

Simultaneous preconcentration and determination of U(VI), Th(IV), Zr(IV) and Hf(IV) ions in aqueous samples using micelle-mediated extraction coupled to inductively coupled plasma-optical emission spectrometry

Shahab Shariati, Yadollah Yamini^{*}, Mohammadreza Khalili Zanjani[✱]

*Department of Chemistry, Faculty of Sciences, Tarbiat Modares University,
P.O. Box 14115-175, Tehran, Iran*

Received 15 October 2007; received in revised form 15 December 2007; accepted 17 December 2007
Available online 20 February 2008

Abstract

A simple cloud point extraction method followed by inductively coupled plasma-optical emission spectrometry (ICP-OES) was developed for simultaneous preconcentration and determination of trace amounts of U(VI), Th(IV), Zr(IV) and Hf(IV) ions in aqueous samples. The metal ions in 50 ml of aqueous solution (containing 0.1 M sodium acetate, pH 6.0) were formed complexes with dibenzoylmethane (DBM). Then, Triton X-114 (0.2%, w/v) was added to the solution. By increasing the temperature of the solution up to 50 °C, a phase separation occurred. After centrifugation at 4000 rpm for 6 min, the surfactant-rich phase (sediment phase) was diluted with 1.0 ml of 20:80 (v/v) of methanol/1 M HNO₃. The metal ions were then determined using ICP-OES. Finally, the main factors affecting the cloud point extraction were evaluated and optimized. Under optimized conditions, enhancement factors in the range of 37.0–43.6 were obtained. The calibration graphs were linear in the range of 0.5–1500 μg l⁻¹ for Th and Zr, 0.5–500 μg l⁻¹ for Hf and 2.5–1240 μg l⁻¹ for U with correlation coefficients (*r*²) better than 0.9926. The detection limits were between 0.1 and 1.0 μg l⁻¹ and the R.S.D. values for seven replicates were lower than 6.1%.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Cloud point extraction; Uranium; Thorium; Zirconium; Hafnium

1. Introduction

Uranium (U) and thorium (Th) have special significance among actinides as nuclear fuel for electricity production in power plants. They are known to cause acute toxicological effects for human and their compounds are potential occupational carcinogens. They are highly toxic which cause progressive or irreversible renal injury that in acute cases may lead to kidney failure and death. The WHO, Health Canada and

Australian drinking water guidelines fixed the maximum uranium concentration in drinking water to be less than 9, 20 and 20 μg l⁻¹, respectively [1–3]. Uranium is present in sea water, though in very small concentrations of about 3.3 μg l⁻¹ or lower. In view of the extensive usage of uranium and thorium for various industrial purposes and their toxicity, precise determination of these elements in environmental and biological samples is a challenging task [4,5].

Zirconium (Zr) and hafnium (Hf) are strategic elements, thus their identification and determination are very important. Zr alloys are employed in the production of optical glasses with high refractive index and in the ceramic industry to produce enamels. Its transparency to thermal neutrons has made Zr as a good structural material in nuclear reactors and chemical plants. Hf is found only in natural zirconium compounds. It has also been found to be a good absorber of neutrons, leading

^{*} Corresponding author. Tel.: +98 21 82883417; fax: +98 21 88006544.

E-mail address: yyamini@modares.ac.ir (Y. Yamini).

[✱] In the memory of our dear friend, Mohammadreza Khalili Zanjani, Ph.D. student of Analytical Chemistry at Tarbiat Modares University, who died unexpectedly at the age of 26. He will stay with us in memory through his words and works and we will miss him sincerely.

to its use as a moderator in control rods for nuclear reactors [6,7].

Most zirconium compounds have low systemic toxicity due to their poor solubility. However, some soluble compounds, such as zirconium tetrachloride, are irritants and may cause corrosive injury. In addition, skin and lung granulomas have been reported following repeated zirconium exposure. Hafnium has no known biological function. Very little information is available concerning its toxicity, but it is generally regarded as being of low toxicity.

Direct determination of U(VI), Th(IV), Zr(IV) and Hf(IV) by instrumental techniques is still difficult because of the very low concentrations of these elements in nature and presence of complex matrix. To solve these problems, various preconcentration and separation techniques including solvent extraction, solid phase extraction, ion-exchange, electrodeposition, extraction chromatography, etc. have been developed [8–18].

Cloud point extraction (CPE) is a simple and powerful method for separation and preconcentration of metal ions. CPE is based on the fact that under cloud point conditions the original surfactant solution easily separates into two apparently immiscible phases: a bulk-diluted aqueous phase containing surfactant at a concentration below or equal to critical micelle concentration (CMC), and a surfactant-rich phase [19–22]. This phenomenon is especially observed with polyoxyethylene surfactants and can be attributed to the two ethylene oxide segments in the micelle that repel each other at low temperatures, when they are hydrated. They attract each other as the temperature increases due to dehydration, causing a decrease in the effective area occupied by the polar groups on the micelle surface and increasing the size of the micelle, resulting in phase separation [23,24].

Upon such cloud point phase separation, dissolved hydrophobic, amphiphilic or even ionic species, originally present in the aqueous solution, will be distributed between immiscible phases in a way analogous to liquid–liquid extractions. The use of preconcentration steps based on CPE permits the design of extraction schemes that are simple, low cost, high efficient and of lower toxicity rather than the extractions that use organic solvents. Also, CPE has high preconcentration factors as well as environmental and personal safety characteristics [25–29].

