

Research Article, Issue 3 Analytical Methods in Environmental Chemistry Journal Journal home page: www.amecj.com/ir



# Thallium extraction in urine and water samples by nanomagnetic 4-Aminothieno[2,3-d] pyrimidine-2-thiol functionalized on graphene oxide

Seyed Jamilaldin Fatemi <sup>a,\*</sup>, Mohammad Reza Akhgar <sup>b</sup> and Masoud Khaleghi Abbasabadi <sup>c</sup>

<sup>a</sup> Department of Chemistry, Shahid Bahonar University of Kerman, 133 -76169, Kerman, Iran
 <sup>b</sup> Department of Chemistry, Faculty of Science, Kerman Branch, Islamic Azad University, Kerman, Iran
 <sup>c</sup> Researcher in Nano Technology Center, Research Institute of Petroleum Industry (RIPI), P.O. Box 1998-14665, Tehran, Iran

## **ARTICLE INFO:**

Received 20 May 2021 Revised form 18 Jul 2021 Accepted 13 Aug 2021 Available online 28 Sep 2021

## **Keywords:**

Thallium, Water and urine, Nanomagnetic 4-Aminothieno[2,3-d] pyrimidine-2-thiol functionalized on graphene oxide,

Dispersive magnetic micro solid-phase extraction

### ABSTRACT

Thallium is a water-soluble metal and extra dosage has toxicological effect in human body. Thallium is readily absorbed by inhalation, ingestion and skin contact. The symptomatology of thallium toxicity was seen in patients with hemorrhage, bone/gastrointestinal problems, delirium, convulsions and coma. So, accurate determination of thallium in water and human urine is necessary. In this research, a novel and applied method based on 25 mg of nanomagnetic 4-Aminothieno[2,3-d] pyrimidine-2-thiol functionalized on graphene oxide (Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO) was used for thallium extraction in 50 mL of water, wastewater and urine samples by dispersive magnetic micro solid-phase extraction (DM-µ-SPE). After extraction and back-extraction of solid phase by 1 mL of nitric acid solution, the concentration of thallium ions determined by flame atomic absorption spectrometry (F-AAS). The working/linear range, the limit of detection (LOD), and preconcentration factor (PF) were achieved (4-1400 µg  $L^{-1}$ ; 4-300 µg  $L^{-1}$ ), 0.9 µg  $L^{-1}$ , and 50, respectively (Mean RSD%=1.8) water; 2.1 urine). The absorption capacity of GO and Fe<sub>2</sub>O<sub>4</sub>-ATPyHS@ GO adsorbent were achieved 7.2 mg g<sup>-1</sup> and 137.5 mg g<sup>-1</sup> for 5 mg L<sup>-1</sup> of thallium, respectively. The procedure was validated by ICP-MS analyzer.

# 1. Introduction

The Thallium use as in semiconductor and optical industries. The concentration of thallium in rocks and soil (limestone, granite) ranges between 0.05-1.7 mg kg<sup>-1</sup> and 1.7-55 mg kg<sup>-1</sup>, respectively [1]. The organic slates and carbon source have 1000 mg kg<sup>-1</sup> thallium [2], and high concentration of thallium exist sulfur salts of thallium [3]. Contamination with thallium is effected on the environmental and

\*Corresponding Author: Seyed Jamilaldin Fatemi Email: fatemijam@uk.ac.ir https://doi.org/10.24200/amecj.v4.i03.150 human health. Thallium has toxic effect even at sub ppb concentration and accumulate in plant, vegetables, fruit, microorganisms, animals and human tissues due to water soluble [4,5]. The occupational exposure of thallium is 0.1 mg m<sup>-2</sup> for skin and more than 15 mg m<sup>-2</sup> is dangerous for human. Thallium can be absorbed from inhalation, ingestion and skin. So, the thallium toxicity must be evaluated in patients through determination in water, wastewater, urine, hair, nail and blood samples. The toxicity of this element is higher compared to mercury, cadmium and lead [6,7]. The mean daily diet contains 2 ng L<sup>-1</sup> thallium

