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A NOVEL METHOD FOR THE DETERMINATION OF TRACE THORIUM BY DISPERSIVE LIQUID-LIQUID MICROEXTRACTION BASED ON SOLIDIFICATION OF FLOATING ORGANIC DROP

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In this study, dispersive liquid-liquid microextraction based on the solidification of floating organic droplets was used for the preconcentration and determination of thorium in the water samples. In this method, acetone and 1-undecanol were used as disperser and extraction solvents, respectively, and the ligand 1-(2-thenoyl)-3,3,3-trifluoracetone reagent (TTA) and Aliquat 336 was used as a chelating agent and an ion-paring reagent, for the extraction of thorium, respectively. Inductively coupled plasma-optical emission spectrometry was applied for the quantitation of the analyte after preconcentration. The effect of various factors, such as the extraction and disperser solvent, sample pH, concentration of TTA and concentration of aliquat336 were investigated. Under the optimum conditions, the calibration graph was linear within the thorium content range of 1.0-250 μg L^{-1} with a detection limit of 0.2 μg L^{-1}. The method was also successfully applied for the determination of thorium in the different water samples.

Keywords: dispersive liquid-liquid microextraction; solidification of floating organic droplets; thorium.

INTRODUCTION

Thorium find extensive application as nuclear fuel in power plants and their main sources are soil, rocks, plants, sand and water. Thorium is known to cause acute toxicological effects for human and their compounds are potential occupational carcinogens.[1] This element is highly toxic which cause progressive or irreversible renal injury. The low concentration of this ion in the presence of relatively high concentration of diverse ions makes it difficult to determine thorium ion. Inductively coupled plasma-optical emission spectrometry (ICP OES), often referred to simply as ICP, is a multi-element analysis technique that uses an inductively coupled plasma source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength. A detector measures the intensity of the emitted light, and calculates the concentration of that particular element in the sample. Separation and preconcentration is mandatory prior to their determination by highly versatile techniques such as ICP OES. To solve these problems, enrichment and separation techniques including solvent extraction, coprecipitation, ion-exchange, etc.[2-6] have been used in the analytical chemistry laboratories for thorium.

A novel microextraction technique, dispersive liquid–liquid microextraction (DLLME), was recently introduced by Rezaee and co-workers[7] based on the formation of tiny droplets of the extractant in the sample solution using a water-immiscible organic solvent (extractant) dissolved in a water-miscible organic dispersive solvent.[8-11] The advantages of the DLLME method are speed, low cost, and high enrichment factors (EFs). However, the required extraction solvent is limited; these solvents, such as chlorobenzene, chloroform, and tetrachloromethane, have a higher density than water and are toxic and environment-unfriendly.

In 2007, Khalili Zanjani and co-workers[12] developed a novel mode of liquid phase microextraction based on the solidification of floating organic droplets (LPME-SFO), in which a small volume of extractant with low density, low toxicity, and a melting point near room temperature (ranging from 10 to 30 °C) was used. LPME-SFO is simple, low cost, with minimum organic solvent consumption, and a high EF. However, the rate of extraction is somewhat slower.

A novel dispersive liquid-liquid microextraction method based on solidification of floating organic drop (DLLME-SFO) was introduced by Leong *et al.*[13] It is based on DLLME and solidification of floating organic drop. In this method, the appropriate mixture of 1-undecanol (as extraction solvent) and dispersive solvent is injected into aqueous sample by syringe, rapidly. Thereby, cloudy solution is formed. The extraction solvent after DLLME, were collected in the top of the test tube and then was cooled by inserting it into an ice bath for 5 min. The solidified of 1-undecanol was transferred into a suitable vial and immediately melted; then it was dissolved in 100 µL of 1-propanol (as eluent in ICP OES) and finally was injected into an ICP OES by using flow injection system. DLLME-SFO was developed for the determination of different compounds.[14-18] This technique is easily carried out. The large contact surface between the sample and the droplets of extractants speeds up mass transfer, as fast as DLLME and shorter extraction time than liquid-liquid microextraction based on solidification of floating organic droplet (LLME-SFO). In this method there is no need to use conical bottom glass tubes, which are easily damaged and hard to clean. The floated extractant is solidified and is easily collected for analysis. In this work, the application of the DLLME-SFO technique combined with ICP OES for the extraction and determination of thorium in the water samples was investigated.

