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To cite this article: Farzaneh Javedani-Asleh, Mohammad Eftekhari & Mahmoud Chamsaz (2016) Determination of total thallium in water and spinach samples by ligandless microextraction using ion pair-based dispersive liquid-liquid microextraction followed by electrothermal atomic absorption spectrometry, *Spectroscopy Letters*, 49:6, 420-425, DOI: [10.1080/00387010.2016.1186099](https://doi.org/10.1080/00387010.2016.1186099)

To link to this article: <http://dx.doi.org/10.1080/00387010.2016.1186099>



Accepted author version posted online: 12 May 2016.
Published online: 12 May 2016.



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Determination of total thallium in water and spinach samples by ligandless microextraction using ion pair-based dispersive liquid–liquid microextraction followed by electrothermal atomic absorption spectrometry

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ABSTRACT

An efficient, simple, and sensitive ligandless, ion pair-based dispersive liquid–liquid microextraction technique was used for preconcentration and determination of trace levels of total thallium followed by electrothermal atomic absorption spectrometry. In this method, thallium(III) was complexed by bromide ion to produce negative charged thallium bromide complex followed by addition of cetylpyridinium chloride as a counterion to form hydrophobic complex which was extracted into the extraction solvent by DLLME. In this method, a mixture of 1.5 mL of methanol (as disperser solvent) containing 150 μL of chloroform (as extraction solvent) was injected as extractant.

Under the optimum conditions, the calibration curve was linear in the range of 0.1–2 $\mu\text{g L}^{-1}$ of thallium (III) with a correlation coefficient of 0.9983. The limit of detection was 0.03 $\mu\text{g L}^{-1}$ and the relative standard deviation based on six replicate analysis of 1 $\mu\text{g L}^{-1}$ thallium(III) was 4.1%. The accuracy of the method was checked by the analysis of certified reference material and spike methods. The method was applied for determination of trace levels of thallium in water and spinach samples.

ARTICLE HISTORY

Received 1 April 2016
Accepted 1 May 2016

KEYWORDS

Cetylpyridinium chloride; electrothermal atomic absorption spectrometry; ion pair-based dispersive liquid–liquid microextraction; ligandless; thallium

Introduction

Thallium (Tl) is a hazardous element which may have harmful effects on the living organism at low concentrations.^[1] It exists usually in nature as Tl(I) and Tl(III) ionic forms that exhibit different bioavailability and toxicity properties.^[2] Its monovalent state has higher stability, whereas its trivalent state forms complexes of greater stability. Its compounds have been extensively used for manufacturing of products such as superconductive materials, alloys, optical lenses, dyes, and pigments.^[3] Concentrations of Tl in surface water usually range from 10 to 100 ng L^{-1} , whereas in human foods it lies typically between 250 and 500 ng g^{-1} .^[4,5] The Canadian guideline for Tl level in fresh water aquatic life is 0.8 $\mu\text{g L}^{-1}$ and in edible plants it is in the range of 0.02–0.125 $\mu\text{g g}^{-1}$.^[5]

Since Tl determination is difficult at low concentrations, a preconcentration step is necessary to achieve reliable results and eliminate matrix interferences. Various techniques have been used for preconcentration of Tl(I)/(III) such as liquid–liquid microextraction,^[6–9] solid phase extraction,^[10–12] and cloud point extraction.^[13] Dispersive liquid–liquid microextraction (DLLME)^[14,15] is a miniaturized sample preconcentration/separation method which has the advantage of large interface area between extractant and aqueous sample. In DLLME, by rapid injection of the mixture of extraction and disperser solvent into the sample, the extraction occurs in a few seconds. DLLME is an appropriate tool for analysis of samples with relatively simple matrix, such as water. However, applications in other fields such as food analysis have increased during the last few years.^[16,17] Up to now, the

greater parts of microextraction applications to preconcentrate of metal ions are based on the formation of hydrophobic chelate with organic chelating agents; as some of these reagents are toxic, application of ligandless microextraction techniques is preferable.^[18,19]

The aim of the present work is the complexation of Tl(III) with bromide anion as thallium tetrabromide (TlBr_4^-).^[20] Cetylpyridinium chloride (CPC) was used as counterion to produce the hydrophobic TlBr_4^- –CPC complex (Fig. 1), which was extracted into the fine droplets of extractant by DLLME. There is no publication on the use of bromide anion as complexing agent for ion pair-based DLLME of Tl(III). Different parameters affecting the extraction efficiency such as concentration of HBr, CPC concentration, and type of disperser and extraction solvent were investigated and optimized.

