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Ligandless, ion pair-based and ultrasound assisted emulsification solidified floating organic drop microextraction for simultaneous preconcentration of ultra-trace amounts of gold and thallium and determination by GFAAS

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ABSTRACT

In the present work, a new, simple and efficient method for simultaneous preconcentration of ultra-trace amounts of gold and thallium is developed using an ion pair based-ultrasound assisted emulsification-solidified floating organic drop microextraction procedure before graphite furnace atomic absorption spectrometry determination. This methodology was used to preconcentrate the ion pairs formed between $AuCl_4^-$ and $TlCl_4^-$ and $[C_{23}H_{42}]N^+$ in a microliter-range volume of 1-undecanol. Several factors affecting the microextraction efficiency, such as HCl volume, type and volume of extraction solvent, sonication time, sample volume, temperature, ionic strength and $[C_{23}H_{42}]NCl$ volume were investigated and optimized. Under the optimized conditions, the enrichment factor of 441 and 443 and calibration graphs of 2.2–89 and 22.2–667 ng L^{-1} for gold and thallium were obtained, respectively. The intra- and inter-day precision of ±4.4 and ±4.9% for Au and ±4.8 and ±5.4% for Tl were obtained. The detection limit was 0.66 ng L^{-1} for Au and 4.67 ng L^{-1} for Tl. The results show that the liquid–liquid pretreatment using ion pair forming, is sensitive, rapid, simple and safe method for the simultaneous preconcentration of gold and thallium. The method was successfully applied for determination of gold and thallium in natural water and hair samples.

1. Introduction

Gold is a dense, soft, shiny, malleable and ductile metal. It is one of the most ancient metals used in the arts and jewelry and it is of growing importance in technology because of its resistance to corrosion. It commands a premium price because of its low abundance in nature. Gold is extensively used in various areas such as the electronic apparatus [1]. It is widely distributed in nature and the chemistry of gold remains an active research area [2].

The determination of hazardous elements in environmental samples can provide important information concerning pollution, since they are usually released in the environment from anthropogenic sources, such as agricultural and industrial activities [3]. Tl is used as a catalyst, in making alloys, optical lenses, jewelry, low temperature thermometers, dyes and pigments and in scintillation counters. Its compounds have also been used as medicines, rodenticides and insecticides [4]. It is extremely toxic to humans, plants and animals and plays no role in their metabolisms. Soluble univalent thallium compounds, e.g., thallium(I) sulfate, nitrate, acetate and carbonate are very toxic because they are easily absorbed into the human body by skin contact or ingestion [5]. The estimated lethal dose in humans is 8–12 μg g^{-1} [6]. Tl(I) is highly toxic to the biosphere even more than Hg, Cd, Pb and Cu [7,8]. Industrial use of thallium is very extensive, mostly in specialized electronic equipments.

In natural samples, Au concentration is about 4 ng g^{-1} in basic rocks and 1 ng g^{-1} in soils. The values of 0.05 and 0.2 ng mL^{-1} were found in seawater and river water, respectively [9] whereas Tl concentration in surface water usually is in the range of 10–100 ng L^{-1} [10] and in non-polluted soils lies typically between 0.3 and 0.55 mg kg^{-1} [11]. On the basis of these considerations, the determination of Au and Tl is difficult for the low concentration in most environmental and geological materials (even below the detection limit of the instrument) and the high concentration of interfering matrix components. Therefore preconcentration procedures, selective separation and purification methods are often needed. Some analytical techniques are available for determination of trace amounts of Au and Tl in geological and environmental samples such as flame atomic absorption spectrometry (FAAS) [12,13], neutron activation [14,15], spectrophotometry [16,17],

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electrochemical methods [18,19] and inductively coupled plasma mass spectrometry (ICP-MS) [20,21]. Electrothermal atomic absorption spectrometry is a good technique for determination of ultra-trace amounts of gold and thallium in several types of samples in view of its sensitivity. The direct determination of trace and ultra-trace amounts of species by graphite furnace atomic absorption spectrometry (GFAAS) sometimes is problematic. By reason of ultra-low concentration of gold and thallium and high concentration of interfering matrix components in most real samples, GFAAS often requires a suitable pretreatment. Pretreatment step (preconcentration/separation) of the sample before analysis is caused to facilitate the desired sensitivity and selectivity of measurement [22]. Various techniques have been used for separation and preconcentration of gold and thallium such as liquid–liquid extraction (LLE) [23,24], solid-phase extraction [25,26] and cloud point extraction [27,28].

LLE is one of the most popular extraction methods. In the last decades, the scientific interest for the environmental burden, have led to green analytical methods. The main target of green analytical chemistry (GAC) is to replace or minimize toxic reagents and wastes [29]. Hence study activities have been placed on miniaturizing the traditional LLE procedure by reducing the organic solvent to aqueous phase ratio, resulting in the development of microextraction techniques such as single drop microextraction (SDME) [30–32], homogenous liquid–liquid microextraction [HLLME] [33,34], solid phase microextraction (SPME) [35,36] and dispersive liquid–liquid microextraction (DLLME) [37,38]. The main advantages of these techniques are; the negligible volume of solvents and their ability to detect analytes at very low concentration. Recently a new liquid–liquid microextraction method namely, solidified floating organic drop microextraction (SFODME), which is a modified solvent extraction method, was proposed for extraction and determination of organic analytes [39]. It has the advantages of simplicity, low cost, minimum organic solvent consumption and achievement of high enrichment factor. We extend its application to inorganic analysis.

