

Cloud Point Extraction and Spectrophotometric Determination of Uranium (VI) in Water Samples after Mixed Micelle-Mediated Extraction Using Chromotrope 2R as Complexing Agent

M. B. Gholivand,* M. Omidi, and M. Khodadadian

Faculty of Chemistry, Razi University, Kermanshah, Iran

RECEIVED APRIL 27, 2011; REVISED JANUARY 29, 2012; ACCEPTED JUNE 15, 2012

Abstract. A rapid, selective and sensitive method for the preconcentration and determination of uranium (VI) by cloud point extraction (CPE) was developed. The method was based on the color reaction of 5.00 ng mL⁻¹ uranium (VI) with 1.5 × 10⁻⁴ mol L⁻¹ of chromotrope 2R in the presence of 0.015 mol L⁻¹ potassium iodide at pH 8 in HEPES buffer and mixed micelle-mediated extraction of complex. The mixture of a nonionic surfactant (0.2 % (v/v) of (Triton X-114) and a cationic (2.0 × 10⁻⁴ mol L⁻¹ of CTAB) was utilized as a suitable micellar medium for preconcentration and extraction of uranium (VI) complexes. Effect of extraction and reaction parameters was studied and optimum parameters were established. The analytical characteristics of the method (*e.g.* linear range, limit of detection, preconcentration and improvement factors) were obtained. Linearity was obeyed in the range of 0.2–10 ng mL⁻¹ of uranium (VI) with a detection limit of 0.035 ng mL⁻¹. The diverse ion effect of some anions and cations on the extraction efficiency of target ions was tested. The proposed method was successfully applied for the determination of uranium (VI) in various water samples. (doi: 10.5562/cca1922)

Keywords: mixed micellar medium; cloud point extraction; spectrophotometry; uranium (VI), chromotrope 2R

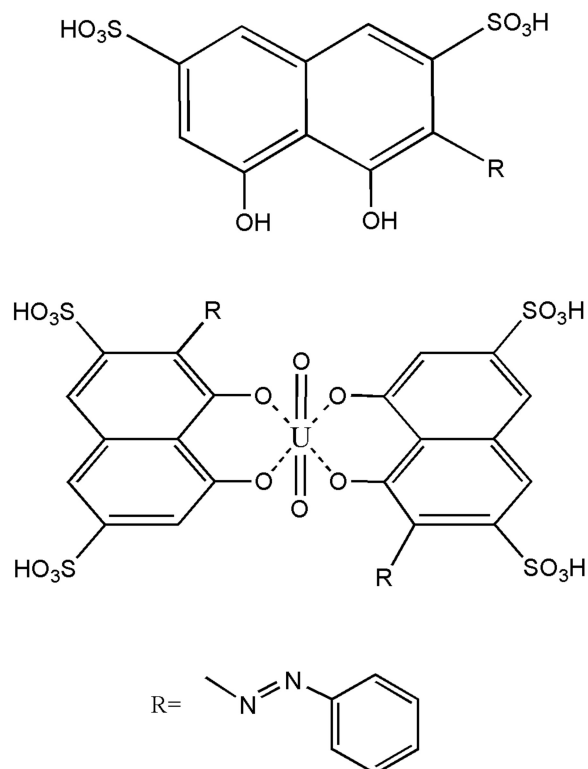
INTRODUCTION

Uranium poses health risks because of its toxicity, primarily to the kidneys, and is known to cause acute renal failure as well as delayed (several weeks or months) kidney problems.¹ Uranium presents a radiological hazard because the metal and its decay products have been demonstrated to deposit in bones and cause cancer and birth defects.² The major sources of uranium in the environment are industrial effluents and other wastes, primarily due to mining and weapons manufacturing.³ Uranium toxicity and mobility is highly dependent on its oxidation state, being the oxidation state +VI the most toxic. The maximum allowed concentration of uranium in drinking water is 20 µg per liter. Thus, highly sensitive methods are required for preconcentration and determination of uranium in water samples.^{4,5} However, conventional spectrometric analytical techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma optical emission spectrometry (ICP OES) cannot be used for determination of trace amounts of ura-

nium. Low sensitivity,^{6,7} the problem with the pyrolysis temperature⁶, uranium carbides formation in a graphite furnace⁸ are drawbacks of these methods. Considering this, inductively coupled plasma mass spectrometry (ICP-MS) is a good alternative for the determination of uranium at low concentrations but is very expensive.

