

Ultra-trace determination of thallium(I) using a nanocomposite consisting of magnetite, halloysite nanotubes and dibenzo-18-crown-6 for preconcentration prior to its quantitation by ET-AAS

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Abstract A nanocomposite modified with dibenzo-18-crown-6 was synthesized and applied as a new sorbent for the preconcentration of thallium(I) via ultrasound assisted-solid phase extraction. This extraction step was combined with electrothermal atomic absorption spectrometry to determine ultra-trace amounts of thallium(I). The nanocomposite was characterized by Fourier transform infrared spectroscopy, X-ray diffraction spectrometry, field emission scanning electron microscopy and transmission electron microscopy. Under the optimized conditions, a dynamic linear range from 7.0 to 435 ng L⁻¹, a detection limit of 1.8 ng L⁻¹ and a quantification limit of 6.0 ng L⁻¹ were obtained. Also, the intra- and inter-day relative standard deviations for 20.0 ng mL⁻¹ Tl(I) were calculated as ±4.8% and ±5.1%, respectively. The adsorbent was applied to the determination of thallium(I) in the environmental, biological and standard samples with satisfactory results.

Keywords Magnetic nanocomposite · Graphite furnace AAS · Crown ether · Reference material · Hair analysis · Water analysis

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Introduction

Thallium (Tl), is a bluish white, inelastic, soft and easily fusible metal [2]. The United States Environmental Protection Agency has located thallium in the list of important pollutants in drinking water, specifying 0.5 µg L⁻¹ Tl as maximum allowed concentration. Tl mainly presents in trivalent [Tl(III)] and monovalent [Tl(I)] forms and each oxidation state is different in terms of toxicity; Tl(III) is more toxic than Tl(I) [3].

Tl has many applications, and the large number of Tl's applications can cause human exposure to toxic thallium compounds. Therefore, the development of selective and sensitive analytical techniques for the determination of this metal is very important [4]. Different analytical techniques have been applied for the determination of thallium amounts including ICP-MS [5], spectrophotometry [6], electrolyte cathode discharge atomic emission spectrometry [7] and electrochemical methods [8].

The abundance of thallium is extremely low in environmental compounds. Tl concentration in non-polluted soils is in the range of 0.3–0.55 mg kg⁻¹ [9] and in surface waters between 10 to 100 ng L⁻¹ [10]. According to the above, determination of Tl is difficult because of its low levels (below the detection limit of the analytical apparatus) and the high amounts of interfering components. Therefore, a preconcentration and separation step is often required. Various techniques have been applied for the separation of Tl from different matrices such as solidified floating organic drop microextraction [11], cloud point extraction [12] and dispersive liquid-liquid microextraction [13].

Solid phase extraction (SPE) is a favorite technique due to its benefits including high recovery, low cost, high preconcentration factor, ease of automation, fast

phase separation, low consumption of toxic organic solvents and simplicity of combination with different detection instruments [14]. Several types of adsorbents such as octadecyl silica membrane disk [15], ion imprinted polymer [16], silica gel [17], chromosorb 105 [18], alumina [19], nitrate resin [20] and some other solid substances, have been utilized for the preconcentration and separation of thallium from diverse samples.

The purpose of the present work was to develop a simple and novel ultrasound assisted-solid phase extraction (USA-SPE) system for Tl preconcentration. In the first step, a crown ether modified magnetic nanocomposite was synthesized and characterized by FT-IR, FE-SEM, TEM and XRD. Then, it was applied in USA-SPE process of ultra-trace levels of thallium(I) ions in some environmental and biological samples. The main parameters influencing the extraction efficiency of thallium(I) such as pH, type, concentration and volume of eluent, sorption and desorption times, adsorbent reusability, temperature, sample volume and adsorption capacity were studied and optimized. Also, the accuracy of the suggested method was checked by analyzing the standard reference material and spiked real samples.