and the average content of thallium in the human body was 0.1 mg. The concentrations in blood is less than 3  $\mu$ g L<sup>-1</sup> and due to reference values thallium has low concentration between 0.15-0.6  $\mu$ g L<sup>-1</sup> in blood and 0.02– 0.3  $\mu$ g L<sup>-1</sup> in serum [8,9]. Groesslova and Wojtkowiak showed that the toxicity of thallium is mainly related to the similarity between Tl (I) ions and K ions, which cause to the thallium interference with potassium and disorder of potassiumassociated metabolic processes. Also, thallium disrupts the disulfide bonds and cysteine cross-linking and cause to the keratin reduction [10,11]. The thallium-201, a radioactive isotope, was used for evaluating coronary artery disease. This type of thallium is more than 4000 times less potent. Thallium-201 is useful in distinguishing toxoplasmosis from Primary CNS lymphoma (PCNSL)in HIV patients. Also, the thallium-201 scintigraphy is useful to diagnose the Kaposi sarcoma, the thyroid imaging and various tumors of the lungs [12]. the acute thallium toxicity has been reported between 6-15% in humans by health organization and the dosage from 10 to 15 mg kg<sup>-1</sup> is a lethal dose for humans. Elimination phase for thallium stats about 24 hours' post-exposure and is mainly achieved through renal excretion and the elimination phase may take up to 30 days with long time. Symptoms of acute exposure of thallium are gastrointestinal, CNC problem, and skin [13,14]. The chronic exposure is gastrointestinal symptoms include, the abdominal pain, the vomiting and the diarrhea. Therefore, due to adverse effect of thallium in human health, the determination human urine, foods and waters must be considered [15]. Based on the thallium toxicity, the power technique must be used for determining of thallium in environmental (water) and human biological (urine) samples. Numerous papers showed that the measurement of this topic with different analytical methods in various matrixes such as, the laser excited atomic fluorescence spectrometry (LE-AFS) [16], the anodic stripping voltammetry (ASV) [17], the inductively coupled plasma optical

emission spectrometry (ICP-OES) [18], the flame atomic absorption spectrometry (FAAS) [19], the electrothermal atomic absorption spectrometry (ET-AAS) [19] and the high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) [20].

In this research, a novel method based on nanomagnetic 4-Aminothieno[2,3-d] pyrimidine-2-thiol functionalized on graphene oxide as a  $Fe_3O_4$ -ATPyHS@GO adsorbent was used for the extraction of thallium in the water, wastewater and the urine samples. The thallium concentration was determined based on dispersive magnetic micro solid-phase extraction by F-AAS.

#### 2. Experimental

#### 2.1. Apparatus and Characterization

The thallium value was determined by flame atomic absorption spectrometer coupled (F-AAS, Varian, USA). The Air-acetylene  $(C_2H_2)$  and the deuterium lampas was adjusted The limit of detection (LOD) and sensitivity of F-AAS obtained 0.2 mg L<sup>-1</sup> and 0.15 mg L<sup>-1</sup>. The HCL of Tl was adjusted based on catalog book with wavelength of 276.8 nm, slit of 0.5 nm and current of 10 mA. All samples injected to F-AAS by auto-injector (0.5-3 mL). The working range and linear range of AT-AAS were obtained 0.2-75 mg L<sup>-1</sup> and 0.2- 15 mg L<sup>-1</sup>, respectively. The electrothermal atomic absorption spectrophotometer (ET-AAS, Varian, USA) was used for validation of thallium in urine and water samples. For suppress of ionization in F-AAS, the reagent of KNO, or KCl was used as a 2000 mg L<sup>-1</sup> of K in final solution. The pH was calculated by digital pH meter (Metrohm 744, Swiss). The different buffer of the acetate (PH 3-6) were used for adjusting pH. The ultra-sonication (Grant, U.K) and the Sigma 3K30 magnetic centrifuge (30.000 rpm, UK) was used. The natural flake graphite (325 mesh, 99.95%), were purchased from Merck chemical Company. The Perkin Elmer Spectrum spectrophotometer (65 FT-IR, USA) was used for FT-IR spectra. The PRO X-ray diffractometer was used for The XRD spectra. The images of field emission scanning electron microscope (FE-SEM) were prepared by SEM of Tescan Mira-3.



**Fig.1.** Synthesis of nanomagnetic ATPyHS@GO adsorbent by 4-aminothieno[2,3-d] pyrimidine-2-thioland and Fe<sub>3</sub>O<sub>4</sub> on GO [22-24]

## 2.2. Materials

All reagents with analytical grade such as; the thallium solution (Tl NO<sub>3</sub>), the acids and base solutions (HNO<sub>3</sub>, HCl, NaOH) were purchased from sigma Aldrich (Germany). The standard solution of thallium nitrate (CAS N: 10102-45-1, Sigma, Germany) was prepared from stock of 1000 mg L<sup>-1</sup> solution in 1 % HNO<sub>3</sub> for further studies. The standard solutions for calibration were daily prepared by distilled water (DW) from Millipore (USA). The other reagents such as acetone and ethanol with analytical grade were purchased from Merck (Germany). The citric acid was used for phosphate citrate buffer for PH between 2.1–7.4 and the acetate buffer was used for pH from 2.8 to 6.2 which was purchased from Merck.

