J. Chil. Chem. Soc., 62, Nº 2 (2017)

FLOTATION-ASSISTED HOMOGENEOUS LIQUID-LIQUID MICROEXTRACTION FOR TRACE DETERMINATION OF URANIUM IN WATER SAMPLES BY ICP-MS

*SOMAYEH VEYSEH, ALI NIAZI **

Department of Chemistry, Faculty of Science, Arak Branch, Islamic Azad University, Arak, Iran

ABSTRACT

In this study, a novel method based on floatation assistance of homogeneous liquid-liquid microextraction (FA-HLLME), combined with inductively coupled plasma-mass spectroscopy (ICP-MS) was proposed, for the determination of trace uranium in environmental water samples. As one of the miniaturized separation and extraction techniques, homogenous liquid–liquid microextraction (HLLME) has been widely applied in the field of environmental monitoring and assessment. 1,2-pyridylazo-2-naphthol (PAN) was used as the complexing agent while toluene and methanol were selected as the extraction and homogeneous solvents, respectively. The factors that influenced the extraction efficiency for uranium determination (including pH, extraction and homogeneous solvents, concentration of PAN and NaCl, extraction time) were studied statistically. Under optimum conditions (pH=7.0, 100 μL toluene, 500 μL methanol, 6.4×10^{-5} mol L^{-1} PAN, 1.5 mol L^{-1} NaCl and 60 sec of extraction time), the linear dynamic range for uranium determination was 1.0-500.0 ng L^{-1} (R^2=0.9995), with a corresponding limit of detection (LOD) of was 0.27 ng L^{-1}. The relative standard deviation (R.S.D.) (C=50.0 ng L^{-1}, n=9) was 1.13%, with a corresponding enrichment factor of 360 for uranium extraction. The proposed method was successfully applied for the determination of uranium in different water samples.

Keywords: Uranium: Determination; Liquid-liquid homogeneous microextraction; ICP-MS; Water samples.

INTRODUCTION

Uranium is one of the most significant radioactive heavy metals found in low levels within many different kinds of rocks, sediments, soils and waters. The average uranium concentration in soils, ground, underground waters and plant increases by processes such as mineral extractions, nuclear industries and fertilizers that are used in agriculture and contain uranium in common[1-3]. Due to its radioactive and toxic potential (oncogenic potential to human), uranium is considered an environmental pollutant and plays an important role in our daily life. The world Health Organization (WHO) suggests 0.015 mg L^{-1} as the safe concentration of uranium in drinking water[4,5]. Thus, the use of very precise methods for the pre-concentration and determination of uranium in water samples is of great necessity. Different processes have been recommended for the separation and pre- concentration of low concentration of uranyl ions[6]. These methods, include the immersion and adsorption on porous materials or materials with large adsorption cross sections (active carbon membrane and ash), supercritical fluid extraction, electro-synthetic techniques (electron flow or electro-osmosis), using microorganisms as biosorbent (bacteria, fungus, yeasts, algaes), soil pollution (use of absorbent plants for the removal of toxic compounds from water), cloud point micro extraction, homogeneous liquid-liquid micro extraction, etc., to mention a few. In addition, many other techniques, such as ICP-MS[7], voltammetry[8,9], active neutron analysis[10], fluorescence[11,12] are useful in the determination and analysis of this element.

There has been a small revolution in Inductively Coupled Plasma (ICP) in the past 40 years, leading to the development and variability of this technique. ICP-MS is one of the most significant analytical techniques used for the determination of concentration of elements, especially at trace and ultra-trace concentration. For environmental samples features such as very high sensitivity, low detection limit and also analyzing very low sample quantities make the technique attractive[13]. ICP-MS is applied the quantitative measurement of 1-10 ng L^{-1} analytes. This technique exhibits more sensitivity of in the direct determination of elements is better than other techniques. The use of this technique makes the analysis of non-metal elements with very good sensitivity, possible, thus, ICP-MS is an effective analytical tool for the measurement of very low concentrations. Some other advantages include high linear dynamic range, high precision and accuracy in measurement, and minimum interferences.

