Highly sensitive and selective determination of uranium in natural waters through a novel solidified floating organic drop microextraction method coupled to spectrophotometric determination

Ali Reza Ghiasvand*, Nahid Heidari, Payman Hashemi
Department of Chemistry, Lorestan University, Khoramabad, Iran

Addresses:

A.R. Ghiasvand:

Postal Address: Department of Chemistry, Lorestan University, 5th km Khoramabad-Tehran

Hwy, Khoramabad, Iran; Postal Code: 67138-17133, P.O. Box: 465

Tel.-Fax: +98 661 6200610-12

E-mail: a_ghiasvand@yahoo.com

N. Haydari:

E-mail: nheidari44@yahoo.com

P. Hashemi:

E-mail: payman_hashemi@yahoo.com

**Corresponding Author: E-mail:* a_ghiasvand@yahoo.com*; Tel-Fax: + 98 661 6200610-12.*

Abstract

Ultra trace amounts of uranyl ions was extracted using a reliable, simple and selective solidified floating organic drop microextraction (SFODME) method and determined by UV-Vis spectrophotometry. Di-2-ethylhexylphosphoric acid (HDEHP) was applied as complexing ligand during the microextraction process and Arsenazo III (AIII) was used as the chromogenic reagent through spectrophotometric determination. The effects of the important experimental parameters on UO_2-AIII complex formation and color development were studied. Other important experimental parameters affected microextraction recovery, such as; type and volume of extracting organic solvent, acid concentration of sample solution, ligand concentration, stirring rate, extraction time and temperature, and salt addition effect were also evaluated and optimized. Under the optimized conditions a linear response was obtained over the range of 0.8-75 ng mL^{-1} for uranyl ions. The interfering effect of some foreign ions on extraction and determination of uranyl ions were also investigated. Limit of detection, relative standard deviation and enrichment factor of the proposed SFODME-UV method were obtained as 0.1 ng mL^{-1}, 3.7% and 125 for uranyl ions, respectively. The proposed method was applied successfully for the extraction and determination of uranyl ions in natural water samples. Good agreement was observed between the results of proposed SFODME method and those reported by official standard method.

Keywords: Uranyl ion; Solidified floating organic drop microextraction (SFODME); Di-2-ethylhexylphosphoric acid (HDEHP); Arsenazo III**;** UV-Vis spectrophotometry.

1. Introduction

Uranium is known to have both chemical and radioactive toxicity for human body. Its compounds are carcinogenic and have irreversible effects on some tissues such as kidney [1, 2]. Due to elevated levels of uranyl ions in natural waters and also require proper storage and disposal of uranium nuclear fuel wastes, its extraction and determinations techniques need to be improved. In recent years several techniques have been used to extract and measure uranyl ions from aqueous samples, including solvent extraction (SE) [3], ultrafiltration [4] solid phase extraction (SPE) [5-8], supercritical fluid extraction (SFE) [9], cloud-point extraction (CPE) [10-

12], homogeneous liquid-liquid extraction (HLLE) [13], dispersive liquid-liquid microextraction (DLLME) [14] and membrane methods consisting of bulk liquid membrane (BLM) [15] emulsion liquid membrane (ELM) [16] and supported liquid membrane (SLM) [17]. However, there are still difficulties due to the increase of uranium in natural waters. So, development of reliable, simple, low cost and practical methods for the determination of uranyl ions in water samples is still of paramount importance. Neutron activation analysis (NAA) [18], energy dispersive X-ray fluorescence (ED-XRF) [19], inductively coupled mass spectrometry (ICP-MS) [20] and radiochemical methods such as alpha spectrometry [21], gamma spectrometry [22], and liquid scintillation counting [23], are suitable for sensitive determination of uranyl ions. But these methods are expensive and are available mostly in equipped and specialized laboratories [24]. However, spectrophotometric methods, provided sufficient sensitivity, are cost-effective, common and easiest ways for the determination of uranyl ions [25,26]. Several organic and inorganic reagents have been used for the spectrophotometric determination of uranyl ions, between them dibenzoylmethane (DBM) and Arsenazo III (AIII) have the ability to measure very low concentrations of uranyl ions selectively [27,28]. However, AIII is the most sensitive reagent for the spectrophotometric determination of uranyl ions [29,30].

