



# Solid Phase Extraction Method for Separation and Pre-concentration of Thallium in Water Samples Using a Novel Adsorbent

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## Abstract

In this study, a new and simple column-mode separation method has been proposed for the pre-concentration and removal of trace amounts of thallium(III) (Tl) from water samples. The procedure was based on sorption of Tl(III) ions by a solid phase extraction column filled with 4-[(2-hydroxy, 3-methoxy benzylidene)4-amino]1,2,4-triazol-5-thione on microcrystalline naphthalene. The determination was performed directly using flame atomic absorption spectrometry (FAAS) method. The main factors affecting the extraction recovery were investigated and optimized. The interference effect of various ions on the determination of Tl(III) was also studied. In optimum conditions, the precision of the proposed method for sample solutions containing 0.2 µg/mL of Tl(III) was 2.0%, and the enrichment factor was found to be 35. The proposed method was evaluated and employed for pre-concentration and removal of Tl(III) from spiked natural (Tap and well) and industrial water samples.

**Keywords:** Pre-concentration, Thallium (Tl), Solid phase extraction (SPE), Removal, Flame atomic absorption spectrometry (FAAS), Water samples

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## 1. Introduction

Among all the pollutants, heavy metals have received considerable attention owing to their role in the pollution of the environment. Thallium (Tl) as a heavy metal has been identified to be an environmentally important element due to its toxic effects. It is regarded as one of the most toxic heavy metals causing both chronic and acute poisoning. In the long term, Tl has the potential to cause changes in blood chemistry, damage to liver, kidney, intestinal and testicular tissues, and hair loss. Generally, it exists in nature as Tl(I) and Tl(III) ions that exhibit different bioavailability and toxicity properties. It has been stated that Tl(III) is more toxic than Tl(I). Tl exists in the environment commonly together with lead, zinc, iron, tellurium, and alkalis. It is used as a catalyst in making alloys, optical lenses, low temperature thermometers, dyes, pigment in scintillation counters. Additionally, it is used as medicine, rodenticide, and insecticide (1-5). Therefore, considerable interest in sample preparation and determination of Tl has been seen in the research literature.

Various analytical procedures have been presented for pre-concentration (extraction) and removal of Tl, mainly based on liquid-liquid extraction and dispersive liquid-liquid extraction (6-8), single drop liquid-phase micro-extraction (9), solid-phase extraction (SPE) and dispersive

SPE (10-15), co-precipitation and ion-exchange (16-19).

Among these techniques, SPE is one of the most effective procedures because of its simplicity, rapidity, and capability to reach a high enrichment factor. Furthermore, SPE can eliminate the interfering matrix effects and also has the ability to combine with some detection methods.

In SPE technique, the sorbent is a critical factor to obtain suitable recovery and selectivity. In the present paper, a simple and accurate pre-concentration methodology, based on sorption of Tl(III) by an SPE column filled with 4-[(2-hydroxy, 3-methoxy benzylidene)4-amino]1,2,4-triazol-5-thione on microcrystalline naphthalene as a new sorbent, has been established. The determination process was directly carried out by flame atomic absorption spectrometry (FAAS). The influence of various factors in the adsorption and removal of Tl(III) from sample solutions was investigated and optimized. Finally, the practical capability of the proposed method was tested using the spiked natural and industrial water samples.

## 2. Materials and Methods

### 2.1. Instrumentation

FAAS (Varian Spectra 220, Australia) equipped with D2 lamp for background correction and air-acetylene burner was used for absorbance measurements. Hollow cathode lamp was employed as a radiation source at the

wavelength of 276.8 nm (12). The operating parameters (10 mA and bandwidth 0.5 nm) were according to the manufacturer's recommendation. In order to obtain the maximum absorbance signal, the acetylene flow rate and burner height were also adjusted. A pH meter (ISTEK-720P, South Korea) was used for measuring the acidity of sample solutions.

## 2.2. Chemicals and Standards

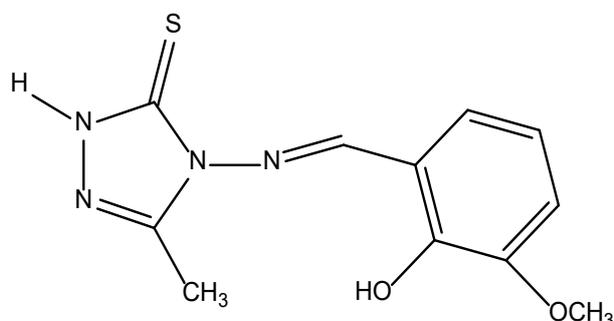
Chemicals and solvents from Merck were used. A stock solution of 100 µg/mL of Tl(III) was prepared by dissolving an accurate weight of  $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  (98%) in distilled water in a 100 mL flask and diluting to the mark with solvent. Working solutions were prepared by appropriate dilution of it with distilled water. The Excel software program (2010) was used for statistical analysis.

