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PRECONCENTRATION OF URANIUM IN WATER SAMPLES USING DISPERSIVE LIQUID-LIQUID MICROEXTRACTION COUPLED WITH SOLID-PHASE EXTRACTION AND DETERMINATION WITH INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETRY

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ABSTRACT. A new liquid phase microextraction method based on the dispersion of an extraction solvent into aqueous phase coupled with solid-phase extraction was investigated for the extraction, preconcentration and determination of uranium in water samples. 1-(2-Pyridylazo)-2-naphthol reagent (PAN) at pH 6.0 was used as a chelating agent prior to extraction. After concentration and purification of the samples in SPE C_{18} sorbent, 1.5 mL elution sample containing 40.0 µL chlorobenzene was injected into the 5.0 mL pure water. After extraction and centrifuging, the sedimented phase was evaporated and the residue was dissolved in nitric acid (0.5 M) and was injected by injection valve into the ICP-OES. Some important extraction parameters, such as sample solution flow rate, sample pH, type and volume of extraction and disperser solvents as well as the salt addition were studied and optimized. Under the optimum conditions, the calibration graph was linear in the range of 0.5-500 µg L^{-1}. The detection limit was 0.1 µg L^{-1}. The relative standard deviation (RSD) at 5.0 µg L^{-1} concentration level was 6.6%. Finally, the developed method was successfully applied to the extraction and determination of uranium in the well, river, mineral, waste and tap water samples and satisfactory results were obtained.

KEY WORDS: Dispersive liquid-liquid microextraction, Solid-phase extraction, Inductively coupled plasma-optical emission spectrometry, Uranium, Water samples

INTRODUCTION

Uranium finds extensive application as nuclear fuel in power plants and their main sources are soil, rocks, plants, sand and water. Uranium 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. Spent nuclear fuels generally contain actinides like uranium, thorium and various fission products [2]. In view of the extensive usage of uranium for various industrial purposes and its toxicity, precise determination of this element in environmental samples is a challenging task [3]. The low concentration of this element in the presence of relatively high concentration of diverse elements makes it difficult to determine directly. So, separation and preconcentration procedures are mandatory prior to its determination by highly versatile techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES). Various procedures for the separation and preconcentration of trace amounts of uranium have been developed, including cloud-point extraction [4, 5], solid sorbents such as polymer-XAD resin series [6] and ion imprinting polymer [7, 8]. However, the separation and preconcentration factors obtained by most of these methods are not sufficient for determination of trace amounts of uranium, some of them use expensive reagent and usually require high volume of sample.

Preconcentration and separation techniques including solvent extraction, solid-phase extraction, co-precipitation and ion-exchange, electrodeposition [9-14] have been used in the analytical chemistry laboratories for uranium. Shamsipur *et al.* [14] have proposed a solid phase

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extraction procedure for ultratrace uranium(VI) in natural waters using octadecyl silica membrane disks modified by tri-*n*octylphosphine oxide. A chelating resin has been synthesed by Gladis and Rao [15] by the reaction with Amberlite XAD-4 and 5-aminoquinoline-8-ol for the uranyl ion uptake. Ghiasvand and Mottaabed [16] have proposed a solid phase extraction procedure of ultratrace uranium by mixtures ofdicyclohexyl-18-crown-6 and tri-*n*-octylphosphine oxide.

Traditional solvent extraction has been used as a basic and powerful method of concentrating for a long time. However, it requires extensive amount of organic solvents. A special attention is nowadays focused on techniques, which are characterized by a considerable reduction or complete elimination of organic solvents. Such techniques protect the environment against additional quantities of solvents and reduce the cost of analysis.

A new microextraction technique, which uses extraction solvent at µL volume, is dispersive liquid-liquid microextraction (DLLME). It is simple, rapid, inexpensive, and efficient and has a higher recovery. It was first reported in 2006 by Rezaee *et al.* [17]. This method uses an extracting solvent dissolved in a dispersive solvent, which is miscible with both extraction solvent and water. Methanol, acetonitrile and acetone have been used as dispersive solvents. In DLLME the appropriate mixture of the extraction and disperser solvents is rapidly injected by a syringe into an aqueous solution containing ion complexes with chelating reagent. Up to now, DLLME has been successfully applied to the pre-concentration of several families of organic and inorganic species [18-26]. Despite several advantages of DLLME, this method is not suitable in complex matrices and extra steps were performed in sample preparation before DLLME.