Due to problems associated to classical extraction methods, liquid and solid-phase microextraction procedures were developed to eliminate or minimize these drawbacks. Each of these new microextraction methods also has limitations and disadvantages. Solidified floating organic drop microextraction (SFODME) method is a miniaturized form of liquid-liquid extraction (LLE), which was started in 2007, to be used as a proper alternative to other microextraction procedures [31,32]. In this method, a microdroplet of a proper organic solvent, with melting point close to the room temperature, is floated on surface of the aqueous sample solution, while being agitated. After the completion of the extraction, the aqueous sample is cooled until to solidify the organic drop. Then the solidified organic microdroplet is transferred into a conical micro-vial, and allows melting in the room temperature. Finally, the analyte concentrated into the organic microdroplet is determined by introducing it to a proper analytical instrument.

SFODME coupled to different analytical instruments, specially UV-Vis spectrophotometry [33,34], flame atomic absorption spectrometry (FAAS) [35], electrothermal atomic absorption spectrometry (ET-FAAS) [36], high performance liquid chromatography (HPLC) [37], and gas

chromatography (GC) [38], has been applied for the extraction of organic [33,36,37,39-42] and inorganic analytes [35,38,43-54].

In this research a simple, sensitive and reliable SFODME method was established for selective preconcentration of uranyl ions using HDEHP followed by UV-Vis spectrophotometric determination using AIII. To the best of our knowledge, there has been no report on application of HDEHP, as a commercial low price and selective extracting reagent for the extraction of uranyl ions through SFODME method coupled with spectrophotometric determination.

2. Experimental

2.1. Materials

Organic solvents of 1-undecanol (98%), 1-dodecanol (98%), 2-dodecanol (95%), and n-hexadecane (98%) were purchased from Merck Chemical Co (Darmstadt, Germany). Reagent grade methanol, ethanol, sodium chloride, sodium nitrate and high purity nitric acid (HNO_3), hydrochloric acid (HCl), and perchloric acid ($HClO_4$) were supplied by Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland) companies. Doubly distilled water was used throughout. Di-2-ethylhexyl phosphoric acid (HDEHP) was obtained from Merck (97% pure). Analar grade disodium salt of Arsenazo III (1,8-dihydroxy-2,7-bis(2-arsonophenylazo) naphthalene-3,6-disulphonic acid) was obtained from Merck. A 0.2% (w/v) stock solution of AIII was prepared by dissolving 0.2 g of its disodium salt in 100 mL methanol. Analytical-grade uranyl nitrate supplied by Merck was of the highest purity available and was dried in a vacuum over P2O5. A stock solution of uranyl ions (1000 μg mL^{-1}) was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in 0.5 M HNO_3. Working solutions of uranyl ions were prepared daily by proper dilution of its stock with double distilled water.

2.2. Instruments

A double-beam spectrophotometer (UV-160, Shimadzu, Kyoto, Japan) was used for absorbance measurements. A totally glass Fi-stream double distiller (Fisons Scientific Apparatus, Loughborough, England) was applied for preparation of doubly distilled water. Weight measurements were done using a Shimadzu AX-120 digital balance (Shimadzu, Japan). 20 mL extraction vials obtained from Supelco were used for the SFODME experiments. Stirring of solutions was carried out on a Heidolph MR 3001K heater magnetic-stirrer (Kelheim, Germany)

using a 8 mm×1.5 mm PTFE coated stirring bar. A 100 μL microsyringe (Hamilton Bonaduz AG, Switzerland) was employed for the placing of the HDEHP solution on the top-center surface of the sample solution. A stainless steel mini-spatula was applied to transfer of the solidified organic drop. For the easily clean removing of the solidified organic drop (SFO), the pan of the mini-spatula was slightly tilted, such a tablespoon, and a hole was created on the center of it.

2.3. Methods

A 15 mL portion of sample solution (0.1 M HClO$_4$) containing 50 ng mL^{-1} of uranyl ion was placed into an extraction vial. Using a 100 μL microsyringe, 50 μL of HDEHP solution (5% w/v in 1-dodecanol) was slightly placed on the top-center surface of the sample solution. The cap of the extraction vial was closed and it was placed in a water bath (35 ∘C) and stirred at 900 rpm. After 40 min stirring for the equilibration, the extraction vial was immersed into an ice-bath for 5 min. The solidified organic drop was then transferred to a 2 mL vial using mini-spatula and mixed with 500 μL of AIII solution (0.2% in methanol) as chromogenic reagent. After 10 min to stabilize the color, the absorbance of the solution was recorded at 620 nm (λ_{max}) against a reagent blank. The concentration of uranyl ion was then determined using an external calibration curve (0.1-10 μg mL^{-1}; R^2=0.9993).