## 2.3. Preparation of SPE Cartridge

4-[(2-hydroxy, 3-methoxy benzylidene)4-amino]1,2,4-triazol-5-thione was synthesized according to the literature procedure (20) using 2-hydroxy-3-methoxybenzaldehyde as aldehyde. The solution of 4-amino-5-methyl-2H-1,2,4-triazole-3(4H)-thione (in  $\text{C}_2\text{H}_5\text{OH}$ ) was treated with 2-hydroxy-3-methoxybenzaldehyde in a molar ratio of 1:1.2 and the resulting mixture was acidified by hydrochloric acid (37%, 4 drops). The reaction mixture was refluxed for 10 hours. The solid residue was filtered and washed with cold solvent. The molecular structure of ligand is shown in Fig. 1.

A mixture containing 20.0 g of naphthalene, 2.0 g of the synthesized ligand (as adsorbent), and 60 mL of acetone was prepared in a 500 mL beaker. It was mixed at 40°C for 20 minutes. Then, distilled water was gradually added and the solution was stirred again for 30 minutes. The solid mass was separated using a Whatman filter paper, dried, and washed by distilled water.

The prepared adsorbent was used as a solid matrix material in a homemade SPE cartridge. The SPE column was a plastic syringe with a diameter of 9 mm and a length of 9 cm. The bottom of the column was plugged with Teflon wool to prevent loss of the adsorbent during the



**Fig. 1.** The Molecular Structure of Ligand: E-4-((2-hydroxy-3-methoxybenzylidene)amino)-3-methyl-1H-1,2,4-triazole-5(4H)-thione.

SPE process. Then, it was filled up and packed without gaps by adding 0.20 g of adsorbent and placing a stopcock at the upper end. The length of adsorbent inserted in the column was about 50 mm.

## 2.4. Pre-concentration and Determination of Tl(III)

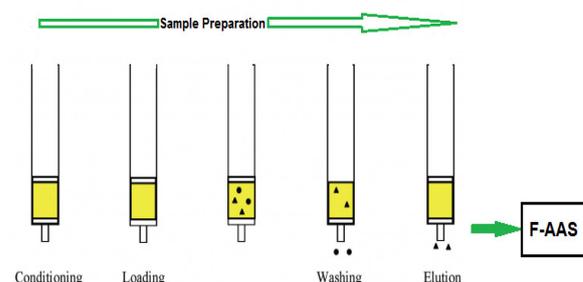
Working solutions containing Tl(III) were prepared and their pH values were adjusted using the  $\text{HNO}_3$  or  $\text{NaOH}$  solutions (0.1 mol/L). The prepared solutions (50 mL) were passed through the column with an appropriate flow rate. In the next step, the column was washed with distilled water to remove the effect of matrix interferences for Tl(III) measurement. Then, the adsorbed analyte ions on the SPE column were separated and eluted using  $\text{HNO}_3$ . Finally, the Tl(III) determination was performed by FAAS method at the wavelength of 276.8 nm and in optimum operating conditions. The schematic diagram of the flow system used for pre-concentration and determination of Tl(III) is shown in Fig. 2.

## 2.5. SPE of Different Spiked Water Samples

Tap and well water samples were obtained from the laboratory and the neighboring areas of the Islamic Azad University of Yazd, respectively. The samples were collected after flowing for a few minutes in 1000 mL PE bottles. Industrial water (used in combined cycle power plant for purposes such as processing, washing, and cooling) samples were prepared from several sites of Yazd power plant and collected in 1000 mL PE bottles. The water samples were stored at 4°C in a refrigerator until analysis. The synthetic samples were prepared and filtered through a 0.45 µm filter to remove any suspended materials and were treated according to the proposed procedure.

