^+	101.4
Fe^{3+}	98.0
Al^{3+}	99.1
Tl^+	97.2
CO_3^{2-}	98.1
CH_3COO^-	99.5

Table 2: Results of determination of thallium in water sample.

Sample	Thallium added (ng/mL)	Recovery (%)
Tap water[a]	0	-
	2	97.0

Interferences

The effects of coexisting ions in real water samples on the recovery of Tl^{3+} were also studied. Interfering ions could affect the determination of Tl^{3+} ions by interaction with brilliant green or Tl^{3+} ions. For this purpose, 10.0 mL of a solution containing 2 mg L^{-1} of Tl^{3+} and the interfering ions at 100 fold excess were treated at the optimized conditions. Table 1 shows the tolerance limits of the interfering ions defined as the concentration of the coexisting ions, which would change the recovery of the metal ions by ± 5%. The results showed this method would be suitable for thallium determination.

Figures of merit for the proposed method

Under the optimized conditions, the calibration curve was linear in the range of 240-6000 ng / mL of Tl^{3+} with a correlation of coefficient(r) of 0.999. The limit of detection, based on $3S_b$ was 90 ng / mL. The enrichment factor, defined as the ratio of the slope of the calibration

graphs before and after the preconcentration, was 17. The Relative Standard Deviation (RSD) for five replicate analysis of 2 µg / mL of Tl^{3+} was 3.6%.

Analysis of real samples and reference material

The proposed procedure was applied to determine thallium content in tap water. The results are given in Table 2. The recovery test for thallium in water sample spiked with thallium under the optimum conditions was studied. According to the results, the added thallium can be quantitatively recovered from the water samples by the proposed procedure. These results demonstrate the applicability of the procedure for determination of thallium in water sample. The accuracy of the proposed procedure was evaluated by analysis of the certified unalloyed zinc (ERM®-EB325) and recovery of 97% was achieved (Table 3). The concentration of Tl was found to be (35.4 ± 1.8) which is in good agreement with the certified value of (36.8 ± 1.2).

Comparison of this method with the Other Sample Preparation Techniques

A comparison between the presented method and the other reported preconcentration methods for the Tl extraction and determination is shown in Table 4. Some of the preconcentration methods of this table are Dispersive Liquid-Liquid MicroExtraction based on solidification of Floating Organic droplet (DLLME- SFO), Dispersive liquid-liquid microextraction. Apparently, this work presented wide linear range. The results demonstrated high accuracy, recovery and applicability of the presented method.

CONCLUSIONS

In the present study, a novel DLLME-SFO was developed for extraction and determination of Tl^{3+} in water sample. DLLME-SFO uses an extraction solvent with lower toxicity instead of highly toxic solvents in DLLME and provides high extraction recovery within a short period of time. The method was successfully applied to determine Tl^{3+} in environmental water sample. Furthermore, it is inexpensive and has higher enhancement factor. Compared to other methods of extraction such as liquid phase microextraction (LPME), DLLME-SFO is fast, simple, inexpensive and consumeslow volumes of organic solvent.

Table 3: Analytical results of thallium for certified reference material.

Sample	Found (mg / kg)	Certified (mg / kg)	Recovery (%)
ERM®-EB325	35.4±1.8	36.8 ±1.2	97.0

Table 4. The comparison between this method and other preconcentration and determination techniques.

Method	LOD	%RS	Linear range (μg / L)	Ref.
DLLME-SFo	2.1 ng / mL	2.5	6 - 900 ng / mL	23
DLLME	3.3 ng / L	5.3	-	24
DLLME-SFo	90ng / mL	3.6	240-6000 ng / mL	This work

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