3. Result and discussion

3.1. The study of important parameters affected the uranyl-AIII complex formation

Arsenazo III (AIII) has different active sites and its complex formation with metal ions is strongly dependent to pH, ionic strength and its concentration [27,55]. Therefore, it is necessary to qualify its reaction with uranyl ions in conditions of the proposed SFODME procedure. So, some important experimental parameters affected the formation of UO$_2^{2+}$-AIII complex were investigated.
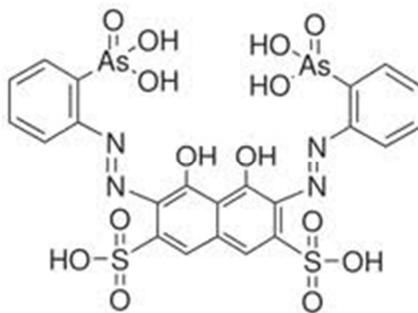
AIII: The simple planer structure of Arsenazo III (1,8-dihydroxy-2,7-bis(2-arsonophenylazo) naphthalene-3,6-disulphonic acid).

For the study of the complete complex formation's time, different concentrations of uranyl ion were mixed with 0.2% AIII solution (both dissolved in methanol) and diluted by methanol in a 10 mL volumetric flask. AIII solution in methanol creates a reddish purple color, while the UO_2^{2+}-AIII complex is blue. Then, during a 25 min period the absorbance of the UO_2^{2+}-AIII complex was recorded each 30 sec, against time. As seen from Fig. 1, the complete complex formation happens after 10 min.
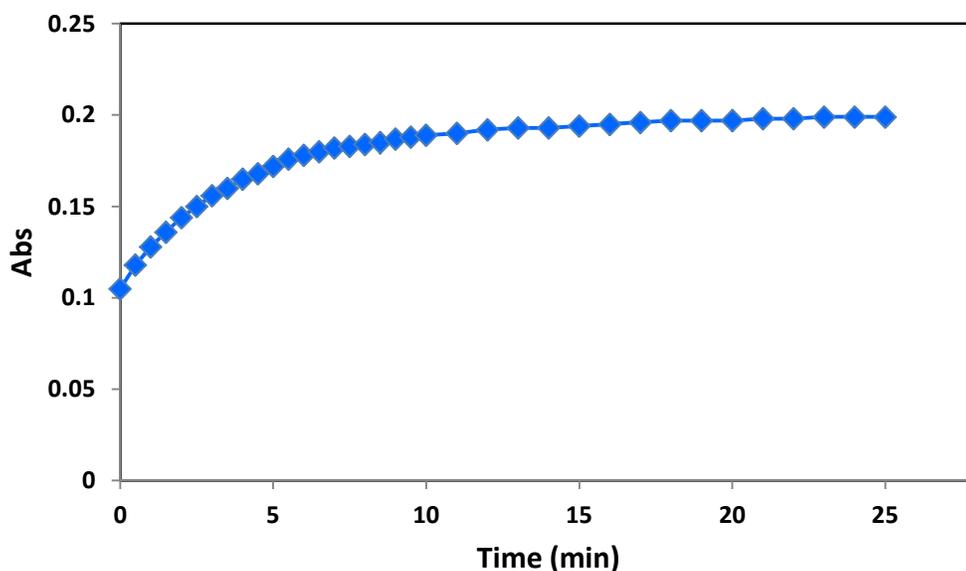
Fig. 1 The effect of time on UO_2^{2+}-AIII complex formation.

The effect of AIII concentration on the complex formation was also studied. For this purpose, different volumes of 0.2% AIII solution were added to constant concentration of uranyl ion in 10 mL volumetric flasks and the absorbance was recorded and plotted against AIII volume. The results showed that the maximum absorbance was achieved using 500 μL of 0.2% AIII solution. Using smaller volumes of AIII solution resulted in a green color, means other types of complexes have been formed between AIII and uranyl ion.

After investigation of the proper condition for UO_2^{2+}-AIII complex formation, an external standard calibration curve was demonstrated to determine uranyl ion concentrations in the future experiments (0.1-10 μg mL^{-1}; R^2=0.9993).