Experimental

Materials and reagents

Halloysite nanotubes (HNTs) were purchased from Auckland Company (New Zealand, www.imerys-ceramics.com). The thallium(I) standard solution (1000.0 mg L^{-1}) was prepared from Merck (Germany, www.merckmillipore.com). Working standard solutions of thallium(I) were prepared freshly at various concentrations by diluting the stock solutions with deionized water. Dibenzo-18-crown-6 (98%) as modifier was purchased from Sigma-Aldrich (USA, www.sigmaaldrich.com). Ethanol (96%), toluene (99.9%), $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ (99%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), HNO_3 (69%), HCl (37%), H_2SO_4 (98%), HClO_4 (70%), NH_3 (25%), NaOH (99%), tetrahydrofuran (THF) (99.8%) and dimethylformamide (DMF) (99.5%) were purchased from Merck (Germany, www.merckmillipore.com). Also, deionized water (pH: 5.5, resistivity: $18.4 \text{ M}\Omega \cdot \text{cm}$, conductivity: $4.1 \mu\text{S cm}^{-1}$, TOC: $42 \mu\text{g L}^{-1}$, sodium: $0.8 \mu\text{g L}^{-1}$, chloride: $0.9 \mu\text{g L}^{-1}$ and silica: $2.7 \mu\text{g L}^{-1}$) was used throughout.

Apparatus

Thallium measurements were performed with an atomic absorption spectrometer (Varian Spectra AA 220,

Australia, www.varianinc.com) with a deuterium lamp background correction, equipped with graphite furnace (GTA-110 series). FT-IR spectra were recorded with a Bruker spectrometer (Tensor-27, Germany, www.bruker.com). A Hitachi field emission-scanning electron microscope (FE-SEM) (S-4160, Japan, www.hitachi-hightech.com) and Omega transmission electron microscopy (TEM) (LEO-912 AB, Germany, www.zeiss.com) were used for the morphological information. A Sonorex Digitec ultrasonic water bath (DT 255H, Germany, www.bandelin.com) with temperature control was applied for the preparation of nanocomposite and preconcentration process. This device features are as follows: capacity: 5.5 lit, frequency: 35 kHz, max peak output: 640 W/Per., HF-Power: $160 \text{ W}_{\text{eff}}$, heating power: 280 W, current consumption: 2.0 A. Also, X-ray diffraction (XRD) images were prepared with a PANalytical instrument (X'Pert³, Holland, www.panalytical.com). Also, the pH measurements were carried out with a Metrohm pH meter (827 pH lab, Switzerland, www.metrohm.com) supplied with a combined glass-calomel electrode.

Samples preparation

Water samples

Two tap water samples (Kerman and Baft drinking water, Kerman, Iran) and a well water (Shahid Bahonar University of Kerman, Kerman, Iran) were selected and filtered. Then, pH was adjusted to pH = 2.0 with HNO_3 to prevent the adsorption of the ions onto the flask walls, stored at $4 \text{ }^\circ\text{C}$ in a refrigerator [21] and the recommended method was applied.

Human hair

Hair samples with different lengths were collected from a men's barber shop in Kerman (Iran) at the end of a working day (about 45 customers). The combined sample was immersed in acetone for 20 min, washed with deionized water and then dried in an oven. An exact amount of sample (0.5 g) was weighed and 30.0 mL of a mixture solution (HClO_4 and HNO_3 , 1:8 v/v) was added to digest it. The resulted solution was dried and several drops of H_2SO_4 (50%) were added to the residue [22]. The final solution was transferred into a 100.0 mL measuring flask, diluted to the mark with deionized water. For Tl determination, an aliquot of last solution was chosen and the assay was performed according to the mentioned method.

Standard reference material

SRM 1643d–Trace Elements in Water: 5.0 mL sample solution was poured into a 100.0 mL measuring flask and diluted to the mark with deionized water. Then, an aliquot of this solution was taken and the thallium content was determined by the suggested method.

Preparation of modified magnetic nanocomposite

In order to prepare the magnetic nanocomposite, 2.5 g HNT and 150 mL deionized water were poured into a beaker. Then, 2.91 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.99 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were added and stirred for 8 h at 70 °C. Its pH was adjusted in the range of 9–10 with ammonia. In the next step, the final solution was placed in the hot water bath (60 °C) for 12 h to complete the reaction. Finally, the prepared magnetic nanocomposite (MNC) were separated by using a Nd magnet, washed 3 times with 50 mL deionized water and 30 mL ethanol and dried in an oven (80 °C) for 8 h.