Considering the low sensitivity of analytical techniques for the determination of uranium, preconcentration procedures are opportune, and several methods have been performed using several separation techniques.^{9–12} Of these, cloud point extraction (CPE) is an impressive alternative to conventional solvent extraction. CPE has frequently been applied in methods for pre-concentration and determination of various ionic and molecular species in several samples.^{13–19} The advantages and limitations of this technique have been summarized in recent reviews.^{20,21} The mixed micelle-mediated extraction (mixed-MME) system is becoming an important and practical application of the use of surfactants in analytical chemistry.^{22,23} Mixed-MME was used to the preconcentration of organic compounds^{24–26} and metal cations.^{27–29}

* Author to whom correspondence should be addressed. (E-mail: mbgholivand@yahoo.com)



Scheme 1. Chemical structures of CTR and CTR-U(VI) complex.

The chromotrope 2R (CTR) (Scheme 1) is a dye derived from the chromotropeic acid and has been used as complexing agent for uranium³⁰ U(IV) reacts with CTR and form a negative charge complex (ML_2) which in the presence of CTAB can subsequently be trapped in the surfactant micelles (*e.g.* Triton X-114) and separated from the aqueous phase.

EXPERIMENTAL

Apparatus

An Agilent-Packard 8453 diode array spectrometer controlled by a Hewlett-Packard computer and equipped with 1 cm path length quartz cell was used for absorption measurements. A Metrohm pH meter (model 632) with a combined glass electrode was utilized for pH measurements. A thermostat (Schvartzart DIN 40050-IP20, Germany) was used to maintain the desired temperature within ± 1.0 °C. A centrifuge (Hittach D-78532, Germany) was used to accelerate the phase separation process.

Reagents

All reagents were of analytical reagent grade. The water utilized in all studies was double-distilled and deionized. The surfactants, polyethylene glycol *tert*-

octylphenyl ether (Triton X-114) and cetyltrimethylammonium bromide (CTAB) (Fluka, Buches, Switzerland) were used without further purification. Stock solution of uranium at a concentration of $1000 \mu\text{g mL}^{-1}$ was prepared by dissolving appropriate amount of uranium acetate salt in double distilled water. Working standard solutions were obtained by dilution of the stock solution. A solution of $1.0 \times 10^{-2} \text{ mol L}^{-1}$ of chromotrope 2R (Fluka, Buches, Switzerland) was prepared by dissolving appropriate amounts of this reagent in double distilled water. The solution pH 8 ± 0.2 was adjusted with 20 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer. *N,N*-dimethylformamide (DMF) and potassium iodide were purchased from Merck (Darmstadt, Germany). These solutions were prepared daily and were stable during the day. The materials and vessels used for trace analysis were kept in 10 % nitric acid for at least 48 h and subsequently washed four times with deionized water before use.

Procedure

For the CPE, a proper amount of a uranium (VI) standard solution was transferred to a 10 mL centrifuge tube, 1.5 mL of the $1.0 \times 10^{-4} \text{ mol L}^{-1}$ chromotrope 2R solution and 1 mL HEPES buffer solution were added. This was followed by the addition of 1.5 mL of $2.0 \times 10^{-4} \text{ mol L}^{-1}$ surfactant CTAB solution, 1.0 mL of 0.2 % (v/v) of Triton X-114 solution and 0.5 mL of 0.015 mol L^{-1} of KI solution. The solution was taken up to the mark with double distilled water. The tubes were kept for 20 min in the thermostatic bath at 70 °C. Subsequently, separation of the phases was accelerated by centrifugation for 15 min at 4000 rpm. The surfactant-rich phase became viscous. The phases were cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted by simply inverting the tube. Later, in order to decrease the viscosity and facilitate sample handling, 0.3 mL of DMF was added to the surfactant-rich phase and a 100 μL of the solution was transferred into a quartz cell containing the blank DMF to measure the absorbance of the solution at 580 nm.