ICP-MS is a widespread technique that has attracted much attention in the measurement of uranium[14], although, little difficulty is experienced in the direct analysis of environmental samples (water) under the special condition, due to the very low concentration of uranium in the presence of interfering ions. One way to overcome this is to dissolve the samples in order to pre-concentrate samples and analyzes those using different analytical instruments. The process of pre-concentration includes a set of different processes used to the increase the ratio of the determinate element to the other dissolved elements. This leads to a promotion in the analytical detection limit, sensitivity and accuracy. This present research utilized the pre-concentration of uranium, based on homogenous liquid–liquid micro extraction.

Up till date, different extractions methods, such solid phase extraction, supercritical fluid extraction, salting-out extraction, liquid-liquid extraction, etc. have been applied, using the effective instruments. Liquid- liquid extraction (LLE) aids in the selective transfer of one or more solute(s) from a liquid phase (usually water) to another immiscible liquid (usually organic phase), and is known as the most common method for the extraction and preparation of environmental samples. In spite of some features, such as appropriate sensitivity and effectiveness, LLE have some disadvantages, such as the high volume use of organic solvent and samples, emulsion formation, time-consuming process, etc. Therefore, the liquid phase micro extraction, which is the miniaturized form of liquid-liquid extraction, is used. In this method, the consumption of extraction solvent has been reduced to microliters.

Some liquid phase micro extraction techniques include single drop microextraction (SDME)[15], dispersive liquid-liquid microextraction (DLLME)[16], cloud point extraction (CPE)[17], hollow-fiber microextraction (HF-LPME)[18], solidified floating organic drop microextraction (SFODME)[19] and homogeneous liquid-liquid microextraction. The homogeneous liquid-liquid micro extraction was used for the first time by Moretta *et. al.,* in 1973 for the extraction of Fe(II) as a complex[20]. Nowadays, this method has found widespread application in extracting different compounds and elements, and satisfactory results have been recorded. Flotation-assisted homogeneous liquid-liquid microextraction which was introduced in 2012 has been applied for the extraction and pre-concentration of polycyclic aromatic compounds (PAC) in soil and water samples[21,22]. This extraction method has some advantages such as simplicity, rapidness, low cost, high recovery and high enrichment factor.

In this paper, the pre-concentration and extraction of low concentration of uranium, using a special extraction cell and analysis of samples using, ICP-MS technique, is addressed. The proposed method was successfully applied for the determination of uranium in different water samples.

EXPERIMENTAL

Materials and Reagents

A standard solution of 1000 mg L^{-1} uranium was purchased in nitrate form and working solutions were prepared at the concentration levels of interest by ultra-pure water. PAN (Fig. 1), purchased from Merck was also applied as chelating agent. The extraction solvents such as n-heptane, hexane, toluene, 1-dodecanol, homogenous solvents such as methanol, ethanol, acetone, acetonitrile, tetrahydrofuran, nitric acid, NaCl and NaOH were purchased from Merck. Nitric acid and NaOH were used for the adjustment of the pH.

e-mail: a-niazi@iau-arak.ac.ir

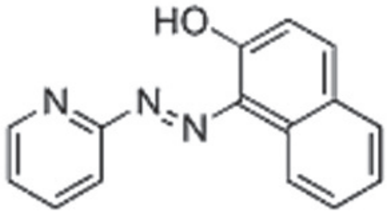

Fig. 1. Chemical structure of PAN reagent.

Instrumentation

The detection system used for determination of uranium was performed in a Perkin-Elmer Sciex ELAN 9000 model. The instrumental operating conditions for the determination of thorium are summarized in Table 1. The pH was determined with a model 780 Metrohm pH-meter with combined glass–calomel electrode.