## 2.3. Synthesis of $Fe_3O_4$ -ATPyHS@GO

The GO was prepared following the modified Hummers method. 5 g of graphite powder was mixed with 250 mL of  $H_2SO_4$  and stirred for 24 h. Then, 30 g of KMnO<sub>4</sub> was gradually added to the mixture based on stirring at 50 °C [21]. Due to previous studies, 4-aminothieno[2,3-d] pyrimidine-

2-thiol (10 g) was added to 150 mL of ethanol and DW (1:1 v/v). Then, 180 mg of GO was added to the resulted solution at 35°C. The  $H_2PO_2(50 \text{ mL}, 50 \text{ mL})$ wt%) was added to product and stirred for 90 min. The product of ATPyHS@GO was washed and dried by DW and oven, respectively. The magnetic nanostructure was prepared by co-precipitation of FeCl, 4H,O and FeCl, 6H,O, in the presence of 4-Aminothieno[2,3-d] pyrimidine-2-thiol graft on GO (ATPyHS@GO). First, the mixture of FeCl, 4H,O and FeCl, 6H,O was prepared with a molar ratio of 1:2. For synthesis nanomagnetic adsorbent, 10 mg of 4-aminothieno[2,3-d] pyrimidine-2-thiol grafted on graphene oxide (ATPyHS@GO) was solved to 10 mL of DW and sonicated for 40 min. Then 125 mg of FeCl, 4H<sub>2</sub>O and 200 mg of FeCl, 6H,O in 10 mL of deionized water were added to remain solution at 25°C. For adjusting of pH=11, the ammonia solution was added at 65°C. After 20 min stirring, the product was cooled at 25°C. Finally, the black Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO was centrifuged at 4000 rpm for 50 min, washed for 10 times (DW) and dried at 70 °C based on vacuum accessory [22-24].

#### 2.4. Extraction Procedure

By the DM- $\mu$ -SPE procedure, 50 mL of water and standard samples (4 - 300  $\mu$ g L<sup>-1</sup>) were used for separation and determination of thallium ions at pH 4-6. Firstly, 25 mg of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO added to water, urine and thallium standard solution and the sample sonicated for 3.0 min at pH=5. After sonication, the Tl ions was chemically absorbed on thiol groups (ATPyHS) of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent (Tl<sup>+</sup>.....:SH-ATPy @ GO) and then, settled down in bottom of magnetic centrifuge conical tube. Then, the thallium ions were back-extracted from Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO at basic pH with NaOH solution (0.1 M, 0.5 mL) and was simply separated by the external magnetic accessory. Finally, the remain solution was determined by FAAS after dilution with DW up to 1 mL (Fig.2). The procedure was round for a blank solution without thallium ions for ten times. The analytical parameters showed in Table 1. The recovery of thallium extraction was calculated by the equation 1. The  $C_i$  and  $C_f$  are the primary and final concentration of thallium, which was determined by F-AAS (n=10).

Recovery (%) = 
$$(C_i - C_f)/C_i \times 100$$
 (Eq.1)

**Table 1.** The analytical parameters for determination thallium in water and urine samples based on  $Fe_3O_4$ -ATPvHS@GO adsorbent by the DM-u-SPE procedure

Parameters	Values				
Working pH	4-6				
Amount of Fe <sub>3</sub> O <sub>4</sub> -ATPyHS@GO adsorbent (mg)	25				
Sample volume of water (mL)	50				
Volume of sample injection	1.0 mL				
Linear range for water working range for water Mean RSD %, n=10	4.0-300 μg L <sup>-1</sup> 4.0-1400 μg L <sup>-1</sup> 1.8				
LOD for water	0.9 µg L-1				
Preconcentration factor	50				
Volume and concentration of NaOH	0.5 mL, 0.4 M				
Shaking time	3.0 min				
Correlation coefficient	$R^2 = 0.9997$				



**Fig.2.** The extraction procedure of thallium in water and urine samples based on Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent by the DM-μ-SPE procedure

# 3. Results and Discussion

# 3.1. TEM Spectra

The TEM of  $Fe_3O_4$ -ATPyHS@GO and GO adsorbent was prepared (Fig. 3a and 3b). Based on the TEM images, both of GO and  $Fe_3O_4$ -ATPyHS@ GO have the thin sheets about 30-80 nm. The  $Fe_3O_4$  was seen as black point on surface of GO in TEM of  $Fe_3O_4$ -ATPyHS@GO adsorbent (Fig. 3a).