3.2. Extracting solvent type and volume

In SFODME, similar to other liquid microextraction methods, the extracting solvent should have low toxicity, volatility and water solubility in order to be safe, stable during the extraction period and have high extraction efficiency. On the other hand, its melting point must be near the ambient temperature, over the range of 10-30 ∘C, due to need for a solidified drop. It also must be soluble in the determination solvent and not interfere in the analytical quantification process of analyte. Limited numbers of extracting solvents have these specifications and are suitable for SFODME, summarized in Table 1. Hexadecane interfered with the spectrophotometric determination of uranyl ion by AIII. On the other hand, 1,10-dichlorodecane was not tested due to its toxicity and also its high density, relatively close to water. However, among the tested solvents 1-undecanol and 1-dodecanol presented the highest extraction efficiencies (1-dodecanol slightly more than1-undecanol). 2-Dodecanol is more expensive than 1-undecanol and 1-dodecanol, whereas didn't show suitable extraction efficiency. Thus, 1-dodecanol was chosen as the proper extracting solvent for more investigation.

Table 1 Generally used solvents in SFODME method as extracting solvents.

Extracting solvent	m.p. (∘C)	b.p. (∘C)	Density (g L^{-1})
1-Undecanol	13-15	243	0.83
1-Dodecanol	22-24	259	0.83
2-Dodecanol	17-18	249	0.80
n-Hexadecane	18	287	0.77
1,10-Dichlorodecane	15.6	167	0.99

The effect of volume of the extracting solvent was also studied. The results (Fig. 2) showed that EF increased with increasing of the solvent volume to 50 μL, due to increasing of the contacting surface between the organic extracting solvent and sample solution. The extraction efficiency slightly decreased when volume of the solvent increased greater than 50 μL. So, 50 μL of 1-dodecanol was selected as the optimal drop volume for the further experiments
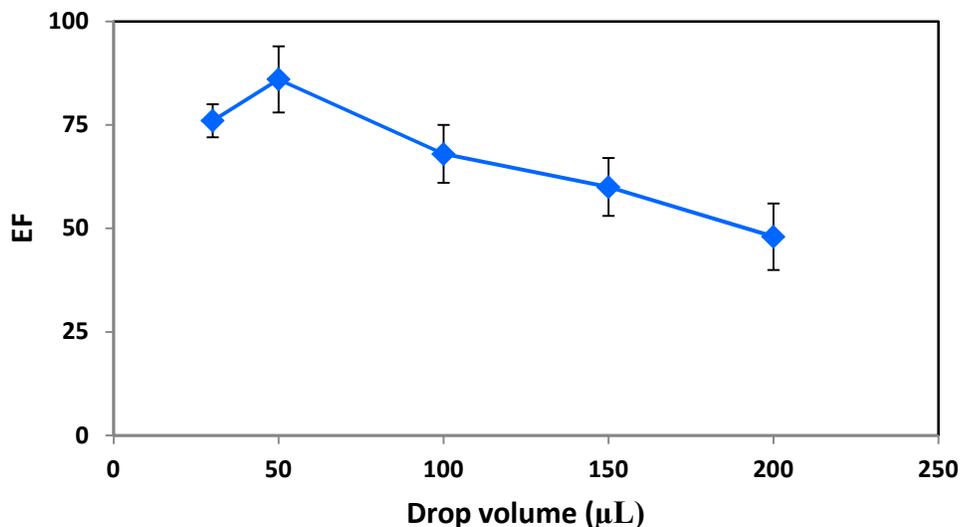
Fig. 2 The effect of drop volume on the enrichment factor (sample solution: 15 mL 0.1 M HClO$_4$ containing 50 ng mL^{-1} of uranium, extractant: 50 μL 5% w/v HDEHP solution in 1-dodecanol, stirring rate: 700 rpm, extraction time and temperature: 30 min and 30 ∘C, cooling time in ice-bath: 5 min).