EXPERIMENTAL

Chemicals and reagents

All chemicals used were of analytical reagent grade. $Th(NO_3)_4.5H_2O$ were purchased from Merck (Darmstadt, Germany). The stock solution of the analyte (1000 mg L^{-1}) was prepared in distilled water. Standard solutions were diluted with distilled water to prepare a stock solution of the above ion in such a way that a concentration

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of it was 10 mg L^{-1} respect to the analyte. Reagent grade 1-(2-thenoyl)-3, 3, 3-trifluoraceton (Merck) was used as chelating agent. A 0.5 mol L^{-1} solution of TTA in methanol was prepared by dissolving proper amount of reagent. Ion-pairing reagent Aliquat 336 from Fluka (Chemie AG, Switzerland) was used. The pH of solutions was adjusted by dissolving proper amount of ammonium acetate in distilled water (2.5 ×10^{-3} mol L^{-1}) and drop wise addition of nitric acid (0.5 mol L^{-1}) and/or sodium hydroxide solutions (0.5 mol L^{-1}). 1-Undecanol, 1-dodecanol, 2-dodecanol and n-hexadecane as extraction solvents were obtained from Merck. Acetone, ethanol, acetonitrile and methanol as dispersive solvents were obtained from Merck. Also, sodium chloride was purchased from Merck. The water used was purified on a ultra pure water purification system (aqua Max^{TM} – ultra, korea).

Apparatus

Determination of metal ion was performed using a simultaneous inductively coupled plasma optical emission spectrometer model Vista PRO from Varian Company (Springvale, Australia) coupled to V-groove nebulizer and equipped with a charge coupled device (CCD) detector. Graphite furnace atomic absorption spectrometry (GF AAS) is essentially the same as flame AA, except the flame is replaced by a small, electrically heated graphite tube, or cuvette, which is heated to a temperature up to 3000 °C to generate the cloud of atoms. GF AAS measurements were carried out by an atomic absorption spectrometer GBC; Avanta PM (Australia) equipped with a graphite furnace atomizer GF 3000 and an autosampler (Pal 3000). Deuterium background correction was employed to correct non-specific absorbance. Peak height absorbance was chosen as the analytical signal. Table 1 shows the optimal instrumental conditions which was selected for determination of the analyte via GF AAS. A six-port two-position injection valve (Tehran University, Iran) equipped with a 200 µL injection loop constructed from silicon tube (L = 4.0 cm, I.D. = 2.52 mm) was applied to introduce the final solution into the ICP OES nebulizer. The pH of the solutions was adjusted and determined using a pH meter model WTW (Inolab, Germany) with a combined glass-calomel electrode. Table 2 shows the optimal instrumental conditions and the emission line, which was selected for determination of the analyte via ICP OES.