The main purpose of this work was to apply CPE as a preconcentration step for simultaneous extraction and determination of low concentrations of U, Th, Zr and Hf ions in aqueous samples. In the developed system, dibenzoylmethane (DBM) was used as a chelating agent and Triton X-114 as a non-ionic surfactant. The target ions were complexed with DBM and the resulted complexes were preconcentrated using Triton X-114 as an extractant. Then, the preconcentrated analytes in the surfactant-rich phase were simultaneously determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Potential factors affecting the cloud point preconcentration and subsequent analytical performance of ICP-OES such as pH, surfactant and reagent concentration, nebulizer pressure, viewing height, etc. were investigated in detail.

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical reagent grade. $ZrOCl_2 \cdot 8H_2O$, $UO_2(NO_3)_2 \cdot 6H_2O$, $Th(NO_3)_4 \cdot 5H_2O$ and 1000 mg l^{-1} of standard solution of Hf(IV) were purchased from Merck (Darmstadt, Germany). The stock standard solution of each analyte (1000 mg l^{-1}) was prepared in distilled water. Standard solutions were diluted with distilled water to prepare a mixed stock solution of the above ions in such a way that the concentration of mixture was 10 mg l^{-1} respect to each analyte. All the working solutions were freshly prepared by the addition of ligand and surfactant and subsequent diluting of the solution with buffer to the required concentration. Reagent grade dibenzoylmethane (DBM) from Merck was used as chelating agent. The standard solution of DBM (0.04 mol l^{-1}) was prepared by dissolving proper amounts of reagent in HPLC grade methanol from Caledon Company (Georgetown, Ont., Canada). The non-ionic surfactant, Triton X-114 from Fluka Company (Chemie AG, Switzerland) was used without further purification.

2.2. Apparatus

A simultaneous inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista-PRO, Springvale, Australia) with a radial torch coupled to a V-groove nebulizer and equipped with a charge-coupled detector (CCD) was used for simultaneous determination of the target elements in the surfactant-rich phase. The argon gas with 99.999% purity for ICP-OES was purchased from Roham Gas Company (Tehran, Iran). A thermostated water-bath from GFL Company (Burgwedel, Germany) was employed for adjusting the temperature of the solutions in CPE experiments and a centrifuge from Ferdous Ray Company (Tehran, Iran) was utilized to accelerate the phase separation process.

2.3. Extraction procedure

For the cloud point extraction, aliquots of the solution containing the analytes were adjusted to the appropriate ionic strength and pH (sodium acetate: 0.1 M, pH 6.0). The ions in the initial aqueous solution were complexed with DBM ($5 \times 10^{-4} \text{ mol l}^{-1}$). Triton X-114 at 0.2% (w/v) concentration was added as non-ionic surfactant. The solutions were kept at 50°C (the temperature above the cloud point temperature of the system) for 15 min in the thermostatic water-bath to become cloudy. Since the surfactant is denser than water, the surfactant-rich phase typically settles through the aqueous phase. The phase separation was accelerated by centrifuging for 6 min at 4000 rpm. Upon cooling in an ice bath (for 5 min), the surfactant-rich phase became viscous and was retained at the bottom of the tube that could facilitate separation of the aqueous phase by means of a suitable pipette. After separation of the bulk aqueous phase, in order to decrease the viscosity of the extract, 1.0 ml of a solution containing 20:80 (v/v) methanol/1 M HNO_3 in water

was added to the surfactant-rich phase. The final volume of the sample was 1.2 ml. Finally, the samples were introduced into the ICP nebulizer with a peristaltic pump and the intensity was measured at the proper wavelength for each ion.

All the optimizing experiments were done using Falcon tubes with 10 ml volume. To draw calibration graphs and to extract the ions from the real samples in order to increase the concentration factor; Falcon tubes with 50 ml volumes were applied. Calibration was performed against the aqueous standards submitted to the same cloud point extraction procedure. A blank, submitted to the same procedure described above, was measured parallel to the samples and calibration solutions.

3. Results and discussion

3.1. Method development

In the proposed procedure, to achieve maximum extraction efficiency, various parameters affecting the emission intensities of the ions in ICP-OES as well as the parameters influencing the complexation of target ions and cloud point extraction were optimized using univariate optimization approach. The optimized conditions of ICP-OES are summarized in Table 1.

3.2. Influence of pH

pH of solution plays a unique role on metal–chelate formation and subsequent extraction. The extraction yield depends on the pH at which the complex formation occurs. In the present work, the effect of pH upon the complex formation of target ions was studied within the pH range of 2.2–10.7 using sodium acetate solution and addition of NaOH or HNO₃. As shown in Fig. 1, the emission intensities were nearly constant in the pH range of 6.0–7.0. Hence, the pH of 6.0 was chosen for the subsequent extractions.