## 3. Results and Discussion

In order to obtain a better extraction recovery, the effects of various factors on SPE including pH, eluent (type, concentration, and volume), and sample solution (flow rate and volume) were investigated and optimized by one-factor-at-a-time method. The extraction recovery of Tl(III) was calculated based on the following formula:



**Fig. 2.** The Schematic Diagram of Pre-concentration and Determination Steps for Tl(III) Using the Proposed Method.

$$\text{Recovery}(\%) = \frac{\text{response}_{\text{extracted sample}}}{\text{response}_{\text{non-extracted sample}}} \times 100$$

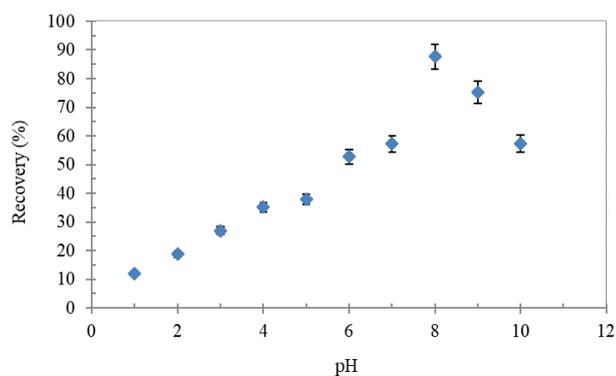
### 3.1. Effect of pH

The pH value of the sample solution plays an important role in the adsorption process (12) of the Tl(III) on the prepared SPE column. The effect of pH on the extraction recovery of Tl(III) was investigated in the range of 1–10, according to the proposed procedure. The results are shown in Fig. 3, which indicated that the maximum recovery of Tl(III) (87.7%) occurs at pH=8 and then it decreased. The low extraction recovery at the acidic pH values is due to the competition of proton with Tl(III) for adsorption on the adsorbent and also at the basic pH values, Tl(III) can precipitate as Tl(OH)<sub>3</sub>. Therefore, pH=8.0 was selected as the optimum value in the following experiments.

### 3.2. Effect of Type, Concentration, and Volume of Elution Solvent

The eluent is another important factor to be considered for obtaining quantitative extraction recovery in SPE studies (21). It must be able to desorb the analyte ions in a low volume while being compatible with the determination method (FAAS). In order to choose the best eluent among the potential solvents, under obtained conditions, different solvents such as nitric acid, phosphoric acid, and ammonia were examined and their extraction recoveries were 90.6%, 47.4%, and 15.2%, respectively. Therefore, it was found that nitric acid can provide the complete desorption and best extraction recovery.

The effect of nitric acid concentration (0.5–3.0 mol/L) on the extraction recovery of Tl(III) ions from aqueous solutions was also tested (Fig. 4). According to the results shown in Fig. 4, the best extraction recovery (>90%) for HNO<sub>3</sub> was achieved at the concentration of 3.0 mol/L. Further increases in nitric acid concentration can lead to the destruction of adsorbent structure and decreased



**Fig. 3.** Effect of pH on Recovery of Tl(III) Ions Using the Proposed SPE Column

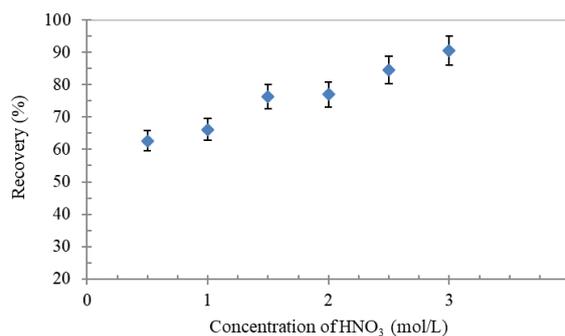
Conditions: Tl(III) concentration: 0.2 µg/mL; sample volume: 40 mL; sample flow rate: 4 mL/min; HNO<sub>3</sub> (1 mol/L, 3 mL).

extraction recovery. Therefore, 3.0 mol/L was used for subsequent investigations.

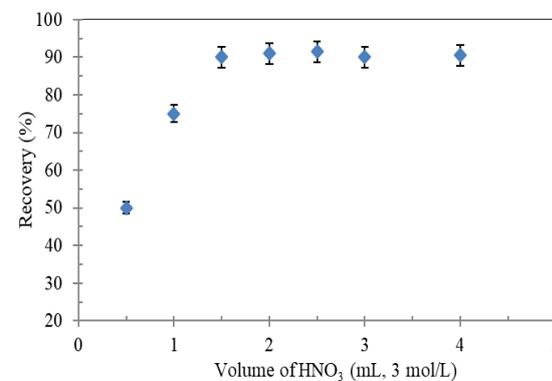
Different volumes (0.5–5 mL) of nitric acid (3.0 mol/L) were examined for elution of adsorbed Tl(III) from homemade SPE cartridge. The experimental results are depicted in Fig. 5. As it is seen, the extraction recovery of metal ions increased up to a volume of 1.5 mL and then it reached a constant level. Therefore, 1.5 mL of nitric acid (3.0 mol/L) was found to be a sufficient value for both quantitative recovery of the analyte ions and solvent saving.