To the best of our knowledge, there is no previous literature report on the use of ion pair formation and GFAAS technique for simultaneous preconcentration and determination of gold and thallium ions in real samples. In the present investigation, a simultaneous and green separation and preconcentration of gold and thallium based on ion pair formation-ultrasound assisted emulsification-solidified floating organic drop microextraction (IP-USAE-SFODME) method combined with GFAAS was developed for separation, enrichment and determination of gold and thallium in several samples. It was used the ion pair formed between $AuCl_4^-$ and $TlCl_4^-$ and $[C_{23}H_{42}]N^+$ as ion pair forming agent in a microliter-range volume of 1-undecanol. In order to obtain a high enhancement factor, the influence of some experimental parameters affecting the ion pair formation and extraction conditions such as HCl volume, type and volume of extraction solvent, sonication time, sample volume, temperature, volume of ion pair forming agent and ionic strength were studied and optimized.

2. Experimental

2.1. Reagents and standards

All chemical reagents which were of analytical-reagent grade and deionized water was used for preparation of the sample solutions. Au(III) stock solutions (100 mg L^{-1}) were prepared by dissolving appropriate amount of $HAuCl_4 \cdot 4H_2O$ (Merck, Darmstadt, Germany) into a 100.0 mL volumetric flask and were diluted to the mark with deionized water. A stock solution of 1000 mg L^{-1} thallium(I) ion was purchased from Merck (Darmstadt, Germany). Working standard solutions of Au(III) and Tl(I) were prepared freshly at various concentrations by diluting the stock standard solution with deionized water. The ion pair forming agent (0.5 mol L^{-1}) solution was prepared daily by dissolving the proper amount of benzyldimethyltetradecyl ammonium chloride dihydrate (Merck, Darmstadt, Germany) in deionized water. 1-undecanol, 2-dodecanol, 1-hexadecanethiol, acetonitrile, acetone, ethanol, methanol and hydrochloric acid (37%) were purchased from Merck (Darmstadt, Germany). All reagents used were of the highest available purity and of at least analytical reagent grade. Deionized water was used throughout the work. The laboratory glassware and conical-bottom tubes were kept in 10% nitric acid for 24 h and before using were washed with deionized water and dried.

2.2. Instrumentation

Gold and thallium measurements were performed with a Varian Spectra AA 220 atomic absorption spectrometer (Australia, http://www.varianinc.com) with a deuterium lamp background correction, equipped with graphite furnace (GTA-110 series). Optimum operating parameters for GFAAS are given in Table 1. Fine droplets of organic solvent were obtained using a Sonorex Digitec DT 255 H ultrasonic water bath (Frequenz: 35 kHz, Germany) with temperature control was used for assisting the emulsification process of the microextraction technique and a centrifuge (6000 rpm, serial: 88–2750, Sahand Teb Aria Co. Iran) was used to accelerate the phase separation.

2.3. IP-USAE-SFODME procedure

For IP-USAE-SFODME, a 20 mL standard solution containing 1.0 ng of Au(III) and 5.0 ng Tl(I), 2 mL of hydroxylamine hydrochloride (0.1 mol L^{-1}), 2.5 mL of concentrated HCl (37%) and 1.6 mL of benzyldimethyltetradecyl ammonium chloride dihydrate (0.5 mol L^{-1}) were poured into a 50-mL conical-bottom tube. Then 30 μL of 1-undecanol (as the extraction solvent) was added to the tube and sonicated for 3 min (or use of 300 μL of ethanol as disperser solvent). In this stage, a white cloudy solution was formed in the test tube. The mixture was centrifuged for 5 min at 3000 rpm and the organic solvent droplet was floated on the surface of the aqueous solution due to its low density. Then it was transferred into an ice bath and the organic solvent was solidified after 10 min. Then the solidified solvent was transferred into a conical vial where it melted quickly at room temperature. After separation, in order to reduce the viscosity of the organic phase and facilitate sample handling prior to GFAAS analysis, the extract was made up to 100 μL by adding methanol and finally, 20 μL of resultant solution automatically injected by the autosampler into the graphite tube and the absorbance of gold and thallium were measured under the operating conditions summarized in Table 1.

2.4. Samples preparation

2.4.1. Water samples

Three water samples, including; tap water (Kerman drinking water, Kerman, Iran), well water (Shahid Bahonar University of Kerman, Kerman, Iran) and waste water (Iron Factory, Bafgh, Yazd, Iran) were selected. These samples were filtered to remove suspended particulate matters, stored at 4 °C in a refrigerator and the proposed method was applied for the determination of gold and thallium content.