Flotation-assisted homogeneous liquid-liquid microextraction (FA-HLLME)

At first, about 1 mL methanol (homogenous solvent) was transferred to a small beaker and about 120 µL toluene (extraction solvent) was added. The two solvents were gently mixed and injected into the extraction cell by a syringe[23,24]. Fig. 2 shows the schematic procedure of the proposed method. Then, 1.5 mol L^{-1} NaCl was prepared as a salting-out agent. The organic phase which was selected lighter than the aqueous phase was placed on the surface of the extraction cell. Then, 0.1 mg L^{-1} uranium solution was prepared from 1000 mg L^{-1} standard solution by serial dilution and 50 µL of this solution was transferred into the saline solution. The uranium solution concentration increased to 50 ng L^{-1} in the 100 mL beaker was due to the limit of quantification (LOQ) associated with ICP-MS analysis (about 20 ng L^{-1}). Shortly following this, the pH of the provided solution was adjusted to 7.0 by adding NaOH due to the better reaction of PAN as a chelating agent. Finally, 22 mL of this solution was collected based on the volume of the reaction cell and transferred into a small beaker. Then, 50 µL PAN (0.01 mol L^{-1}) was added. The solution was collected by a syringe and injected into the reaction cell. The injecting of water via a large syringe resulted in mixing of water and air in a ratio of half to half giving rise to good aeration. The extracted sample was placed on the surface of mixture and collected by a micro-syringe. The sample volume was measured and transferred into a 1 mL falcon tube. The organic solvent was allowed to evaporate for a few minutes. Shortly, 0.5 mL nitric acid at a concentration of 0.5 mol L^{-1} was added. Finally, the sample was injected into ICP-MS for subsequent analysis.

Preparation of real samples prior to FA-HLLME

The accuracy of this method was validated using different water samples for analysis. The samples were collected from different cities in order to determine uranium concentrations in samples of tap, well, river and spring water. All water samples were filtered through a 0.45 µm filter prior to pre-concentration. Then, the pH of samples was adjusted to 2 and stored at 4 °C until they could be analyzed.

RESULTS AND DISCUSSION

In order to obtain the optimum condition for the microextraction and determination of uranium in water samples, the effect of parameters such as pH, concentration of PAN, type and volume of extraction and homogeneous solvents, and the required time were investigated. The results were reported based on the ratio of recovery percentage to the factor of interest.

Effect of type and volume extraction solvent

The selection of extraction solvents is of great significance and their densities should be less than that of water. Based on these features, four solvents including n-hexane, heptane, toluene, 1-dodecanol were selected. The results obtained showed that toluene demonstrated the highest recovery compared to the other solvents. It should be noted that the recovery percentage was calculated by the average of 3 times results which were obtained by the analysis of each sample. Fig. 3 shows the recovery according to the type of extraction solvents. The selection of an extraction solvent is followed by an optimization of its volume. Therefore, the effects of toluene volume were investigated in a range of 80 to 180 µL. As shown by the results in Fig. 4, toluene, with a volume of 120 µL had the best recovery for extraction of uranium.

Table 1: The optimal condition of ICP-MS in order to measuring uranium ion.

RF Power	1000 Watts
Plasma Gas Flow	15 L min^{-1}
Auxiliary Gas Flow	1 L min^{-1}
Nebulizer Gas Flow	0.81 L min^{-1}
Solution Pump Rate	1.50 mL min^{-1}
Sample Introduction System	Cross-flow with Scott spray chamber
Rinse Time	35 seconds @ 48 rpm
Sample Uptake Time	25 seconds @ 48 rpm
Equilibration Time	10 seconds @ 24 rpm
Analysis Time (total)	2:06 minutes
Detector Mode	Dual Mode
Lens	6.25
Sampler/Skimmer Cones	Nickel
Scanning Mode	Peak Hopping
Number of Points/Peak	1
Dwell Time	100 ms per point
Number of Sweeps/Reading	8
Number of Readings/Replicate	1
Number of Replicates	3
Total Acquisition Time	3 : 16 minutes

