



Preconcentration and speciation of thallium by ferrofluid based dispersive solid phase extraction and flame atomic absorption spectrometry



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ABSTRACT

A dispersive solid phase extraction method based on ferrofluid has been proposed for the separation and preconcentration of thallium (I) before its determination by flame atomic absorption spectrometry. The ferrofluid was rapidly injected into the aqueous sample containing the thallium (I) and dibenzo-18-crown-6 (DB18C6) as the chelating agent with a syringe. The separation of the sorbent from the aqueous phase was achieved by the application of an external magnet. The main factors affecting the extraction of thallium (I) were investigated and optimized. Total thallium was determined after the reduction of Tl(III) to Tl(I) by hydroxylamine hydrochloride. Under the optimized conditions with a sample volume of 150.0 mL, the detection limit (based on $3S_b/m$) and the enhancement factor were found to be $0.85 \mu\text{g L}^{-1}$ and 298, respectively. The relative standard deviation at $50 \mu\text{g L}^{-1}$ concentration level of Tl(I) was 3.2%. The method was successfully applied to the determination of thallium species in water and waste water samples as well as total thallium in nail, hair, cabbage and iron ore samples. The validity of the method was checked through the recovery experiments besides the analysis of a certified reference material.

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1. Introduction

Ferrofluids are colloidal mixtures consisted of magnetic nanoparticles dispersed in a carrier liquid such as water or the organic solvents [1]. Ferrofluids have both magnetic and fluid properties, and possess only a small percentage of the magnetic material. Some properties of ferrofluids such as density, pour point, vapor pressure and chemical properties of the liquid are similar to those of the base fluid [2]. To form the ferrofluids, the magnetic nanoparticles must be prevented from agglomeration by coating the single domain magnetic nanoparticles with a suitable material [3]. Thus, the coating material and the carrier liquid are the two important factors of the ferrofluids formation. The ferrofluids have been classified into two groups according to the coating process, namely, surfactant ferrofluid (SFF) and ionic ferrofluid (IFF). In SFF, the coating is surfactant/polymer molecules which prevents the particle agglomeration by a steric repulsion, whereas in IFF, the nanoparticles are coated with electric shell and the stability is due to the repulsion of electric charges. The carrier liquid in IFFs is usually water and in SFFs, it is an organic solvent such as 1-octanol [4].

Up to now, only tetramethylammonium hydroxide [5], perchloric acid [6,7] and acetic acid [8–12] have been used as coating agents for the stabilization of ferrofluids used in sensors, color removal and extraction, but to the best of our knowledge, there is no report on the use of fatty acids.

Thallium is a natural element widely distributed in the earth's crust at very low concentrations. This element can be found in nature as Tl(I) and Tl(III) ions that have different chemical, bioavailability and toxicity properties [13]. The Tl(I) chemistry resembles that of the alkali metals and can replace K^+ due to their similar ionic radii (Tl(I): 164 pm, K^+ : 152 pm). Tl(I) can be absorbed through the skin and bind to sulphhydryl groups to accumulate in the body. The estimated lethal dose in humans is $8\text{--}12 \mu\text{g g}^{-1}$ [14]. The main threat of thallium to humans is through occupational exposure, water contamination, and accumulation in vegetables grown on contaminated soils. Although the exact mechanism of thallium toxicity is still unknown, the impaired glutathione metabolism, oxidative stress, and disruption of potassium-regulated homeostasis may affect this mechanism. The thallium toxicity can lead to some neurological problems such as encephalitis, brain tumors, epilepsy, polyneuritis of the feet and legs, optic and nervous atrophy, and tingling pain at the extremities [15]. Therefore, the determination of thallium species in water as well as biological samples is important. However, due to the low concentration of thallium, its

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determination required analytical methods with a low detection limit and a high sensitivity. Flame atomic absorption spectrometry (FAAS) is a simple and well available technique for the thallium determination in real samples. But, its main drawbacks are the low sensitivity, interference of high concentration of matrix components and inability of speciation. These problems can be solved by using a separation and preconcentration method. Different preconcentration/separation methods including liquid-liquid extraction [16–19], cloud point extraction [20], hydride generation [21] and solid phase extraction (SPE) [22–26] have been designed for this purpose. However, these methods are usually laborious, time and reagent consuming, and in need of a large sample volume. To solve these problems, the sample preparation has to be moved toward simplification, miniaturization, automation, high-throughput performance, and low solvent consumption.

Recently, dispersive solid phase extraction (DSPE) in which a small amount of sorbent is dispersed in the sample solution, was introduced for the sample preparation [27]. The advantages of DSPE are simplicity, rapidity, low cost and low consumption of the solvent compared with the traditional SPE. In 2013, for the first time, ferrofluid in 1-octanol was used in DSPE of the crystal violet and palladium [8,9]. Ionic liquid-based ferrofluid has been used for the DSPE of complexes of lead, copper and cationic dye [10–12]. A selective ionic liquid based ferrofluid-DSPE for the extraction of lead and cadmium has also been reported [28]. The selectivity of ionic liquid (1-hexyl-3-ethylimidazolium tetrafluoroborate) ferrofluid was improved through coating the surface of $\text{Fe}_3\text{O}_4@ \text{TiO}_2$ nanoparticles with 1-(2-pyridylazo)-2-naphthol as the chelating agent [28]. However, up to now, there is no report on the use of ferrofluids based DSPE for the speciation of metal ions.