2.4.2. Human hair

Human hair sample was immersed in acetone for 30 min, washed by water and then dried. 0.5 g of sample was weighed accurately, digested by 30.0 mL of a mixture solution of $HClO_4$

Table 1
Instrumental parameters and thermal program of GFAAS for determination of Au and Tl.

a) Instrumental parameters

Parameter	Tl	Au
Wavelength (nm)	276.8	242.8
Spectral bandwidth (nm)	0.5	1.0
Lamp current (mA)	10	4
Signal measurement	Peak Height	Peak height
Sample volume (μL)	20	20
Modifier volume (1000 ppm)	5 ($Pd(NO_3)_2$)	5 ($Pd(NO_3)_2$)

b) Temperatures programs

Step	Furnace temp. (°C)	Time (s)	Argon flow rate ($L\ min^{-1}$)
Drying	85	5	3.0
Drying	95	40	3.0
Drying	120	10	3.0
Ashing	250[a],500[b]	5	3.0
Ashing	250[a],500[b]	1	3.0
Ashing	250[a],500[b]	2	0
Atomization	2200[a],2600[b]	1[a],1.2[b]	0
Atomization	2200[a],2600[b]	2[a],2[b]	0
Cleaning up	2400[a],2800[b]	2	3.0

[a] Tl.
[b] Au.

and HNO_3 (1:8 v/v) at low temperature. The digested solution was dried under elevated temperature and then several drops of H_2SO_4 (1:1 v/v) were added to the residue. After leaching with water, the residue was transferred to a 100.0 mL measuring flask, diluted to the mark with deionized water [44], an aliquot of solution were selected and the experiment was carried out according to the procedure mentioned earlier.

2.4.3. *Certified reference material*

In order to confirm the validity of the developed procedure, this method has also been applied for the determination of the content of gold and thallium in certified Reference Materials; (MA-1b reference gold ore) and (SRM 1643d-Trace Elements in Water).

For Au, a 500.0 mg sample (MA-1b reference gold ore) was taken and dissolved completely in a mixture of HNO_3, HCl and HF (2:4:1 volume ratio) with heating. The solution was cooled, diluted and filtered. The volume of the filtrated was raised to 1.0 L with deionized water in a volumetric flask. 5 mL of this solution was diluted to 1.0 L and an aliquot of the sample solution was taken individually, and the gold content was determined by the recommended procedure.

In the case of Tl, 2 mL of the solution (SRM 1643d-Trace Elements in Water) was poured into a 100.0 mL measuring flask, diluted to the mark with deionized water and the thallium content was determined by the proposed method.

Since used standard reference materials were not containing both of Au and Tl, gold and thallium (from their standard stock solutions) were added to SRM 1643d-Trace Elements in Water and MA-1b reference gold ore before their preparation, respectively.

3. Results and discussion

In this study, a combination of IP-USAE-SFODME with GFAAS was developed for determination of ultra-trace amounts of gold and thallium ions. In order to achieve the best efficiency, various factors influenced the ion pair formation, extraction and analysis process, were investigated. These factors are; nature and volume of extraction solvent, nature and volume of disperser solvent, HCl volume, benzyldimethyltetradecyl ammonium chloride dihydrate volume, furnace temperature program, ionic strength, sonication time, volume of aqueous solution and temperature. The optimization process was performed by modifying one at a time and keeping the remaining parameters constant. The enrichment factor (EF) was defined as the ratio of the curve slope of preconcentration sample to that obtained from extraction with the proposed method and was used to evaluate the extraction efficiency under different experimental conditions. The calculate methods of preconcentration factor and extraction recovery were expressed as Eqs. (1) and (2), respectively:

$$PF = the\ \ initial\ volume/the\ final\ volume \quad (1)$$

$$Recovery\% = [(C_{org} \times V_{org})/(C_{aq} \times V_{aq})] \times 100 \quad (2)$$

where PF, $Recovery\%$, C_{org}, V_{org}, C_{aq} and V_{aq} are the preconcentration factor, extraction recovery, concentration of extraction solvent after the extraction process, volume of extraction solvent after the extraction process, concentration of water sample before the extraction process and volume of water sample, respectively. The proposed method was also employed for the determination of Au and Tl in several samples.

3.1. *GFAAS determination*

Drying, pyrolysis and atomization temperature for determination of Au and Tl in the extracts were optimized and the optimum conditions are presented in Table 1. Under the optimum conditions, the peak was sharp and the background was minimized. With regard to the boiling point of 1-undecanol (243 °C), it was proved that for evaporation of solvent, a drying temperature of 270 °C with the hold time of 10 s is necessary. $Pd(NO_3)_2$ is a common chemical modifier that has previously been used in GFAAS and good results have been obtained [40]. Therefore, it was decided to use this modifier in our experiments.

3.2. *Effect of HCl concentration*

An acidic medium is suitable for the extraction of ion pairs in conventional SFODME [41]. For this purpose, the effect of three acids such as HCl, HBr and HNO_3 were investigated. The result of this study shows that HCl is the most suitable acid for proposed method. HCl concentration is a very important factor on the formation of the $AuCl_4^-$ and $TlCl_4^-$ complexes, previous to the formation of their ion pairs. The excess of HCl has a positive effect on both of the ion pair formation and also extraction. As shown in Fig. 1, an increase in the extraction efficiency of the ion pairs occurred with increasing HCl volume up to 2.5 mL (1.5 mol L^{-1}), therefore it was decided to carry out further experiments at this concentration.

3.3. *Effect of the ion pair forming agent*

Benzyldimethyltetradecyl ammonium chloride dihydrate was chosen due to its ability to form ion pairs with the $AuCl_4^-$ and $TlCl_4^-$ ions, which can be extracted into 1-undecanol. The effect of ion pair forming agent (0.5 mol L^{-1}) volume was studied in the range 0.4 to 4 mL. As it can be seen in Fig. 2, an increase in the extraction recovery of the ion pair occurred with increasing the ion pair forming agent volume up to 1.6 mL and remains constant even the amount of ion pair forming agent increased. Thus this volume was selected accordingly for subsequent experiments.