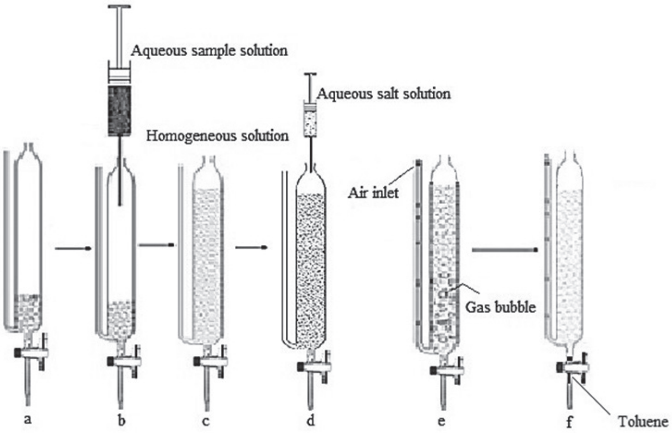

Fig. 2. Schematic procedure of FA-HLLME (a) Home-designed microextraction cell, (b) Injection of the sample solution into the microextraction cell, (c) a homogeneous solution was formed in the cell, (d) aqueous salt solution was added into the cell, (e) flotation was used, to complete the extraction, (f) the high-density extractant was collected on the bottom of the cell.

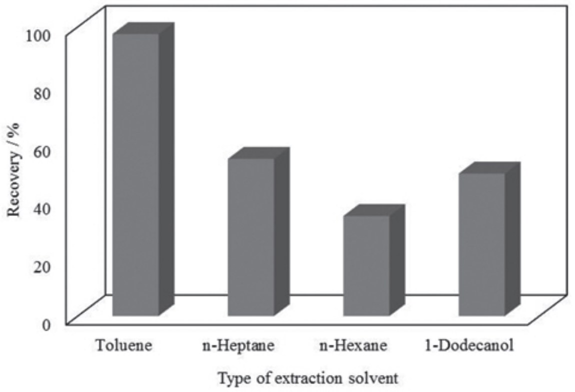

Fig. 3. Effect of extracting solvent at optimum condition (pH=7, 0.5 mL methanol, 6.363×10^{-5} mol L^{-1} of PAN, 1.5 mol L^{-1} of NaCl and extraction time 1 min).

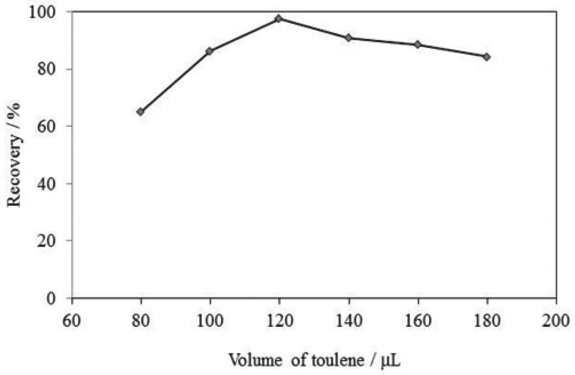

Fig. 4. Effect of volume of toluene at optimum condition (pH=7, 0.5 mL methanol, 6.363×10^{-5} mol L^{-1} of PAN, 1.5 mol L^{-1} of NaCl and extraction time 1 min).

Effect of type and volume of homogeneous solvent

The homogeneous solvent should be miscible in both organic (extraction solvent) and liquid (sample solution) phase. The type of homogeneous solvent should be effective on the homogenization of injection phase, stability of homogeneous solution and extraction recovery. In this work, different solvents such as acetone, acetonitrile, ethanol and methanol were examined. The results showed that the recoveries of different extractions using various homogeneous solvents were different and the best result was obtained with methanol (Fig. 5). The effect of methanol volume was investigated in a range of 0.5 to 2.0 mL. The obtained results showed that 0.5 mL methanol had the best recovery for extraction and determination (Fig. 6). It is necessary to refer at this point, that volumes smaller than 0.5 mL have no effect on extraction.

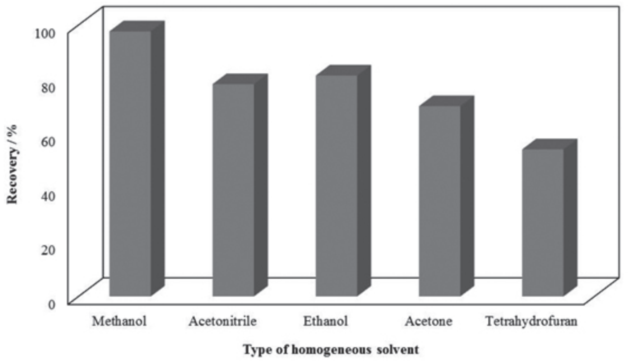

Fig. 5. Effect of homogenous solvent at optimum condition (pH=7, 120 µL toluene, 6.363×10^{-5} mol L^{-1} of PAN, 1.5 mol L^{-1} of NaCl and extraction time 1 min).