RESULTS AND DISCUSSION

Method Development

The chromotrope 2R (CTR) is a dye derived from the chromotropeic acid. It presents a chelating power for U(VI) and forms a ML_2 (metal to ligand) complex with uranium (VI).²⁹ In addition, in the primary experiment, it was found that the addition of some equivalent of U(VI) to aqueous solution of CTR resulted in a fast change in the color of the solution. CTR as an anionic dye shows maximum absorbance at 520 nm at pH 8.

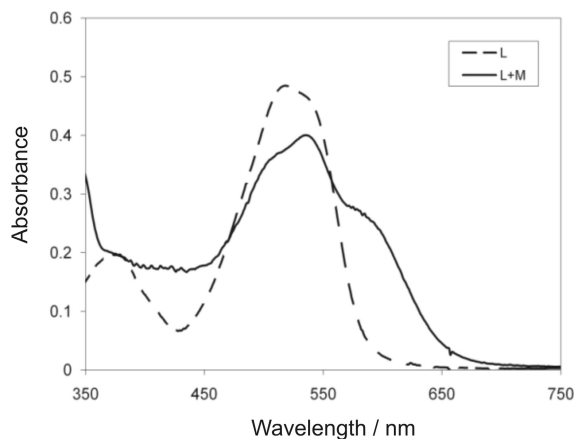


Figure 1. Absorption spectra for chromotrope 2R (discrete line) and its complex with uranium (VI) (solid line) in surfactant-rich phase. Conditions: chromotrope 2R, 1.5×10^{-4} mol L^{-1} ; uranium (VI), 5.00 ng mL^{-1} ; KI, 0.015 mol L^{-1} ; CTAB, 2×10^{-4} mol L^{-1} ; Triton X-114, 0.2 % (v/v); pH = 8.0 .

U(VI) in this medium reacts with CTR in the presence of CTAB and Triton X-114, the absorbance of solution decreases at 520 nm and produces a new band with maximum absorbance at about 580 nm (Figure 1). The solution became turbid after addition of the iodide ion. Therefore the ternary complex of U(IV)–CTR–CTAB can be extracted by CPE method. Thus, for finding the optimum conditions, the influence of various parameters on extraction efficiency was investigated.

Effect of pH

The separation of uranium (VI) by CPE method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase. The pH plays an important role on metal–chelates formation and subsequent extraction. The effect of pH on the signal intensity of uranium (VI) with CTR was studied in pH range 2.0 – 12.0 , and the experimental results are shown in Figure 2. As can be seen, when the medium pH was lower than 8.0 , only part of the uranium (VI) were extracted into the surfactant-rich phase due to the incomplete formation of U(VI)–CTR complexes in this pH range. Maximum absorbance was obtained at pH 8.0 . When the medium pH was higher than 8.0 , the hydrolysis reaction plays a dominant role, the hydrolysis of uranium (VI) would occur prior to their chelation with CTR which lead to the low extraction efficiency. Hence, pH 8.0 was chosen as the working pH.

Effect of CTR Concentration

In general, the concentration of the chelating reagent has a remarkable influence on the extraction efficiency. In order to select the optimal concentration of CTR, with the

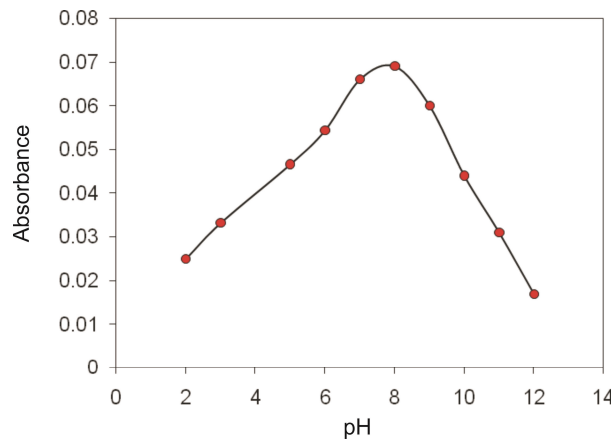


Figure 2. Effect of pH on the CPE of 5.00 ng mL^{-1} uranium (VI). Other conditions are as in Figure 1.

other experimental parameters remaining constant, the effect of CTR concentration in the range of $(0.33$ – $2.5) \times 10^{-4}$ mol L^{-1} was investigated. By increasing the ligand concentration (Figure 3), the conditions of complex formation will be better and the concentration of the formed complex will be increased, therefore, the absorbance will be increased too (to 1.5×10^{-4}). But from the optimum concentration on, the whole amount of metal ions will be consumed for the formation of the complex and no signal is detected for uranium in aqueous phase and the conditions for complex formation are not suitable anymore, therefore, the amount of ligand doesn't have any role on forming the complex and the absorbance will be fixed.