3.4. *Nature and volume of extraction solvent*

In order to obtain high recovery and enrichment factor, the selection of organic solvent and its volume have an important role in the SFODME system. The extractant phase should have lower density than water, low volatility and water solubility. In addition, the extractant phase should show appropriate extraction efficiency of the target analyte. On the basis of these considerations, three organic solvents with different physicochemical properties (Table 2) including; 1-undecanol, 2-dodecanol and 1-hexadecanethiol were investigated. 1-undecanol was found to give the best extraction efficiency. In the case of 2-dodecanol, the extraction efficiency was about 68% of 1-undecanol, while 1-hexadecanethiol produced high backgrounds during the analysis with GFAAS, which interfere with determination of the analytes. Thus, in the present study, 1-undecanol was selected as the extraction solvent. The influence of the volume of 1-undecanol on the extraction efficiency was studied. For this purpose, different volumes of 1-undecanol (20–100 μL) were subjected to the same SFODME (Fig. 3). As can be seen, the extraction recovery increased with an increase in 1-undecanol volume up to 30 μL and remained constant up to 100 μL. Because 1-undecanol is toxic and also too expensive, therefore minimum volume of this compound was used for extraction. Moreover 1-undecanol is a viscose solvent and needs to be diluted before injection to GFAAS. Thus 30 μL of 1-undecanol was selected for the further experiments.

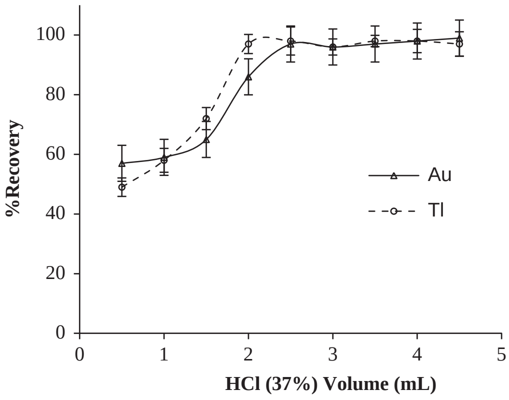

Fig. 1. Effect of HCl volume on the extraction efficiency of gold and thallium. Experimental conditions were the following: amount of gold(III) and Tl(I), 1 ng and 5 ng; sample volume 20 mL; volume of ion pair forming agent, 1.6 mL; extraction solvent volume, 30 μL; extraction temperature, room temperature; sonication time, 3 min; centrifugation time and rate, 5 min and 3000 rpm.

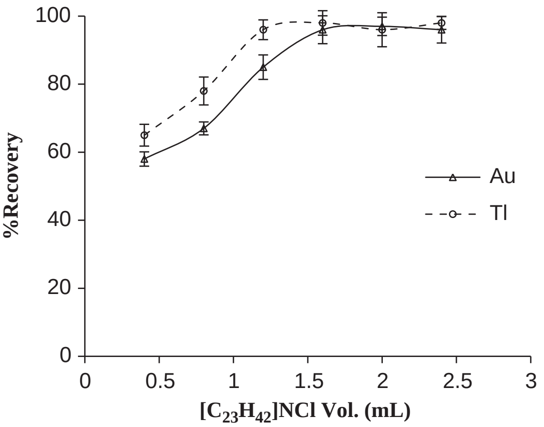

Fig. 2. Effect of ion pair forming agent volume on the extraction efficiency of gold and thallium. Experimental conditions were the same as in Fig. 1. except ion pair forming agent volume (HCl concentration, 1.5 mol L^{-1}).

3.5. *Nature and volume of disperser solvent*

For the sake of acquiring the most suitable disperser solvent, four types of disperser solvents such as acetonitrile, acetone, ethanol and methanol were investigated. The results of these studies show that the analyte signal with ethanol as the dispersive solvent was higher in comparison with methanol, acetone and acetonitrile (Fig. 4). Thus in this study ethanol was selected as the most suitable disperser solvent due to its low toxicity, low cost and high analyte signal. Subsequently, the experiment was performed with different volumes of ethanol (100–1000 μL) (Fig. 5) in order to obtain the best result. At the low volume of ethanol, the 1-undeconol was not completely dispersed and the extraction efficiency was also low. The absorbances of analytes were maximized from 300 to 700 μL of ethanol and then decreased with further increase of the ethanol volume. The decrease in extraction recovery at more volumes of ethanol is due to dissolution of the 1-undecanol drop by ethanol. Thus 300 μL of ethanol was used as the optimal volume of disperser solvent.

3.6. *Effect of ultrasound energy without the use of disperser agent*

To avoid the use of the disperser agent, ultrasound energy could be applied, which leads to the technique known as ultrasound assisted emulsification microextraction. Ultrasound irradiation can facilitate the dispersion of the extraction solvent in the aqueous phase without using disperser agent [42]. A comparative study on the extraction efficiency of the ion pair by a micro-volume of 1-undecanol was performed by applying different dispersion systems, including; the use of a disperser solvent (ethanol) and an ultrasonic bath. The application of ultrasound energy by means of an ultrasonic bath with 1-undacanol (30 μL) as organic extractant allows achieving an extraction efficiency of 96%, very close to that obtained by adding 1-undecanol (30 μL) and ethanol (300 μL) (i.e., 98%). In spite of the fact, that our method using a disperser solvent, provided good performance, because the organic solvents are toxic and they are harmful to the environment, therefore it was decided to choose ultrasonic bath.