In this study for the first time, an attempt was made to stabilize the magnetic nanoparticles through the modification of their surface by a fatty acid; and a ferrofluids based DSPE method was designed for the separation/preconcentration and speciation of thallium. In this regard, DB18C6 macrocyclic polyether was used as a selective complexing agent for Tl(I) and the complex was extracted on the ferrofluids modified with palmitic acid. Palmitic acid is the most common long chain fatty acid widely used for manufacturing of metallic palmitate, pharmaceuticals, soap, cosmetics, and food packaging, however, its application in analytical chemistry is limited [29,30] and there is no report on its usage in the modification of sorbent. After the optimization of the extraction and desorption conditions, the application of the method for the determination of thallium species in water and waste water samples as well as total thallium in different matrices was examined.

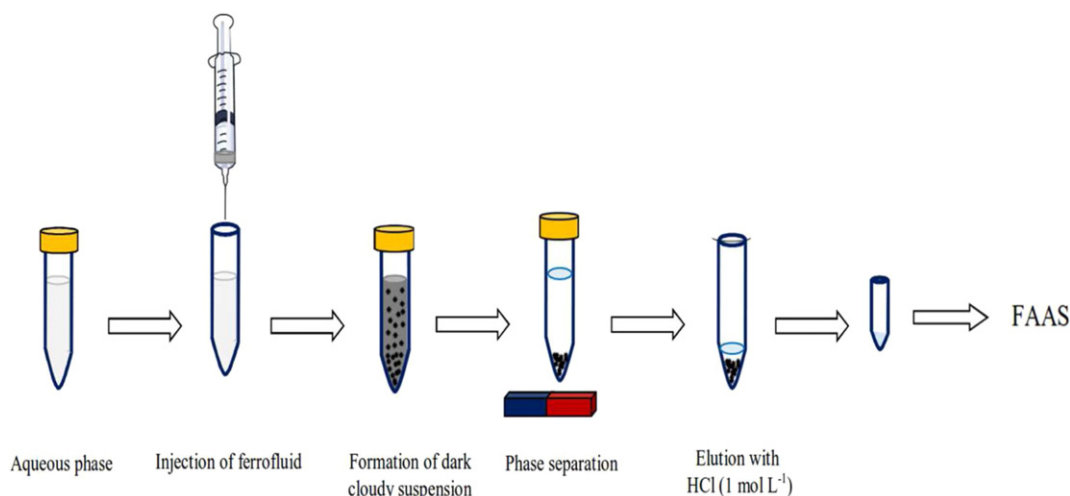
2. Experimental

2.1. Apparatus

An Analytik Jena novAA 300 (model 330, Germany) atomic absorption spectrometer, equipped with a hollow cathode lamp and an air-acetylene flame was used for the thallium measurement. The operating conditions were as follows: wavelength 276.8 nm, slit width 0.7 nm and lamp current 10.0 mA. An off line flow injection system consisted of a rotary injection valve (Rheodyne, CA, USA) with a loop of 300 μL capacity and a peristaltic pump (Ismatic, MS-REGLO/8-100, Zurich, Switzerland) was used for the control of the amount of eluent and precision of the measurements. A Metrohm pH meter (model 691, Switzerland) equipped with a combined glass-calomel electrode was used for the pH measurements. A strong neodymium-iron-boron ($\text{Nd}_2\text{Fe}_{12}\text{B}$) magnet (1.2 T, 10 cm \times 5 cm \times 2 cm) was applied for the magnetic separation.

2.2. Reagents and materials

Iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, tetraethyl orthosilicate (TEOS) and DB18C6 were purchased from Sigma-Aldrich (St. Louis, MO, USA). Double distilled water was used throughout the procedure. A stock solution of 1000 mg L^{-1} of Tl(I) and Tl(III) was prepared by dissolving an appropriate amount of TlNO_3 (Merck, Darmstadt, Germany) or $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Merck, Germany) in a 100 mL flask and diluting to the mark with distilled water. Working solutions were prepared daily from the stock solution by serial dilutions with distilled water. Ethanol, 1-octanol, hexadecanoic acid (palmitic acid), hydrochloric acid, nitric acid, and ammonia were purchased from Merck Company (Darmstadt, Germany). A 2.6×10^{-3} mol L^{-1} solution of DB18C6 was prepared by dissolving 100.0 mg of DB18C6 in 100.0 mL of acetone. 1% (w/v) hydroxylamine hydrochloride solution was prepared by dissolving 1.0 g of the reagent in double distilled water in a 100.0 mL volumetric flask. A phosphate buffer (pH = 7.0) was prepared by mixing 1.0 mol L^{-1} of sodium dihydrogen phosphate and 1.0 mol L^{-1} disodium hydrogen phosphate solution in an appropriate ratio. All the glassware used for the trace analysis was kept in 10% nitric acid solution overnight and subsequently rinsed twice with distilled water before use.



Scheme 1. Schematic diagram of experimental set-up.

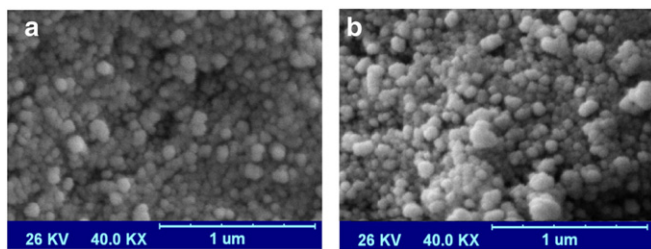


Fig. 1. The SEM images of Fe_3O_4 nanoparticles (a) and silica-coated Fe_3O_4 nanoparticles (b).