Experimental

Instrumentation

A graphite furnace atomic absorption spectrometer (HGA 700 model 4100, Perkin Elmer Norwalk, CT, USA), equipped with deuterium lamp as a background correction system, was used for the determination of Tl(III). Pyrolytic-coated graphite tubes (HGA 700, PerkinElmer) with L'vov platform were used. A Tl hollow cathode lamp (Beijing Shuguang-Ming Beijing, China) at a wavelength of 276.8 nm was used as radiation source, and measurements were carried out in the peak height mode, using a spectral bandwidth of

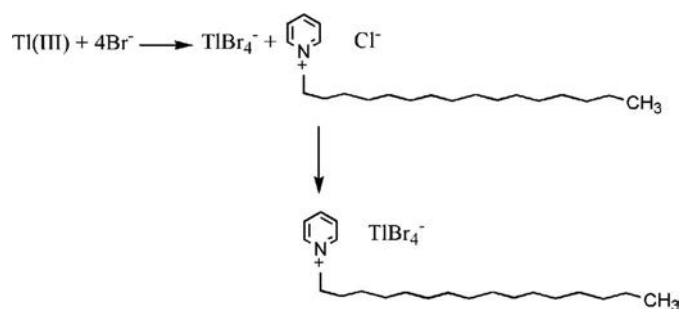


Figure 1. Scheme of the reaction of TlBr_4^- with cetylpyridinium chloride.

0.7 nm. Argon of 99.99% purity was used as inert gas, the flow rate being 300 mL min^{-1} during all stages, except during atomization when the flow was stopped. Phase separation was assisted using a centrifuge (Centurion Scientific, Andreas Hettich, Tuttingen, Germany).

Reagents

All reagents were of analytical reagent grade, and deionized water was used throughout. Deionized water ($18.1 \text{ M}\Omega\text{cm}^{-1}$) was obtained from a purification system (Nanopure Diamond, Barnstead, CA, USA). A solution of 1000 mg L^{-1} Tl(III) standard was prepared by dissolving appropriate amounts of Tl (NO_3)₃ (Sigma Aldrich, St. Louis, MO, USA) in 2% (v/v) HNO_3 (65%, Merck KGaA, Darmstadt, Germany). Working standard solutions were prepared by dilution with deionized water. A solution of $10^{-2} \text{ mol L}^{-1}$ CPC (Merck KGaA) was prepared in deionized water. Concentrated HBr (48% w/w, Sigma Aldrich) was used as a source of bromide anion and concentrated hydrogen peroxide (H_2O_2 , 30% v/v) (Merck KGaA) was used as an oxidizing agent to convert total Tl to Tl(III). $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and ascorbic acid (Merck KGaA) were used as chemical modifiers. Concentrated HBr was standardized by titration with aqueous sodium hydroxide (1 mol L^{-1}) and it was 8.6 mol L^{-1} . Stock solutions of 1.0% (w/v) Pd in 1% (v/v) HNO_3 , 2.0% (w/v) Mg in 1% HNO_3 , and 5.0% (w/v) ascorbic acid in deionized water were used as chemical modifiers.