Table 2
Physicochemical properties of some extraction solvents at 25 °C.

Name	Molecular formula	Molar mass (g mol^{-1})	Density (g mL^{-1})	Melting point (°C)	Boiling point (°C)
1-undecanol	$CH_3(CH_2)_{10}OH$	172.31	0.83	11	146
2-dodecanol	$CH_3(CH_2)_9CH(OH)CH_3$	186.33	0.83	19	249–250
1-hexadecanethiol	$CH_3(CH_2)_{15}SH$	258.51	0.84	18–20	184–191

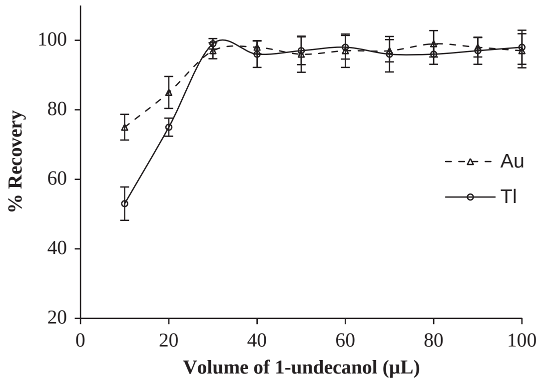

Fig. 3. Effect of extraction solvent volume on the extraction efficiency of gold and thallium. Experimental conditions were the same as in Fig. 1. except extraction solvent volume (HCl concentration, 1.5 mol L^{-1}).

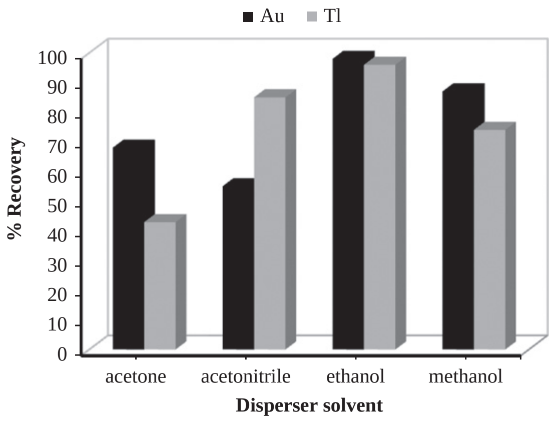

Fig. 4. Effect of disperser solvent type on the extraction efficiency of gold and thallium. Experimental conditions were the same as in Fig. 1. except disperser solvent type (HCl concentration, 1.5 mol L^{-1}).

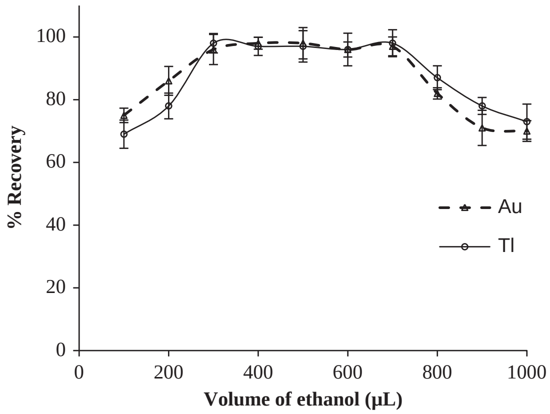

Fig. 5. Effect of disperser solvent volume on the extraction efficiency of gold and thallium. Experimental conditions were the same as in Fig. 1. except disperser solvent volume (HCl concentration, 1.5 mol L^{-1}).

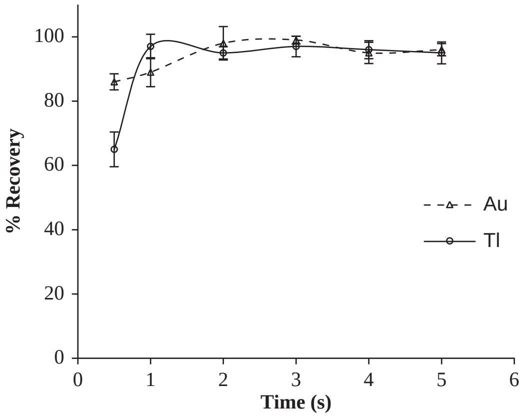

Fig. 6. Effect of sonication time on the extraction efficiency of gold and thallium. Experimental conditions were the same as in Fig. 1. except sonication time (HCl concentration, 1.5 mol L^{-1}).

3.7. *Effect of sonication time*

Dispersion is the key step in determining whether extraction is successfully carried out or not. Sonication produces fine droplets of organic solvent into the aqueous bulk and results in the generation of a high contact area between the aqueous phase and the extraction solvent. Sonication time was examined in the range of 0.5–10 min under constant experimental conditions. As shown in Fig. 6, the extraction recovery increased with increasing the sonication time up to 2 min and remains constant for longer times which mean 2 min was sufficient for 1-undecanol dispersion to fine droplets and extraction of ion pairs to extractant phase. Thus, 3 min was selected for dispersion procedure in the subsequent experiments.

3.8. *Effect of temperature*

The effect of temperature on extraction was studied by varying the temperature from 10 to 60 °C. Based on the resulting data; the extraction was quantitative in all of these temperatures. On the other words the proposed method is independent of temperature. Thus, the extraction was performed at room temperature (~27 °C) for its more convenience.