Effect of Surfactants Concentration

In the preliminary experiments it is observed that the addition of the neutral surfactant such as Triton X-114

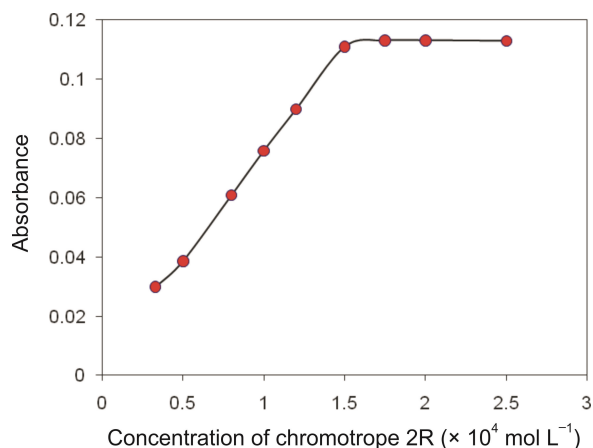


Figure 3. Effect of concentration of complexing agent on CPE of 5.00 ng mL^{-1} uranium (VI). Experimental conditions: Triton X-114, 0.2 % (v/v); CTAB, 2×10^{-4} mol L^{-1} ; KI, 0.015 mol L^{-1} and pH = 8.0 .

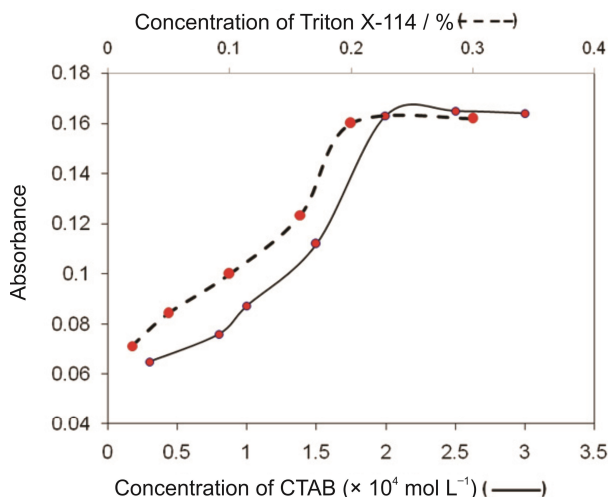


Figure 4. Absorbance of the complex as a function of CTAB (solid line) and Triton X-114 (dashed line) concentrations. Conditions: 5.00 ng mL^{-1} U (VI); $1.5 \times 10^{-4} \text{ mol L}^{-1}$ CTR; 0.015 mol L^{-1} KI; pH = 8.0.

to ternary complex of U(VI) ion-CTR-CTAB and heating, makes the solution turbid. This shows that the ternary complex can be extracted by CPE method. Therefore, the effect of ionic (CTAB) and nonionic surfactant (Triton X-114) concentrations on the analytical response of 5 ng mL^{-1} of uranium (VI) were investigated. The results are shown in Figure 4. As can be seen the measured absorbance reached its maximum at more than 0.2 % (v/v) of Triton X-114 and $2.0 \times 10^{-4} \text{ mol L}^{-1}$ of CTAB, indicating that quantitative extraction by cloud point method was obtained. By increasing the concentrations of the surfactants due to increase the amount of formed micelles, the extraction percentage will be increased. Therefore, $2.0 \times 10^{-4} \text{ mol L}^{-1}$ and 0.2 % (v/v) were selected as the optimum amounts of ionic and nonionic surfactants for subsequent uses. Thus, by using Triton X-114 and CTAB as a mixed surfactant agent, the test solution could be separated easily into two phases and the bulk aqueous phase could be decanted after centrifugation.