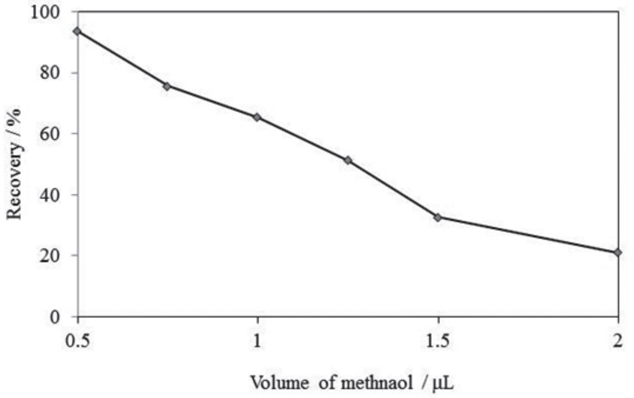

Fig. 6. Effect of extraction solvent at optimum condition (pH=7, 120 µL toluene, 6.363×10^{-5} mol L^{-1} of PAN, 1.5 mol L^{-1} of NaCl and extraction time 1 min).

Effect of pH

The separation and preconcentration of metal ions by FA-HLLME is based on the formation of a complex with sufficient hydrophobicity that can be extracted into small volume of toluene. Thus the pH of aqueous phase has a unique role in the extraction method as it affects the metal-chelate formation and its subsequent extraction. The extraction of uranium was studied in the pH range of 2.0-12.0 using nitric acid and sodium hydroxide solution and other variables were kept constant. The results shown in Fig. 7 demonstrated that the recovery of extractions was pH dependent.

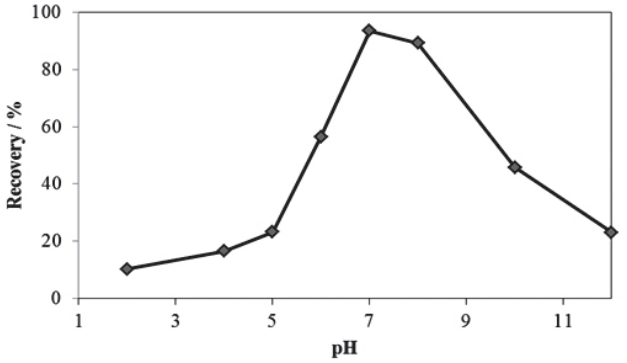

Fig. 7. Effect of pH at optimum condition (120 µL toluene, 6.363×10^{-5} mol L^{-1} of PAN, 1.5 mol L^{-1} of NaCl and extraction time 1 min).

Fig. 7 showed that, there was a significant increase in the extraction recovery from pH 2.0 to 7.0, in which the maximum amounts of complexes were formed and then the progressive decrease in extraction of uranium at pH<7.0 might be due to the competition of proton with the analyte for reaction with PAN, also there was decrease in the recovery at pH larger than 7.0 that might be due to the hydrolysis of the uranium ions. Therefore, a pH of 7.0 was selected as the optimum pH for subsequent work[25)].

Effect of PAN concentration

The effect of concentration of PAN reagent at complexation and extraction were investigated. An appropriate amount of PAN should be carefully selected and used to ensure the effective complexation of all metal ions and to obtain a high recovery. The effect of PAN concentration from 5.0×10^{-6} to 5.5×10^{-5} mol L^{-1} on recovery was studied, and the results are shown in Fig. 8. As shown in the results in Fig. 8, the best PAN concentration was 6.4×10^{-5} mol L^{-1} in this study. It is necessary at this point to explain that PAN is a reactant which can form complex with a large number of metals. However, ICP-MS method overcame this problem due to its high selectivity.