3.9. *Effect of ionic strength*

Salting-out is a process of addition of electrolytes to an aqueous phase in order to increase the distribution ratio of a particular solute. The term also suggests reduction in the mutual miscibility of two liquids by addition of electrolytes. Weak intermolecular forces, e.g., hydrogen bonds between organic molecules or non-electrolytes and water are easily disrupted by the hydration of electrolytes [43]. For investigation the influence of ionic strength on Au and Tl extraction, several experiments were studied by varying the concentration of NaCl within the range 1–5% (w/v). The resulting data showed that the extraction efficiency was independent of the salt concentration.

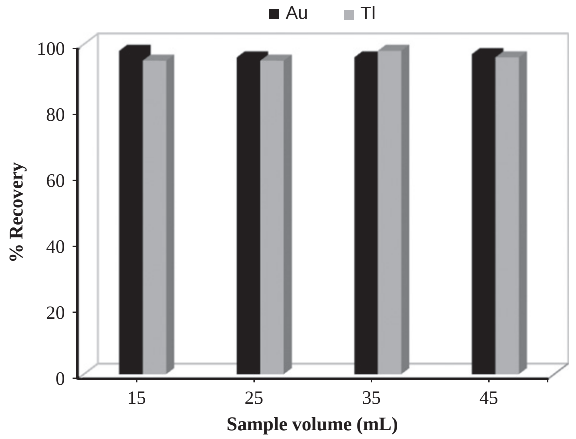

Fig. 7. Effect of sample volume on the extraction efficiency of gold and thallium. Experimental conditions were the same as in Fig. 1. except sample volume (HCl concentration, 1.5 mol L^{-1}).

3.10. Effect of sample volume

The preconcentration capability of IP-USAE-SFODME system was further considered by studying the effect of aqueous volume on recovery of 1.0 ng of gold and 5.0 ng of thallium from different sample volumes (15–45 mL). The results showed that the extraction was quantitative with the aqueous phase volume up to 45 mL (Fig. 7). Due to the limitation in the size of our centrifuge tubes, extraction from higher aqueous volume was not considered. Based on the final extract volume (100 μL) and the maximum sample volume that the extraction was quantitative (45 mL), therefore a preconcentration factor of 450 was determined.

3.11. Interference study

The efficiency of the proposed method in extraction and preconcentration of gold and thallium in the presence of various cations and anions was examined. The cationic interference refers to the competition of the other metal ions for the ion pair forming agent and anionic interference refers to the competition of anions for ion pair formation or precipitation with gold and thallium. The tolerance level was defined as the maximum amount of foreign species producing an error of ±5% in Au and Tl determination. The study was performed by analyzing 20 mL of 50.0 ng L^{-1} of gold and 250.0 ng L^{-1} of thallium solution containing concomitant ions at different concentration, according to the recommended procedure. The tolerance level of each potentially interfering ion species was tested at mole ratio of 1000 and if interference occurred, the ratio was reduced until it ceased. Table 3 shows the studied substances and their maximum tolerable amounts. As can be seen, several species did not interfere even at high concentrations and is applicable to analysis of Au and Tl in different samples.

Table 3
Effect of coexisting ions.

Foreign ion	Foreign ion/Au(III) ratio	Foreign ion/Tl(I) ratio	Recovery (%)	
			Au	Tl
Ca^{2+}	1000	1000	103.5 ± 4.7	99.1 ± 5.5
Mn^{2+}	1000	650	97.6 ± 3.9	96.9 ± 3.8
Cu^{2+}	1000	1000	99.6 ± 4.2	104.1 ± 4.1
Co^{2+}	250	1000	96.9 ± 3.5	100.2 ± 4.8
Ni^{2+}	500	1000	101.2 ± 3.8	98.6 ± 3.7
Pb^{2+}	600	500	97.1 ± 4.2	102.1 ± 5.9
Al^{3+}	1000	1000	99.8 ± 5.1	97.5 ± 4.6
Mg^{2+}	1000	500	95.7 ± 4.7	97.0 ± 3.8
NH_4^+	750	1000	96.1 ± 3.7	98.6 ± 5.4
K^+	1000	750	104.5 ± 6.1	102.0 ± 6.2
Na^+	1000	1000	103.3 ± 4.0	97.2 ± 5.1
Zn^{2+}	500	250	100.1 ± 6.3	103.0 ± 5.7
Hg^{2+}	250	1000	102.8 ± 3.7	95.7 ± 4.6
Fe^{2+}	250	750	100.9 ± 5.3	101.2 ± 5.9
CH_3COO^-	850	750	99.7 ± 3.5	95.6 ± 3.6
NO_3^-	1000	1000	98.7 ± 3.9	103.3 ± 5.0
CO_3^{2-}	1000	1000	104.2 ± 4.3	95.3 ± 4.6
SO_4^{2-}	650	750	98.8 ± 5.0	96.9 ± 3.5
$C_2O_4^{2-}$	1000	1000	104.7 ± 4.8	98.5 ± 3.9

Table 4
Analytical characteristics of the method.

