Supramolecular solvent microextraction of uranium at trace levels from water and soil samples

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Abstract: A supramolecular solvent microextraction procedure was established for the separation/preconcentration of uranium(VI) (U(VI)) prior to its determination by UV-Vis spectrophotometry. 1-(2-Pyridylazo)-2-naphthol (PAN) was used to form a red chelate (U-PAN) with U(VI) at pH 10. U-PAN was extracted by undecanol in tetrahydrofuran. All the parameters that affect extraction efficiency like solution pH, amount of ligand, type and volume of supramolecular solvent, sample volume, and diverse ion effect were optimized. The preconcentration factor was 17. The detection limit was 0.31 μg L^{-1}. The method was validated using GBW07424 (GSS-10 certified reference material). Microextraction was also applied to water and soil samples.

Key words: Supramolecular solvent, microextraction, spectrophotometric determination, uranium, 1-(2-pyridylazo)-2-naphthol

1. Introduction

Due to its toxicological chemical and radioactive nature the determination of uranium in water and other environmental sample is a subject of immense interest among scientists.[1−3] Uranium is also one of the most important energy sources because it is used as nuclear fuel in nuclear power plants. Pitchblende, monazite sand, and seawater are the main sources of U(VI).[2,4] The maximum tolerable level of U(VI) stated by the WHO in drinking water is 9 μg L^{-1}, while the concentration of U(VI) in seawater is approximately 3 μg L^{-1}.[3] Therefore, the performances of different nuclear processes can be evaluated by determining U(VI) at trace level in water and other environmental samples.[5,6]

Highly sophisticated analytical techniques like inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry cannot be used directly for the determination of U(VI) without preliminary treatment of the samples, because of low sensitivity, lack of selectivity, high interferences of the complex matrix, and low precision and accuracy.[3,7] The other most important factor is that these analytical techniques are expensive and laboratory technicians with high expertise are required to conduct them. Therefore, due to their simplicity, low cost, and high accuracy, UV-Vis spectrophotometric methods of determination are still preferable and widely used for determination of U(VI).[2,8−10] For U(VI) to be determined by UV-Vis spectrophotometry, a selective chelating agent is necessary that forms a stable chelate with U(VI) and has maximum absorption ($\lambda_{\max}$) in the UV-Vis region. A variety of chromogenic reagents

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like anthranilic acid and rhodamine 6G,[11] pyrocatechol,[12] 2-(5-bromo-2-pyridylazo-5-diethylaminophenol),[13] dibenzoylmethane (DBM),[14] 2-(2-benzothiazolylazo)-3-hydroxyphenol (BTAHP),[15] and thiocyanate[16] have been used for the spectrophotometric determination of U(VI).

However, UV-Vis spectrophotometry cannot be used successfully without preliminary chemical separations due to spectral interference of the complex matrix nature for the determination of the analytes. These problems can be overcome by using a selective preconcentration and separation step prior to its determination.

Various preconcentration analytical techniques such as solvent extraction,[17] solid-phase extraction (SPE),[18] cloud-point extraction (CPE),[19] and dispersive liquid–liquid microextraction (DLLME)[20] have been employed for the extraction and measurement of U(VI) from aqueous and soil samples.[21] Among all these preconcentration techniques, liquid–liquid microextraction is superior to the others because it has certain advantages such as being faster and cheaper and there is no need for special synthesis and characterization as in SPE.[22] Various microextraction techniques like DLLME,[23] headspace liquid microextraction,[24] and the combination of LLE and LSE have been employed for preconcentration of heavy metals.[25] Soylak et al. have proposed a microextraction procedure for the separation/preconcentration of uranium as PAN chelates in different matrices using switchable solvent.[26]

Supramolecular solvent (Ss) has greatly attracted the attention of scientists in the field of microextraction of organic and inorganic compounds due to its special tendency towards (e.g., hydrophobic and hydrogen bonding) these compounds.[27] Supramolecular solvent-based liquid–liquid microextraction (SsLLME) is an environmentally friendly, fast, cost effective, and highly efficient extraction technique as compared to traditional liquid–liquid microextraction techniques.[28−30] According to our literature survey, the supramolecular solvent microextraction of U(VI)-PAN chelates is firstly used for the separation/preconcentration of uranium at trace levels from soil and water samples.