DLLME-SFO procedure

Aliquots of the solutions were adjusted to the appropriate ionic strength and pH using ammonium acetate (ammonium acetate: 2.5 ×10^{-3} mol L^{-1}, pH = 8). A 20.0 mL of this solution was placed in a 40 mL screw cap glass tube and spiked at the level of 100 µg L^{-1} of metal ion and 70 µL 0.5 mol L^{-1} of TTA and 250 µL Aliquat 336 (10 % (*w/v*)) were added. The ion in the aqueous solution were complexed. 2.0 mL of acetone (as disperser solvent), containing 140 µL of 1-undecanol (as extraction solvent), was rapidly injected into the sample solution by using 5.0 mL of gastight syringe. A cloudy solution (water, 1-undecanol and disperser solvent) was formed in a test tube (the cloudy state was stable for a long time). Then the mixture was centrifuged for 3 min at 6000 rpm. Accordingly, the dispersed fine particles of extraction phase were collected on the top of test tube. The sample solution was transferred into a breaker containing ice pieces and the organic solvent was solidified after 5 min and then, the solidified solvent was transferred into a conical vial where it melted immediately. In spite of the fact that under a given set of nebulization conditions, an organic solvent induces increases in W_{tot} as compared to water, many studies have reported lower ICP OES signals than for water.[19] The high mass of solvent delivered to the plasma when organic solvents are present degrades the plasma thermal characteristics. This is attributed to the fact that the solvent evaporation and dissociation consumes a fraction of the plasma energy. The consequences of this process can be a decrease in the plasma excitation temperature and the electron number density. The solvent dissociation causes an increase in the background noise and level. This may lead to a drop in the plasma excitation conditions, although in some cases, a more energetic plasma has been observed as a result of a mechanism called plasma thermal pinch.[20,21] The effect caused by organic solvents on the plasma depends on the solvent nature. Thus, it has been claimed that the H:C ratio precludes the extent of the interference. Solvents with high values of this ratio deteriorate the plasma more severely than others having low H:C ratios.[22] According to Maessen *et al.*,[23] organic solvents can be classified into two different groups: (i) solvents that have low vapour pressure values and, hence, do not affect the plasma stability and (ii) solvents with high vapour pressure values that deteriorate the plasma behaviour. The first group includes water, xylene and 1-propanol, whereas chloroform, methanol and ethanol would belong to the second group. A different criterion has also been established to classify the solvents based on the carbon content and the molecular weight.[24] In a different study, it has been concluded that the solvent C:O ratio affects the plasma appearance.[25] Finally, the extraction solvent was dissolved in of 1-propanol to decrease the viscosity and increase nebulization efficiency in ICP OES instrument, because of having stable and good conditions. The final solution was injected by injection valve into the ICP OES for subsequent analysis (Figure 1). 1-propanol was used as a suitable eluent to introduce the extraction phase into ICP OES.

Table 1. Instrumental parameters for metal ion determination using GF AAS

Spectrometer parameter		Th		
Wavelength (nm)		570.7		
Slit width (nm)		0.2		
Lamp current (mA)		7.0		
Step	Temperature (°C)	Time (s)		Gas flow (L min^{-1})
		Ramp	Hold	
	Electrothermal atomizer			
Pre-warming	50°	1	2	3.0
Inject step	Inject sample	-	-	3.0
Drying I	90°	10	15	3.0
Drying II	120°	15	10	3.0
Ashing	850°	10	5	3.0
Atomization	2600°	0.9	1.2	0
cleaning	2600°	1	2	3.0

Table 2. ICP OES operating conditions and metal ion emission line

RF generator power	1.65 kW
Frequency of RF generator	40 MHz
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.5 L min^{-1}
Viewing height (above coil)	6 mm
Nebulizer pressure	170 kPa
Pump rate	16 rpm
Analytical lines (nm)	283.730

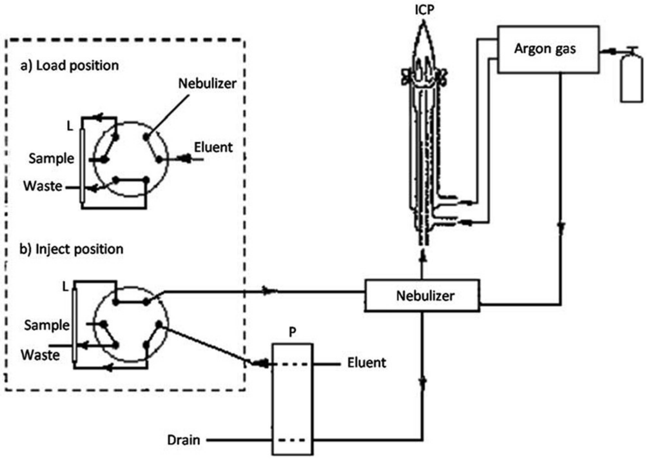

***Figure 1.** Schematic of flow injection system**;** a) Load position; sample introduction into the loop; b) Injection position, the eluent carry the sample into the nebulizer using a peristaltic pump (L: Loop; P: Peristaltic pump)*

RESULTS AND DISCUSSION

In order to obtain the most effective extraction, it is important to determine the optimum DLLME-SFO conditions for the analysis of thorium including the type and volume of extraction and disperser solvents, pH, concentration of TTA and concentration of aliquat336.