For preparation of modified magnetic nanocomposite (MMNC), 3.0 g of prepared nanocomposite (as described above) and 300 mL toluene were poured into a 250.0 mL measuring flask and sonicated for 3 min to disperse the MNCs. Then, 1.404 g dibenzo-18-crown-6 was added and refluxed for 24 h at 110 °C. After cooling, the prepared adsorbent was washed 3 times with 50 mL deionized water and 30 mL ethanol and dried in an oven.

General procedure

For thallium preconcentration and extraction step, 10.0 mL solution containing known amount of Tl(I) was poured into a 100 mL beaker and its pH was adjusted in 10 by NaOH solution (0.1 mol L^{-1}) and HNO_3 (0.1 mol L^{-1}). A 40.0 mg prepared MMNC was added to the beaker, put in an ultrasonic bath, sonicated for 4 min and then, the adsorbent was collected and removed with a Nd magnet.

For the desorption step, 2.0 mL HNO_3 (3.0 mol L^{-1}) was added to the MMNC and sonicated for 5 min. Finally, the eluted adsorbent was removed from the solution with a magnet and the resulted solution was introduced to ETAAS directly for thallium determination.

Results and discussion

Some adsorbents such as carbon active, silica gel, zeolite, carbon nanotube and HNT were examined to Tl(I)

determination, but the best extraction recovery was performed by using modified magnetic nanocomposite with HNT and dibenzo-18-crown-6.

FT-IR spectra (Figs. S1(a–d)) confirmed that dibenzo-18-crown-6 was settled on the surface of adsorbent. These spectra have some backbones including; 431.17 cm^{-1} for Fe–O, 539.14 cm^{-1} for Fe–O–Fe, $750\text{--}1100 \text{ cm}^{-1}$ for Si–O or Al–O of HNT, 1384.01 cm^{-1} for CH_2 , 1631 cm^{-1} for C = C, $2800\text{--}3000 \text{ cm}^{-1}$ for C–H and $3100\text{--}3500 \text{ cm}^{-1}$ for stretching O–H. The comparison between the FT-IR spectra of halloysite nanotubes (Fig. S1(a)), magnetic nanocomposite (Fig. S1(b)), dibenzo-18-crown-6 (Fig. S1(c)) and modified magnetic nanocomposite by dibenzo-18-crown-6 (Fig. S1(d)) show the adsorbent synthesis process was done successfully.

Also in XRD pattern (Fig. S2(a)) of modified magnetic nanocomposite and its interpretation (Fig. S2(b)), the peaks of Fe_3O_4 nanoparticles and dibenzo-18-crown-6 are clearly visible. FE-SEM images of magnetic nanocomposite (Fig. S3(a)) and modified nanocomposite by dibenzo-18-crown-6 (Fig. S3(b)) show the surface morphology and size of nanoparticles. In TEM image (Fig. S4), the tubular structure of HNTs, Fe_3O_4 and dibenzo-18-crown-6 can be seen clearly and confirmed the successful synthesis of desirable adsorbent.

Optimization of method

After characterization and confirmation of MMNC synthesis, some preconcentration and extraction parameters including pH, type, concentration and volume of eluent, sorption and desorption times, adsorbent reusability, temperature, sample volume and adsorption capacity were investigated and optimized. The related explanations were presented in [Electronic Supplementary Material](#) file, but the results are summarized below:

- Sample pH value: pH = 10 was chosen as optimized pH.
- Type, concentration and volume of eluent: 2.0 mL HNO_3 (3.0 mol L^{-1}) was applied as the best eluent.
- Sorption and desorption times: For quantitative sorption and desorption processes, 4 and 5 min were sufficient, respectively.
- Adsorbent reusability: The thallium preconcentration efficiency decreased slightly when MMNC was reused 6 times.
- Temperature: 25 °C was selected as optimum temperature.
- Sample volume: The preconcentration process can perform quantitatively until 550 mL.
- Adsorption capacity: The maximum adsorption capacity of 16.7 mg g^{-1} was obtained for the synthesized MMNC.