# 3.2. FE-SEM Spectra

The morphology of  $Fe_3O_4$ -ATPyHS@GO and GO adsorbent is prepared by the field emission scanning electron microscopy (FE-SEM) (Fig. 4a and 4b).



Fig. 3a. TEM of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO

100 nm

Based on the SEM images, both of GO and  $Fe_3O_4$ -ATPyHS@GO have the thin sheets nearly related to each other. The SEM images of GO and  $Fe_3O_4@4$ -PhMT-GO showed us, the HS and  $Fe_3O_4$  had no effect on the morphology of the GO sheets. Also, the nanoparticles of  $Fe_3O_4$  have a spherical morphology on HS-GO with a diameter of 40 nm.

# 3.3. FTIR diagram

The infrared spectra of pure GO and  $Fe_3O_4$ -ATPyHS@GO are presented in Figure 5. The spectra of GO and  $Fe_3O_4$ -ATPyHS@GO are showed to the stretching bands of (O-H;



Fig. 3b. TEM of the GO adsorbent



Fig. 4a. FE-SEM of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO



Fig. 4b. FE-SEM of the GO



Fig. 5. The FTIR spectra of pure GO and Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbents

3415), (C=O; 1730), (C=C; 1624), and (C-O; 1061). Also, the peak of FTIR at range of 2600-3500 cm<sup>-1</sup> belong to to the O-H and C=C(OH) function. Moreover, the peak of 1400 cm<sup>-1</sup> and 2234 cm<sup>-1</sup> related to tertiary hydroxyl groups(OH) and HS function on GO. In –addition the peaks at 628 cm<sup>-1</sup> and 583 cm<sup>-1</sup> belong to the Iron oxide [22-24].

#### 3.4. X-ray diffraction (XRD) patterns

The X-ray diffraction patterns of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO was shown in Figure 6. GO have a single original peak at  $2\theta = 12^{\circ}$  which is related to the O<sub>2</sub> groups. In both of GO and Fe<sub>3</sub>O<sub>4</sub>@4-PhMT- GO adsorbent, the XRD peaks were observed at  $2\theta = 12^{\circ}$  and  $41.58^{\circ}$  which are belonged to (002) and (100), respectively. Based on the XRD peak of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO, the intensity of the peak at  $2\theta = 12^{\circ}$  has decreased due to function on GO with HS and Fe<sub>3</sub>O<sub>4</sub>. In addition, the peak at  $2\theta = 12^{\circ}$  showed that the stability of O<sub>2</sub> functionalities even after the functionalization of GO with HS or Fe<sub>3</sub>O<sub>4</sub> groups. The similar XRD peak of Fe<sub>3</sub>O<sub>4</sub> can be seen for the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent which are confirmed to the cubic spinel crystal structure of Fe<sub>3</sub>O<sub>4</sub>. So, the functionalities of HS and Fe<sub>3</sub>O<sub>4</sub> were successfully done without changing in structure of GO.



Fig. 6. XRD patterns of (a) GO adsorbent and (b) Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent [22]

#### 3.5. Optimizing extraction parameters

By DM- $\mu$ -SPE procedure, the separation/extraction of thallium in water, wastewater and urine samples was achieved by a novel Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO adsorbent between 4-300 µg L<sup>-1</sup> thallium concentration. For the efficient extraction of thallium based on Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent, the extraction conditions must be optimized. So, the effective parameters such as pH, the amount of adsorbent, the eluent, the sample volume, and the adsorption capacity must be studied.