2.3. Preparation of ferrofluid

2.3.1. Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles

Fe_3O_4 nanoparticles were prepared by the coprecipitation method as described elsewhere with minor modifications [31]. In a typical procedure, 50.0 mL of an aqueous solution containing 5.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was heated at 80 °C under nitrogen gas for 15 min. Then, 10.0 mL of concentrated NH_3 was rapidly added to it under vigorous stirring (1000 rpm) using a glass stirrer. The solution temperature was maintained at 80 °C and nitrogen gas was used to prevent the intrusion of the oxygen during the whole experiment. After the completion of the reaction, the black precipitate was collected using a magnet, washed with double distilled water and ethanol, and dried in an oven at 60 °C.

The Fe_3O_4 nanoparticles (2.0 g) were dispersed throughout a mixture of ethanol (80.0 mL), deionized water (40.0 mL) and aqueous ammonia (2.4 mL). Then, 1.0 mL of TEOS was added dropwise to the suspension and the mixture was sonicated for 12 h. The silica-modified nanoparticles were isolated by magnetic separation and were rinsed with ethanol three times and then they dried in oven at 65 °C for 12 h [31].

2.3.2. Preparation of ferrofluid

Palmitic acid was used as the modifier and the stabilizer in preparation of ferrofluids. For this purpose, 10 mg of the prepared silica-coated magnetic nanoparticles (SCMNPs) was mixed with 1.0 mL of 3% w/v palmitic acid in ethanol in a vial and the mixture was heated at 70 °C under continuous stirring for 10.0 min. Then, the ferrofluid was obtained by dispersing the modified magnetic nanoparticles in 0.2 mL of 1-octanol while it was sonicated for 20 min.

2.4. Preparation of real samples

2.4.1. Water and waste water samples

The water and waste water samples were filtered through a 0.45 μm Millipore filter, the pH was adjusted to 7.0 upon the addition of phosphate buffer (pH = 7.0) and was treated according to the developed procedure [16].

2.4.2. Hair and nail

The hair and nail samples were prepared according to the literature [32]. These samples were rinsed with acetone, chloroform and double distilled water, and were dried at 60 °C. 1.5 g of each dried sample was weighed accurately in a 50.0 mL beaker and 5.0 mL concentrated HNO_3 was added. The content of the beaker was heated on a hot plate (initially at 100 °C for 30 min and then at 150 °C for 15 min). After dissolution, the solution was cooled to 70 °C and 2.0 mL of 30% w/v H_2O_2 was added. The mixture was heated to dryness at 200 °C to yield a white residue. After this, approximately 10 mL of 0.1 mol L^{-1} HNO_3 was added to the beaker and the content was heated at 100 °C for a few minutes. Then, its thallium content was reduced to Tl(I) upon the addition of 0.5 mL of hydroxylamine hydrochloride (1% w/v), the pH was adjusted to 7.0 with 1.0 mL phosphate buffer and was diluted to 50.0 mL. The total thallium was determined according to the developed procedure.

2.4.3. Cabbage

The cabbage was purchased from a local market in Yazd, Iran. The sample was washed in tap water as well as distilled water and was dried at 110 °C in an oven. Then, the sample was ground to decrease the particle size and was mixed thoroughly to ensure its homogeneity. 10.0 mL of concentrated nitric acid was added to 250.0 mg of the sample in a 100.0 mL beaker and the mixture was heated on a hot plate (130 °C) for 3 h. After cooling to the room temperature, 5.0 mL concentrated perchloric acid was added dropwise. The content of the beaker was heated up to the completion of the sample decomposition which resulted in a clear solution. Then, the solution was transferred to a 50 mL volumetric flask, the pH was adjusted to 7.0 with phosphate buffer, and was diluted to the mark with distilled water [33].

2.4.4. Iron ore

An exact amount of the dried iron ore sample (1.0 g) was placed in the beaker and 10 mL of concentrated nitric acid was added to it. The content was heated on a hot plate to dryness. After cooling, a second 10 mL portion of the concentrated nitric acid was added, and the

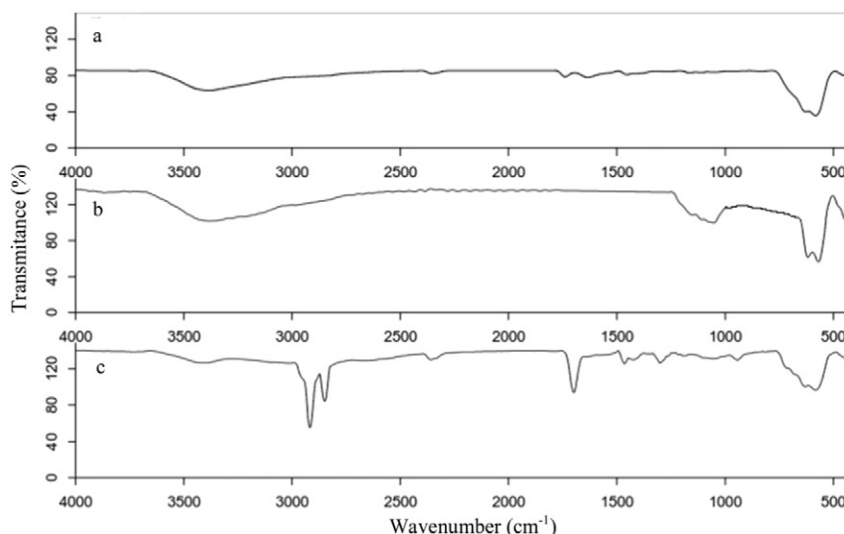


Fig. 2. FT-IR spectra of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4/\text{SiO}_2$ (b), and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{palmitic acid}$ (c).