Microextraction procedure

An aliquot of 10 mL of sample solution containing $0.1\text{--}2 \text{ }\mu\text{g L}^{-1}$ of Tl(III), $60 \text{ }\mu\text{L}$ of concentrated HBr (48%), and $6.5 \times 10^{-4} \text{ mol L}^{-1}$ of CPC was transferred into the conical bottom glass centrifuge tube. A mixture of 1.5 mL of methanol containing $150 \text{ }\mu\text{L}$ of chloroform was rapidly injected into the sample solution. The resulting cloudy solution (water, methanol, and chloroform) was centrifuged for 10 min at 3000 rpm. The volume of the sedimented phase was determined using a $100 \text{ }\mu\text{L}$ micro-syringe which was about $40.0 \text{ }\mu\text{L}$. Finally, $20 \text{ }\mu\text{L}$ of the sedimented phase was removed by syringe and diluted to $40 \text{ }\mu\text{L}$ with ethanol, and subsequently, $20 \text{ }\mu\text{L}$ of the resulting solution and chemical modifier ($15 \text{ }\mu\text{g}$ Pd and $10 \text{ }\mu\text{g}$ Mg) were injected into the electrothermal atomizer for determination of Tl.

Preparation of real samples

Water samples

Different water samples including tap (Mashhad, Iran), river (Kashaf Rood, Mashhad, Iran), and spring waters (Nowchah, Mashhad, Iran) were collected from their local sources and filtered through No. 42 Whatman[®] paper to remove any suspended particles and then acidified with 2 mL of 2 mol L^{-1} nitric acid and stored in glass bottles at 5°C . To 8 mL of each sample, $10 \text{ }\mu\text{L}$ of concentrated H_2O_2 (30%) was added to convert Tl(I) to Tl(III), and it was placed for 10 min in $60\text{--}70^\circ\text{C}$ heated water to remove excess amounts of H_2O_2 . Finally, after addition of other reagents and dilution to 10 mL , it was analyzed for its Tl content according to the microextraction procedure.

Spinach samples

Spinach leaves were purchased from the local market, washed with deionized water several times, and dried in an oven at 50°C for 6 hr. Spinach leaves were finely milled using a multi-function grinder and then 1000 g of powdered sample was weighted and digested in 15 mL HNO_3 (65%) on a heating block to $60\text{--}70^\circ\text{C}$ for 2 hr to near dryness. In order to complete digestion, 5 mL of H_2O_2 was added to the sample solution which was heated to $60\text{--}70^\circ\text{C}$ for another 30 min. The resulting solution was filtered through No. 42 Whatman[®] paper and diluted to 50 mL with deionized water. An aliquot of 1 mL of this solution was analyzed according to the microextraction procedure.

Results and discussions

Modification of graphite furnace program

Drying, pyrolysis, and atomization temperature for determination of Tl in the extraction solvent were optimized and the optimum conditions are presented in Table 1. Since the extraction solvent (chloroform) and ethanol have low boiling points, the drying step of 90°C was selected, and to remove nitric acid, the drying step of 130°C with a hold time of 15 s was chosen. The influence of pyrolysis temperature on the absorbance of Tl was studied in detail within a range of $400\text{--}800^\circ\text{C}$. Optimal pyrolysis temperature was observed at 600°C , with a hold time of 20 s. The effect of atomization temperature on the absorbance of Tl was studied within the interval of $1800\text{--}2200^\circ\text{C}$. Maximum absorbance was observed at 2000°C with a hold time of 5 s. Finally, a temperature of 2400°C and a hold time of 3 s was chosen for the cleaning step. Several modifiers such as Pd ($15 \text{ }\mu\text{g}$; by injection of $7.5 \text{ }\mu\text{L}$ of 0.2% (w/v) Pd), a mixture of Pd and Mg ($15 \text{ }\mu\text{g}$ Pd + $10 \text{ }\mu\text{g}$ Mg; by injection of $7.5 \text{ }\mu\text{L}$ of 0.2%

Table 1. Instrumental parameters and temperature program for thallium analysis.