3.3. Type and concentration of acid in sample solution

Organic phosphorus compounds possess high extractive properties and have frequently been used as reagents in extraction of rare-earth elements [27]. The extractive properties of the organophosphorus ligands depend on the number of ester oxygen atoms and the nature of substituents present in their structures. Usually, elements in their highest oxidation state (e.g., UO$_2{}^{2+}$ or U(VI)) yield the most extractable complexes with these ligands in the presence of inorganic acids such as nitric and hydrochloric acid [56]. So, the effect of the presence of different inorganic acids such as, HNO$_3$, HCl, and HClO$_4$, in the sample matrix, on the extraction of uranyl ion using HDEHP by the proposed SFODME method was investigated. The results are summarized in Fig. 3.
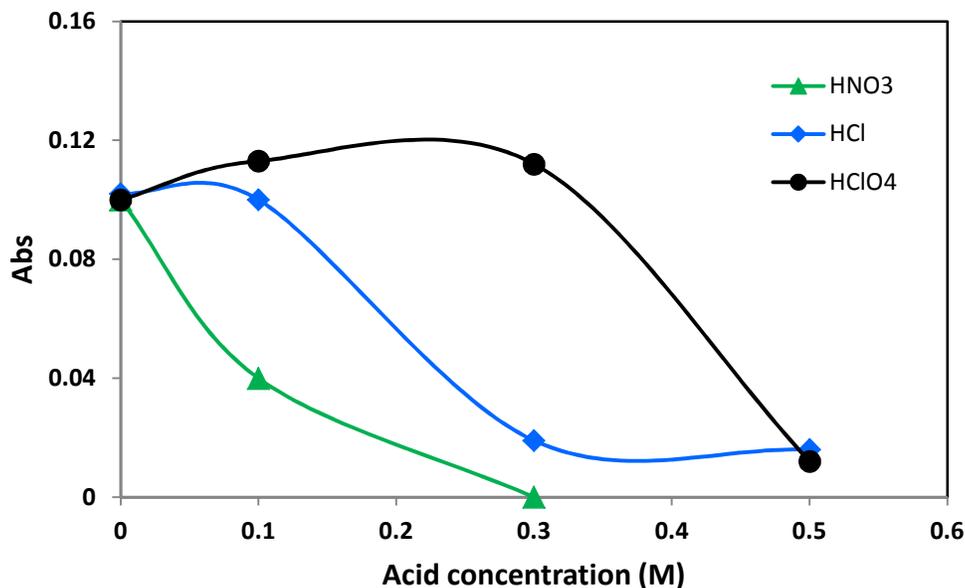
Fig. 3 The effect of different concentrations of HNO_3, HCl and $HClO_4$ on the SFODME of uranium (sample solution: 15 mL containing 50 ng mL^{-1} of uranium, extractant: 50 μL 5% w/v HDEHP solution in 1-dodecanol, stirring rate: 700 rpm, extraction time and temperature: 30 min and 30 ◦C, cooling time in ice-bath: 5 min).

From the results, it is clear that presence of HNO_3 and HCl diminish the extraction of uranyl ion using HDEHP. It was predictable because, di-2-ethylhexyl phosphoric acid (HDEHP) has itself acidic property. On the other hand, the improving effect of HNO_3 and HCl on the extraction of uranyl by organophosphorus compounds is generally due to incorporation of nitrate and chloride in the complex structure, as in the case of extraction of uranyl ions using tri-*n*-octylphosphine oxide (TOPO) [9,13,26]. TOPO-uranyl is a solvated salt complex [28] and so, nitrate or chloride can improve its formation by involving in the complex compartment. They can also incorporating in salting-out effect [9]. However, nitrate or chloride can't participate in complex formation of UO_2^{2+}-HDEHP, because it is chelating complex [57, 58] and doesn't affected by salting-out reagents. It may even be possible to nitrate or chloride ions to compete with HDEHP in binding with uranyl ion. However, $HClO_4$ showed the highest efficiency in the SFODME of uranyl ions using HDEHP, because chlorate ion has donating oxygen atoms which can participate in the complex formation and probably in the structure of UO_2^{2+}-HDEHP associate.

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The results showed that maximum absorbance is related to 0.1-0.3 M concentration of $HClO_4$, therefore 0.1 M of $HClO_4$ was applied as the sample matrix for the future experiments of SFODME of uranyl ions by the proposed method.

3.4. Ligand concentration

For the study of the effect of HDEHP concentration on the extraction of uranyl ions by the proposed SFODME method, different concentrations of HDEHP in the extracting solvent were carried out. The results showed that with increasing of HDEHP concentration to 4% (w/v), EF increases and then remains constant. Therefore, to ensure of complete complex formation between uranyl ion and HDEHP in higher concentrations of uranyl ion, 5% (w/v) of HDEHP was selected as the optimum amount of ligand for further studies.