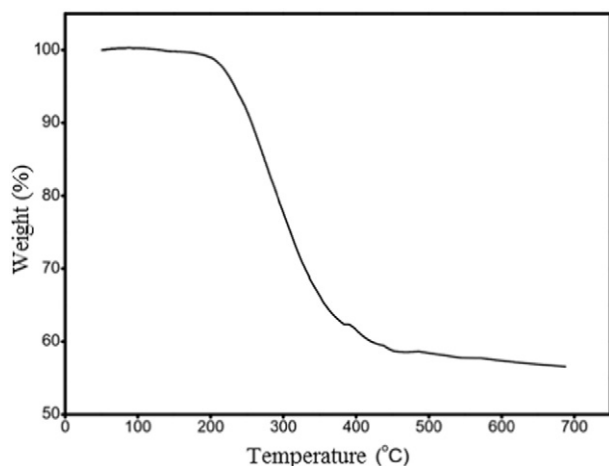


Fig. 3. TGA thermogram of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{palmitic acid}$.

procedure of heating was repeated. Then, 10 mL of a concentrated hydrochloric acid was added to the beaker, and the solution was gently heated to complete dryness. After cooling, the residue was dissolved in 10 mL of 1 mol L^{-1} HCl, the mixture was filtered through a $0.45 \mu\text{m}$ Millipore filter, and the filtrate was diluted to 50 mL with distilled water [34]. The pH was adjusted to ~ 7.0 and treated according to the given procedure. For the recovery study of solid sample, a precise amount of analyte was added to the sample prior to the digestion procedure.

2.4.5. Certified reference material

5.0 mL of concentrated nitric acid was added to 0.3 g of the certified ore sample (BCR, no. 288). The solution was heated over a water bath for 10 min. Then, 3.0 mL of 30% H_2O_2 was added and the solution was heated for 5 more minutes. The solution was filtered and 0.5 mL of hydroxylamine hydrochloride (1.0% w/v) was added. The pH was adjusted to 7.0, the solution was transferred to a 50 mL flask and diluted to the mark with distilled water. The complete digestion of reference material was assured through the direct determination of Tl in the digested sample by ETAAS. The result ($2.30 \pm 0.07 \mu\text{g g}^{-1}$) suggests that at the 95% confidence level the digestion of reference material is completed and there is no significant difference with the accepted value of $2.31 \pm 0.09 \mu\text{g g}^{-1}$.

2.5. Extraction procedure

2.5.1. Determination of Tl(I)

One milliliter of DB18C6 ($2.6 \times 10^{-3} \text{ mol L}^{-1}$) was added to 50.0 mL of the sample or the standard solution containing not $>22.5 \mu\text{g}$ of

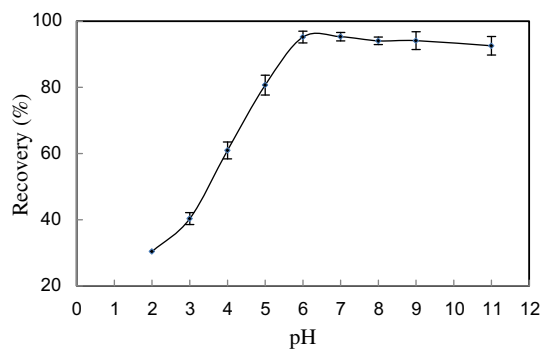


Fig. 4. Effect of pH on the extraction recovery of thallium (I). Conditions: sample volume, 50.0 mL; Tl(I) concentration, $50.0 \mu\text{g L}^{-1}$; sorbent, 10 mg; DB18C6 concentration: $6.0 \times 10^{-5} \text{ mol L}^{-1}$; 1-octanol, 0.2 mL and eluent volume (HCl 1 mol L^{-1}), 0.5 mL.

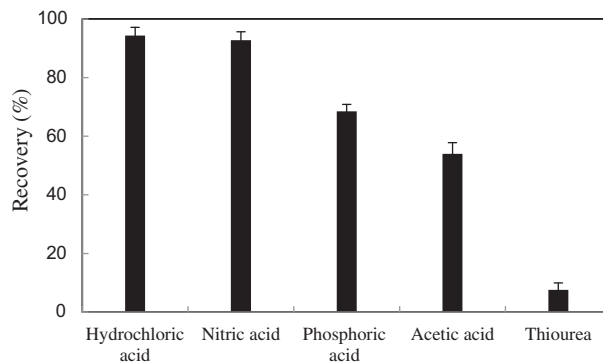


Fig. 5. The effect of type of eluent on the extraction recovery of thallium (I). Conditions: sample volume, 50.0 mL; Tl concentration, $50.0 \mu\text{g L}^{-1}$; pH = 7.0; sorbent, 10 mg; DB18C6 concentration: $5.0 \times 10^{-5} \text{ mol L}^{-1}$; 1-octanol, 0.2 mL and eluent volume, 0.5 mL.

thallium (I) and the pH was adjusted to 7.0 upon the addition of 1.0 mL of 1.0 mol L^{-1} phosphate buffer. Then, the prepared ferrofluid (palmitic acid- $\text{Fe}_3\text{O}_4/\text{SiO}_2$) was rapidly injected into the sample solution using 1.0 mL syringe. A dark cloudy suspension was immediately formed and the complex of thallium with DB18C6 was sorbed quickly onto the nanoparticles. Subsequently, a strong magnet was placed at the bottom of the tube and the ferrofluid containing the complex was separated. The supernatant was discarded by decantation, 0.5 mL of 1.0 mol L^{-1} hydrochloric acid was added and the mixture was sonicated for 3 min to desorb the extracted analyte. Finally, the sorbent was separated with a strong magnet and the amount of Tl(I) in the solution was determined by FAAS. Schematic diagram of experimental set-up is shown in Scheme 1.