Solid-phase extraction (SPE) is a widely used sample preparation technique for the isolation of selected analytes. The principal goals of SPE are trace enrichment (concentration), matrix simplification (sample clean-up) and medium exchange. It is now the most common sampling technique in many areas of chemistry, including environmental, pharmaceutical, clinical, food and industrial chemistry [27]. SPE-DLLME is an efficient hyphenated technique that offers the advantages of both methods such as simplicity, low solvent usage and exposure, low disposal costs and extraction time, with high recovery and enrichment factor and it can be also used in complex matrices [28-31]. The main purpose of this work was to apply SPE-DLLME as preconcentration step for extraction and determination of low concentrations of uranium in aqueous samples. Compared with the conventional SPE procedure, the SPE-DLLME method provided higher enrichment factor and higher purification ability and selectivity.

EXPERIMENTAL

Chemicals and reagents

All chemicals used were of analytical reagent grade. $UO_2(NO_3)_2.6H_2O$ was purchased from Merck (Darmstadt, Germany). The stock solution of 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 of 10 mg L^{-1} respect to analyte. Reagent grade 1-(2-pyridylazo)-2-naphthol (PAN) (Merck) was used as chelating agent. A 0.01 mol L^{-1} solution of PAN in methanol was prepared by dissolving proper amount of reagent. 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}). Carbon tetrachloride (GR), tetrachloroethylene (GR), chloroform and chlorobenzene as extraction solvents were obtained from Merck. Acetone, acetonitrile and methanol as dispersive solvents were obtained from Merck. Also, sodium chloride was purchased from Merck. The water used was purified on a youngling ultra pure water purification system (Aqua Max^{TM} – ultra, Korea).

Apparatus

Determination of the metal ion was performed using a simultaneous inductively coupled plasma-optical emission spectrometry (ICP-OES) model Vista PRO from Varian Company (Springvale, Australia) coupled to V-groove nebulizer and equipped with a charge coupled device (CCD) detector. 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 1 shows the optimal instrumental conditions and the emission line, which was selected for determination of the analyte via ICP-OES.

Table 1. 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 line (nm)	367.007

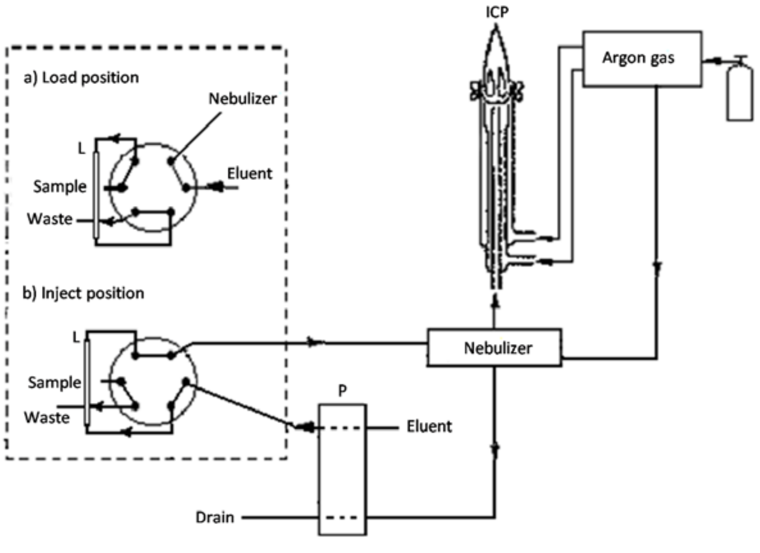

Figure 1. Schematic of flow injection system; a) Load position; sample introduction into the loop; b) Injection position, the eluent carry the sample into the nebulizer using a peristaltic pump (L: Loop; P: Peristaltic pump).