3.3. Influence of reagent concentration

CPE can be used for preconcentration of metal ions after the formation of sparingly water-soluble complexes. The nature of the chelating agent and its concentration are important factors that should be considered. CPE efficiency depends on the

Table 1
The optimized conditions for ICP determination of the target ions

ICP-OES conditions (radial torch)	
RF generator power (kW)	1.65
Frequency of RF generator (MHz)	40
Plasma gas flow rate (l min ⁻¹)	15.0
Auxiliary gas flow rate (l min ⁻¹)	1.5
Nebulizer pressure (kPa)	240
Viewing height (mm)	9
Pump rate (rpm)	15
Hf wavelength (nm)	282.023
Zr wavelength (nm)	343.823
U wavelength (nm)	367.007
Th wavelength (nm)	339.203

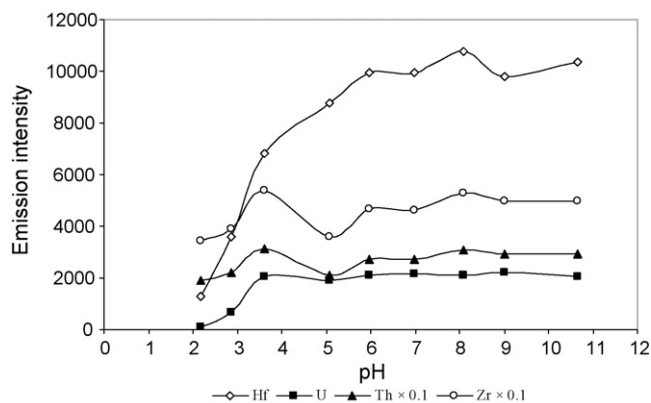


Fig. 1. Influence of pH on the CPE of the ions. Extraction conditions—500 $\mu\text{g l}^{-1}$ of the ions in the solution (pH 6.5), 0.2% (w/v) Triton X-114, equilibration temperature: 60 °C (for 10 min) and centrifugation time: 10 min.

hydrophobicity of the ligand and the formed complex, the apparent equilibrium constants in the micellar medium, the kinetics of the complex formation and the transference between the phases [22,30]. In the present study, dibenzoylmethane was used as a β -diketone reagent that forms 1:2 complexes (metal:ligand) with target ions.

The variation of emission intensities with DBM concentration in the range of 0 to $1 \times 10^{-3} \text{ mol l}^{-1}$ is shown in Fig. 2. Concentration of the target ions was fixed at 500 $\mu\text{g l}^{-1}$ and the molar ratio of DBM was changed within 0–50. The results revealed that at the reagent concentration of 1×10^{-4} to $2 \times 10^{-4} \text{ mol l}^{-1}$, more extraction occurred. Therefore, $2 \times 10^{-4} \text{ mol l}^{-1}$ was selected as the optimal chelating agent concentration value. After studying the effect of foreign ions on the extraction of analytes, in order to prevent the reduction of extraction efficiency in the presence of interferences, higher concentrations of DBM was utilized.

3.4. Influence of surfactant concentration

Triton X-114 was chosen for the extraction due to its low cloud point temperature (CPT) and high density of the

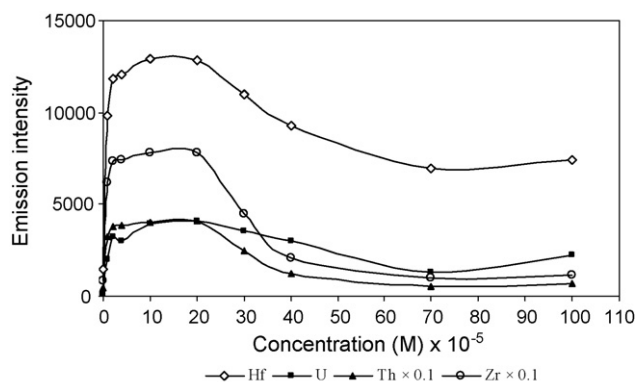


Fig. 2. Effect of reagent concentration on the CPE of the ions. Extraction conditions—500 $\mu\text{g l}^{-1}$ of the ions in the solution (0.1 M of sodium acetate, pH 6.0), 0.2% (w/v) Triton X-114, equilibration temperature: 60 °C (for 10 min) and centrifugation time: 10 min.

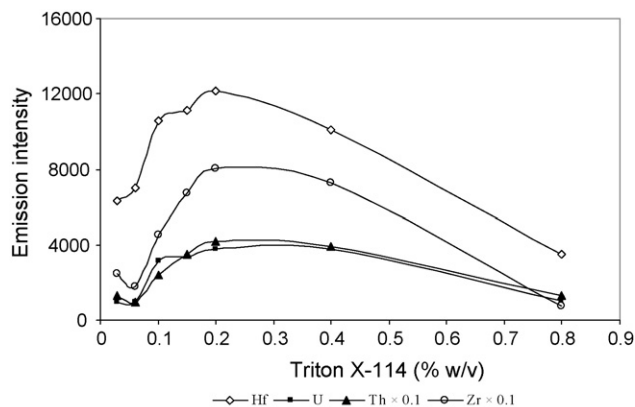


Fig. 3. Effect of Triton X-114 on the CPE of the ions. Extraction conditions— $500 \mu\text{g l}^{-1}$ of the ions in the solution (0.1 M of sodium acetate, pH 6.0), $2 \times 10^{-4} \text{ mol l}^{-1}$ DBM, equilibration temperature: 60°C (for 10 min) and centrifugation time: 10 min.

surfactant-rich phase, which facilitates phase separation by centrifugation. A successful cloud point extraction should maximize the extraction efficiency and minimize the phase volume ratio to improve preconcentration factor. The effect of Triton X-114 concentration on the extraction efficiency was studied in the range of 0.03–0.8% (w/v). The variation of emission intensity as a function of surfactant concentrations is shown in Fig. 3.

Extraction rate of the analytes increased with the increase of Triton X-114 concentration from 0.03% to 0.2% (w/v). At lower concentrations of surfactant, the extraction efficiency was low, probably due to inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. Further increase in the concentration of Triton X-114 (higher concentrations than 0.2% (w/v)) resulted in a decrease in the magnitude of the emission signals of the analytes likely due to the increasing of the surfactant-rich phase volume. So a concentration of 0.2% (w/v) was chosen as the optimum surfactant concentration in order to achieve the highest possible extraction efficiency and preconcentration factor.