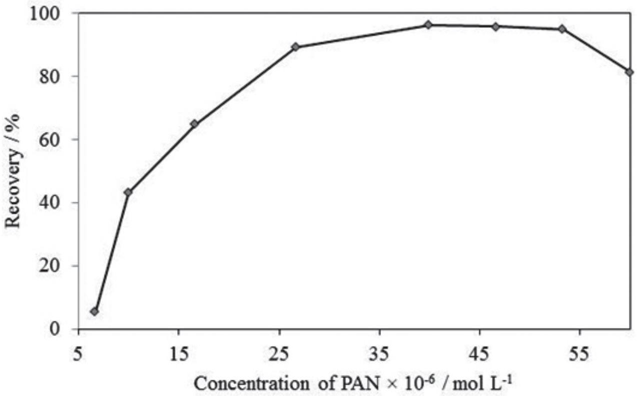

Fig. 8. Effect of concentration of PAN at optimum condition (pH=7, 120 μL toluene, 0.5 mL methanol, 1.5 mol L^{-1} of NaCl and extraction time 1 min).

Effect of salt addition

Salt addition on the water sample may have several different effects on the extraction (salting-out, salting-in or no effect). The influence of ionic strength of the aqueous solutions on the extraction efficiency was evaluated by changing the concentration of NaCl from 0.5 to 5.0 mol L^{-1}. By increasing the NaCl concentration up to 1.5 mol L^{-1}, the extraction efficiency of the analyte increased because of salting-out effect. By using the salt with the amounts higher than 1.5 mol L^{-1} extractions, the efficiency decreased. Thus, 1.5 mol L^{-1} of NaCl was used in subsequent studies.

Effect of extraction time

In HLLME, the extraction time is defined as the interval between the injections of the extraction mixture into solvents and flotation. In this work, the effect of extraction time in the range of 0 to 20 min was investigated under the same condition of other parameters. The results showed that, the extraction time demonstrated no remarkable effect on the procedure. Following the aeration procedure, the surface contact area between the liquid and extraction phase increased and the transfer of analyte from liquid phase (sample) into the extraction solvent rapidly occurred. Due to the very short extraction time, the equilibrium time occurred at a faster rate. The short extraction time is one aspect of HLLME. Therefore, the extraction time of 1 min was considered.

Interferences

In this work, the interfering effect of different ions; for example, 21 cations and anions were investigated on the extraction procedure of uranium under the optimal condition. The results of water samples showed that the interferences demonstrated no significant effect on extracting and determining uranium in the presence of the aforementioned ions (Table 2).

Table 2: Interfering effect study of different ions under optimal conditions (pH=7, 120 μL toluene, 0.5 mL methanol, 6.363×10^{-5} mol L^{-1} of PAN 1.5 mol L^{-1} of NaCl and extraction time 1 min).

Interference ion	Ratio of concentration of interference to concentration of uranium	Concentration of extracted uranium in presence of interference ion after condensation (ng L^{-1})	Calculated uranium concentration in calibration curve before condensation (ng L^{-1})	Recovery (%)
Li^+	100	15.29	45.89	90.8
Na^+	100	17. 26	51.77	102.5
K^+	100	16.98	50.95	100.9
Rb^+	100	14.42	43.26	85.5
Ca^{2+}	100	14. 58	43.74	86.5
Mg^{2+}	100	15.08	45.24	89.5
Sr^{2+}	100	15.18	45.55	90.1
Ba^{2+}	100	16.19	48.58	96.2
Fe^{3+}	50	15.09	45.28	89.6
Zn^{2+}	50	15.15	45.45	90.0
Cd^{2+}	50	14.97	44.85	88.7
Al^{3+}	50	14.65	43.98	86.9
Co^{2+}	50	15.21	45.62	90.3
Ni^{2+}	50	15.36	46.07	91.2
Pb^{2+}	50	15.69	47.08	93.2
Sn^{4+}	50	14.37	43.11	85.2
Cs^+	50	15.31	45.93	90.9
Be^{2+}	50	14.84	44.52	88.0
Ru^+	50	16.49	49.48	98.0
Sm	50	16.70	50.09	99.2
Mn^{2+}	50	14.95	44.86	88.7