Effects of Equilibration Temperature and Time

Equilibration time and temperature are among the most important parameters to be optimized in order to achieve easy phase separation and efficient pre-concentration in cloud point extraction processes. It is reported that the greatest analyte pre-concentration factor is achieved when the CPE process is conducted with equilibration temperatures that are well above the cloud point temperature of the surfactant.³¹ Increasing time and temperature is necessary for having complete reaction, facile separation and complete pre-concentration, therefore, by increasing them the absorbance will be

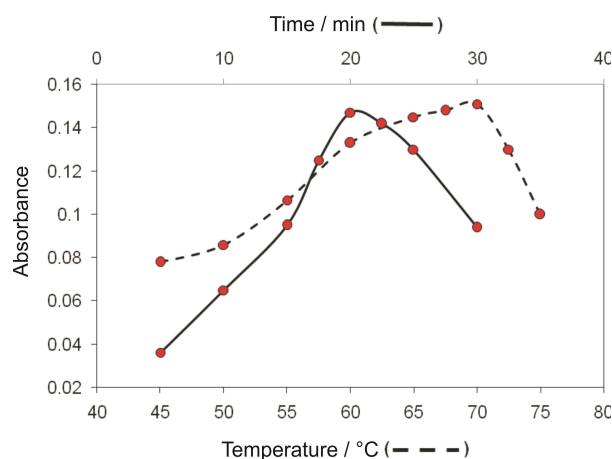


Figure 5. Effect of equilibration time (solid line) and temperature (dashed line) on the CPE of 5.00 ng mL^{-1} U(VI). Experimental conditions: $1.5 \times 10^{-4} \text{ mol L}^{-1}$ CTR; Triton X-114, 0.2 % (v/v); CTAB, $2 \times 10^{-4} \text{ mol L}^{-1}$; KI, 0.015 mol L^{-1} ; pH = 8.0.

increased. From the optimum points on, there is a probability for collapsing the formed complex and weak clouding of the surfactants, therefore, absorbance will be decreased. The dependency of extraction recovery to the incubation time and temperature was studied in the range 5–30 min and 45–75 °C, respectively. The results showed that an equilibration time of 20 min and equilibration temperature of 70 °C are adequate to obtain quantitative extraction (Figure 5).

Optimization of other Cloud Point Extraction Parameters

Addition of salts can cause cationic surfactant solutions to separate into immiscible surfactant rich and surfactant-poor phases. Therefore, the effects of a few salts, such as NaCl, NaF, KNO_3 , KBr and KI, on the CPE behavior were investigated. It was found that the presence of KI induced the phase separation and resulted in extraction of maximal efficiency. As mentioned before the resulted complex of uranium and CTR is an anionic complex and it must be converted to an uncharged form in order to be trapped in the surfactant micelles. CTAB can interact with the complex as an individual molecule or aggregates. On the other hand, cationic surfactants react by ion pair formation with the anionic uranium complex to form a ternary complex involving surfactant monomers. This uncharged complex can be trapped in the triton X-114 as surfactant micelles. Furthermore, the excess of CTAB monomers may be used as co surfactant and thus, potassium iodide was used to reduce the repulsion between the monomers. On the other hand, potassium and iodide ions with large ionic size and less charge density reduces the repulsion of cationic surfac-

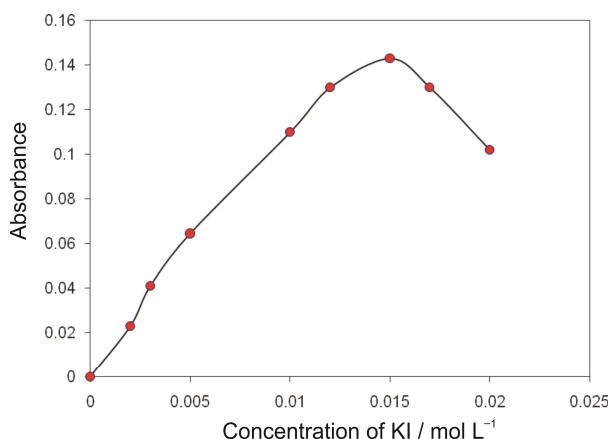


Figure 6. Effect of iodide concentration on the CPE of 5.00 ng mL⁻¹ U(VI). Conditions: CTAB, 2×10⁻⁴ mol L⁻¹; Triton X-114, 0.2 % (v/v); CTR 1.5×10⁻⁴ mol L⁻¹ and pH= 8.0.