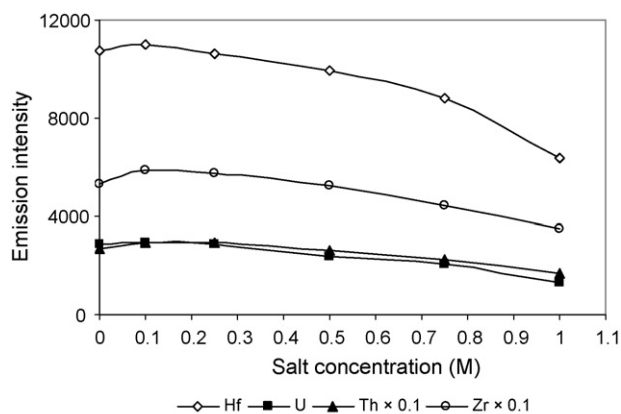


Fig. 4. Effect of salt concentration on the CPE of the ions. Extraction conditions— $500 \mu\text{g l}^{-1}$ of ions in the solution (0.1 M of sodium acetate, pH 6.0), $2 \times 10^{-4} \text{ mol l}^{-1}$ DBM, 0.2% (w/v) Triton X-114, equilibration temperature: 60°C (for 10 min) and centrifugation time: 10 min.

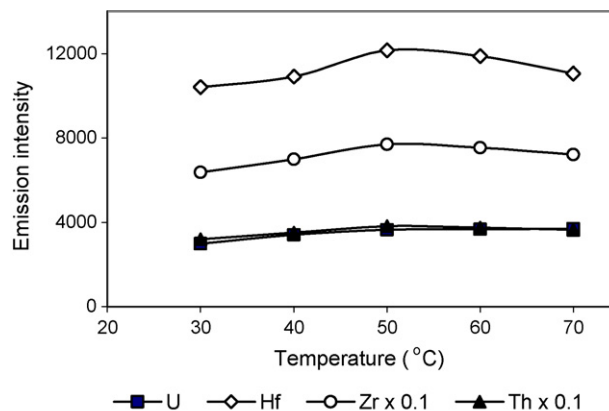


Fig. 5. Effect of equilibration temperature on the CPE of the ions. Extraction conditions— $500 \mu\text{g l}^{-1}$ of ions in the solution (0.1 M of sodium acetate, pH 6.0), $2 \times 10^{-4} \text{ mol l}^{-1}$ DBM, 0.2% (w/v) Triton X-114, centrifugation time: 10 min.

3.5. Influence of salt concentration

Salt effect was studied by the addition of NaNO_3 to the solution in the range of 0–1.0 mol l^{-1} . The results presented in Fig. 4 show that salt addition had no significant effect on the extraction efficiency which is in agreement with the literature results which demonstrated that an increase in ionic strength in micellar systems does not seriously alter the extraction efficiency of the analytes.

3.6. Influence of incubation time, equilibration temperature and centrifugation time

Optimal incubation time and equilibration temperature are necessary to complete extraction and to achieve easy phase separation. It is also desirable to employ the shortest equilibration time and the lowest equilibration temperature, which compromise the completion of reaction and efficient separation of the phases. It appears that the phase volume ratio of all non-ionic

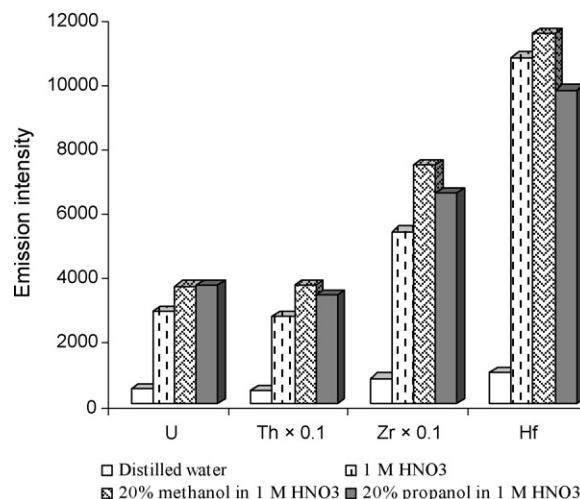


Fig. 6. Influence of type of the diluent. Extraction conditions— $500 \mu\text{g l}^{-1}$ of the ions in the solution (0.1 M of sodium acetate, pH 6.0), $2 \times 10^{-4} \text{ mol l}^{-1}$ DBM, 0.2% (w/v) Triton X-114, equilibration temperature: 50°C and centrifugation time: 6 min.

Table 2
The optimized conditions for cloud point extraction of the target ions

Optimum CPE conditions	
Chelating agent (mol l ⁻¹)	2 × 10 ⁻⁴
Surfactant percent (w/v)	0.2
Buffer	Acetic acid/acetate solution (0.1 M, pH 6.0)
Equilibrium temperature (°C)	50
Centrifugation time (min)	6
Equilibrium time (min)	15
Diluent	20% (v/v) methanol/1 M HNO ₃

surfactants decreases as the equilibration temperature increases. The greatest analyte preconcentration factors can be obtained when the CPE is conducted at the temperatures well above the CPT of the surfactant [31].