2.5.2. Determination of total thallium and Tl(III)

Total concentration of thallium was determined according to the given procedure in part A after the quantitative reduction of Tl(III) to Tl(I) upon the addition of 0.5 mL 1.0% w/v hydroxylamine hydrochloride to 50 mL of the sample and leaving the solution at the room temperature for 10 min. The concentration of Tl(III) was calculated by subtracting Tl(I) from the total thallium concentration.

3. Results and discussion

Different sorbents including Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{acetic acid}$, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{acetic acid}$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{palmitic acid}$ were prepared and their capability in formation of a stable ferrofluid was examined in the preliminary experiments. The stability of the ferrofluid was investigated by qualitative observation of its sedimentation in 1-octanol, the most common carriers used in the preparation of ferrofluid. The results showed that the rate of sedimentation of $\text{Fe}_3\text{O}_4/\text{acetic acid}$ and $\text{Fe}_3\text{O}_4/$

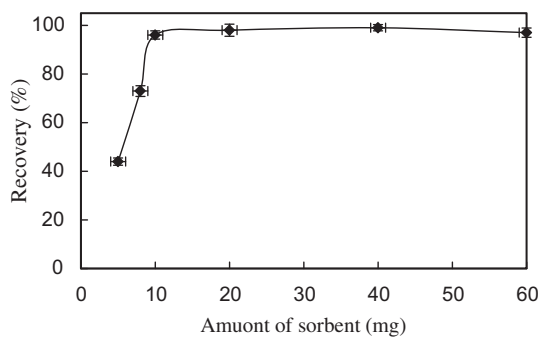


Fig. 6. Effect of amount of sorbent on the extraction recovery of thallium (I). Conditions: sample volume, 50.0 mL; DB18C6 concentration, $5.0 \times 10^{-5} \text{ mol L}^{-1}$, pH = 7.0; 1-octanol, 0.2 mL and eluent volume, 0.5 mL.

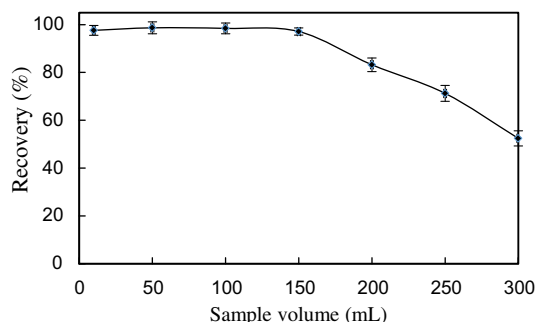


Fig. 7. Effect of sample volume on the extraction recovery of thallium (I). Conditions: 0.5 μg of Tl(I); DB18C6 concentration, 5.0×10^{-5} mol L $^{-1}$, sorbent, 10 mg; pH = 7.0; 1-octanol, 0.2 mL and eluent volume, 0.5 mL.

SiO $_2$ was lower than that of the bare magnetic nanoparticles (Fe $_3$ O $_4$). However, they formed sediments in > 1 h, whereas, the suspension of Fe $_3$ O $_4$ /SiO $_2$ /acetic acid and Fe $_3$ O $_4$ /SiO $_2$ /palmitic acid were stable even after 10 h. This observation indicated that modification of the surface of nanoparticle has an important role in stability of ferrofluids. Furthermore, it was found that the ferrofluid of Fe $_3$ O $_4$ /SiO $_2$ /palmitic acid has a higher capability in the extraction of the complex of DB18C6 with Tl(I). The palmitic acid adsorbs onto the surface of silica coated Fe $_3$ O $_4$ nanoparticles through its carboxylic acid group with electrostatic or hydrogen bonding interactions. The long hydrocarbon chain of palmitic acid has good compatibility with the 1-octanol. Thus, in addition to the confidence of the formation of ferrofluid, it helps the rapid extraction of the complex through intramolecular hydrophobic interactions. So, Fe $_3$ O $_4$ /SiO $_2$ /palmitic acid was selected as the sorbent for further studies. Then, the effect 1-octanol volume (0.1 to 0.5 mL) on the formation of ferrofluids and the extraction of analyte by 10.0 mg of Fe $_3$ O $_4$ /SiO $_2$ coated by palmitic acid was studied. When the volume of 1-octanol was < 0.2 mL, the resultant ferrofluid was very viscous and its handling was difficult, however, with higher amount of 1-octanol, the extraction efficiency was almost constant. Therefore, a volume of 0.2 mL of 1-octanol was selected for the subsequent studies.

3.1. Characterization of the sorbent

The scanning electron microscopy (SEM) images of the nanoparticles before and after the modification (Fig. 1) indicates that the size of Fe $_3$ O $_4$ nanoparticles before coating with SiO $_2$ is below 50 nm, whereas, after coating with SiO $_2$ their size changes to 60–75 nm. Thus, it can be concluded that the Fe $_3$ O $_4$ nanoparticles are coated successfully with SiO $_2$ and their size is still in nanoscale. Also Fig. 1b indicates that the SiO $_2$ is uniformly distributed on the magnetic nanoparticles.

The modification of Fe $_3$ O $_4$ nanoparticles with SiO $_2$ was confirmed by the Fourier transform infrared spectroscopy (FTIR) using KBr pellet method (Fig. 2). Comparing Fig. 2a and b revealed that upon the modification with SiO $_2$, in addition to the characteristic absorption band of Fe—O—Fe of Fe $_3$ O $_4$ around 600 cm $^{-1}$, new bands around 975 and

1130 cm $^{-1}$ related to the Si—O—H and Si—O—Si stretching, respectively, are appeared. The spectrum of Fe $_3$ O $_4$ @SiO $_2$ modified with palmitic acid showed additional bands at 1702, 2918 and 2845 cm $^{-1}$ corresponding to C=O and C—H stretching of —CH $_2$ and —CH $_3$ groups of palmitic acid, respectively, indicating that the surface of the SCMNPs is modified with palmitic acid.