In the present work, SsLLME was carried out for U(VI) with 1-(2-pyridylazo)-2-naphthol (PAN), which was used as chelating agent that forms a red chelate (U-PAN) in basic media.[31] The measurement of uranium concentration in the supramolecular solvent phase as U-PAN chelate was measured by a UV-Vis double beam spectrophotometer at 580 nm.

2. Results and discussion

2.1. Effect of pH

pH is one of the most important parameters that affect the % recovery and also the formation of U-PAN complex during SsLLME. Uranium(VI) forms a complex with PAN at basic pH.[31,32] Therefore, the effect of pH on the formation of U-PAN complex and the percent recoveries were studied at a pH range of 7–13 (Figure 1). The recoveries of uranium increased with increasing pH from 7 to 10 and reached quantitative values at the pH range of 10–11. These results are in agreement with the literature.[26,31,32] Subsequent optimization studies were carried out at pH 10.

2.2. Effect of amount of PAN

PAN is a complexing reagent that forms a stable complex with U(VI) in basic media.[31,32] Therefore, the amount of PAN has a great influence on the percent recovery of U(VI). In order to investigate the effect of the amount of PAN on percent recoveries of U(VI), microextraction studies were carried out using different amounts of PAN
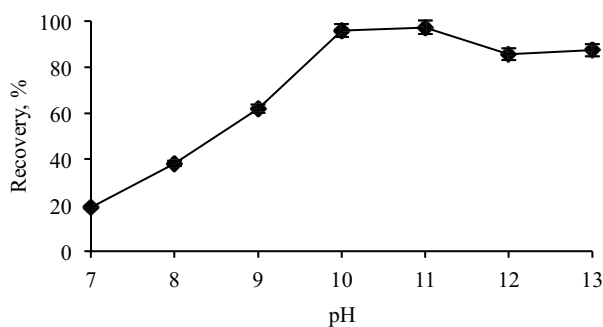
Figure 1. Effect of pH on formation of U-PAN complex and % recovery of U(VI) (N = 3).

in the range of 0.1–0.8 mg (Table 1). The results indicate that the percent recovery of U(VI) increases with an increase in the amount of PAN and reaches its maximum value at 0.4 mg of reagent amount. It can be explained that maximum complex formation was obtained when 0.4 mg of ligand was added. A further increase in the amount of PAN had no significant effect on the percent recoveries of U(VI) (Table 1). Therefore, 0.4 mg of PAN was used in the subsequent microextraction studies of U(VI).

Table 1. Effect of ligand amounts on % recoveries of U(VI), pH: 10, volume of the sample solution: 15 mL, final volume: 1.5 mL (N = 3).

Amount of ligand (mg)	Recovery, %
0.1	19 ± 3^a
0.2	29 ± 6
0.3	54 ± 4
0.4	96 ± 3
0.5	99 ± 3
0.6	97 ± 2
0.7	97 ± 2
0.8	99 ± 2

[a]Mean ± standard deviation.

2.3. Effect of type of supramolecular solvent

The type of extraction solvent has a significant effect on the extraction of U-PAN complex. Therefore, to improve the extraction of U-PAN, selection of the best supramolecular solvent is essential. The supramolecular solvent should have low solubility in water, high dissolubility for the U-PAN complex, and low solubility for the interfering agents present in the sample matrix.[33] Based on these facts, three supramolecular solvents, namely 1-decanol-THF, undecanol-THF, and decanoic acid-THF, were used and the extraction efficiencies of the three supramolecular solvents (Ss) are compared in Table 2. The recoveries with undecanol-THF and decanol-THF were the same. Because undecanol-THF has stronger dissolving ability for the U-PAN complex than 1-decanol-THF, undecanol-THF was used as the extraction solution in all experiments.

2.4. Effect of volume ratio of undecanol and THF

The volume of undecanol was investigated in the range of 0.1 to 0.7 mL, in order to achieve the highest % recovery of U(VI) while keeping the volume of THF constant. As can be seen from Figure 2, an increase in volume of undecanol from 0.1 to 0.4 mL resulted in an increase in % recoveries of U(VI), and no significant change in the

Table 2. Effect of type of extraction solution on % recoveries of U(VI), pH: 10, volume of the sample solution: 15 mL, final volume: 1.5 mL, volume of THF: 0.4 mL (N = 3).