3.5. Stirring rate

Making stress methods in sample solution, e.g. stirring, is a crucial parameter in many extraction methods for improving the extraction dynamics and to reducing the thermodynamic equilibration time, according to the convective-diffusive mass transfer theory [35, 43]. On the other hand, in SFODME method, very high stirring rates can cause spatter and damage the organic microdroplet, resulting in decrease in extraction efficiency. Hence, the effect of stirring rate on the extraction efficiency of uranyl ions using the proposed SFODME method was investigated. As is clear from the results (Fig. 4), EF increases slightly with increasing the stirring rate from 200 to 500 rpm, and then its slope rises when the stirring rate exceeded 500 rpm. Besides, the floating microdroplet could be sputtered into very small droplets in stirring rates greater than 900 rpm, which is difficult to collect and resulting in organic solvent loss and poor precisions. Hence, stirring rates greater than 900 rpm weren't examined. Accordingly, 900 rpm was selected as the suitable stirring rate for the sample solution.
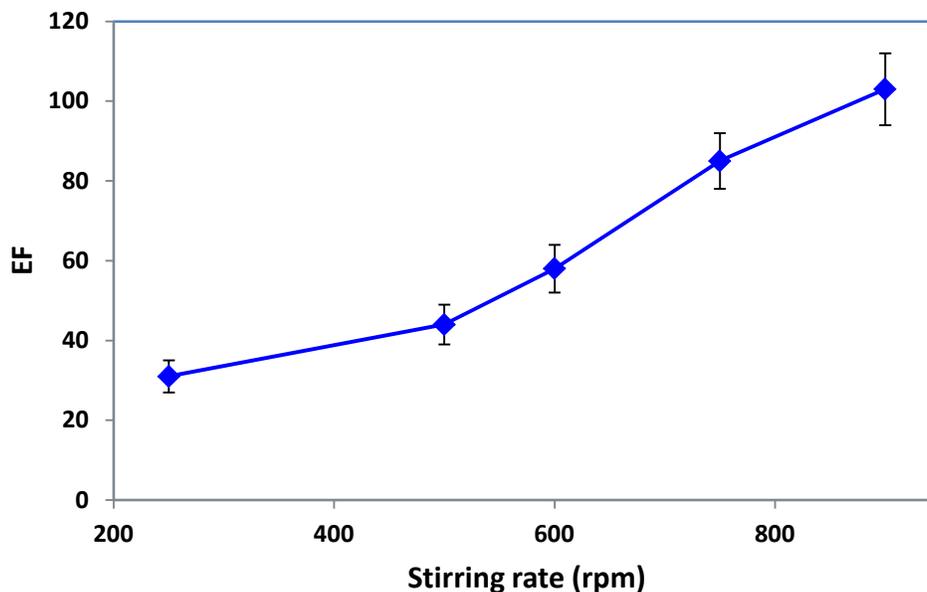
Fig. 4 The stirring rate effect on the extraction efficiency of uranium by the proposed SFODME method (sample solution: 15 mL 0.1 M HClO$_4$ containing 50 ng mL^{-1} of uranium, extractant: 50 µL of 5% w/v HDEHP solution in 1-dodecanol, extraction time and temperature: 30 min and 30 °C, cooling time in ice-bath: 5 min).

3.6. Extraction time

The extraction time of analyte is an important experimental parameter that has significant effects on the extraction efficiency. In SFODME it is mainly dependent on mass transfer rate of analyte from aqueous sample solution to the organic microdroplet. Thus, the effect of extraction time on the extraction of uranyl ions was studied over the range of 5-60 min under the optimal amounts of the other studied parameters. The results showed that EF increases by the increase in time up to 40 min and then remained constant. Thus, 40 min was chosen as the sufficient extraction time for the further studies.

3.7. Extraction temperature

The effect of temperature on the extraction of uranyl ions using the proposed SFODME procedures was also studied. For this purpose, the SFODME extraction vial was placed in a water bath and its temperature varied between 25-55 °C. It was clear from the results that EF increases by increasing of temperature up to 35 °C. However, further increase in temperature

cause a slight decrease in EF, which might be due to increase in solubility of organic solvent in aqueous sample solution at higher temperatures. Based on the results 35 ∘C was considered as the optimal extinction temperature for the further experiments.