The amount of palmitic acid sorbed onto the SCMNPs was studied by thermogravimetric analysis (TGA). As shown in Fig. 3, when the temperature rose from 100 to 400 °C, about 42% of the sorbent weight is lost and then remained constant up to 700 °C. Thus, based on the TGA curves, the amount of palmitic acid sorbed onto the SCMNPs is about 42%.

3.2. Optimization of the extraction conditions

In order to obtain a suitable sensitivity for the speciation and determination of thallium ions, DSPE was combined with FAAS. The different parameters affecting the extraction of the analyte such as pH of the sample solution, concentration of the chelating agent, the nature and volume of eluent, time of the extraction and desorption, amount of the sorbent, and sample volume were investigated and optimized. For optimization of the procedure, the univariate method was applied.

3.2.1. Effect of sample pH

The effect of the sample pH on the extraction of Tl(I) from 50 mL of sample solution (50 μg L $^{-1}$) was studied by varying the pH in the range of 1.0–11.0. The pH of solution was adjusted using 0.1 mol L $^{-1}$ of hydrochloric acid or ammonia solution (0.1 mol L $^{-1}$). The results showed that the extraction efficiency increased with an increase in the pH up to 6.0 and then leveled off at higher pH (Fig. 4). The decrease in the extraction efficiency at lower pH can be related to the competition of proton with Tl(I) for complexation with DB18C6 (log K $_f$ (Tl $^+$ /DB18C6) = 5.05, and log K $_f$ (H $^+$ /DB18C6) = 2.3) [35]. A pH of 7.0 was selected for the subsequent experiments.

3.2.2. Effect of the DB18C6 concentration

The effect of DB18C6 concentration within the range of 5.0×10^{-6} to 6.0×10^{-5} mol L $^{-1}$, on the extraction of 50 mL sample solution with a concentration of 50 μg L $^{-1}$ of Tl(I) at pH = 7.0 was evaluated. The results revealed that the extraction efficiency increased with an increase in DB18C6 concentration up to 3.0×10^{-5} mol L $^{-1}$ and then remained constant. So, a concentration of 5.0×10^{-5} mol L $^{-1}$ of DB18C6 was chosen for the further studies.

3.2.3. Effect of type, concentration and volume of desorbing solution

The type of desorbing solution is important for the analytical performance of ferrofluids based DSPE method. The proper desorbing solution must be able to desorb the analyte in a minimum volume while being compatible with the atomic absorption spectrometer. In order to select a suitable desorbing solution, 1.0 mL of different eluents including nitric acid, hydrochloric acid, acetic acid, phosphoric acid and thiourea at a concentration level of 1.0 mol L $^{-1}$ under the above optimized

Table 1
Tolerance limits of diverse ions for the determination of thallium (I).

Ions	Molar ratio (ion/Tl(I))	Recovery (%)	Foreign ion	Molar ratio (ion/Tl(I))	Recovery (%)
Mg $^{2+}$	1000 ^a	99.7 \pm 4.3	Ag $^+$	500	101.8 \pm 3.1
Ba $^{2+}$	1000 ^a	99.2 \pm 3.5	Cs $^+$	500	98.5 \pm 3.4
Na $^+$	10,000	96.7 \pm 3.8	K $^+$	400	98.3 \pm 2.5
Ni $^{2+}$	1000 ^a	98.7 \pm 2.6	NO $_3^-$	10,000	103.2 \pm 3.1
Zn $^{2+}$	1000 ^a	98.5 \pm 2.5	Br $^-$	1000 ^a	102.4 \pm 3.8
Cd $^{2+}$	1000 ^a	99.1 \pm 3.1	SO $_4^{2-}$	1000 ^a	104.1 \pm 4.1
Pb $^{2+}$	1000 ^a	97.7 \pm 3.8	I $^-$	1000 ^a	96.5 \pm 3.1
Ca $^{2+}$	750	97.9 \pm 4.2	Cl $^-$	750	101.5 \pm 3.8
Cu $^{2+}$	600	101.8 \pm 2.5	CO $_3^{2-}$	500	103.2 \pm 3.1
Co $^{2+}$	600	98.7 \pm 2.8	PO $_4^{3-}$	500	101.5 \pm 3.8

^a Above which was not considered.

conditions was examined. The results (Fig. 5) showed that with hydrochloric acid and nitric acid the desorption was more complete. However, as nitric acid can affect the magnetic property of the sorbent, hydrochloric acid was selected for further studies. Then, the effect of the hydrochloric acid concentration on the desorption efficiency was studied by varying its concentration in the range of 0.1 to 1.5 mol L⁻¹. The results indicated that the extraction efficiency increased with increasing the hydrochloric acid concentration up to 0.75 mol L⁻¹ and then leveled off at higher concentration. Therefore, subsequent tasks were performed with 1.0 mol L⁻¹ hydrochloric acid. The effect of the volume of the desorbing solution in the range of 0.2–1.5 mL was also studied, and a volume of 0.5 mL was found to be sufficient for the quantitative recovery of the analyte.

3.2.4. The Effect of extraction and desorption time

The extraction time is an important factor affecting the speed of extraction and is defined as the time interval between the injection of ferrofluid sorbent and the application of external magnetic field for phase separation. So, the effect of the extraction time under the other optimized conditions (sample volume, 50.0 mL; DB18C6 concentration, 5.0×10^{-5} mol L⁻¹, sorbent, 10 mg; pH = 7.0; 1-octanol, 0.2 mL and eluent volume, 0.5 mL) was investigated in the range of 30 s to 5 min. The results showed that the extraction time has no significant effect on the extraction efficiency. This observation can be related to the extremely large surface area between the dispersed sorbent and the aqueous phase. Thus, the formed complex of Tl(I) and DB18C6 was instantly diffused into dispersed sorbent so, the equilibrium was achieved rapidly and the extraction process was completed within a few seconds. This can be cited as the most important advantage of the ferrofluids based DSPE method.