Step	Temperature ($^\circ\text{C}$)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min^{-1})
Drying 1	90	3	15	300
Drying 2	130	10	20	300
Ashing	600	30	20	300
Atomization	2000	0	5	0
Cleaning	2400	2	3	300

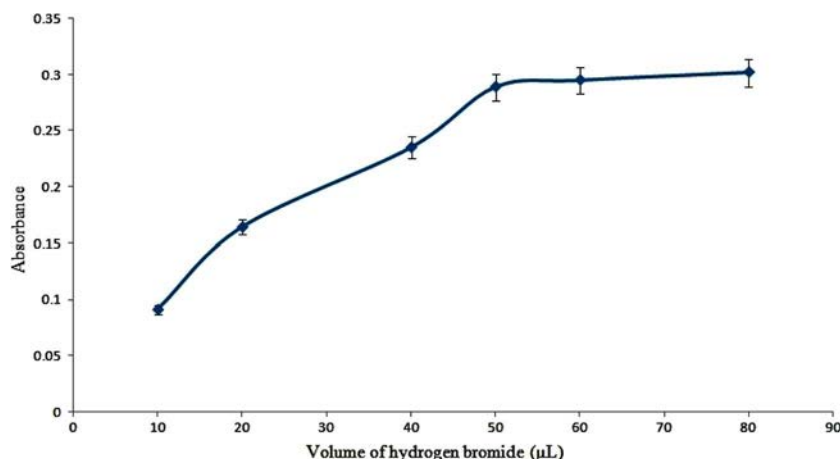


Figure 2. Effect of volume of hydrogen bromide on the absorbance of thallium(III). Conditions: $1 \mu\text{g L}^{-1}$ thallium(III), $6.5 \times 10^{-4} \text{ mol L}^{-1}$ cetylpyridinium chloride, 1.5 mL of methanol containing 150 μL chloroform.

(w/v) Pd and 5 μL of 0.2% (w/v) Mg), and a mixture of Pd + ascorbic acid (15 μg Pd + 200 μg ascorbic acid; by injection of 7.5 μL of 0.2% (w/v) Pd and 10 μL of 2% (w/v) ascorbic acid) were tested. Based on the results, a mixture of Pd and Mg (15 μg Pd + 10 μg Mg) provided maximum absorbance for determination of Tl.

Effect of hydrogen bromide concentration

Concentrated HBr provides bromide anion to produce TlBr_4^- in the sample solution; therefore, its optimum concentration has an important effect on the extraction efficiency of Tl(III). The effect of concentration of HBr on the absorbance of Tl(III) was studied by addition of different volumes of HBr (48% w/w) in the range of 10–130 μL . The results are shown in Fig. 2. As can be seen, the absorbance reaches its maximum value at a volume of 50 μL HBr, and it remains constant afterward. Therefore, to ensure an efficient concentration of HBr remaining in solution 60 μL of concentrated HBr (48% w/w), 51.6 m mol L^{-1} bromide ion, was used as optimum value.

Effect of cetylpyridinium chloride concentration

In this study, CPC was used as a counterion to produce hydrophobic complex with TlBr_4^- which can be extracted into the chloroform by DLLME. The effect of CPC concentration on the absorbance of Tl(III) was studied in the range of 1.0×10^{-4} – $8.0 \times 10^{-4} \text{ mol L}^{-1}$ CPC. Based on the results shown in Fig. 3, the absorbance reaches its maximum value at a concentration of $6.0 \times 10^{-4} \text{ mol L}^{-1}$ of CPC and remained constant afterward. Therefore, a concentration of $6.5 \times 10^{-4} \text{ mol L}^{-1}$ CPC was selected as optimum value.