Analytical performance	Au	Tl
Linear range (ng L^{-1})	2.2–89	22.2–667
Correlation coefficient (r^2)	0.9987	0.9984
Repeatability (%) (n=7)	±4.4	±4.8
Reproducibility (%) (n=5)	±4.9	±5.4
Detection Limit (ng L^{-1})	0.66	4.67
Enrichment factor	441	443
Preconcentration factor	450	450

3.12. Analytical figures of merit

Under the optimum conditions, performance characteristics of the proposed IP-USAE-SFODME method were obtained by processing standard solutions of gold and thallium and are summarized in Table 4. The calibration curves for the determination of gold and thallium under the optimized conditions were obtained that showed the linearity over the range of 2.2–89 ng L^{-1} (R^2=0.9987) for Au and 22.2–667 ng L^{-1} (R^2=0.9984) for Tl. The detection limit based on $3S_b/m$ (where S_b is standard deviation of the blank signals and m is the slope of calibration curve after extraction) was 0.66 ng L^{-1} for Au and 4.67 ng L^{-1} for Tl. The repeatability (intra-day) and reproducibility (inter-day) of the method were evaluated by carrying out seven replicate extractions and determination of gold and thallium at a concentration level of 50.0 ng L^{-1} for Au(III) and 250.0 ng L^{-1} for Tl(I) during a day (intra-day) and five replicates in five subsequent days (inter-day). Intra- and inter-day precisions of the method were satisfactory with a relative standard deviation (RSD) of ±4.4 and ±4.9% for Au(III) and ±4.8 and ±5.4% for Tl(I), respectively. The enrichment factor, which was calculated based on the slopes of the calibration curves with or without the extraction, was 441 and 443 for Au and Tl, respectively. The preconcentration factor is 450 for Au and Tl.

Also the regression parameters were analyzed for gold and thallium:

$$\text{For Au}: \quad S_y/x = \pm 5.85 \times 10^{-3} \quad S_b = \pm 7.81 \times 10^{-2} \quad S_a = \pm 3.70 \times 10^{-3}$$

$$\text{For Tl}: \quad S_y/x = \pm 6.24 \times 10^{-3} \quad S_b = \pm 1.08 \times 10^{-2} \quad S_a = \pm 3.30 \times 10^{-3}$$

where S_y/x, S_b and S_a are the random errors in the y-direction, standard deviation for the slope and standard deviation for the intercept, respectively.

3.13. Analytical application

In order to establish the validity of the procedure, the proposed method was applied to simultaneous extraction of gold and thallium in water samples (tap water, well water and waste water) and human hair with diverse matrix cation and anion concentrations. The reliability of the method was checked by the analysis of the samples spiked with the known amount of gold

Table 5
Determination of gold and thallium in real samples.

Sample	Added		Found[a]		Recovery (%)	
	Au	Tl	Au	Tl	Au	Tl
(μg L^{-1})						
Tap water[b]	–	–	0.014	0.028	–	–
	0.020	0.070	0.035	0.095	105.0 ± 5.4	95.7 ± 5.3
	0.040	0.300	0.053	0.331	97.5 ± 3.7	101.0 ± 3.2
	0.070	0.500	0.081	0.551	95.7 ± 4.4	104.6 ± 5.1
Well water[c]	–	–	0.031	0.087	–	–
	0.020	0.050	0.050	0.135	95.0 ± 3.9	96.0 ± 4.8
	0.030	0.300	0.062	0.385	103.3 ± 4.2	99.3 ± 4.1
	0.050	0.500	0.079	0.569	96.0 ± 4.5	96.4 ± 5.7
Waste water[d]	–	–	0.035	0.541	–	–
	0.020	0.030	0.045	0.570	100.0 ± 4.6	96.7 ± 4.4
	0.030	0.050	0.064	0.593	96.7 ± 3.8	104.0 ± 4.8
	0.050	0.100	0.083	0.643	96.0 ± 5.4	102.0 ± 3.9
(ng g^{-1})						
Human hair	–	–	N.D.[e]	75.00	–	–
	1.50	20.00	1.56	94.87	104.0 ± 3.8	99.4 ± 4.3
	7.50	35.00	7.44	110.62	99.2 ± 4.1	101.8 ± 3.8
	15.50	50.00	14.76	127.36	95.2 ± 5.6	104.7 ± 4.0

[a] Mean ± standard deviation (*n*=3).
[b] Kerman drinking water, Kerman, Iran.
[c] Shahid Bahonar University of Kerman, Kerman, Iran.
[d] Iron Factory, Bafgh, Yazd, Iran.
[e] N.D: Not Detected.

Table 6
Analysis of gold and thallium in certified reference materials.

Sample	Composition	Added		Found[a]		Recovery (%)	
		Au	Tl	Au	Tl	Au	Tl
SRM 1643d Trace elements in water	Li;16.50,Be;12.53,B;144.8,Na;22.07 Mg;7.989,Al;127.6,K;2.356,Ca;31.04 V;35.1,Cr;18.53,Mn;37.66,Fe;91.2, Co;25.00,Ni;58.1,Cu;20.5,Zn;72.48, As;56.02,Se;11.43,Sr;294.8,Mo; 112.9,Ag;1.270,Cd;6.47,Sb;54.1 Ba;506.5,Pb;18.15,**Tl;7.28 μg L^{-1}**	–	–	–	7.43 ± 0.3	–	102.1
		2.0 μg L^{-1}	–	1.93 ± 1.6	7.54 ± 0.4	96.5	103.6
MA-1b reference gold ore	Si;24.5,Al ;6.11,Fe ;4.62, Ca;4.60, K;4.45, Mg;2.56, C;2.44 ,Na;1.49, S;1.17,Ti;0.38, Ba; 0.18, P;0.16 , Mn;0.09%, Cr;200.0,Pb;200.0, Rb;160.0,Zr;140.0,Cu; 100.0,Zn;100.0, Bi;100.0,Ni;90.0,Mo;80.0, Te;40.0, Co;30.0 ,Y;20.0,W;15.0, Sc;13.0, As; 8.0,Ag;3.9,Sb;3.0,**Au;17.0 μg $^{g-1}$**	–	–	16.61 ± 0.7	–	97.7	–
		–	20.0 μg g^{-1}	16.43 ± 0.9	19.67 ± 6.4	96.6	98.3