3.8. Salting-out effect

To investigate of the influence of ionic strength on the performance of SFODME method of uranyl ions, various experiments were carried out by adding varying amount of NaCl and NaNO3 over the range of 0-3% (w/v), while other experimental parameters were kept constant. Based on the obtained results (Fig. 5), salt addition causes a slight decrease in extraction efficiency of analyte. Therefore, salt addition was not used in further experiments.
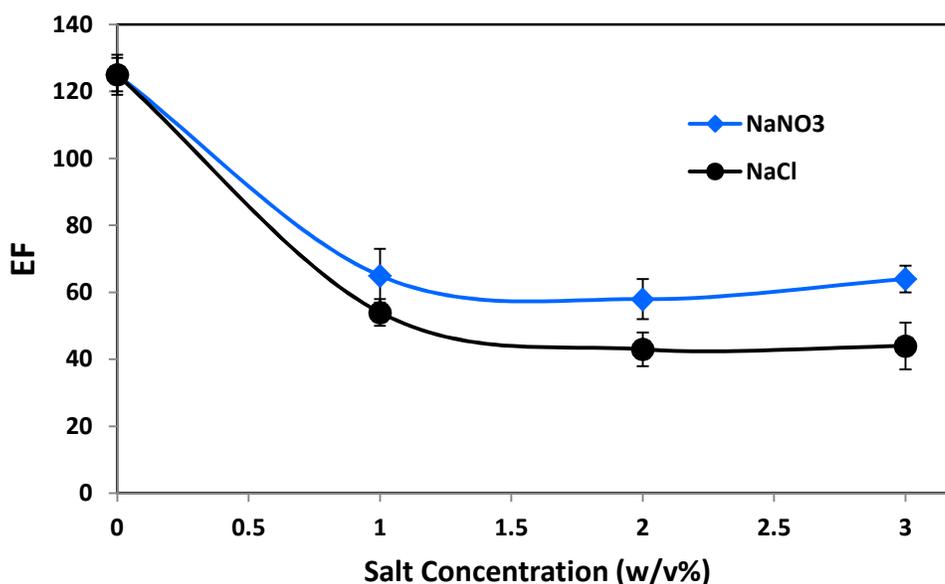
Fig. 5 The influence of ionic strength on the extraction recovery of uranium using proposed SFODME procedure (sample solution: 15 mL 0.1 M HClO$_4$ containing 50 ng mL^{-1} of uranium, extractant: 50 μL of 5% w/v HDEHP solution in 1-dodecanol, stirring rate: 900 rpm, extraction time and temperature: 40 min and 35 ∘C, cooling time in ice-bath: 5 min).

Finally, the optimum amounts of the examined experimental parameters were obtained as: sample solution; 15 mL 0.1 M HClO$_4$, extracting microdroplet; 50 μL of 5% w/v HDEHP

solution in 1-dodecanol, stirring rate; 900 rpm, extraction time; 40 min, extraction temperature; 35 ∘C..

3.9. Interference effect of foreign ions

In order to evaluate the reliability of the proposed SFODME method for the extraction and determination of uranyl ions in real matrices containing different ions, the influence of several added ions on the SFODME and determination of uranyl ions was studied. Twice of the standard deviation of measurements was considered as tolerable relative error. Table 2 shows a summary of the results. Most of the examined cations do not interfere with the extraction and determination of uranyl ions, and some of them are tolerated at very high levels. However, some of the species tried such as Fe^{3+}, Pb^{2+}, and Zr^{6+} interfere with the determination of uranyl ions. Zirconium reacts with Arsenazo-III in acidic medium. However, its complexation condition is relatively different from uranyl ion [27]. Fe(III) can also forms associate with Arsenazo-III. However, in the optimized conditions for uranyl-AIII complex formation, obtained from the published reports [27-30, 55], uranyl ion can forms more stable complex than Zr(VI) and Fe(III). However, these interferences were eliminated or reduced considerably in the presence of EDTA, because in acidic medium only uranyl ions form a stable associate with EDTA (Table 2).

Table 2 Tolerance limits of interfering ions in the determination of 50 ng mL^{-1} uranium.

Foreign ion	Tolerated ratio of foreign ion to uranium
Na^+, Cl^-, NO_3^-	100
K^+	100[a]
Mg^{2+}, SO_4^{2-}	15
Fe^{3+}	50[b]
Cu^{2+}	20
Ni^{2+}	100[a]
Zn^{2+}	10[a]

Ag^+	10^a
Pb^{2+}	10^b
Cr^{3+}	100
Hg^{2+}	100^a
Zr^{6+}	10^b

[a] Above of which was not tested.

[b] After application of 0.0035 M EDTA in sample solution as masking agent.

3.10. Analytical quantitative aspects

3.10.1. Linearity, limit of detection, repeatability, enrichment factor and extraction recovery

The analytical characteristics of the developed SFODME strategy including; linear dynamic range (LDR), limit of detection (LOD), and repeatability were obtained by processing standard solutions of uranyl ions under the optimal experimental conditions. A series of sample solutions spiked with varying concentrations of uranyl ion, over the range of 0.8- 75 ng mL^{-1}, exhibited a correlation coefficient of 0.998. The regression equation for the calibration curve was y=0.0803x+0.0668 (y: absorbance, x: concentration of uranyl ion). LOD of the method for the determination of U(VI) was determined as 3Sb/m (S: the standard deviation of the blank signals, m: the slope of calibration curve of the SFODME method) was 0.1 ng mL^{-1}. The relative standard deviation (RSD) was found as ±3.7% (n=6) for 50 ng mL^{-1} of uranyl ion. LDR can be extended by lowering the preconcentration factor, i.e. by lowering the sample volume or diluting of the extract depending on the analyte concentration in sample.