The effect of desorption time in the range of 1–15 min was also evaluated. The results showed that 3 min was sufficient for the quantitative desorption of the analyte from the sorbent.

3.2.5. Effect of the amount of sorbent and sample volume

Another important factor affecting the extraction efficiency is the amount of sorbent. So, in the next step, the amount of the sorbent was optimized through the injection of varying amounts of the prepared sorbent (5.0–60.0 mg) and 10 mg of it was found to be sufficient for the quantitative recovery (>95%) of the thallium (I) ions (Fig. 6). The extraction efficiency was almost constant for higher amounts of modified magnetic nanoparticles ferrofluid.

Manifestation of the capability of the method concerning the extraction of trace amounts of analyte from large sample volume is another important aspect of the method development. For this purpose, different volumes of sample solution (10.0–300.0 mL) containing 0.5 µg of thallium (I) were extracted under the optimized conditions (Fig. 7). The result of this study showed that the extraction efficiency was constant while it was maximum up to a sample volume of 150.0 mL. Thus, a preconcentration factor of 300 could be achieved based on the maximum initial sample volume whereby the extraction was quantitative (150.0 mL) and the final volume of desorbing solution (0.5 mL).

3.2.6. Effect of the ionic strength

The effect of the ionic strength on the extraction of Tl(I) from the solution (sample volume, 50.0 mL; DB18C6 concentration, 5.0×10^{-5} mol L⁻¹, sorbent, 10 mg; pH = 7.0; 1-octanol, 0.2 mL and eluent volume, 0.5 mL) was investigated by the addition of varying amounts of sodium nitrate (0.0 to 1.0 mol L⁻¹). The results indicated that up to a concentration of 0.5 mol L⁻¹ of NaNO₃, the ionic strength had no considerable impact on the extraction efficiency of thallium. However, a further increase in salt concentration caused a decrease in the extraction efficiency. This observation can be attributed to the increase in the viscosity of the sample solution which prevents through dispersion of the sorbent. Thus, the extraction experiments were carried out without any addition of salt.

Table 2

Determination and speciation of thallium in water and waste water samples (sample volume = 150 mL).

Sample	Added (µg L ⁻¹)		Found ^d (µg L ⁻¹)		Recovery (%)	
	Tl(I)	Tl(III)	Tl(I)	Tl(III)	Tl(I)	Tl(III)
Tap water	0	0	ND ^b	ND	–	–
	10	10	9.5 ± 0.3	10.3 ± 0.3	95.0	103.0
	20	20	20.5 ± 0.8	19.1 ± 0.9	102.5	95.5
River water	0	0	ND	ND	–	–
	10	10	10.1 ± 0.4	9.6 ± 0.1	101.0	96.0
	20	20	19.1 ± 0.5	20.6 ± 0.7	95.5	103.0
Well water	0	0	ND	ND	–	–
	10	10	9.7 ± 0.4	9.9 ± 0.3	97.0	99.0
	20	20	19.3 ± 0.5	20.5 ± 0.7	96.5	102.5
Sea water (Caspian)	0	0	8.5 ± 0.5	4.8 ± 0.1	–	–
	10	10	18.4 ± 1.1	14.5 ± 0.6	99.0	97.0
	20	20	28.8 ± 1.5	24.6 ± 0.8	101.5	99.0
Waste water ^c	0	0	6.2 ± 0.3	4.1 ± 0.2	–	–
	10	10	15.9 ± 0.5	14.3 ± 0.6	97.0	102.0
	20	20	26.5 ± 1.2	23.7 ± 1.1	101.5	98.0

^a Mean and standard deviation of three independent analyses.

^b ND = not detected.

^c Waste water from Koushk industry, Bafgh.

3.2.7. Sorbent capacity

The capacity of the sorbent, defined as the maximum amount of the analyte which was retained by a certain amount of the sorbent, was determined by dispersing 0.8 mL of ferrofluid equivalent to 40.0 mg of dried sorbent into 50 mL of 50.0 mg L⁻¹ thallium (I) solution under the optimized conditions. After the phase separation, the amount of thallium in the supernatant was determined by flame atomic absorption spectrometry. The capacity of the sorbent was determined from the differences in the amounts of Tl(I) in the initial and final solutions. The capacity of the sorbent for Tl(I) was found to be 8.9 mg g⁻¹ of dried sorbent.

3.2.8. Influence of interfering ions

The selectivity of the designed extraction system was examined by extracting the analyte from 50.0 mL of solution containing 50.0 µg L⁻¹ of Tl(I) and varying amounts of other ions present in the real samples or those capable of forming complex with DB18C6. A relative error less than ±5% in the determination of Tl(I) was considered to be within the range of the experimental error. The results of this study presented in Table 1, indicate that at the given mole ratio, the examined cations and anions do not interfere with the determination of Tl(I). Thus, the procedure has good selectivity toward the analyte ion.

3.3. Analytical performance

The analytical performance of the developed method was evaluated by processing 50.0 and 150.0 mL of standard solutions of the thallium (I) under the optimized conditions. The calibration graph was linear in the concentration range of 10.0–450.0 and 4.0–150.0 µg L⁻¹ of thallium

Table 3

Determination of total thallium in nail, hair, cabbage and iron ore samples (n = 3).