SPE-DLLME procedure

The ionic strength and pH of the solutions were adjusted to an appropriate amount (ammonium acetate: 2.5×10^{-3} mol L^{-1}, pH = 6.0). 100.0 mL of the solution containing 100 µg L^{-1} of uranium was placed in a test tube and 150 µL 0.01 M of PAN (as chelating agent) was added. The uranium ions in the aqueous solution were complexed with PAN. SPE of U from the water samples was carried out using C_{18} sorbent (3 mL syringe barrel, waters, USA). The sorbent was conditioned with 2.0 mL of acetone. A volume of 100.0 mL of the sample was loaded at a flow rate of about 6.7 mL min^{-1} with the aid of a vacuum pump (Rotavac, Heidolph, Germany). The C_{18} syringe barrels were rinsed with 2.0 mL of water to remove the matrix interferences. After ventilating of the solid phase, U was eluted with 1.5 mL methanol, the eluent collected into a test tube and was used as disperser solvent in the subsequent DLLME procedures. A volume of 5.0 mL aqueous solution was placed in a 10 mL screw cap glass test tube with conical bottom. Methanol (disperser solvent) with the volume of 1.5 mL containing 40.0 µL chlorobenzene (extraction solvent) was injected into the aqueous solution, using a 5.0 mL syringe (gas tight, Hamilton, Reno, NV, USA). A cloudy solution, resulting from the dispersion of the fine chlorobenzene droplets in the aqueous solution was formed in the test tube. In the final step, U was extracted into fine chlorobenzene droplets in a few seconds. The mixture was then centrifuged for 3 min at 5000 rpm. After this procedure, the dispersed fine chlorobenzene droplets were sedimented at the bottom of the conical test tube.After vaporization of the sedimented phase, it was dissolved in nitric acid (0.5M) and injected to ICP-OES by using flow injection system (Figure 1).

RESULTS AND DISCUSSIONS

In the present research, the SPE and DLLME conjunction was designed and employed for the preconcentration of uranium from water samples. This combination not only resulted in a high enrichment factor, but also it could be used in complex matrices. To achieve a high extraction recovery and enrichment factor with the employment of SPE-DLLME, the SPE and DLLME conditions must be examined and optimized.

Effect of type of the extraction solvent

Careful attention should be paid to the selection of the extraction solvent. The extraction solvent must have some properties, such as higher density than water, high extraction capability of the analyte and low solubility in water. Carbon tetrachloride (CCl_4), tetrachloroethylene (C_2Cl_4), chlorobenzene (C_6H_5Cl) and chloroform ($CHCl_3$) was examined in this study. A series of sample solutions were tested using 1.5 mL acetonitrile, containing different volumes of the extraction solvents to achieve constant volume of the sedimented phase. Thereby, 60.0, 40.0, 35.0 and 48.0 µL of $CHCl_3$, C_6H_5Cl, C_2Cl_4 and CCl_4 were used, respectively. The results (Figure 2) indicated that the chlorobenzene has the higher extraction efficiency in comparison with the other tested solvents. It is probably, because of higher solubility of complex in chlorobenzene in comparison with the other tested solvents. Therefore, chlorobenzene was selected as the main extraction solvent.

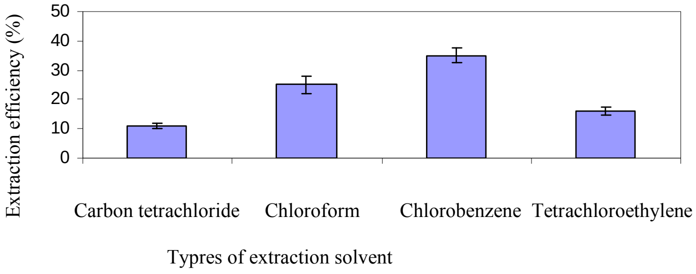

Figure 2. Effect of type of the extraction solvent on the extraction recovery of U obtained from SPE-DLLME.

Effect of pH

In order to extract the metal ion it must be converted into a hydrophobic species. Thus, optimization of the solution pH may help the formation of an extractable species of uranium. So, the effect of pH on the extraction of U was studied by varying the pH within the range of 2-8. The pH was adjusted by using either nitric acid or NaOH while keeping the other variables constant. The results (Figure 3) showed that extraction efficiency was maximum at the pH = 6. Thus, pH = 6 was selected as a optimum amount.

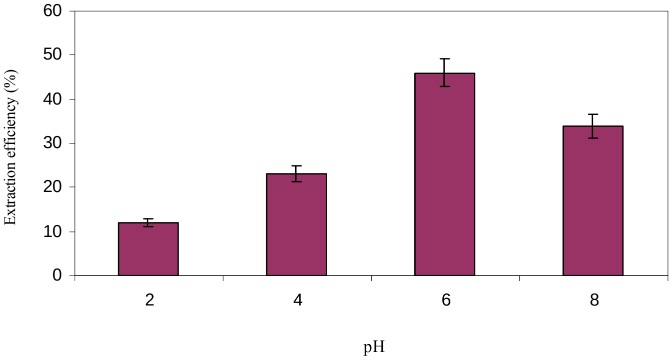

Figure 3. Effect of pH on the extraction recovery obtained from SPE-DLLME.