Extraction solution	Volume (mL)	Recovery, %
Decanol–THF	0.2	92 ± 3^a
Undecanol–THF	0.2	95 ± 4
Decanoic acid–THF	0.2	< 10

^{a}Mean $\pm$ standard deviation.

percent recovery of U(VI) occurred when the volume of undecanol increased beyond 0.4 mL. Therefore, 0.4 mL of undecanol, which was the optimized volume of undecanol, was used in further microextraction studies.
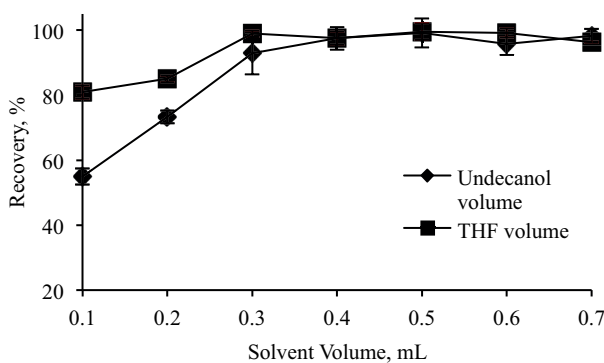

Figure 2. Effect of volume of undecanol and THF on % recovery of U(VI) (N = 3).

After optimization of the volume of undecanol, the volume of tetrahydrofuran (THF) was also optimized by carrying out microextraction studies of U(VI) at different volumes of THF in the range of 0.1–0.7 mL (Figure 2) while keeping the volume of undecanol constant. A gradual increase in % recovery of U(VI) occurred in the volume range of 0.1–0.3 mL and reached its maximum value at 0.3 mL volume of THF. Therefore, 0.3 mL was the most suitable volume of THF for the microextraction studies of U(VI) because further increases in volume had an insignificant effect on % recoveries. The results indicate that improved microextraction efficiency was obtained using 0.3 mL of THF.

2.5. Effect of sample volume

In order to obtain a high preconcentration factor, the proposed microextraction method was carried out with different sample volumes (5–30 mL) while keeping the other parameters constant. The results obtained indicate that the extraction of U(VI) was not altered by a sample volume below 25 mL. Hence, a preconcentration factor of 17 can be achieved by using 25 mL of sample and 1.5 mL final volume.

2.6. Effects of concomitants

In the determination of analyte elements using instrumental techniques, the effect of matrix components should be determined by preconcentration/separation techniques.[34−45] Some transition metal ions form a stable complex with PAN and also with the salt components in real samples, being a possible source of interference with the proposed method for U(VI). Therefore, the effect of common coexisting ions on the LLME of U(VI)

was investigated. The effects of the investigated matrix ions were analyzed separately. The obtained results for % recovery are given in Table 3 and show that the presence of a higher concentration of these interfering ions had no effect on % recovery of U(VI). This shows that the method is highly selective and free of interferences. The tolerable levels of the transition elements including Ni(II), Co(II), and Cu(II) using the presented method were approximately 10 mg/L level. Higher levels of these elements affected the method. These were not a problem for our study as the levels of transition elements were at μg/L level.

Table 3. Interference effect of some matrix ions on percent recoveries of U(VI), pH: 10, volume of sample: 15 mL, final volume: 1.5 mL, amount of PAN: 0.4 mg, volume of THF: 0.4 mL, volume of extraction solution: 0.4 mL (N = 3).

Matrix ion	Added as	Concentration, mg L^{-1}	Recovery, %
Na$^+$	NaNO$_3$	2500	96 ± 3^a
K$^+$	KCl	2500	94 ± 6
Al^{3+}	Al(NO$_3$)$_3$.9H$_2$O	250	103 ± 4
Mg^{2+}	Mg(NO$_3$)$_2$.6H2O	500	98 ± 3
Fe^{3+}	Fe(NO$_3$)$_3$.9H$_2$O	10	94 ± 3
Zn^{2+}	Zn(NO$_3$)$_2$.6H2O	10	95 ± 6
Co^{2+}	Co(NO$_3$)$_2$.6H$_2$O	10	96 ± 6
Cu^{2+}	Cu(NO$_3$)$_2$.3H$_2$O	10	95 ± 4
Ni^{2+}	Ni(NO$_3$)$_2$.6H$_2$O	10	98 ± 6
Cd^{2+}	Cd(NO$_3$)$_2$.6H$_2$O	10	97 ± 5
Cl$^-$	KCl	2500	94 ± 6
SO$_4^{2-}$	Na$_2$SO$_4$	250	95 ± 0

^{a}Mean ± standard deviation.