Table 1 Effect of potentially interfering ions

Potentially interfering ion	Potentially interfering ion/Tl(I) ratio	Recovery (%)
Cd ²⁺	250	102.3
Bi ³⁺	1800	98.3
Ca ²⁺	2000	100.0
Co ²⁺	2000	96.9
Ni ²⁺	2000	96.7
Pb ²⁺	1000	95.7
Al ³⁺	2000	96.9
Mg ²⁺	850	96.6
Cu ²⁺	2000	97.1
Hg ²⁺	2000	95.7
Na ⁺	2000	97.3
Zn ²⁺	500	96.5
Mn ²⁺	800	95.4
Fe ²⁺	2000	97.1
CH ₃ COO ⁻	2000	99.6
NO ₃ ⁻	2000	99.8
CO ₃ ²⁻	1200	95.7
SO ₄ ²⁻	2000	100.9
C ₂ O ₄ ²⁻	2000	98.7

Effect of interferences

Crown ethers let only some ions to enter and complex formation that their sizes are equal to ether cavity. So, use of crown ether strongly improves selectivity. The interference effect of different ions including anions and cations, those can affect on the method performance was tested by using a solution containing 100.0 ng mL⁻¹ thallium(I) and addition of diverse concentrations of the interferences. The tolerance level was described as the maximum quantity of interferences those can produce a ± 5% error in thallium determination. The tolerance level of every interference ion was studied and if interference happened, the ratio was decreased until it stopped. Table 1 shows the studied species and their maximum tolerable quantities. As can be seen, several ions did not have any interference even at high levels and this means the suggested method can be applied to the analysis of thallium in different samples.

Analytical figures of merit

Under the optimized conditions, the performance was studied using the thallium(I) standard solutions. The results showed that the calibration graph for seven points was linear in the concentration range of 7.0–435 ng L⁻¹ in the initial solution (Fig. 1). The regression equation can be expressed as $Y = 2.8015X + 0.0137$, with

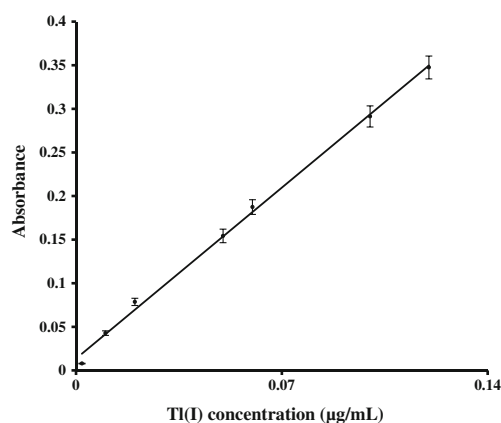


Fig. 1 The calibration plot of Tl(I) determination. Experimental conditions were as following: amount of thallium(I): 0.002, 0.01, 0.02, 0.05, 0.06, 0.1 and 0.12 µg mL⁻¹, pH = 10, type and volume of eluent: 2.0 mL HNO₃ (3 mol L⁻¹), sorption and desorption time: 4 and 5 min and temperature: 25 °C

the correlation coefficient $R^2=0.9974$. As can be seen from this plot, the slope is sharp and this shows that the sensitivity is high. In the regression equation, in addition to the slope, there is another parameter: intercept. Whatever the intercept is closer to zero, the method's sensitivity is higher.

The repeatability (intra-day) and reproducibility (inter-day) were evaluated by carrying out eight replicate extractions and determinations of thallium at a concentration level of 20.0 ng mL⁻¹ during a day (intra-day) and five replicates in five subsequent days (inter-day). Intra- and inter-day precisions were satisfactory with a relative standard deviation (RSD) of ±4.8% and ±5.1%,

Table 2 Determination of thallium(I) in real samples

Sample	Added	Found ^a	Recovery (%)
(µg L ⁻¹) Tap water ^b	-	0.036 ± 0.002 ^c , 0.002 ^d	-
	0.100	0.132 ± 0.007, 0.008	96 ± 5.3
	0.200	0.244 ± 0.010, 0.012	104 ± 5.4
Well water ^c	-	0.093 ± 0.005, 0.007	-
	0.100	0.194 ± 0.010, 0.013	101 ± 5.1
	0.200	0.287 ± 0.014, 0.016	97 ± 3.7
Tap water ^f	-	0.023 ± 0.001, 0.001	-
	0.100	0.119 ± 0.006, 0.008	96 ± 4.4
	0.200	0.221 ± 0.011, 0.014	99 ± 5.2
(µg g ⁻¹) Human hair	-	0.082 ± 0.005, 0.006	-
	0.100	0.179 ± 0.010, 0.012	97 ± 4.4
	0.300	0.377 ± 0.019, 0.021	98 ± 4.8