Effect of amount of ligand

The extraction efficiency of the analyte depends on the amount of PAN as a complexing agent. Thus different volume of PAN (70, 150, 300 and 700 µL) with the concentration of 0.01 M was used. The results (Figure 4) showed that by increasing the volume of PAN up to 150 µL, the extraction efficiency increases and then it decreases slightly. This reduction could be due to the extraction of PAN itself, which can easily saturate the small volume of the extraction solvent. Therefore, the 150 µL of PAN was selected for the subsequent works.

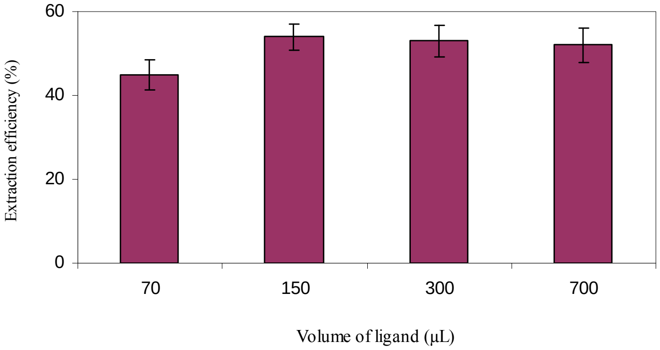

Figure 4. Effect of volume of PAN on the extraction recovery obtained from SPE-DLLME.

Effect of type of disperser solvent

When combining SPE with DLLME, the elution solvent of SPE must also play the role of the disperser solvent at the DLLME stage. The main criterion for selecting the disperser solvent is its miscibility with the extraction solvent and the aqueous sample. For this purpose, different solvents such as acetonitrile, acetone and methanol were examined. A series of sample solutions were tested using 1.5 mL of each disperser solvent, containing 40.0 µL volume of C_6H_5Cl (as extraction solvent). The results (Figure 5) indicated that methanol has higher extraction efficiency in comparison with the other tested solvents. It seems that it is due to interaction hydroxyl group in PAN structure with methanol and methanol has more eluent strength for the complex. Thus, methanol was chosen as the disperser or eluent solvent for subsequent experiments.

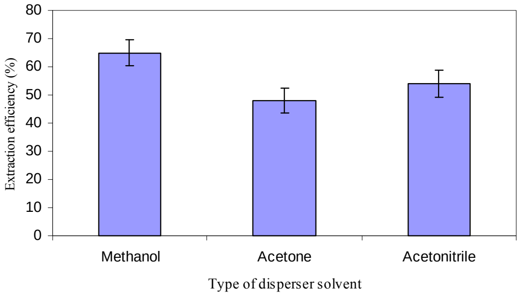

Figure 5. Effect of the type of disperser solvent on the extraction recovery of U obtained from SPE-DLLME.

Effect of volume of the extraction solvent

In order to examine the effect of the extraction solvent volume, 1.5 mL methanol containing different volumes of C_6H_5Cl (30.0, 40.0, 50.0, 60.0 and 70.0 µL) was subjected to the same SPE-DLLME procedures. According to the equation:

$$ER(\%) = \frac{K_d}{K_d + \frac{V_{aq}}{V_{org}}} \times 100$$

by increasing the volume of chlorobenzene (V_{org}) from 30.0 to 40.0 µL, the extraction efficiency (ER%) increases, but according to the equation:

$$ER(\%) = \frac{C_{sedimented} \times V_{sedimented}}{C_{sample} \times V_{sample}} \times 100$$

by increasing the volume of chlorobenzene from 40.0 to 70.0 µL, the extraction efficiency (ER%) decreases. Because the concentration of the complex in the sedimented phase decreases and dilution effect. Therefore, 40.0 µL of C_6H_5Cl was selected as the volume of extraction solvent.