Calibration and figure of merits

The calibration curve under the optimized conditions for uranium was obtained between 1.0-500.0 ng L^{-1} with a proper correlation coefficient of R^2=0.9991 for Y=0.0107+0.3346X calibration equation. The preconcentration factor (PF) of 500 and enrichment factor (EF) (calculated from the ratio of the slopes of the calibration curves obtained with and without pre-concentration) of 360 for uranium was determined, respectively. Precision, accuracy and repeatability were evaluated by intra-day and inter-day analyses. The intra-day precision was determined by performing five replicates extraction and determination of the analyte ions during a day. The inter-day precision was achieved by five replicates at five subsequent days. Intra-day and intra-day precision were found to be 1.13 and 1.38%, respectively. Finally, limit of detections (LOD) based on $3S_b/m$ (where S_b is the standard deviation of the blank signals and m is the slope of the calibration curve after extraction) was calculated as, 0.27 ng L^{-1} for the determination of uranium.

Table 3 shows the comparison of this work with different reported methods for determining uranium. As can be seen, this method has a wide linear dynamic range, good detection limit, and high preconcentration factor, making it suitable for the trace analysis of uranium with better or comparable precision as those presented by other methods.

Table 3: Comparison of current proposed method with other extraction methods for determining uranium.

Method	Detection system	PF[a] or EF[b]	LDR[c] (ng mL^{-1})	LOD[d] (ng mL^{-1})	RSD[e] (%)	Ref.
FA-HLLME	ICP-MS	500 [a] and 360 [b]	1.0–500.0	0.27	1.13	This work
SPE [f]	UV–Vis	100 [b]	200–3500	0.50	< 4	[26]
SPE	UV–Vis	143 [a]	100-15000	6.14	1.7	[27]
CPE [g]	ICP-OES	37 [b]	2.5–1240	1.0	6.1	[28]
SPE	ICP-MS	30[b]	–	0.063	2.3	[29]

[a] PF: Preconcentration factor.
[b] EF: Enrichment factor.
[c] LDR: Linear dynamic range.
[d] LOD: Limit of detection.
[e] RSD: Relative standard deviation.
[f] SPE: Solid phase extraction.
[g] CPE: Cloud point extraction.

Real samples

In order to measure uranium in real samples under optimal conditions, the extraction was performed 3 times without adding element and 3 times by adding 50 ng mL^{-1} uranium. Then, the recovery percentage of the real samples was collected from different water sources such as tap, qanat, river and spring water. The analyzed results for different water samples are presented in Table 4 which shows the efficiency of this method for uranium determination in water samples.

Table 4: Analytical results of a uranium sample under optimum conditions.

Water sample	Uranium concentration without standard addition (ng L^{-1})	Additional concentration (ng L^{-1})	Extracted concentration after standard addition (ng L^{-1})	Recovery (%)
Tap water	1.07 ± 0.18	50.0	50.48 ± 0.48	98.8
Underground water	8.59 ± 1.27	50.0	58. 27 ± 1.16	99.4
Water of Sea	173.07 ± 5.56	50.0	221.32 ± 2.23	87.9
Duct water	24.22 ± 0.68	50.0	75.16 ± 1.30	101.9
River water	38.72 ± 1.42	50.0	87.81 ± 2.73	98.2
Underground water	388.85 ± 1.86	50.0	436.77 ± 2.62	96.4
Underground water	373.29 ± 2.73	50.0	421.41 ± 3.02	96.3

CONCLUSION

In this study, a novel sensitive FA-HLLME for preconcentration of uranium in different water samples is proposed as prior step to their determination by ICP-MS. This method is simple, rapid, sensitive and cheap and has low toxicity, since only very small amounts of solvents are used instead of large organic solvents. This technique was successfully applied for microextraction of uranium with a recovery of 96.3 to 100.0% in real water samples such as seas, rivers, springs, qanat and drinking water. The advantage and novelty of this study is for coupling FA-HLLME with ICP-MS technique, therefore figure of merits were improved. Using this proposed method, the measurement of uranium with limit of detection of 0.27 ng L^{-1} was permitted, and without using this microextraction method, low LOD was not achieved. By ICP-MS micro-sampling technique, the consumption of the extractant phase was minimized and the enrichment factor of the microextraction technique was improved. The proposed method has good repeatability and reproducibility with low LODs, a high preconcentration factor and a wide linear range.