Selection of extraction and dispersive solvents

The selection of an appropriate extraction solvent is crucial in DLLME-SFO. It should have some properties: high affinity to analyte, low solubility in water, lower density than water, low volatility and proper melting point around room temperature. Based on the above requirements, three organic solvent candidates, including 1-undecanol, 1-dodecanol, 2-dodecanol and n-hexadecane were tested. In the cases of n-hexadecane as extraction solvent, the fine droplets were unable to accumulate together after centrifugation. Thus, it would not be ideal for our research scheme. Subsequently, 1-undecanol, 1-dodecanol and 2-dodecanol were used for further investigation. The experiments showed that the best extraction efficiency for the target analyte was obtained when 1-undecanol was used as the extraction solvent. Therefore, 1-undecanol was selected as the extraction solvent.

On the other hand, the dispersive solvent, which promotes the dispersion of 1-undecanol into water, is an important component in the process of traditional DLLME. The dispersive solvent should be miscible both in the extraction solvent and water. To meet this requirement, methanol, acetonitrile, ethanol and acetone were studied. The results show that the extraction efficiency with using different disperser solvents are not remarkable. Thus, acetone was selected as a disperser solvent, because of lower toxicity and cost.

Effect of extraction solvent volume and dispersive solvent volume

To evaluate the effect of the extraction solvent volume, different volumes of 1-undecanol ranging from 100 to 180 µL were examined. By increasing the volume of 1-undecanol, the extraction efficiency increased, reaching a maximum value at 140 µL and then decreased, because of dilution effect (Figure 2). Therefore, 140 µL was selected as the most suitable extraction solvent volume.

Variation of the volume of acetone (as disperser solvent) causes changes in the volume of the collected organic phase; hence, it is impossible to consider the influence of the volume of acetone on the extraction efficiency. To avoid of this matter and in order to achieve a constant volume of the collected organic phase, the volume of acetone and 1-undecanol were changed, simultaneously to achieve a constant volume of the collected phase. To evaluate the effect of the dispersive solvent volume on the extraction efficiency, the volume of acetone was varied between 1.0 and 6.0 mL. As shown in Figure 3, a cloudy state was not sufficiently formed when the low volume of acetone was employed, and a low extraction efficiency was obtained. Moreover, the extraction efficiency increased as the volume of acetone increased from 1.0 to 2.0 mL, and decreased as the volume of acetone increased from 2.0 to 6.0 mL. This result may be attributed to the increased solubility of the complex in water as the volume of acetone increased. Thus, to obtain a high extraction efficiency, 2.0 mL of acetone was selected as the volume of dispersive solvent in subsequent experiments.

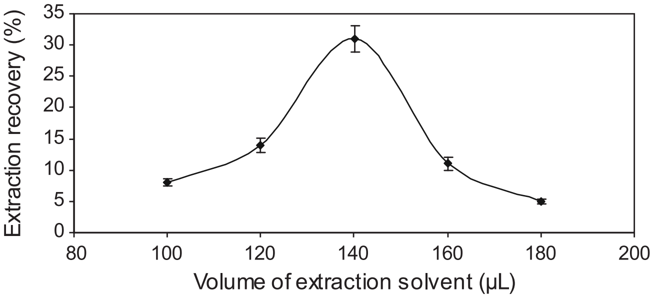

***Figure 2.** Effect of volume of extraction solvent on the extraction efficiency; Extraction conditions: disperser solvent (acetone) volume, 2.0 mL; Volume of TTA (0.5 mol L^{-1}), 35 µL; Volume of Aliquat336 (10 % (w/v)), 100 µL; volume of extraction solvent, 100, 120, 140, 160 and 180 µL; pH, 6*