tant by better ion pair formation induces the phase separation and increases the extraction efficiency. These results are consistent with the previous report.³² The effect of iodide concentration was studied in the range 0.00–0.02 mol L⁻¹. The results demonstrated that the maximum analytical signals of uranium (VI) was achieved at concentration 0.015 mol L⁻¹ and decreased at higher concentrations (Figure 6). Therefore, 0.015 mol L⁻¹ of KI was used in further uses.

The surfactant-rich phase obtained after CPE is very viscous. In order to decrease the viscosity of surfactant-rich phase and facilitate its transfer into a spectrophotometric cell, handling and absorbance measurements various solvents such as carbon tetrachloride (CCl₄), ethanol (C₂H₅OH), methanol (CH₃OH), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), methyl isobutyl ketone (MIBK), and *N,N*-dimethylformamide (DMF) were tested as diluents. The results show that the highest signal was found when DMF was used as diluent. By the use of the other solvents for dissolving the rich surfactant phase, much amount of the solvent is required that not only brings more cost but also causes both environmental pollution and decreasing the pre-concentration factor. Therefore, 0.3 mL of DMF was added to the extracted phase and its absorbance was measured.

The high levels of rate and time are required for centrifuge to have a more suitable separation of two phases, but temperature will be decreased during a long time for this process which causes more mix two phases together and subsequently decreases the extraction yield. It should be noted that high temperature can collapse the formed complex. The effect of the centrifugation time on extraction efficiency was the other parameter that was studied within a range 5–30 min. A Centrifuge time of 15 min at 4000 rpm was selected for the entire procedure, since analyte extraction in this time is

Table 1. Tolerance limit of diverse ions on the determination of 5.00 ng mL⁻¹ U(VI)

Interfering ion	Interfering ion/U(VI) (ng mL ⁻¹)
Bi ³⁺ , Zr ⁴⁺ , Al ³⁺ , Fe ³⁺	40 (500) ^(a)
Ni ²⁺ , Pb ²⁺ , Cd ²⁺ , Co ²⁺ , Ca ²⁺ , Cu ²⁺	2000
Cr ³⁺ , Ce ³⁺ , Ag ⁺	2500
Na ⁺ , Li ⁺ , K ⁺	4000
SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻	60000

^(a) After addition of 0.5 mL EDTA 0.1 %.

almost quantitative, since complete separation occurred at this time, and no considerable improvement was observed for longer periods of time.

Effect of Foreign ions

In order to evaluate the performance of this procedure, the highest tolerability of various common interfering ions were studied. Interferences may occur mainly due to competition of other existing ionic species in the test solution that may form complexes with the CTR. Therefore, the tolerable limits of various foreign ions were studied in solution containing 5.00 ng mL⁻¹ of uranium (VI), by keeping the relative error between ±5 %. It was found that most of the investigated species did not interfere even when present in 2000-fold excess over uranium (VI) (Table 1). The ions Al³⁺, Bi³⁺, Fe³⁺ and Zr⁴⁺ in concentrations higher than the tolerance ratios reported in Table 1 have influence on the proposed CPE of uranium (VI) under the selected conditions. The interfering effect of mentioned ions was completely removed in the presence of 0.1 % of EDTA.