[a] Mean ± standard deviation (*n*=3).

and thallium. The results illustrated in Table 5 reveal that recovery of spiked sample at 95% confidence level is satisfactory.

To verify the accuracy of the method, this procedure was also applied to the determination of gold and thallium in two different certified reference alloys; MA-1b reference gold ore and SRM 1643d-Trace Elements in Water and the analytical results are given in Table 6. As can be seen, the obtained results are in good agreement with the reference values and no significant difference between the results and the accepted values. Thus, the procedure is reliable for analysis of wide range of samples.

3.14. Comparison with other methods

Table 7 compares the characteristic data of the proposed method with other methods for determination of Au and Tl in diverse samples which have been reported in the literature [40,45–56]. As can be seen from Table 7, they are mostly one-element methods, except the following reported [50,55]. For both elements the recommended method possesses wide linear dynamic range, low consumption of organic solvent, high sampling volume, high preconcentration factor and high sensitivity. The proposed method has also the best enrichment factors and the lowest detection limit except the results reported in the following literature [46], for simultaneous extraction of gold and thallium ions. Moreover, because of low toxicity of the proposed method due to the use of only 30 μL of extraction solvent, it is proper to mention this method as a green and environmental-friendly method. Thus this procedure can be coupled with analytical equipment for ultra-trace determination of Au and Tl in ordinary analytical laboratories.

4. Conclusion

In this study, an effective method for preconcentration and determination of gold and thallium was developed. As a widely and commonly used detection method, GFAAS was coupled with

Table 7
Comparison of the proposed method with other reported methods for preconcentration of gold and thallium.

System	Analyte	Enrichment factor	Analysis method	R.S.D. (%)	Linear range ($\mu g\ L^{-1}$)	LOD ($ng\ L^{-1}$)	Ref.
[a]SDME	Tl	50	[b]ETAAS	5.1	3–22	700	[45]
[c]LLE	Tl	–	[d]FAAS	1.9	–	1.25	[46]
[e]SPE	Tl	77	FAAS	2.6	20–200	2500	[47]
SPE	Tl	20	ETAAS	3.9	–	9	[48]
[f]IL-USA-DLLME	Tl	98.2	FAAS	1.43	5–400	640	[49]
[g]GCE	Tl	–	[h]SV	7.2–8.2	5–250	1000	[50]
DLLME	Au	388	ETAAS	4.2	0.03–0.5	5	[40]
SPE	Au	75	FAAS	3.1	5–800	150	[51]
[l]IP-DLLME	Au	220	ETAAS	3.6–9.7	0.075–0.75	8.4	[52]
DLLME	Au	60	ETAAS	–	0.02–1.0	2	[53]
SPE	Au	100	UV–vis	1.28	20–1300	6100	[54]
[j]IL-DLLME	Au	50	ETAAS	4.1	0.02–40	4.8	[55]
USAE-SFODME	Au	34.8	FAAS	1.7	1.5–400	450	[56]
IP-USAE-SFODME	**Au**	**441**	ETAAS	**4.4**	**0.0022–0.089**	**0.66**	**This work**
	Tl	**443**		**4.8**	**0.022–0.667**	**4.67**	

[a] Single drop microextraction.
[b] Electrothermal atomic absorption spectrometry.
[c] Liquid–liquid extraction.
[d] Flame atomic absorption spectrometry.
[e] Solid phase extraction.
[f] Ionic liquid- ultrasound assisted- dispersive liquid–liquid microextraction.
[g] Glassy carbon electrode.
[h] Stripping voltammetry.
[l] Ion-pair based-dispersive liquid–liquid microextraction.
[j] Ionic liquid-dispersive liquid–liquid microextraction.

ion pair formation-ultrasound assisted emulsification-solidified floating organic drop microextraction (IP-USAE-SFODME), which largely minimized toxic organic solvents consumption and greatly increased the sensitivity for determination of gold and thallium. It has also been shown that gold and thallium ions reacted with benzyldimethyltetradecyl ammonium chloride dihydrate and the ion pairs ($AuCl_4$–[$C_{23}H_{42}$]N and $TlCl_4$–[$C_{23}H_{42}$]N) formed were extracted into the fine droplets of 1-undecanol in a few seconds prior to determination by GFAAS.

Besides considerably high preconcentration ability, some other benefits of the system were simultaneous determination of two elements, enhancement of GFAAS sensitivity, decrease of toxic solvent consumption, environmental-friendly property, its simplicity and speed of analysis. Furthermore, the proposed IP-USAE-SFODME method permits effective separation and preconcentration of gold and thallium and final determination by GFAAS in several categories of samples.

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