REFERENCES

1. N.T. Sanaa, M.A. Didi, D. Villemin, J. Radioanal. Nucl. Chem. 293, 789 (2012).
2. S. Regenspurg, D. Schild, T. Schafer, F. Huber, M.E. Malmstrom, Appl. Geochem. 24, 1617 (2009).
3. G.R. Najem, L.K. Voyce, Am. J. Public. Health 80, 478 (1990).
4. C.M. Amakom, N.N. Jibiri, Int. J. Phys. Sci. 5, 1009 (2010).
5. S. Bachmaf, B.J. Merkel, Environ. Earth. Sci. 63, 925 (2011).
6. A. Takahashi, Y. Ueki, S. Igarashi, Anal. Chim. Acta 387, 71 (1999).
7. M.G. Demidova, A.I. Saprykin, J. Anal. Chem. 59, 45 (2004).
8. M. Mlakar, Anal. Chim. Acta 276, 367 (1993).
9. R. Djogic, M. Branica, Anal. Chim. Acta 305, 159 (1995).
10. H. Bem, D.E. Ryan, Anal. Chim. Acta 166, 189 (1985).
11. K.B. Hong, K.W. Jung, K.H. Jung, Talanta 36, 1095 (1989).
12. G.I. Romanovskaya, V.I. Pogonin, A.K. Chibisov, Talanta 34, 207 (1987).
13. C. Moulin, C. Beaucaire, P. Decambox, P. Mauchien, Anal. Chim. Acta 238, 291 (1990).

14. M. Rozmaric, A.G. Ivsic, Z. Grahek, Talanta 80, 352 (2009).
15. M.A. Jeannot, A. Przyjazny, J.M. Kokosac, J. Chromatogr. A 1217, 2326 (2010).
16. A. Niazi, S. Habibi, M. Ramezani, J. Chil. Chem. Soc. 58, 1899 (2013).
17. S.A.M. Fathi, M.R. Yaftian, J. Colloid Inter. Sci. 334, 167 (2009).
18. K.E. Rasmussen, S.P. Bjergaard, Trends Anal. Chem. 23, 1 (2004).
19- Sh. Dadfarnia, A.M. Haji Shabani, Anal. Chim. Acta 658, 107 (2010).
20. S. Kinaree, S. Chanthai, Chem. Papers 68, 342 (2014).
21. M.H. Hosseini, M. Rezaee, S. Akbarian, F. Mizani, M.R. Pourjavid, M. Arabieh, Anal. Chim. Acta 762, 54 (2013).
22. M.H. Hosseini, M. Rezaee, H.A. Mashayekhi, S. Akbarian, F. Mizani, M.R. Pourjavid, J. Chromatogr. A 1265, 52 (2012).
23. M.H. Hosseini, P. Asaadi, M. Rezaee, M. Rezaei, M.R. Pourjavid, M. Arabieh, A.A. Abhari, Chromatographia 76, 1779 (2013).
24. J. Hassan, A. Farahani, M. Shamsipur, F. Damerchili, J. Hazard. Mater. 184, 869 (2012).
25. A. Niazi, N. Khorshidi, P. Ghaemmaghami, Spectrochim. Acta Part A 135, 69 (2015).
26. J. Ghasemi, E. Zolfonoun, Talanta 80, 1191 (2010).
27. V.K. Jain, R.A. Pandya, S.G. Pillai, P.S. Shrivastav, Talanta 70, 257 (2006).
28. Sh. Shariati, Y. Yamini, M. Khalili Zanjani, J. Hazard. Mater. 156, 583 (2008).
29. F.A. Aydin, M. Soylak, Talanta 72, 187 (2007) 187.