## 3.5.1. pH effect

The pH of extraction of thallium in water and urine samples must be evaluated and optimized. The favorite pH cause to increase the adsorption of thallium ions by the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent. So, the different pH between 2-11 was examined for thallium extraction in water and urine samples by adjusting pH with different buffer solutions. The results showed us, the maximum extraction of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent for Tl(I) was obtained at pH of 4-7. Also, the recoveries for thallium were decreased at acidic pH less than 4 and basic pH more than 7. So, the pH 5 was selected as the optimal pH for extraction of thallium in water and urine samples by the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO adsorbent (Fig.7). The mechanism of extraction of thallium was occurred by the dative bond of thiol

group  $[2(Ti^+) \dots^2:$ SH-ATPyHS@GO-Fe<sub>3</sub>O<sub>4</sub>) with the positively charged of thallium(Tl<sup>+</sup>) at optimized pH. In addition, the thallium ions participated (Tl(OH)) at more than pH 7.5.

## 3.5.2. Amount of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent

Foe high extraction of thallium in water/urine samples, the amount of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO adsorbent evaluated at thallium concentration between 4-300  $\mu$ g L<sup>-1</sup>. For this purpose, the various amount of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent between 5-50 mg were studied for Tl(I) extraction in water and standard solutions by the DM- $\mu$ -SPE method. As Figure 8, the best recovery for thallium extraction was created by 20 mg of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO adsorbent. So, 25 mg of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@ GO adsorbent was used for further work.

## 3.5.3. Effect of eluents

The various eluents such as  $HNO_3$ ,  $H_2SO_4$ , NaOH and  $CH_3COOH$  were used for back extraction thallium ions from the  $Fe_3O_4$ -ATPyHS@GO adsorbent. In acidic and basic pH, the dative bonding between the thiol group (HS) and thallium (Tl) was started to dissociate (4>pH>6). So, after break down the bonging, the thallium ions released in eluent solution by elution. At pH more than 7, the thallium participated as thallium hydroxyl (Tl-OH)



Fig.7. The effect of pH on thallium extraction in water and urine samples by  $Fe_3O_4$ -ATPyHS@GO adsorbent



**Fig.8.** The effect of amount of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent on thallium extraction in water and urine samples by the DM-μ-SPE method

and in low pH, the bonding of Tl-SH dissociated. Due to results, the  $HNO_3$  and NaOH has more recovery as compared to  $H_2SO_4$  and  $CH_3COOH$ . The different acid solution with different volume and concentration was used for back extraction Tl(I) in water and urine samples (0.2-2.0 mol L<sup>-1</sup>, 0.1-0.5 mL) by the DM- $\mu$ -SPE procedure. Due to results, the Tl ions were completely back-extracted from the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent by nitric acid and NaOH solutions more than 1.0 mol L<sup>-1</sup> and 0.1 mol L<sup>-1</sup>, respectively. Therefore, 0.1 mol L<sup>-1</sup> of NaOH was used as an optimum eluent for this study. Also, the effect of different volumes of eluents from 0.1 mL to 0.5 mL for thallium was checked. Therefore, 0.5 mL of NaOH (0.1 M) selected as optimum elution (Fig. 9). Also, the more concentration of NaOH (M>0.2) caused to the thallium participation (Tl-OH).



**Fig.9.** The effect of eluent concentration on thallium extraction in water and urine samples by the  $Fe_3O_4$ -ATPyHS@GO adsorbent

#### 3.5.4.Effect of sample volume

The main factor for efficient extraction of Tl ions from water/urine samples is sample volume. The effect of different volumes between 10-200 mL for Tl extraction based on the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent was studied and optimized in water and urine samples (4-300  $\mu$ g L<sup>-1</sup>). By results, the high recovery (%) was occurred for 55 mL for urine and 70 mL for water samples. So, 50 mL of sample volume was used for further work by the DM- $\mu$ -SPE procedure (Fig. 10).

#### 3.5.5. Effect of sonication time

The dispersion of Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent increased the interaction between thiol group (HS) and thallium ions at pH 5. By uniform dispersion of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent, the chemical adsorption of thallium occurred. Therefore, the extraction recovery increased due to physical adsorption of GO and chemical bonding of HS group in Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent. Moreover, the sonication times was effected on extraction rate. The various sonication times (1-10 minute) was used and the recoveries obtained. The best recoveries were achieved at the sonication time of 2.5 min. Therefore, 3.0 min was used as the optimum time for thallium extraction in water and urine samples. After sonication, the magnetic adsorbent (Tl- Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO) was collected from the liquid samples by extra magnet accessory.