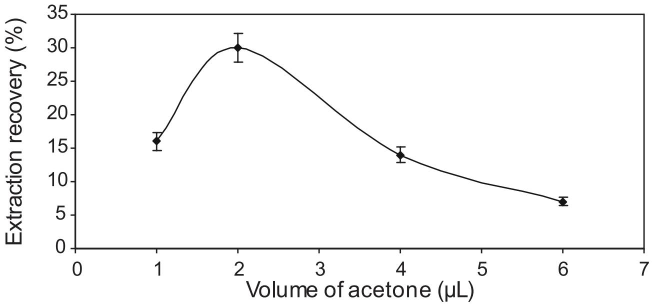

***Figure 3.** Effect of volume of disperser solvent on the extraction efficiency; Extraction conditions: disperser solvent (acetone) volume, 1.0, 2.0, 4.0, 6.0 mL; extraction solvent (1-undecanol) volume, 124.0, 140.0, 161.0, 178.0 µL; Volume of TTA (0.5 mol L^{-1}), 35 µL, Volume of Aliquat336 (10 % (w/v)), 100 µL; pH, 6*

Influence of pH

The pH of the sample solution is one of the important factors that affect the formation of complexes and their subsequent extraction. The effect of pH on the DLLME-SFO extraction of Th was studied in the pH range of 4.0–12.0. As shown in Figure 4, the highest extraction efficiency was obtained at pH 8.0 which was selected for the subsequent study.

Concentration of the chelating reagent

The chelating reagent used in this DLLME-SFO procedure was TTA, which was studied in the volume of 10.0 to 150.0 µL at the concentration level of 0.5 mol L^{-1}. The effect of TTA on the amount of Th extracted is shown in Figure 5. It can be observed that the extraction efficiency reached a maximum at the volume of 70 µL. It

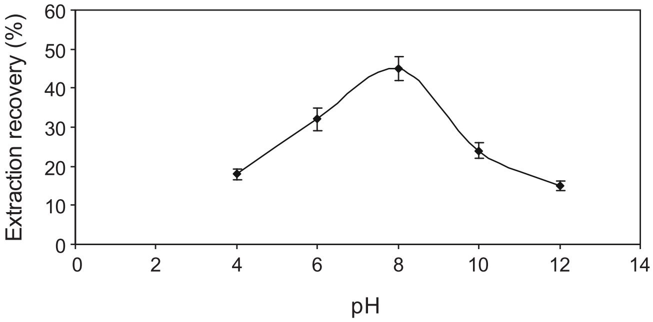

Figure 4. *Effect of pH on the extraction efficiency; Extraction conditions: disperser solvent (acetone) volume, 2.0 mL; extraction solvent (1-undecanol) volume, 140.0 μL; Volume of TTA (0.5 mol L^{-1}), 35 μL, Volume of Aliquat336 (10 % (w/v)), 100 μL; pH, 4, 6, 8, 10, 12*

seems that reduction of extraction in high concentration of TTA is due to the extraction of TTA itself, which can easily saturate the small volume of the extraction solvent. Thus, for further studies, we used the volume of 70 μL of TTA with the concentration of 0.5 mol L^{-1}.