Effect of type and volume of extraction solvent

In this study, chloroform, carbon tetrachloride, and dichloromethane were used as the extraction solvents. In order to study the effect of type of extraction solvents on the absorbance of Tl (III), different volumes of extraction solvents (150 μL , 80 μL , and 60 μL of chloroform, dichloromethane, and carbon tetrachloride, respectively) were diluted to a volume of 1.5 mL with methanol and injected into the sample solution to obtain 40 μL of sedimented extraction solvent. The results show that

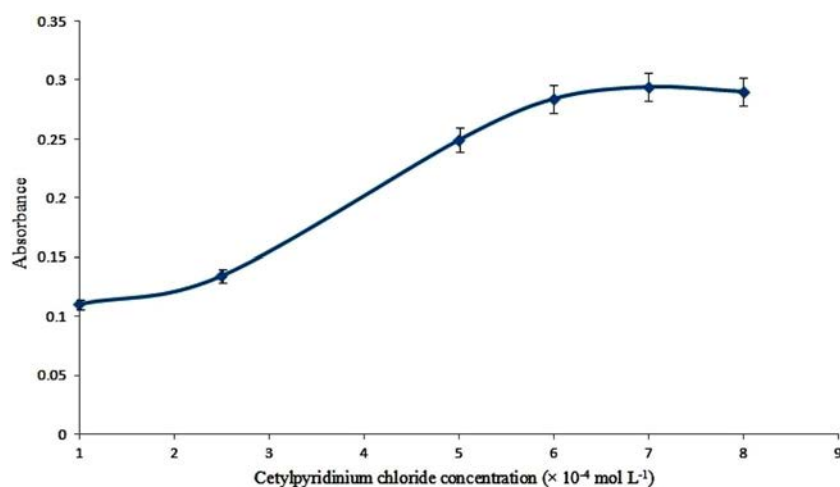


Figure 3. Effect of cetylpyridinium chloride concentration on the absorbance of thallium(III). Conditions: $1 \mu\text{g L}^{-1}$ thallium(III), 60 μL of hydrogen bromide (48%), 1.5 mL of methanol containing 150 μL chloroform.

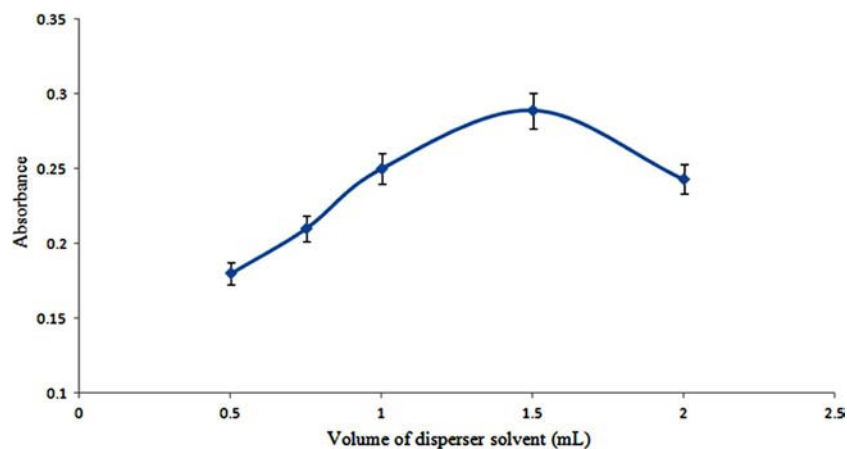


Figure 4. Effect of volume of disperser solvent on the absorbance of thallium(III). Conditions: $1 \mu\text{g L}^{-1}$ thallium(III), $60 \mu\text{L}$ of hydrogen bromide (48%), $6.5 \times 10^{-4} \text{ mol L}^{-1}$ cetylpyridinium chloride, $150 \mu\text{L}$ of chloroform.

chloroform provides maximum extraction efficiency for micro-extraction of Tl(III), and it was selected as the extraction solvent. The effect of volume of extraction solvent on the absorbance of Tl(III) was studied in the range of 100–350 μL . Different volumes of chloroform were diluted to a volume of 1.5 mL with methanol and injected into the sample solutions. The results show that 150 μL of chloroform provides maximum extraction efficiency for determination of Tl(III). Therefore, 150 μL of chloroform was selected as the optimum volume.