#### 3.5.6. The adsorption capacity

The Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent was dispersed in water samples and the extractions of thallium ions from liquid samples were followed many times and re-usage of adsorbent calculated. The results showed, the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent can be used for 18 extraction cycles at pH of 5.0. The absorption capacities (AC) of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent depended on the BET, the function group and size of adsorbent. In batch system, 25 mg of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO nanoparticles was used in 50 mL of thallium solution (5 mg L<sup>-1</sup>; ppm) at pH 5.0. After 10 minutes' sonication, the AC of adsorbent calculated by F-AAS. The adsorption capacities of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent for Tl ions were obtained 137.5 mg g<sup>-1</sup>.

#### 3.5.7. Interference of coexisting ions

The effect of main coexisting ions on thallium extraction based on the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent was evaluated in water and urine samples by the DM- $\mu$ -SPE procedure. So, the effect of various concentrations of interfering ions (1-3 ppm) was studied for 50 mL of water samples by proposed procedure at pH 5.0. The main concomitant ions in water and urine were selected and used for thallium extraction by the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent. The results showed that the interference coexisting ions do not affect on the thallium extraction in optimum conditions (Table 2).



**Fig.10.** The effect of sample volume on thallium extraction in water and urine samples by the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent

1						
Mean ratio (C <sub>1</sub> /C <sub>TI(I)</sub> )	Mean ratio (C <sub>1</sub> /C <sub>TI (I)</sub> )	Recovery (%)	Recovery (%)			
Urine	Water	Urine	Water			
400	650	98.1	97.0			
700	900	96.5	98.3			
550	700	98.6	99.2			
900	1200	97.9	98.5			
1000	1300	97.3	98.8			
350	400	97.1	97.6			
600	600	97.4	98.7			
800	950	97.7	98.6			
200	300	96.8	97.4			
500	700	98.2	97.9			
	Mean ratio (C 1/C 10)           Urine           400           700           550           900           1000           350           600           800           200           500	Mean ratio (C $_1$ /C $_{TI(0)}$ )         Mean ratio (C $_1$ /C $_{TI(0)}$ )           Urine         Water           400         650           700         900           550         700           900         1200           1000         1300           350         400           600         600           800         950           200         300           500         700	Mean ratio (C 1/C 10)         Mean ratio (C 1/C 10)         Recovery (%)           Urine         Water         Urine           400         650         98.1           700         900         96.5           550         700         98.6           900         1200         97.9           1000         1300         97.3           350         400         97.1           600         600         97.4           800         950         97.7           200         300         96.8           500         700         98.2			

 Table 2. The effect of interferences ions on extraction of thallium in human urine and water samples by the DM-µ 

 SPE procedure

## 3.5.8. Validation in real samples

The DM- $\mu$ -SPE procedure was used for extraction and determination of thallium in water and urine samples. The validation of results for the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent were shown in Table 3. For validation, the real samples were spiked to different concentration of standard solutions of thallium and process continued by the DM- $\mu$ -SPE procedure at pH 5.0 (Table 3). As Table 3, the efficient extraction and high recovery for thallium ions were obtained in water and human urine samples by nanoparticles of the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent. Moreover, the standard reference materials were prepared in water and urine samples with ICP-MS analyzer for validating of the DM- $\mu$ -SPE procedure based on the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent (Table 4).

**Table 3.** Validation of methodology for thallium ions in water and urine samples based on Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent by spiking of real samples

Sample*	Added (µg L-1)	*Found (μg L <sup>-1</sup> )	Recovery (%)
<sup>a</sup> Well water		56.4 ± 2.4	
	50	$104.6\pm4.5$	96.4
<sup>b</sup> Wastewater		$146.6 \pm \hat{\tau}/\delta$	
	150	$294.3 \pm 13.4$	98.5
Wastewater <sup>c</sup>		$122.9 \pm 5.9$	
	100	$225.7 \pm 11.2$	102.8
WT T		$4.7\pm0.2$	
*Orine	5	$9.6\pm0.5$	98.0
Urine <sup>⊮</sup>		$11.9 \pm 0.4$	
	10	$21.6\pm0.9$	97.0
		28.9±1.3	
<sup>v</sup> Urine	30	$59.8 \pm 2.7$	103

\*Mean of three determinations of samples  $\pm$  confidence interval (P = 0.95, n =10)

<sup>a</sup>Well water prepared from Varamin garden, Tehran, Iran

<sup>b</sup>Wastewater prepared from chemical factory, Karaj, Iran

°Wastewater prepared from petrochemical factory, Arak, Iran

<sup>v</sup>Urine prepared from workers from car, chemical and paint factories, Iran