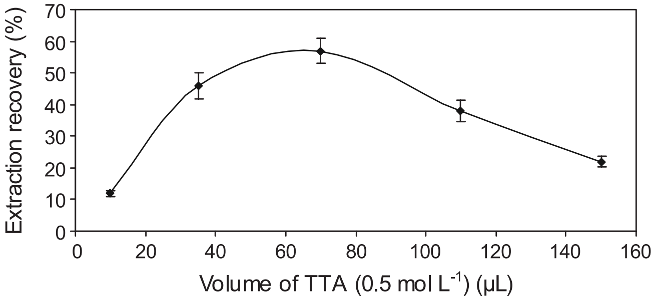

Figure 5. *Effect of concentration of the chelating reagent on the extraction efficiency; Extraction conditions: disperser solvent (acetone) volume, 2.0 mL; extraction solvent (1-undecanol) volume, 140.0 μL; Volume of TTA (0.5 mol L^{-1}), 10, 35, 70, 110, 150 μL, Volume of Aliquat336 (10 % (w/v)), 100 μL; pH, 8*

Effect of the concentration of the ion-pairing reagent

Complex between thorium and TTA is ionic. Aliquat336 was used as a ion-pairing reagent which produced ion-paired complex with Th in the presence of TTA. The effect of concentration of Aliquat336 was studied by using the concentration 10 (*w/v*)% of it in different volumes (0, 100, 250, 400 and 600 μL). The results was shown in the Figure 6. As can be seen, the volume of 250 μL, give the best extraction efficiency. Thus, 250 μL volume of Aliquat336 10 (*w/v*)% was selected as a optimum amount.

Interferences

The potential interferences of some ions on the preconcentration and determination of metal ion were examined by using ICP OES. In these experiments, solutions of 100 μg L^{-1} of the analyte containing the interfering ions were treated according to the optimized procedures. Table 3 shows tolerance limits of the interfering ions. Some of cations such as Cd^{2+}, Mn^{2+}, Co^{2+} and Cr^{3+} have interference at the concentration up to 200 mg L^{-1}. It seems that at this level concentration, they compare with thorium for complexation and extraction into the solvent extraction. By reducing the concentration of these cations up to the 50 mg L^{-1}, the interferences of them was removed. Also, Fe^{3+} has interference for the determination of thorium and by reducing the level concentration of it and by using the complexing agent SCN^-, the interferences of it was removed. It seems that SCN^- give better complex with Fe^{3+} in comparison with the reagents which used for complexation of thorium in the presented work. In addition, a number of common anions like Cl^-, SO_4^{2-}, NO_3^-, I^- and F^- were tested. The results showed that they did not interfere at the concentration up to 100 mg L^{-1}.

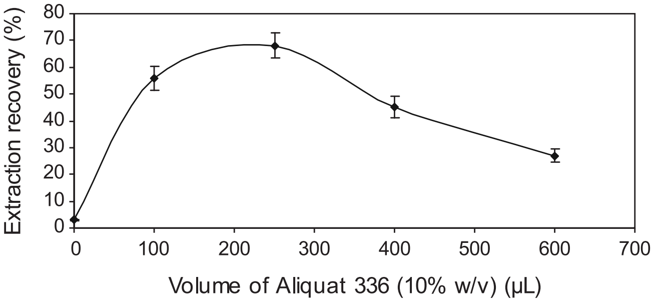

Figure 6. *Effect of concentration of the ion-pairing reagent on the extraction efficiency; Extraction conditions: disperser solvent (acetone) volume, 2.0 mL; extraction solvent (1-undecanol) volume, 140.0 μL; Volume of TTA (0.5 mol L^{-1}), 70 μL, Volume of Aliquat336 (10 % (w/v)), 0, 100, 250, 400, 600 μL; pH, 8*

Table 3. Effect of interference on the preconcentration and determination of metal ion

Interference	Interference to metal ion ratio[a]	Th
		Recovery %
Ca^{2+}	1000	98
Mg^{2+}	1000	95
Ba^{2+}	1000	93
K^+	2000	97
Zn^{2+}	200	95
Na^+	2000	97
Cd^{2+}	200	56
Cd^{2+}	50	91
Mn^{2+}	200	68
Mn^{2+}	50	94
Pb^{2+}	200	91
Co^{2+}	200	41
Co^{2+}	50	93
Cr^{3+}	200	62
Cr^{3+}	50	97
Al^{3+}	200	90
Fe^{3+}	200	18
Fe^{3+}	50	61
Fe^{3+} + 0.02 M SCN^-	5	91
Ni^{2+}	200	95
Cl^-	1000	95
SO_4^{2-}	1000	97
NO_3^-	1000	94
F^-	2000	61
F^-	1000	91