Dependence of extraction efficiency upon equilibration temperature was studied in the range of 30–70 °C. As shown in Fig. 5, the optimal temperature was found to be in the range of 50–60 °C. Therefore, an equilibration temperature of 50 °C was chosen for further experiments. The effect of incubation time on the extraction efficiency was studied in the range of 5–20 min and it was found that an incubation time of 15 min was adequate for the extraction of the metal ions. The effect of centrifugation time upon the analytical signals was studied in the range of 2–15 min. Since complete separation occurred within this time and no significant improvements were observed for longer times a centrifugation time of 6 min at 4000 rpm was selected as the optimum centrifugation time.

3.7. Influence of the surfactant-rich phase viscosity

After centrifugation, the surfactant-rich phase (150 µl) with high viscosity was sedimented. In order to reduce the viscosity of the sediment phase and to facilitate its transfer into the ICP nebulizer, several diluents were used. As shown in Fig. 6, 20% (v/v) methanol in 1 M HNO₃ was chosen as the proper diluent

and 1.0 ml of this diluent was added to the surfactant-rich phase to reduce the viscosity and to ensure a sufficient volume of the sample for aspiration. The final surfactant-rich phase volume was 1.2 ml. The optimized conditions of CPE are summarized in Table 2.

3.8. Interference effect of metal ions

Due to high selectivity provided by inductively coupled plasma spectrometry, the only interferences investigated were the cations that may form complexes with DBM and decrease the extraction efficiency. To investigate the interference effect of different species, 10 ml of a solution containing 200 µg l⁻¹ of the target ions and foreign ions in different interference-to-analyte ratios were subjected to the extraction procedure. The obtained results (Table 3) showed that under the conditions specified in the procedure, the major cations in the water samples had no obvious influence on CPE of the target ions. On the other hand, some ions including Cr³⁺ and Hg²⁺ could interfere in CPE of the ions. Further experiments showed that interference effect of these elements could be eliminated by increasing the reagent concentration up to 5 × 10⁻⁴ mol l⁻¹.

3.9. Figures of merit

Calibration curves were obtained using 50 ml of the standard solutions buffered at pH 6, containing 0.2% (w/v) Triton X-114 and known amounts of the target ions in the concentration range of 0.5–1500 µg l⁻¹. For this purpose, each standard sample was extracted by the suggested CPE method at optimum conditions and the calibration curves were obtained by plotting the intensity of the signal against concentration of the analytes in the aqueous phase. The calibration curves exhibited good linearity with correlation coefficients better than 0.9926 in a wide range of concentrations. The limit of detections (LODs), calculated as the concentration equivalent to three times of the blank stan-

Table 3
Effect of foreign ions on the recovery of 200 µg l⁻¹ of target ions

Foreign ion	Hf(IV)	Th(IV)	U(VI)	Zr(VI)
Ag ⁺	200 ^a (>92%) ^b	200 (100%)	200 (>100%)	200 (>96%)
Pb ²⁺	200 (>100%)	200 (>98%)	200 (>98%)	200 (>100%)
Co ²⁺	220 (102%)	220 (99%)	220 (100%)	220 (98%)
Ni ²⁺	220 (99%)	220 (102%)	160 (>100%)	220 (102%)
Mn ²⁺	160 (>100%)	220 (>96%)	220 (>98%)	220 (>95%)
Cd ²⁺	160 (>100%)	220 (>95%)	220 (>99%)	220 (>92%)
Zn ²⁺	160 (>92%)	220 (>94%)	220 (>98%)	220 (>92%)
Fe ³⁺	200 (>94%)	150 (>100%)	50 (>99%)	150 (>93%)
Li ⁺	200 (>100%)	200 (>95%)	200 (>99%)	200 (>92%)
K ⁺	200 (>100%)	200 (>95%)	200 (>99%)	200 (>92%)
Hg ²⁺	5 ^c (>100%)	5 ^c (>95%)	5 ^c (>99%)	5 ^c (>92%)
Cu ²⁺	160 (>94%)	160 (>100%)	30 (>99%)	30 (>93%)
Cr ³⁺	5 ^c (>90%)	5 ^c (>90%)	5 ^c (>90%)	5 ^c (>90%)
Mg ²⁺	200 (>94%)	150 (>100%)	50 (>99%)	150 (>93%)
Ca ²⁺	200 (>93%)	200 (>100%)	200 (>95%)	150 (>96%)

^a Foreign ion concentration (mg l⁻¹).

^b Recovery of target ions in the presence of the mentioned amount of the foreign ion.

^c Due to high interference effect of the ion, the ligand to metal ratio increased to 30.

Table 4
Analytical characteristics of the proposed CPE method

Element	LOD ($\mu\text{g l}^{-1}$)	Regression equation	r^2	DLR ($\mu\text{g l}^{-1}$)	R.S.D. (%)	EF
Hf	0.15	$I = 99.427 C (\mu\text{g l}^{-1}) - 412.54$	0.9995	0.5–500	5.1	39.5
Th	0.10	$I = 269.64 C (\mu\text{g l}^{-1}) + 1616.1$	0.9948	0.5–1500	3.6	43.6
U	1.00	$I = 21.118 C (\mu\text{g l}^{-1}) - 123.64$	0.9931	2.5–1240	6.1	37.0
Zr	0.20	$I = 467.82 C (\mu\text{g l}^{-1}) + 8296.8$	0.9926	0.5–1500	3.9	41.7

standard deviation divided into the slope of calibration curve, were in the range of 0.1–1.0 $\mu\text{g l}^{-1}$. The relative standard deviations (R.S.D.s), resulted from CPE–ICP–OES of seven replicates of 200 $\mu\text{g l}^{-1}$ of the metal ions from a 50 ml solution, were in the range of 3.6–6.1%.