Effect of type and volume of disperser solvent

Acetone, acetonitrile, ethanol, and methanol were studied as disperser solvents. About 150 μL of chloroform for ethanol, methanol, and 135 μL of chloroform for acetonitrile and acetone were diluted to 1.5 mL with disperser solvents (to obtain 40 μL of sedimented extraction solvent) and rapidly injected into the sample solution. Based on the results, methanol provides maximum absorbance for determination of Tl(III); therefore, it was selected as optimum disperser solvent. Also, in order to study the effect of volume of disperser solvent on the absorbance of Tl(III), different volumes of methanol in the range of 0.5–2 mL containing 150 μL of chloroform were injected into the sample solution. The results in Fig. 4 show that 1.5 mL of methanol provides maximum absorbance for determination of Tl(III). Therefore, 1.5 mL of methanol was used as optimum volume.

Effect of extraction time

The extraction time, defined as the interval between injection of the mixture of methanol and chloroform and the time of centrifugation process started, was evaluated in the range of 0–240 s. The results show that extraction time has no impact on the absorbance of Tl. It may be related to the large contact surface area between extraction solvent and aqueous phase. Therefore, in this method, extraction time is very short.

Effect of centrifugation time

The effect of centrifuge time was studied in the interval time of 4–15 min at a constant rate of 3000 rpm. The results show that

10 min centrifuge time at 3000 rpm is adequate to separation of two immiscible phases.

Effect of ionic strength

In order to study the effect of ionic strength on the absorbance of Tl(III), different concentrations of KNO_3 , 0.3–4.0% (g mL^{-1}), were tested in the presence of $1 \mu\text{g L}^{-1}$ Tl(III). The results show that the absorbance remains constant up to 1% g mL^{-1} KNO_3 , and it decreases gradually at higher KNO_3 concentrations. Therefore, all experiments were performed without addition of salt into the sample solution.

Effect of interfering ions

The effects of diverse cations and anions on the absorbance of Tl(III) were checked to study the applicability of the proposed method in different real samples. An interfering ion was considered to interfere if it resulted in absorbance variation of $\pm 5\%$. The study was performed by analyzing 10 mL of $1 \mu\text{g L}^{-1}$ Tl(III) containing contaminant ions at different concentrations. The results indicated there were no interferences from the following ions each at a concentration of 200, 000 microgram per liter: potassium (I), sodium (I), sulfate, and nitrate; 100,000 $\mu\text{g L}^{-1}$ of chloride anion; 1000 $\mu\text{g L}^{-1}$ zinc (II), copper (II), manganese (II), nickel (II); and 500 $\mu\text{g L}^{-1}$ lead (II), cadmium (II), iron (III), aluminum (III), and cobalt (II); ions did not show any interferences. Therefore, this

Table 2. Analysis of real samples for determination of thallium(III). Results (mean \pm standard deviation based on three replicate analyses).

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water (Mashhad, Iran)	–	0.84 ± 0.04	–
	0.50	1.30 ± 0.07	97.0
	1.00	1.81 ± 0.12	98.4
Spring water (Now Chah, Mashhad, Iran)	–	0.33 ± 0.02	–
	0.50	0.80 ± 0.05	96.4
	1.00	1.31 ± 0.07	98.5
River water (Kashaf Road, Mashhad, Iran)	–	1.12 ± 0.08	–
	0.50	1.65 ± 0.09	101.8
	Spinach leaves (mg kg^{-1})	–	0.12 ± 0.02
	0.10	0.21 ± 0.04	95.4

Table 3. Comparison of the proposed method for the determination of thallium with other reported methods.