Sample	ICP-MS (µg L <sup>-1</sup> )	Added	Found*( µg L <sup>-1</sup> )	Recovery (%)
CRM1	25.3 ± 0.5		$24.9 \pm 1.2$	
		20.0	$44.3 \pm 1.9$	97.0
CRM 2	62.7 ± 0.7		64.1 ± 2.8	
		50.0	$113.2\pm5.2$	98.2
CRM 3	5.1±0.2		$4.8\pm0.2$	
		5.0	$9.9\pm0.4$	102
CRM 4	$6.4 \pm 0.2$		$6.2 \pm 0.3$	
		5.0	11.0± 0.5	96.0

 Table 4. Validation of D-μ-SPE procedure for thallium determination in water and urine samples by ICP-MS (certified reference materials, CRM, n=10)

\*Mean of three determinations of samples  $\pm$  confidence interval (P = 0.95, n =10)

CRM1: Thallium concentration in Water by ICP-MS (25.3 µg L<sup>-1</sup>)

CRM2: Thallium concentration in Wastewater by ICP-MS (62.7 µg L-1)

CRM3: Thallium concentration in urine by ICP-MS (5.1  $\mu$ g L<sup>-1</sup>)

CRM4: Thallium concentration in urine by ICP-MS ( $6.4 \mu g L^{-1}$ )

## 4. Conclusions

A simple and reliable method was used for preconcentration, separation and determination of Tl (I) in human urine and water samples by DM- µ-SPE procedure. The proposed method was developed based on magnetic Fe<sub>2</sub>O<sub>4</sub>-ATPyHS@GO adsorbent at pH 5.0 without any organic chelating agent and organic solutions. The proposed method based on the Fe<sub>3</sub>O<sub>4</sub>-ATPyHS@GO adsorbent can be considered for Tl extraction in liquid phase as a low cost, efficient, reusability and fast separation phase. The newly developed method was low interference, easy usage for sample preparation in human urine samples and also provides low LOD (0.9  $\mu$ g L<sup>-1</sup>), RSD (1.8-2.1%) values as well as good PF (50) and quantitative recoveries more than 95% for thallium extraction in water and urine human matrixes. So, the proposed method based on magnetic nanoparticles and thiol groups on the  $Fe_3O_4$ -ATPyHS@GO adsorbent can be considered as a fast sample preparation technique with low amount of adsorbent for thallium separation and determination by F-AAS.

# 5. Acknowledgements

The authors wish to thank the Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, Iran and Department of Chemistry of Islamic Azad University, Kerman, Iran.

# 6. References

- [1] T.S. Lin, J.O. Nriagu, Thallium in the environment, New York: Wiley, pp.31-44,1998.
- [2] C. Yang, Y. Chen, P. Peng, X. Chang, C. Xie, Distribution of natural and anthropogenic thallium in the soils in an industrial pyrite slag disposing area, Sci. Total Environ., 341 (2005) 159–172.
- [3] A. Vaněk, Z. Groesslova, M. Mihaljevic, Thallium contamination of soils/vegetation as affected by sphalerite weathering: a model rhizospheric experiment, J. Hazard. Mater., 283 (2015) 148–156. https://doi. org/10.1016/j. jhazmat.2014.09.018.
- [4] M. Sadowska, E. Biaduń, B. Krasnodębska-Ostręga, Stability of Tl(III) in the context of speciation analysis of thallium in plants, Chemosphere, 144 (2016) 1216–1223.
- [5] Z. Ning, L. He, T. Xiao, L. Márton, High accumulation and subcellular distribution of thallium in green cabbage, Int. J. Phytoremed., 17 (2015)1097–1104.
- [6] B. Krasnodebska-Ostrega, Tl I and Tl III presence in suspended particulate matter: speciation analysis of thallium in wastewater, Environ. Chem., 12 (2015) 374–379.
- P. Cvjetko, I. Cvjetko, M. Pavlica, Thallium toxicity in humans, Arch. Ind. Hyg. Toxicol., 61 (2010) 111–119. https://doi.org/ 10.2478/10004-1254-61-2010-1976.