The enhancement factors (EF), defined as the ratio of slope of the preconcentrated samples to that obtained without preconcentration, were in the range of 37.0–43.6. The analytical performance of the proposed method is summarized in Table 4.

A comparison between the figures of merit of the proposed CPE method and some of the published methods are summarized in Table 5. It clearly shows that our proposed method has good sensitivity and precision with a wide dynamic linear range. Also, the obtained LODs are better than those obtained by some presented methods [1,32,33,36,40] and higher than WHO and Health Canada and Australian drinking water guideline levels [1–3]. Higher LOD levels of the proposed method comparing to the inductively coupled plasma-mass spectrometry (ICP-MS) methods are related to the higher sensitivity of the ICP-MS instrument. Accordingly, the main advantages of our proposed method include high sensitivity with good precision,

low consumption of organic solvents, low cost and simplicity to operation.

3.10. Analysis of real samples

In order to demonstrate the applicability and also accuracy of the proposed CPE–ICP–OES method for extraction and determination of Hf, Zr, Th and U in aqueous samples, various matrixes were studied. At first, each sample was extracted using the mentioned method at optimal conditions. The results showed that concentration of the analytes was lower than the limit of detections of our method. Then, for studying the matrix effect on the extraction efficiency, the samples were spiked at 8 and 15 $\mu\text{g l}^{-1}$ concentration levels of the analytes. Finally, the spiked samples were extracted using the described CPE method. For real samples, the calibration curve was plotted against the aqueous standards submitted to the same cloud point extraction procedure. The summarized results in Table 6 are the average of three replicate measurements.

As Table 6 shows, there is a good agreement between the obtained results and the known values, indicating the successful

Table 5
Comparison of the proposed CPE method with other published methods

Ion	Method of extraction/detection system	LOD ($\mu\text{g l}^{-1}$)	DLR ($\mu\text{g l}^{-1}$) ^a	R.S.D. (%)	EF ^b	Ref.
U(VI), Th(IV), Zr(IV), Hf(IV)	CPE/ICP-OES	0.1–1.00	Th, Zr: 0.5–1500, Hf: 0.5–500, U: 2.5–1240	<6.1	37.0–43.6	Proposed method
U(VI)–Th(IV)	SPE with malonamide grafted polymer/UV–vis	20–50	–	<4	400–350	[32]
U(VI)–Th(IV)	SPE with calix[4]arene anchored chloromethylated polystyrene/UV–vis	6.14–4.29	U: 100–15,000, Th: 20–3400	1.7–1.5	143–153	[1]
U(VI)–Th(IV)	Precolumn derivitization/capillary zone electrophoresis	142–16.8	U: 800–100,000, Th: 100–50,000	–	–	[33]
U(VI)–Th(IV)	SPE on Duolite XAD 761 resins/ICP-MS	0.0063–0.0045	–	2.3–4.5	30	[34]
U(VI)–Th(IV)	Coprecipitation/ICP-MS	0.05–0.07	–	<2.8	30	[35]
U(VI)	SPE with modified activated carbon/UV–vis	5.0	5–200	2.5	–	[36]
U(VI)	Modified ODS disk/UV–vis	0.1	–	–	8	[11]
U(VI)	CPE/FIA spectrophotometry	1.1	–	5.1	100	[37]
U(VI)	Homogeneous liquid–liquid extraction/UV–vis	0.14	7.7–630	1.4	330	[38]
Zr(IV), Hf(IV)	Formation of ternary complexes/RP-HPLC	0.2–0.8	Zr: 0.8–160, Hf: 1–200	<1.8	–	[39]
Zr(IV), Hf(IV)	PCA-ANN ^c /UV–vis	20–80	Zr: 30–3400, Hf: 200–7000	–	–	[40]

^a Dynamic linear range.

^b Enrichment factor.

^c Principle component analysis-artificial neural network.

Table 6
Analysis of real samples

Sample		Hf(IV)	Th(IV)	U(VI)	Zr(VI)
Well water	Added ($\mu\text{g l}^{-1}$)	10.00	10.00	10.00	10.00
	Found ($\mu\text{g l}^{-1}$) ^a	8.45 \pm 0.78	10.19 \pm 0.79	9.03 \pm 0.52	10.02 \pm 0.71
	Relative recovery (%)	84.5	101.9	90.3	100.2
Sea water 1 ^b	Added ($\mu\text{g l}^{-1}$)	8.00	8.00	8.00	8.00
	Found ($\mu\text{g l}^{-1}$)	7.50 \pm 1.20	8.38 \pm 0.64	8.22 \pm 0.49	8.39 \pm 0.66
	Relative recovery (%)	93.8	104.8	102.8	104.9
Sea water 1	Added ($\mu\text{g l}^{-1}$)	15.00	15.00	15.00	15.00
	Found ($\mu\text{g l}^{-1}$)	14.97 \pm 0.14	14.90 \pm 0.45	14.57 \pm 0.34	14.55 \pm 0.39
	Relative recovery (%)	99.8	99.3	97.1	97.0
Sea water 2 ^c	Added ($\mu\text{g l}^{-1}$)	15.00	15.00	15.00	15.00
	Found ($\mu\text{g l}^{-1}$)	15.45 \pm 1.7	14.44 \pm 0.52	12.01	14.44 \pm 0.60
	Relative recovery (%)	103.0	96.3	80.1	96.3
Spring water	Added ($\mu\text{g l}^{-1}$)	8.00	8.00	–	–
	Found ($\mu\text{g l}^{-1}$)	7.38 \pm 0.89	7.41 \pm 1.00	–	–
	Relative recovery (%)	92.3	92.6	–	–
Spring water	Added ($\mu\text{g l}^{-1}$)	15.00	15.00	–	–
	Found ($\mu\text{g l}^{-1}$)	14.80 \pm 1.49	13.5 \pm 1.51	–	–
	Relative recovery (%)	98.7	90.0	–	–

^a Mean of three replicates \pm S.D.