2.7. Analytical feature of the proposed method

Various analytical parameters like limit of detection (LOD), relative standard deviation (RSD), enhancement factor (EF), preconcentration factor (PF), and consumptive index (CIn) were explored under the optimized experimental conditions. The LOD was 0.31 μg L^{-1}, which was calculated as the ratio of three times the standard deviation of the ten blank absorbances to the slope of the regression equation, where the LOQ was found as 1.05 μg L^{-1}, which was calculated as the ratio of ten times the standard deviation of the ten blank solutions to the slope of the regression equation. The average RSD was calculated for five repeated determinations of 0.46 μg mL^{-1} of U(VI) and was found as 0.2%. The straight line equation, based on the relationship between the absorbance (A) of U(VI) in the UV-Vis spectrophotometry measurement and the concentration of U(VI) (C), was A = 0.0681 + 0.112 C with a correlation coefficient of R^2 = 0.982. The enhancement factor (EF) and preconcentration factor (PF) were 16 and 17, respectively. The EF was calculated by using the ratio of the U(VI) concentration in the extraction phase to the initial concentration of U(VI) in the sample solution, while the PF was calculated as the ratio of the model solution to the final volume. The CIn, which was calculated as the ratio of the sample volume (in milliliters) to the enhancement factor, was 0.7.

2.8. Validation of the proposed method

Due to the toxicological effect of U(VI) in humans and other living organisms, and also because it is a source of energy in nuclear power plants, the proposed Ss-LLME method was applied to certified reference material, real water, and soil samples. In order to check accuracy, the describe method was applied to a soil certified

reference material (GBW07424 (GSS-10) sample. The quantitative % recoveries of U(VI) in Table 4 show that the method was accurate and valid for the determination of U(VI) at trace level.

Table 4. Application of the method to certified reference material, pH: 10, volume of the sample: 15 mL, final volume: 1.5 mL, volume of THF: 0.3 mL, volume of extraction solution: 0.4 mL (N = 3).

Certified reference material	Certified value, μg g^{-1}	Found value, μg g^{-1}	Recovery, %
(GBW07424 GSS-10)	0.9	0.92 ± 0.04^a	103

^{a}Mean $\pm$ standard deviation.

The method was also applied to real water samples (tap water, seawater) and a soil sample for addition and recoveries. The results are given in Table 5. High percentage recoveries (96%–105%) show that the proposed method can be successfully applied to real samples of complex nature.

Table 5. Application of the proposed method to real samples for addition recoveries, pH: 10, volume of the sample: 15 mL, final volume: 1.5 mL, volume of THF: 0.3 mL, volume of extraction solution: 0.4 mL (N = 3).

Sample	Added, μg	Found, μg	Recovery, %
	0.00	BDL	-
Tap water	1.00	0.97	98 ± 4^a
	2.00	1.93	97 ± 5
	0.00	0.063	-
Seawater	1.00	0.99	99 ± 3
	2.00	1.98	99 ± 5
	0.00	0.06	-
Soil	1.00	1.05	105 ± 4
	2.00	1.86	93 ± 7

^{a}Mean $\pm$ standard deviation.
^{b}BDL = Below the detection limit.

A novel SsLLME method for preconcentration of U(VI) for water and soil samples was established prior to its determination by UV-Vis spectrophotometry. The proposed method was highly sensitive with a low limit of detection value of 0.73 μg L^{-1}, was reproducible with relative standard deviation value of 0.2%, was selective as it is free of interferences, and was cost effective because there is no need for special laboratory equipment.

The described SsLLME method was compared with other preconcentration methods for U(VI) in the literature (Table 6). The method was comparable or superior in performance to the other preconcentration methods for U(VI) in terms of LOD. The proposed method was more sensitive than the other preconcentration methods regarding LOD. The method was successfully applied to certified reference material and real samples (water and soil). The results obtained indicate that the method was highly accurate and can be applied to samples with a complex matrix nature without significant interferences.