^a Mean ± standard deviation ($n = 3$)

^b Kerman drinking water, Kerman, Iran

^c Intra-day RSD

^d Inter-day RSD

^e Shahid Bahonar University of Kerman, Kerman, Iran

^f Baft drinking water, Kerman, Iran

Table 3 Comparison of the process with other reported methods for preconcentration of Tl

Method	Preconcentration factor	RSD (%)	Linear range ($\mu\text{g L}^{-1}$)	LOD ^a (ng L^{-1})	Ref.
Spect. ^b	23	1.12	0.66–100	220	[23]
Spect.	-	1.4	0.5–12	150	[24]
Spect.	100	2.9	0.7–4087.6	290.2	[25]
FAAS ^c	98.2	1.43	5–400	640	[26]
FAAS	50	1.82	2–100	920	[27]
FAAS	-	1.9	-	1.25	[28]
FAAS	77	2.6	20–200	2500	[29]
FAAS	125	2.1	10–700	1500	[30]
FAAS	80	1.7	3.75–17,500	1000	[31]
ETAAS	20	3.9	-	9	[32]
ETAAS	50	5.1	3–22	700	[33]
ETAAS	100	2.6	1–600	20	[34]
ETAAS	100	6.4	0.6–2.5	87	[35]
ETAAS	275	4.8	0.007–0.435	1.8	This work

^a Limit of detection

^b Spectrophotometry

^c Flame atomic absorption spectrometry

respectively. The detection limit based on $3s_b/m$ (where s_b = blank standard deviation and m = slope of the calibration curve) and quantification limit based on $10s_b/m$ were found to be 1.8 ng L^{-1} and 6.0 ng L^{-1} (RSD = 5.0%). Also, 275 was obtained as the preconcentration factor.

Analytical applications

In order to survey the credibility of the suggested technique, it was used for the preconcentration of thallium(I) in water samples and human hair. The trustiness was tested by analysis of the spiked environmental and biological samples with known amount of Tl. The data in Table 2 show that recovery at 95% confidence level is satisfactory.

To consider accuracy, this method was utilized for the thallium(I) determination in a certified reference material; SRM 1643d–Trace Elements in Water. The obtained analytical data are shown in Table S1. As can be seen, the presented results are in good agreement with the registered amounts and there is no remarkable discrepancy between the obtained results and the accepted values. So, the suggested system is valid for analysis of thallium in diverse samples.

Comparison with previously reported methods

In Table 3, figures of merit were compared with other methods for thallium determination. As can be seen from this Table, the recommended method has a wide linear graph, suitable RSD, and

high sensitivity. This method has also the lowest detection limit except only one reported literature [28] and best preconcentration factor. Moreover, due to the non-toxicity of method (without application of toxic and organic solvent), this technique can be regarded as a green method.

Conclusion

A modified magnetic nanocomposite was synthesized and applied for the preconcentration and determination of thallium(I) in combination with ETAAS. The aim of this work is to introduce a green technique that utilizes of magnetic nanocomposite for the preconcentration and determination of thallium ions in environmental, biological and standard samples. The suggested method has many advantages such as environmentally-friendly property, inexpensive, ease of adsorbent collection and enhanced sensitivity. Also, because of application of crown ether as modifier and limitation of other ions (except the Tl ion) entering to its cavities, the method's selectivity was improved significantly. This method has only one weakness and that is the required long time of MMNC preparation (about 52 h), but this time is necessary just for once and all needed nanocomposites are made at the same time. The performance characteristics of the method such as detection limit, linear range and preconcentration factor are superior and comparable in comparison with previously Tl reported analytical protocols. Also, this method was shown to be a good alternative for the determination of ultra-trace amount of thallium in different and complicated matrices.

Compliance with ethical standards The author(s) declare that they have no competing interests.

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