### 3.3. Effect of Sample (Flow Rate and Volume)

The sample flow rate through SPE column has a significant effect on both the analyte adsorption and analysis time (22). The influence of this factor on the extraction recovery was investigated at different flow rate values (1–8 mL/min) (Fig. 6). As it is seen in Fig. 6, the flow rate in the range of 1–6 mL/min had a significant effect on the recovery of Tl(III) while at higher values, it decreased. This can be attributed to incomplete adsorption of Tl(III) ions on the column. Therefore, the flow rate of 6 mL/min was adopted to obtain the maximum recovery of Tl(III)



**Fig. 4.** Effect of Concentration of HNO<sub>3</sub> (Eluent, 3 mL) on Recovery of Tl(III) Ions Using the Proposed SPE Column. Conditions: Tl(III) concentration: 0.2 µg/mL; sample volume: 40 mL; sample flow rate: 4 mL/min; pH: 8.



**Fig. 5.** Effect of Volume of HNO<sub>3</sub> (eluent) on Recovery of Tl(III) Ions Using the Proposed SPE Column.

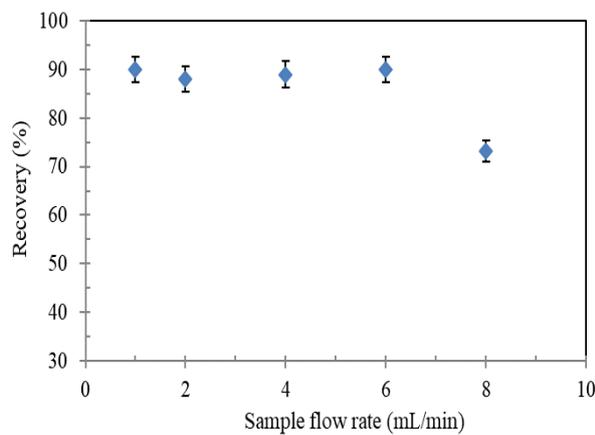
Conditions: Tl(III) concentration: 0.2 µg/mL; sample volume: 40 mL; sample flow rate: 4 mL/min; pH: 8; HNO<sub>3</sub> (3 mol/L).

ions and save time.

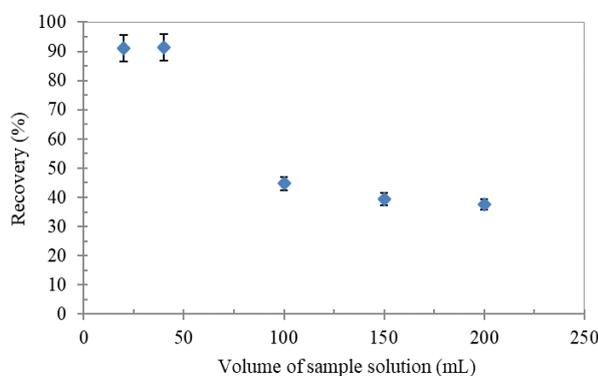
In order to evaluate the breakthrough volume of the SPE cartridge, a constant amount of analyte was added to different volumes of distilled water (20-200 mL) and was loaded on the prepared column and then was treated based on the proposed procedure. According to the recovery results shown in Fig. 7, volumes of up to 50 mL of sample solution could be applied without significant loss of extraction recovery for Tl(III). Consequently, the enrichment factor of 35 was also achieved in the presented work.

### 3.4. Effect of Divers Ions

For selectivity study, the effect of potential interferences from some foreign ions was tested on the recovery of 0.2 µg/mL of Tl(III) using the proposed method. The results are summarized in Table 1. The tolerance limit was defined as the maximum concentration of ions which caused a relative error smaller than ±3% in determination



**Fig. 6.** Effect of Sample Flow Rate on Recovery of Tl(III) Ions Using the Proposed SPE Column  
 Conditions: Tl(III) concentration: 0.2 µg/mL; sample volume: 40 mL; HNO<sub>3</sub> (3 mol/L, 1.5 mL), pH: 8.



**Fig. 7.** Effect of Sample Volume on Recovery of Tl(III) Ions Using the Proposed SPE Column  
 Conditions: Tl(III) concentration: 0.2 µg/mL; sample flow rate: 6 mL/min; pH: 8; HNO<sub>3</sub> (3 mol/L, 1.5 mL).

of the analyte ions. According to this Table, most of the ions did not interfere, even when presented in 500 to 1000-fold excess over analyte. Therefore, the proposed method showed a good selectivity that could be applied in pre-concentration (or removal) and determination of Tl(III) in real water samples.