Samples	Added (µg g ⁻¹)	Found (µg g ⁻¹) ^a	Recovery (%)	GF-AAS (µg g ⁻¹)
Nail	0	0.53 ± 0.02	–	0.54 ± 0.02
	0.2	0.72 ± 0.03	95.0	
Hair	0	0.34 ± 0.01	–	0.33 ± 0.01
	0.2	0.55 ± 0.03	105.0	
Cabbage	0	3.72 ± 0.12	–	3.68 ± 0.18
	0.5	4.21 ± 0.17	98.0	
Iron ore	0	49.77 ± 1.33	–	50.13 ± 2.40
	5	54.86 ± 1.63	101.8	

^a Mean and standard deviation of three independent analyses.

Table 4
Characteristic performance data of the proposed method and other SPE methods for FAAS determination of thallium.

Method	Sorbent	Chelating agent	EF or PF	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Ref.
FI-SPE	SDS-coated Al_2O_3	Oxine	77	2.5	2.6	[36]
SPE	Nanoclay	PAN	150	0.2	1.48	[37]
SPE	Benzophenone	O-Phen	–	1	1.7	[38]
SPE	C_{18} bonded silica	Shift base	100	0.1	1.2	[39]
SPE	MWCNT	PAN	140	5.1	1.5	[40]
DSPE	Ferrofluid	DB18C6	298	0.85	3.2	This work

EF: enrichment factor; PF: preconcentration factor; LOD: limit of detection; RSD: relative standard deviation;

Oxine: 8-hydroxyquinoline; PAN: 1-(2-pyridylazo)-2-naphthol; O-phen: 1,10-phenanthroline; shift base: 4-(4-chloro-phenylazo)-2-[(4-hydroxy-phenylamino)-methyl]-phenol; MWCNT: multiwalled carbon nanotube; DB18C6: dibenzo-18-crown-6.

(I) for the sample volume of 50.0 and 150.0 mL, respectively. The equations of the calibration graphs were $A = 0.00093C + 0.0054$ and $A = 0.0028C + 0.0138$ (where A is the absorbance and C is the concentration of Tl(I) in $\mu\text{g L}^{-1}$) with a correlation coefficient of 0.9991 and 0.9985 for 50 and 150 mL sample volume, respectively. The detection limit defined as $3S_0/m$ (where S_0 is the standard deviation of eight replicate analysis of the blank and m is the slope of the calibration graph) for was found to be 2.5 and $0.85 \mu\text{g L}^{-1}$ for the sample volume of 50.0 and 150.0 mL, respectively. The relative standard deviation (RSD) for six replicate extractions and measurement of Tl(I) from 50.0 mL of the sample at the concentration level of $50.0 \mu\text{g L}^{-1}$ was found to be 3.2%.

The enhancement factor defined as the ratio of slope of calibration curve after ferrofluids based DSPE using 150.0 mL sample solution to that of without extraction was found to be 298. The closeness of the enhancement factor (298) and the preconcentration factor (300) indicated that the extraction of Tl(I) is almost quantitative (>99%).

3.4. Validation and application of method

The method was applied to the determination of Tl(I) and Tl(III) species in tap, well, river (Zayandeh Roud River, Isfahan, Iran), sea (Caspian sea) and waste water samples (waste water sample was collected from the Koushk industry in state of Yazd). The accuracy of the method was evaluated through the recovery experiments by spiking each samples at two level with Tl(I) and Tl(III). The results (Table 2) indicate that the recovery of both species of thallium at the spiked levels are almost quantitative (95.0–103.0%). Thus, the procedure is reliable for speciation of thallium in water samples.

The applicability of the developed procedure was also assessed by its application to the determination of the total thallium in cabbage, nail, hair and iron ore samples. The validity was evaluated through the recovery experiments and the comparison of the results with the data obtained by electrothermal atomic absorption spectrometry (ETAAS). The results (Table 3) showed that the recoveries of spiked samples were satisfactory (95.0–105.0%) and at the 95% confidence level, there is no significant difference between the results obtained by the developed procedure and those obtained by ETAAS. Furthermore, the accuracy of the method was evaluated through the analysis of an ore certified reference material (BCR, no. 288). The concentration of thallium in the sample was found to be $2.29 \pm 0.08 \mu\text{g g}^{-1}$ which at 95% confidence level is in agreement with the certified value of $2.31 \pm 0.09 \mu\text{g g}^{-1}$. Thus, the proposed method is reliable for the determination of thallium in a wide range of samples.

3.5. Comparison of the method with other SPE methods combined with FAAS

The figures of merit of the developed method were compared with some recent reported SPE methods combined with FAAS for determination of thallium (Table 4). As it is shown the enhancement factor of the developed method is higher and consequently, with two exceptions, its detection limit is lower than the other reported methods.

4. Conclusion

In the present study, for the first time, the magnetic nanoparticles were stabilized through the modification of their surface by a fatty acid, and a ferrofluids based DSPE method was designed for the separation/preconcentration and speciation of thallium. DB18C6 macrocyclic polyether was used as a selective complexing agent for Tl(I) and the complex was extracted to the ferrofluids modified with palmitic acid. The palmitic acid with long hydrocarbon chain showed good compatibility with the 1-octanol and in addition to the formation of stable ferrofluid it helped the rapid extraction of the complex through intramolecular hydrophobic interactions. The developed DSPE method proved to be effective for the separation/preconcentration and speciation of thallium in water and waste water samples as well as determination of total thallium in cabbage, nail, hair, and iron ore samples prior to FAAS. The magnetic separation greatly improved the sample extraction time by avoiding the time consuming column passing or filtration process. The other advantages of the developed method are simplicity, rapidity, selectivity, sensitivity and relatively low cost.

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