^b Sea water 1 was collected from Anzali Lagoon (Caspian Sea, Iran).

^c Sea water 2 was collected from Ghazian Coast (Caspian Sea, Iran).

applicability of this method for simultaneous determination of target analytes in aqueous samples containing high concentrations of salts such as sea water.

4. Conclusion

The use of micellar systems as an alternative to other methods of separation and preconcentration offers several advantages including experimental convenience, safety and being an inexpensive method. Further, in comparison to solvent extraction methods, it is much safer, since only a small amount of the surfactant, which has a low toxicity, is used.

In the present study, we investigated the application of the cloud point extraction method for preconcentration of Zr, Hf, Th and U as a prior step to their subsequent determination by ICP-OES. This method gives low limit of detection as well as good R.S.D. and linearity for the analytes. The method was verified by determination of the analytes concentration in the real samples and satisfactory results were obtained. Also, our findings showed that it is possible to obtain a better limit of detection by extraction of the analytes from large volumes of the sample solution and diluting the surfactant-rich phase into a smaller volume, or using the flow injection method to introduce smaller volumes of the sample into the ICP nebulizer.

References

- [1] V.K. Jain, R.A. Pandya, S.G. Pillai, P.S. Shrivastav, Simultaneous preconcentration of uranium(VI) and thorium(IV) from aqueous solutions using a chelating calix[4]arene anchored chloromethylated polystyrene solid phase, *Talanta* 70 (2006) 257–266.
- [2] WHO: Guidelines for Drinking Water Quality, 2nd ed., Addendum to vol. 2, Health Criteria and Other Supporting Information, WHO/EOS/98.1, Geneva, 1998, p. 283.
- [3] WHO: Guidelines for Drinking Water Quality, vol. 1, third ed., Geneva, 2003.
- [4] M. Tamada, N. Seko, F. Yoshii, Application of radiation-graft material for metal adsorbent and crosslinked natural polymer for healthcare product, *Radiat. Phys. Chem.* 71 (2004) 223–227.
- [5] P.G. Barbano, L. Rigali, Spectrophotometric determination of uranium in sea water after extraction with aliquat-336, *Anal. Chim. Acta* 96 (1978) 199–201.
- [6] P. Peralta-Zamora, J.W. Martins, Anomalies in the spectrophotometric and extractive behavior of zirconium and hafnium: evidence of a synergistic effect, *Talanta* 49 (1999) 937–941.
- [7] A. Abbaspour, L. Baramakeh, Simultaneous determination of zirconium and molybdenum by first-derivative spectrophotometry, *Anal. Sci.* 18 (2002) 1127.
- [8] S. Dadfarnia, C.W. McLeod, On-line trace enrichment and determination of uranium in waters by flow injection inductively coupled plasma mass spectrometry, *Appl. Spectrosc.* 48 (1994) 1331–1336.
- [9] D. Dojozan, M.H. Pournaghi-Azar, J. Toutounchi-Asr, Preconcentration of trace uranium from sea water with solid-phase extraction followed by differential pulse polarographic determination in chloroform eluate, *Talanta* 46 (1998) 123–128.
- [10] T. Prasada Rao, P. Metilda, J. Mary Gladis, Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination, *Talanta* 68 (2006) 1047–1064.
- [11] M. Shamsipur, A.R. Ghiasvand, Y. Yamini, Solid-phase extraction of ultra trace uranium(VI) in natural waters using octadecyl silica membrane disks modified by tri-*n*-octylphosphine oxide and its spectrophotometric determination with dibenzoylmethane, *Anal. Chem.* 71 (1999) 4892–4895.
- [12] E.R. Unsworth, J.M. Cook, S.J. Hill, Determination of uranium and thorium in natural waters with a high matrix concentration using solid-phase extraction inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 442 (2001) 141–146.
- [13] F. Hao, B. Paull, P.R. Haddad, Determination of thorium and uranyl in nitrophosphate solution by on-line matrix-elimination reversed-phase chromatography, *Chromatographia* 42 (1996) 690–696.
- [14] C.A. Moody, S.E. Glover, D.B. Stuit, R.H. Filby, Preconcentration and separation of thorium, uranium, plutonium and americium in human soft tissues by extraction, *J. Radioanal. Nucl. Chem.* 234 (1998) 183–187.