Effect of volume of disperser solvent

In order to examine the effect of disperser solvent volume, the volume of the sedimented phase was kept constant and the volume of methanol and chlorobenzene was changed, simultaneously. The different volumes of methanol (0.5, 1.0, 1.5 and 2.0 mL) were in concomitant with the corresponding volumes of 26.0, 32.0, 40.0 and 45.0 µL of chlorobenzene, respectively. The results showed that 1.5 mL methanol has higher extraction efficiency than that of others. It seems that, at the volume of 1.5 mL, the amount of methanol is enough for sufficient elution of the complex. At a low volume of methanol, cloudy state is not formed well, thereby, the extraction recovery decreases. At the high volume of methanol, the solubility of the complex in water increases, therefore, the extraction efficiency decreases. Therefore, 1.5 mL was selected as the optimum volume of methanol.

Effect of the flow rate of the sample solution

The flow rate of the sample solution through the solid phase is an important factor, because it controls the time of analysis. The flow rate, on the one hand, must be low enough to perform an effective retention of the analyte. On the other hand, it must be high enough not to waste time. The flow rate influence of the sample solutions from the solid-phase cartridge on the U recovery was investigated in the range of 0.65-8.6 mL min^{-1}. It was found that in the range of 0.65-6.7 mL min^{-1}, the U recovery by the cartridge was not affected considerably by the flow rate of the sample solution (Figure 6). According to the result, 6.7 mL min^{-1} was used as the best sample flow rate.

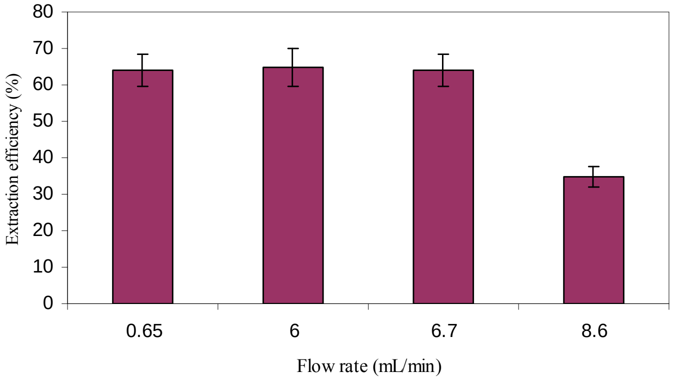

Figure 6. Effect of the flow rate on the extraction recovery of U obtained from SPE-DLLME.

Effect of salt addition

The influence of ionic strength was evaluated at 0-8% (*w/v*) NaCl levels while other parameters were kept constant. The experimental results showed that salt addition had no significant effect on the extraction efficiency of the analyte. This is possibly because of two opposite effects of addition of salt. One is to increase the volume of the sedimented organic phase and decrease the concentration of the complex in the sedimented organic phase and dilution effect which reduces the extraction efficiency; another is the salting-out effect, which increases the extraction efficiency. It is mentioned that by increasing the salt concentration, the volume of the sedimented organic phase increases, because of the decrease of solubility of the extraction solvent in the presence of salt. Therefore, all the following experiments were carried out without adding salt.

Interferences

The potential interferences of some ions on the preconcentration and determination of metal ion were examined. In these experiments, solutions of 100 µg L^{-1} of the analyte containing the interfering ions were treated according to the optimized procedures. Table 2 shows tolerance limits of the interfering ions. 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}.

Table 2. Effect of interference on preconcentration and determination of metal ion

Interference	Interference to metal ion ratio	Recovery (% U)	Interference	Interference to metal ion ratio	Recovery (% U)
Ca^{2+}	1000	97	Co^{2+}	200	44
Mg^{2+}	1000	100	Co^{2+}	50	95
Ba^{2+}	1000	91	Cr^{3+}	200	51
K^{+}	2000	101	Cr^{3+}	50	96
Zn^{2+}	200	100	Al^{3+}	200	91
Na^{+}	2000	102	Cu^{2+}	50	45
Cd^{2+}	200	70	Cu^{2+}+0.01M SCN^{-}	50	73
Cd^{2+}	50	93	Cu^{2+}+ 0.01M Ascorbic acid + 0.01 M KI	50	92
Mn^{2+}	200	72	Fe^{3+}	200	15
Mn^{2+}	50	96.4	Fe^{3+}	50	56
Pb^{2+}	200	101	Fe^{3+} + 0.02 M SCN^{-}	5	95
Hg^{2+}	200	35	Ni^{2+}	200	94
Hg^{2+}	50	95			

Figures of merit of the proposed method

The figures of merit of the proposed method are summarized in Table 3. The percent relative standard deviation (RSD %) was 6.6. 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 DL was obtained 0.1 µg L^{-1}. Dynamic linear range of the method were evaluated and obtained in the range of 0.5-500 µg L^{-1}. The coefficient of determination of the calibration curves was 0.9969.