The enrichment factor (EF) was calculated as the ratio between concentrations of the analyte in the organic drop (C_{drop}) and in the aqueous sample solution (C_{aq}) [40], as follows:

$$EF = C_{drop}/C_{aq} \tag{1}$$

The extraction recovery (ER) was obtained as the percentage of total analyte (n_0) extracted into the organic drop (n_{drop}):

$$ER = (n_{drop}/n_0) \times 100 = (C_{drop} \times V_{drop})/(C_{aq} \times V_{aq})) \times 100 \tag{2}$$

$$ER = EF \times (V_{dropt}/V_{aq}) \times 100 \tag{3}$$

V_{drop} and V_{aq} are the volumes of the organic floated drop and sample solution, respectively. However, by conducting the developed SFODME method under the optimal experimental parameters EF and ER were obtained as 125 and 41%, respectively.

3.10.2. Analysis of real samples

To evaluate the accuracy and applicability of the proposed SFODME method to real samples, it was applied to the recovery and determination of uranyl ions from two water samples. A tap water sample (from Lorestan University) and a river water sample (from Bisheh waterfall located 65 km from Khoramabad) were analyzed using added-found procedure. No uranyl ion was detected in the real samples. Therefore, these real samples were spiked with the target analyte at the concentration of 50 ng mL^{-1}. The proposed SFODME method was also applied to extract and determine of uranyl ions contents in two water samples collected from two different springs around Gachin uranium mine near Bandar Abbass city. The results showed satisfactory agreement between the concentration obtained by the proposed SFODME method and those obtained by ICP-MS. The results summarized in Table 3 indicate that the developed method can be successfully applied for the determination of uranyl ions in real water samples.

Table 3 Extraction and determination of uranium in water samples using the proposed SFODME method.

Water sample	Uranium added (ng mL^{-1})	Uranium determined (ng mL^{-1})	
		SFODME method	ICP-MS[a]
Tap water (Lorestan University, Khoramabad)	50	49.2 (3.5)[b]	---
River water (Bisheh waterfall, Khoramabad)	50	48.5 (4.1)	---
Spring water 1(Gachin mine, Bandar Abbass)	0	65.2 (2.8)	63.7 (2.2)
Spring water 2(Gachin mine, Bandar Abbass)	0	52.8 (3.1)	51.4 (3.8)

[a] Results reported by Applied Geological Research Center of Geological Survey of Iran

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[b] RSD of three replicate experiments.

4. Conclusion

In this research, a sensitive, effective and reliable method for the preconcentration and determination of uranyl ions in natural water samples was developed. UV-Vis spectrophotometry, as a simple, low coast and commonly used method, was applied for detection of uranyl ions. The developed SFODME-UV method largely minimizes consumption of the toxic organic solvents and greatly increases the sensitivity for the determination of uranyl ions. Simplicity of operation, sensitivity, selectivity, low sample volume, low cost and high enrichment factor are some advantages of the proposed strategy relative to the others reported methods (Table 4) in the literature [5,7,11,26,34,59,60]. The proposed SFODME-UV method was successfully conducted for the recovery and determination of uranyl ions in natural water samples.

Table 4 Comparison of the proposed SFODME-UV method to some preconcentration procedures for the extraction and determination of uranium.

Method	LOD (ng mL^{-1})	RSD	EF	Ref
SFODME-UV	0.1	3.7	125	Present work
SPE-UV	0.5	4	---	[34]
SPE-UV	2.7	<10	100	[5]
CPE-UV (Triton X-114)	0.5	2.3	---	[59]
SPE-ICP-AES	6.14	---	143	[60]
SPE-DPP	20	1.6	100	[7]
SPE-UV	0.1	3	---	[26]
CPE-ICP-OES	1	6.1	43.7	[11]

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Graphical Abstract

1

50 μL of 1-dodecanol (5% w/v HDEHP)

15 mL sample solution (0.1 M $HClO_4$) containing U(VI) and a magnet

2

Stirred for 40 min in water bath (35 °C) at 900 rpm

3

5 min in ice-bath and then removing the solid drop by spatula

4

Transfer to 2 mL vial+500 μL of 0.2% in methanol. After 10 min record Abs at 620 nm (λ_{max})