Method	Linear range ($\mu\text{g L}^{-1}$)	Limit of detection ($\mu\text{g L}^{-1}$)	Relative standard deviation (%)	Preconcentration factor	Reference
Single-drop microextraction–electrothermal atomic absorption spectrometry	3–22	0.7	5.1	50	[7]
Solid-phase extraction–electrothermal atomic absorption spectroscopy	1–600	0.02	2.6	–	[10]
Ultrasound-assisted- dispersive liquid–liquid microextraction–electrothermal atomic absorption spectroscopy	0.2–10	0.03	3.3	–	[6]
Solid-phase extraction–electrothermal atomic absorption spectroscopy	0.6–2.5	0.087	6.4	100	[11]
Dispersive liquid–liquid microextraction–electrothermal atomic absorption spectroscopy	0.033–4	0.003	5.3	28.6	[21]
Ultrasound-assisted emulsification solidified floating organic drop–electrothermal atomic absorption spectroscopy	0.022–0.66	0.0047	4.8–5.4	450	[18]
Dispersive liquid–liquid microextraction–inductively coupled plasma mass spectrometry	0.04–0.08	0.004	1.3–1.5	–	[22]
Ultrasound-assisted microextraction–inductively coupled plasma optical emission spectrometry	1–1000	0.52	4.19	–	[23]
Ion pair-based DLLME–ETAAS	0.1–2	0.03	4.1	125	Present work

method is applicable to analysis of Tl(III) in different real samples.

Analytical figures of merit

Under the optimum conditions, the calibration curve was linear in the range of $0.1\text{--}2\ \mu\text{g L}^{-1}$ of Tl(III) with a correlation coefficient of 0.9983. The equation of calibration graph was $A = 0.2692 C_{\text{Tl(III)}} + 0.0372$, where A is the analytical signal measured as absorbance and C is the concentration of Tl(III) in $\mu\text{g L}^{-1}$. The relative standard deviation (RSD, %), based on six replicate analysis of $1\ \mu\text{g L}^{-1}$ of Tl(III) was 4.1% and the limit of detection (LOD) which is defined as three times of standard deviation of blank ($n = 5$) was $0.03\ \mu\text{g L}^{-1}$ ($0.6\ \text{pg Tl}$). The preconcentration factor (PF), calculated as the ratio between the volume of the aqueous phase and the final volume of the extraction phase, was 125. The enhancement factor as calculated by the slope ratio of the calibration curves for Tl(III) determination with and without ion pair-based DLLME was 112. The sensitivity of the proposed method for the determination of Tl based on $0.0044/m$ (where m is the slope of calibration curve) was $0.016\ \mu\text{g L}^{-1}$.

Analysis of real samples

In order to check the applicability of the proposed method for the determination of trace levels of Tl(III), different water and spinach leaf samples were analyzed for monitoring the total levels of Tl. Spike tests ascertain that recoveries are satisfactory (Table 2). Also, certified reference material–trace metals in drinking water (High Purity Standards Company, Charleston, South Carolina, USA; <http://www.highpuritystandards.com/store/home.php?cat¼44>), with a declared Tl concentration of $10.0\ \mu\text{g L}^{-1}$, have been analyzed. Since the certified concentration value in the certified reference material (CRM) was higher than the upper limit of the linear range of this method, a 10-fold dilution had to be implemented prior to the analysis. By using the proposed method, Tl(III) concentration was found to be $9.91 \pm 0.51\ \mu\text{g L}^{-1}$, indicating an acceptable accuracy of the method.

Comparison to other methods

The proposed ion pair-based dispersive liquid–liquid microextraction technique was compared with other preconcentration methods used for the determination of Tl, and the results are shown in Table 3. The linear range, and detection limit of the proposed method are better or comparable to other reported methods.

Conclusions

Ligandless, ion pair-based DLLME as an efficient, rapid, and sensitive preconcentration method followed by electrothermal atomic absorption spectrometry was used for the determination of trace levels of total Tl. The method is based on complexation of Tl(III) with bromide ion to form TlBr_4^- followed by addition of CPC as counterion to produce hydrophobic complex of $\text{TlBr}_4\text{--CPC}$ which can be extracted into the extraction solvent (chloroform) by DLLME. Based on our knowledge, there is no publication on the use of bromide anion as complexing agent for ion pair-based DLLME of Tl(III). The results show that this extraction procedure is noticeable due to its outstanding advantages which are minimum organic solvent consumption, simplicity, rapidity, low cost, and high extraction efficiency.

Funding

The authors acknowledge the financial support of the Ferdowsi University of Mashhad, Iran.

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