- [15] P. Peralata-Zamora, L. Cornejo-Ponce, M.I. Maretta, S. Bueno, J.W. Martins, Zirconium and hafnium determination by energy dispersive X-ray fluorescence with solid-phase preconcentration, *Talanta* 44 (1997) 811–816.
- [16] M.D. Palmieri, J.S. Fritz, Determination of metal ions by high-performance liquid chromatographic separation of their hydroxamic acid chelates, *Anal. Chem.* 59 (1987) 2226–2231.
- [17] S. Oszwaldowski, J. Jakubowska, Simultaneous determination of zirconium and hafnium as ternary complexes with 5-Br-PADAP and fluoride using solid-phase extraction and reversed-phase liquid chromatography, *Talanta* 60 (2003) 643–652.
- [18] X.J. Yang, C. Pin, Determination of niobium, tantalum, zirconium and hafnium in geological materials by extraction chromatography and inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 458 (2002) 375–386.
- [19] H. Watanabe, H. Tanaka, A non-ionic surfactant as a new solvent for liquid–liquid extraction of zinc(II) with 1-(2-pyridylazo)-2-naphthol, *Talanta* 25 (1978) 585–589.
- [20] W.L. Hinze, E. Pramauro, A critical review of surfactant-mediated phase separations (cloud point extractions): theory and applications, *Crit. Rev. Anal. Chem.* 24 (1993) 133–177.
- [21] J.L. Manzoori, G. Karim-Nezhad, Development of a cloud point extraction and preconcentration method for Cd and Ni prior to flame atomic absorption spectrometric determination, *Anal. Chim. Acta* 521 (2004) 173–177.
- [22] C.D. Stalikas, Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis, *TRAC, Trends Anal. Chem.* 21 (2002) 343–355.
- [23] M. Corti, C. Minero, V. Degiorgio, Cloud point transition in nonionic micellar solutions, *J. Phys. Chem.* 88 (1984) 309–317.
- [24] G. Komaromy-Hiller, R. von Wandruszka, Anisotropy changes of a fluorescent probe during the micellar growth and clouding of a non-ionic detergent, *J. Colloid Interface Sci.* 177 (1996) 156–161.
- [25] C. García-Pinto, J.L. Pérez-Pavón, B. Moreno-Cordero, Cloud point preconcentration and high-performance liquid chromatographic determination of organophosphorus pesticides with dual electrochemical detection, *Anal. Chem.* 67 (1995) 2606–2612.
- [26] S.R. Sirimanne, J.R. Barr, D.G. Patterson, L. Ma, Quantification of polycyclic aromatic hydrocarbons and polychlorinated dibenzo-*p*-dioxins in human serum by combined micelle-mediated extraction (cloud-point extraction) and HPLC, *Anal. Chem.* 68 (1996) 1556–1560.
- [27] A. Eiguren-Fernández, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Determination of polychlorinated biphenyls by liquid chromatography following cloud point extraction, *Anal. Chim. Acta* 358 (1998) 145–155.
- [28] S. Shariati, Y. Yamini, Cloud point extraction and simultaneous determination of zirconium and hafnium using ICP-OES, *J. Colloid Interface Sci.* 298 (2006) 419–425.
- [29] L. Tavakoli, Y. Yamini, H. Ebrahimzadeh, A. Nezhadali, S. Shariati, F. Noormohamadian, Development of cloud point extraction for simultaneous extraction and determination of gold and palladium using ICP-OES, *J. Hazard. Mater.* 152 (2008) 737–743.
- [30] R. Carabias-Martínez, E. Rodríguez-Gonzalo, B. Moreno-Cordero, J.L. Pérez-Pavón, C. García Pinto, E. Fernández Laespada, Surfactant cloud point extraction and preconcentration of organic compounds prior to chromatography and capillary electrophoresis, *J. Chromatogr. A* 902 (2000) 251–265.
- [31] A. Safavi, H. Abdollahi, M.R. Hormozi Nezhad, R. Kamali, Cloud point extraction, preconcentration and simultaneous spectrophotometric determination of nickel and cobalt in water samples, *Spectrochim. Acta A* 60 (2004) 2897–2901.
- [32] C.S.K. Raju, M.S. Subramanian, Selective preconcentration of U(VI) and Th(IV) in trace and macroscopic levels using malonamide grafted polymer from acidic matrices, *Microchim. Acta* 150 (2005) 297–304.
- [33] B.-F. Liu, L.-B. Liu, J.-K. Cheng, Separation and determination of thorium, uranium and mixed rare-earth elements as their UV–vis absorbing complexes by capillary zone electrophoresis, *Talanta* 47 (1998) 291–299.
- [34] F.A. Aydin, M. Soylak, Solid phase extraction and preconcentration of uranium(VI) and thorium(IV) on Duolite XAD 761 prior to their inductively coupled plasma mass spectrometric determination, *Talanta* 72 (2007) 187–192.
- [35] F.A. Aydin, M. Soylak, A novel multi-element coprecipitation technique for separation and enrichment of metal ions in environmental samples, *Talanta* 73 (2007) 134–141.
- [36] A.M. Starvin, T. Prasada Rao, Solid phase extractive preconcentration of uranium(VI) onto diarylazobisphenol modified activated carbon, *Talanta* 63 (2004) 225–232.
- [37] M.E.F. Laespada, J.L.P. Pavon, B.M. Cordero, Micelle-mediated methodology for the preconcentration of uranium prior to its determination by flow injection, *Analyst* 118 (1993) 209–212.
- [38] A. Takahashi, Y. Ueki, S. Igarashi, Homogeneous liquid–liquid extraction of uranium(VI) from acetate aqueous solution, *Anal. Chim. Acta* 387 (1999) 71–75.
- [39] S. Oszwaldowski, R. Lipka, M. Jarosz, Simultaneous determination of zirconium and hafnium as ternary complexes with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and fluoride by reverse-phase liquid chromatography, *Anal. Chim. Acta* 361 (1998) 177–187.
- [40] A. Abbaspour, L. Baramakeh, Application of principle component analysis-artificial neural network for simultaneous determination of zirconium and hafnium in real samples, *Spectrochim. Acta A* 64 (2006) 477–482.