[a]Concentration of ion is 100 μg L^{-1}

Figure of merit of the proposed method

The figures of merit of the proposed method are summarized in the Table 4. The percent relative standard deviation (RSD %) was 7.4 for thorium. The detection limit (DL) was calculated from C_{LOD}= K S_b/m, where, K is a numerical factor of 3, S_b is the standard deviation of six replicate blank measurement and m is the slop of the calibration graph. The DLs was obtained 0.2 μg L^{-1} for thorium by using ICP OES and DLs was obtained 1.0 μg L^{-1} by using GF AAS. Dynamic linear range of the method were evaluated and obtained in the range of 1.0-250 μg L^{-1}. The correlation coefficient of the calibration curve was 0.9981. The comparison of the proposed method with other reported methods vortex-assisted liquid-liquid microextraction[26] and solid-phase extraction[27] demonstrated that DLLME-SFO method has a wide linear range, lower detection limit, higher preconcentration factor, short extraction time, is easy for operation in extraction and the determination of uranium, also cheap.

Table 4. Figures of merit of the proposed method

Analyte	Enrichment factor	RSD%[a] (n = 5)	Dynamic linear range (μg L^{-1})	R^2
Th	68	7.4	1.0 - 250	0.9981

[a] Percent relative standard deviation at concentration of 10 μg L^{-1}.

Analysis of real samples

To demonstrate the performance of the present method, it was utilized to determine the analyte concentration in different water samples. The obtained results are given in Table 5. As could be seen, the relative recoveries for the spiked samples are in acceptance range (88 -96%). Also, in order to investigate the accuracy of the proposed method, further experiments were done on new water samples and the results were compared with those obtained by determination using GF AAS (Table 5). One can see that satisfactory agreement exits between the results obtained for the cations in the water samples by the proposed method and GF AAS.

Table 5. Determination of metal ion in different water samples

Sample	Concentration (μg L^{-1}) ± RSD[a] (n = 3)	Added (μg L^{-1})	Found (μg L^{-1}) ± RSD[a] (n = 3)	Relative recovery (%)
Tap water[c]	Nd[b]	10	9.6 ± 8.4	96
Well water[d]	4.5 ± 11.1	10	13.5 ± 10.5	90
River water[e]	2.1 ± 9.8	10	10.9 ± 9.7	88
Mineral water[f]	Nd.[b]	10	9.3 ± 8.6	93

Sample	GF AAS method (μg L^{-1})[g]	Proposed method (μg L^{-1})[g]
Tap water[c]	Nd.[b]	Nd.[b]
Well water[d]	4.7 ± 7.9	4.5 ± 11.1
River water[e]	2.6 ± 8.4	2.1 ± 9.8

[a]Relative standard deviation. [b]Not detected. [c]was taken from our laboratory (Tehran. Iran). [d]was taken from saghand area (Yazd, Iran). [e]was taken from Anzaly River (Gilan, Iran). [f]was taken from Pars Company (Shiraz, Iran). [c]Concentration of metal ion was determined using standard addition method.

CONCLUSIONS

DLLME-SFO combined with ICP OES was evaluated for the preconcentration and determination of the trace Th content from various water samples. It has the advantages of both DLLME and LPME-SFO. The analysis time can be as fast as that of DLLME and is much shorter than that of LPME-SFO. DLLME-SFO employs 1-undecanol as the extraction solvent which is less toxic and less dense than the solvents used in DLLME. Due to the mp and density of the extraction solvent, extractant droplets can be easily collected after solidification on the surface of the sample at low temperatures. Furthermore, the solidified phase can be easily separated from the aqueous phase. The developed method has been successfully applied to the preconcentration and determination of trace Th content in river, well, mineral and tap water samples; furthermore, the precision and accuracy of the method are satisfactory.

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