- [8] J.M. Wallace, Kale and thallium: insights from your nutrition team. Permaculture solutions for healing, 2015.
- [9] A. Lansdown, The carcinogenicity of metals: human risk through occupational and environmental exposure, Cambridge: Royal Society of Chemistry, pp. 323–330, 2013.
- [10] Z. Groesslova, A. Vanek, M. Mihaljevic, V. Ettler, M. Hojdovác, T. Zádorováa, Bioaccumulation of thallium in a neutral soil as affected by solid-phase association, J. Geochem. Explor., 159 (2015) 208–212.
- [11] T. Wojtkowiak, B. Karbowska, W. Zembrzuski, M. Siepak, Z. Lukaszewski, Miocene colored waters: a new significant source of thallium in the environment, J. Geochem. Explor., 161 (2016) 42–48. https://doi.org/10.1016/j. gexplo.2015.09.014.
- [12] F.S. Hussain, N.S. Hussain, Clinical utility of thallium-201 single photon emission computed tomography and cerebrospinal fluid epstein-barr virus detection using polymerase chain reaction in the diagnosis of AIDS-related primary central nervous system lymphoma, Cureus., 8 (2016) e606.
- [13] L. Osorio-Rico A. Santamaria S. Galván-Arzate, Thallium toxicity: general issues, neurological symptoms, and neurotoxic mechanisms, Adv. Neurobiol., 18 (2017) 345-353.
- [14] V. Yu, M. Juhász, A. Chiang, N. Atanaskova Mesinkovska, Alopecia and associated toxic agents: A systematic review, Skin Appendage Disord., 4 (2018) 245-260.
- [15] HY. Yu, C. Chang, F. Li, Q. Wang, M. Chen, J. Zhang, Thallium in flowering cabbage and lettuce: Potential health risks for local residents of the Pearl River Delta, South China, Environ. Pollut., 241 (2018) 626-635.
- [16] B. Štádlerová, M. Kolrosová, J. Dědina, S. Musil, Atomic fluorescence spectrometry for ultrasensitive determination of bismuth based on hydride generation – the role of excitation source, interference filter and flame atomizers, J. Anal. At. om., 35 (2020)

993-1002.

- [17] B. Karbowska, T. Rębiś, G. Milczarek, Electrode modified by reduced graphene oxide for monitoring of total thallium in grain products, Int. J. Environ. Res. Public Health, 15 (2018) 653.
- [18] L. Nyaba, T. S. Munonde, Magnetic Fe<sub>3</sub>O<sub>4</sub>@ Mg/Al-layered double hydroxide adsorbent for preconcentration of trace metals in water matrices, Sci. Reports, 11(2021) 2302.
- [19] L. Nyaba, B. Dubazana, A. Mpupa, P. N. Nomngongo, Development of ultrasoundassisted dispersive solid-phase microextraction based on mesoporous carbon coated with silica@iron oxide nanocomposite for preconcentration of Te and Tl in natural water systems, Open Chem., 18 (2020) 412–425.
- [20] T. Kusutaki, M. Furukawa, Preconcentration of Pb with aminosilanized Fe<sub>3</sub>O<sub>4</sub> nanopowders in environmental water followed by electrothermal atomic absorption spectrometric determination, Chem. Eng., 3 (2019) 74.
- [20] W.S.J. Hummers, R.E. Offeman, Preparation of graphitic oxide, J. Am. Chem. Soc., 80 (1958) 1339.
- [21] S. Khodabakhshi, F. Marahel, A. Rashidi, M. Khaleghi Abbasabadi, A green synthesis of substituted coumarins using nano graphene oxide as recyclable catalyst, J. Chin. Chem. Soc., 62 (2015) 389-392.
- [22] H. Shirkhanloo, M. K. Abbasabadi, F. Hosseini, A. Faghihi, Nanographene oxide modified phenyl methanethiol nanomagnetic composite for rapid separation of aluminum in wastewaters, foods, and vegetable samples by microwave dispersive magnetic micro solid-phase extraction, Food Chem., 347 (2021) 129042.
- [23] M.K. Abbasabadi, A. Rashidi, S. Khodabakhshi, Benzenesulfonic acid-grafted graphene as a new and green nanoadsorbent in hydrogen sulfide removal, J. Nat. Gas Sci. Eng., 28 (2016) 87-94.
- [24] M. Khaleghi-Abbasabadi, D. Azarifar, Magnetic  $Fe_3O_4$ -supported sulfonic acidfunctionalized graphene oxide ( $Fe_3O_4@GO$ naphthalene-SO<sub>3</sub>H): a novel and recyclable nanocatalyst for green one-pot synthesis, Res. Chem. Intermed., 45 (2019) 2095-2118.