Table 3. Quantitative results of SPE-DLLME method for uranium

Analyte	Detection limit (µg L^{-1})[a]	RSD%[b] (n = 5)	Dynamic linear range (µg L^{-1})	R^2
U	0.1	6.6	0.5 - 500	0.9969

[a] Detection limits were calculated based on $3S_B$/m. [b] Relative standard deviation (%) at concentration of 20 µg L^{-1}.

Table 4. Determination of uranium in tap, well, mineral, waste and river water andrelative recovery of spiked uranium in them

Sample	Concentration of U (µg L^{-1}) ± RSD[a] , n = 3	Added U (µg L^{-1})	Found U (µg L^{-1}) ± RSD[a] , n = 3	Recovery (%)
Tap water [c]	n.d[b].	10.0	9.4 ± 7.4	94
Well water [d]	4.6 ± 6.1	10.0	13.4 ± 8.6	88
River water[e]	1.1 ± 7.3	10.0	10.2 ± 8.4	91
Mineral water[f]	n.d.	10.0	9.2 ± 6.8	92
Waste water[g]	5.3 ± 8.4	10.0	14.0 ± 7.6	87

[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 Anzali River (Gilan, Iran). [f] Was taken from Pars Company (Shiraz, Iran). [g] Was taken from our laboratory (Tehran. Iran).

Analysis of real samples

To demonstrate the performance of the present method, it was utilized to determine the analyte concentration in different water samples. Water samples were spiked with U standard (10.0 µg L^{-1}) to assess matrix effects. Ultimately, the extractions were performed at optimized conditions and the results are shown in Table 4. The results showed that the water matrices, in our present context had little effect on SPE-DLLME. As could be seen, the relative recoveries for the spiked samples are in acceptable range (87-94%). The validation of the presented procedure was performed by the analysis of certified reference material (NASS-4, open ocean seawater), then the proposed preconcentration procedure was applied. The certified and observed values for NASS-4-CRM are given in Table 5. The results found are in good agreement with the certified values of CRM.

Table 5. Uranium levels of seawater Certified Reference Material (NASS-4-CRM).

	Certified value (μg L^{-1})	Measured value (μg L^{-1}) ± SD (n = 3)
U	2.68 ± 0.12	2.63± 0.15

Table 6 compare the proposed method with the other extraction methods for the determination of the target analyte in water samples. The quantitative results of the proposed method are better than of solid phase extraction [10, 34] and DLLME [35]. The comparison of extraction time of the proposed method with cloud-point extraction [33] for the extraction of the target analyte indicates that this method has a short extraction time. DLLME alone needs extra steps in sample preparation for the extraction of the analyte in complex matrices such as waste samples in comparison with SPE-DLLME method. Also, it needs more dilution in waste samples in comparison with the proposed method which it is causes to have problem in detection in lower concentration, because of more dilution. The comparison of the proposed method with the SPE method alone and without DLLME procedure show that the calibration graphwas in the range of 10-500 μg L^{-1} for the selected analyte and it was indicated that by using DLLME procedure the preconcentration factor increases, because of large surface area between the extraction solvent and the slected analyte.

Table 6. Comparison of the proposed method with other extraction methods for the determination of uranium.

Methods	RSD%	Dynamic linear range (μg L^{-1})	Limit of detection (μg L^{-1})	Extraction time (min)	Ref.
Cloud-point extraction	3.0	0.2-20	0.06	10	[33]
Solid-phase extraction (C-8 SPE cartridge)	1.6	0.5-80 μM	0.4 μM	1	[10]
Solid-phase extraction (murexide modified silica gel)	1.6	1.35-217	1.0	15	[34]
DLLME	5.5	5.0-200	2	A few seconds	[35]
SPE-DLLME	6.6	0.5-500	0.1	1	This work

CONCLUSION

In the present study, novel SPE-DLLMEmethod was employed to extract uranium from water samples. The method is rather simple, rapid, efficient and environmentally friendly. This method provides wide linear range and detection limits at μg L^{-1} from 100.0 mL of water sample. The resulting optimized procedure allowed quantification of trace levels of uranium in water samples whilst using SPE-DLLME coupled to ICP-OES.

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