### 3.5. Application of the Proposed Method for Different Water Samples

In order to evaluate the extraction recovery of the proposed method, it was exploited for sample preparation and determination of Tl(III) from three water samples (well, tap, and industrial water) which have been collected from the local area of Yazd, Iran. The known amounts (2 levels) of the standard solution of Tl(III) were spiked to the water samples. The concentration of Tl(III) in synthetic water samples and their extraction recoveries are listed in Table 2. The values varied within the range of 93.0%–95.0% with RSD of 2-3%. The satisfactory recovery results obtained confirm that the proposed SPE-FAAS is a suitable alternative method for trace determination of Tl(III) in such water samples.

**Table 1.** Tolerance Limit for Diverse Ions in the Determination of 0.2 µg/mL of Tl(III)

Foreign Ion	Tolerance Limit (w <sub>ion</sub> /w <sub>Tl</sub> )
Na <sup>+</sup>	1000
K <sup>+</sup>	1000
Cl <sup>-</sup>	1000
NO <sub>3</sub> <sup>-</sup>	1000
Ca <sup>2+</sup>	750
Mg <sup>2+</sup>	500
Mn <sup>2+</sup>	500
Sn <sup>2+</sup>	100
Fe <sup>3+</sup>	100
Co <sup>2+</sup>	50
Ni <sup>2+</sup>	50
Cu <sup>2+</sup>	10
Ag <sup>+</sup>	5

**Table 2.** Application Studies for Adsorption of Tl(III) in Different Water Samples Using the Proposed Method

Water sample	Tl(III)		Recovery %
	Added (µg/mL)	Found (µg/mL)	
Drinking	-	-	-
	0.10	0.09 <sub>4</sub>	94 ± 1.8
	0.20	0.19	95 ± 2.0
Tap	-	-	-
	0.10	0.09 <sub>3</sub>	93 ± 1.5
	0.20	0.19	95 ± 2.2
Industrial <sup>a</sup>	-	-	-
	0.10	0.09 <sub>3</sub>	93 ± 2.5
	0.20	0.19	95 ± 3.0

<sup>a</sup> Combined cycle power plant.

**Table 3.** Comparison of the Proposed Method with the Other Methods for Pre-concentration and Determination and of Tl

Method	Enrichment or Pre-concentration Factor	Recovery %	RSD %	Ref.
DLLME-ICP-MS	-	96.3-103	1.5	23
ILDLLME-ETAAS	100	97.3-103	5.3	24
CPE-ICP-MS	125	99.6-101.5	2.3	25
UA-CPE-ICP/OES	160	98.5-101	1.7-2.8	26
DSPE-FAAS	298	95.5-103	3.2	21
FI-SPE-FAAS	77	95-103.6	2.6	27
SPE-FAAS	100	98-104	1.2	28
SDME-ETAAS	50	94-96	5.1	9
ET-AAS	100	96.5-101	4	22
FI-SPE-FAAS	105	94-104	3.2	12
SPE-FAAS	35	93-95	2	This work

DLLME: Dispersive liquid-liquid microextraction; ICP: Inductively coupling plasma; MS: Mass spectrometry; IL: Ionic liquid; UA: Ultrasound assisted; CPE: Cloud point extraction; DSPE: dispersive solid phase extraction; FI: Flow injection; SDME: Single drop microextraction; ET: Electrothermal; OES: Optic emission spectrometry; FAAS: Flame atomic absorption spectrometry.

In addition, some analytical parameters of the proposed method were compared with those of other published methods used for the Tl adsorption of different samples (Table 3). As it is shown, the proposed method presented a suitable accuracy that is comparable to other reported methods. Furthermore, low cost, affordability, and simplicity are the other advantages of the presented method over the reported works (9,12,21-28).

#### 4. Conclusion

In this study, a procedure for the determination of trace amounts of Tl(III) ions was described using FAAS, which applied a new SPE-column ((2-hydroxy, 3-methoxy benzylidene)4-amino]1,2,4-triazol-5-thione on microcrystalline naphthalene) for sample preparation. The system was successful in pre-concentrating analyte ions from sample solutions without the need for additional instrumentation. The analytical validation parameters of the proposed method were comparable with other presented methods. Furthermore, it can be considered as a cost-effective and simple method for Tl(III) determination in different water samples.

#### Conflict of Interest Disclosures

The authors declare that they have no conflict of interests.

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