3. Experimental

3.1. Instruments

A Hitachi UH 5300 spectrophotometer with a quartz microcell with a path length of 10 mm and a volume of 700 μL was used for absorbance measurements. pH was adjusted using a pH meter with a Nel pH 900 (Ankara, Turkey) model glass electrode. Phase separation was enhanced by centrifuge with centrifugal vials (Shanghai

Surgical Instrument Factory, 80-2, Shanghai, China). A vortex mixer (Wiggen Hauser, Malaysia) was used for thorough mixing of the solutions.

Table 6. Comparison of the developed method with other preconcentration methods.

Method	Analysis	LOD (μg L^{-1})	Ref.
Solid-phase extraction	ICP-MS	4.5	[1]
Solid-phase extraction	UV-Vis	1.9	[2]
Solid-phase extraction	ICP-OES	0.34	[3]
Solid-phase extraction	UV-Vis	0.8	[33]
Liquid-phase microextraction	UV-Vis	0.87	[46]
Solid-phase extraction	UV-Vis	2	[47]
Supramolecular solvent-based liquid–liquid microextraction	UV-Vis	0.31	This work

3.2. Reagents and solutions

High-purity standards of concentration 1000 mg L^{-1} were diluted in ethanol for the preparation of various standard solutions of U(VI). A standard solution (1000 mg L^{-1}) of 1-(2-pyridylazo)-2-naphthol (PAN) (E. Merck, Darmstadt, Germany) was prepared by dissolving 0.1 g in 100 mL of ethanol. For pH adjustment hydrochloric acid (HCl), ammonium hydroxide (NH$_4$OH), and sodium hydroxide (NaOH) were also provided by E. Merck (Darmstadt, Germany). The supramolecular solvent component, tetrahydrofuran (THF), was provided by Lab-Scan (Ireland) and decanol and undecanol were provided by E. Merck (Schuchardt, Germany), while decanoic acid was provided by Sigma-Aldrich (St. Louis, MO, USA).

3.3. Supramolecular solvent based liquid-liquid microextraction of U(VI)

First, 200 μL of U(VI) was taken in a 50-mL centrifuge tube from a stock solution of 20 mg L^{-1} prepared in ethanol. To this was added 2 mL of NH$_4$OH (25%) solution to obtain the desired basic pH of 10 to 11. The solution was diluted to 5 mL with ethanol. After the addition of 0.5 mg of PAN, a dark red U-PAN complex that was soluble in ethanol was obtained. The solution was allowed to stand for 5 min to ensure that the complex formation was complete and the solution was diluted to 10 mL with ultrapure distilled water. The complex was then extracted to hydrophobic supramolecular solvent phase (0.4 mL of undecanol and 0.4 mL of THF). To enhance the extraction of the U-PAN complex to the extraction solution phase the solution was vortexed for 2 min at a vortex speed of 40 × 100 rpm. The solution was centrifuged at 4000 rpm for 10 min to accelerate the complete separation of water and supramolecular solvent phase. The extraction solution phase was collected and diluted up to 1.5 mL with ethanol. The concentration of uranium in the last volume was measured spectrophotometrically by a UV-Vis double beam spectrophotometer at 580 nm.

3.4. Applications

The method was applied to a tap water sample (our laboratory), seawater sample (Marmara Sea, Turkey), and soil sample from the city of Kayseri, Turkey, for addition and recovery studies. The method was also applied to soil certified reference material (GBW07424 (GSS-10). All the real water samples were filtered through a cellulose membrane filter of 0.45 μm (Millipore) prior to use.

The wet digestion method was performed in which 1 g (3 replicate) of soil samples and 0.5 g (3 replicate) of certified reference material were taken in beakers and digested with 24 mL of aqua regia at room temperature

for 30 min, and then at 95 °C on a hot plate until a dry residue was obtained. After cooling, the residues were again digested with mixtures of 24 mL of aqua regia following the same procedure as described above. When the final residues in beakers were obtained they were dissolved with 15 mL of distilled water and filtered to obtain a clear solution. The resulting solution was subjected to the developed method.

Acknowledgment

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