Analytical Characteristics

Table 2, summarizes the analytical characteristics of the optimized method, including regression equation, linear range, limit of detection, pre-concentration and improvement factors. The limit of detection and limit of quantification are defined as $C_{LOD} = 3S_B/m$ and $C_{LOQ} = 10S_B/m$ where S_B and m are standard deviation of the blank and slope of the calibration curve, respectively. By the use of the foregoing formula 0.035 and 0.116 ng mL⁻¹ are obtained for LOD and LOQ, respectively. Because the amount of uranium (VI) in 10 mL of sample solution is measured after preconcentration by cloud point extraction in a final volume of 0.5 mL (0.2 mL surfactant-rich phase and 0.3 mL DMF), the maximum preconcentration factor of the solution is 20. The improvement factor defined as the ratio of the slope of the calibration graph for CPE method to that of the calibration graph in micellar media without preconcentration, was 100. The relative standard deviation (RSD) was 3.3 % and 2.9 % for concentrations of uranium of 2.0 and 5.0 ng mL⁻¹, respectively (See Table 2).

Table 2. Analytical features of the proposed method

Analytical parameter	Uranium(VI)
Linear range ^(a)	0.2–10.0 (ng mL ⁻¹)
Regression equation ^(a)	0.011C ng mL ⁻¹ + 0.090 (n = 8)
Correlation coefficient (r ²) ^(a)	0.997
Linear range ^(b)	20–1000 (ng mL ⁻¹)
Regression equation ^(b)	0.00011C ng mL ⁻¹ + 0.080 (n = 15)
Correlation coefficient (r ²) ^(b)	0.998
Improvement factor	100
Maximum Preconcentration factor	20
Repeatability (RSD, %)	3.3 (for 2.0 ng mL ⁻¹ , n = 6)
Repeatability (RSD, %)	2.9 (for 5.0 ng mL ⁻¹ , n = 6)
Limit of detection	0.0350 (3S _b / ng mL ⁻¹) (n = 7)
Limit of qualification	0.116 (10S _b / ng mL ⁻¹) (n = 7)

^(a) After preconcentration.^(b) Before preconcentration.**Table 3.** Determination of U(VI) in the water samples

Sample	U(VI) added / ng mL ⁻¹	U(VI) found / ng mL ⁻¹	Recovery U(VI) / %
Tap Water	2.00	2.03 ± 0.04	101.5
	5.00	4.82 ± 0.01	96.4
Well Water	2.00	2.03 ± 0.02	101.5
	5.00	4.80 ± 0.04	96.0

Application

In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of uranium in water samples. Reliability was checked by spiking the sample and the accuracy of the method was examined by recovery experiment. The results of the CPE experimental are shown in Table 3. The obtained recoveries varying between 96 and 102.5 % proved that this procedure is not affected by the matrix and can be applied satisfactorily to the determination of uranium in water samples.

CONCLUSION

We have presented a new concept of increasing the hydrophobic nature of cationic micelles with nonionic surfactant for inducing the cloud point phase separation. The use of micellar systems as an alternative to other methods of separation and preconcentration offers several advantages including experimental convenience, safety and being an inexpensive method with low toxicity. Its analytical applicability has been demonstrated by extraction of hydrophilic anionic species of uranium.

Table 4. Comparison of the performance of the proposed method with that of other reported methods for the preconcentration Spectrophotometric determination of uranium (VI)

Analytical method	Detection limit	Linear range	Preconcentration factor	References
micelle-mediated extraction / spectrophotometric determination	0.06 ng mL ⁻¹	0.20–10.00 (ng mL ⁻¹)	14.3	32
Spectrophotometry	2.0 ng mL ⁻¹	5–200 (µg l ⁻¹)	-	10
Spectrophotometry	11 ng mL ⁻¹	15–300 (ng mL ⁻¹)	62	33
inductively coupled plasma optical emission spectrometry (ICP OES).	0.3 µg L ⁻¹	1–1500 (µg L ⁻¹)	100	34
micelle-mediated extraction / inductively coupled plasma-optical emission spectrometry	1.0 µg L ⁻¹	2.5–1240 (µg L ⁻¹)	-	35
Solid phase extraction/ spectrophotometric determination	1 µg L ⁻¹	1.35–217 (µg mL ⁻¹)	400	36
Colorimetry	0.3 µg mL ⁻¹	-	-	37
Membrane optode	50 ng mL ⁻¹	0.01–0.11 (µmol L ⁻¹)	-	38
Preconcentration/spectrophotometric determination	0.50 µg L ⁻¹	-	100	39
CPE	0.035 ng mL ⁻¹	0.20–10.00 (ng mL ⁻¹)	20	Proposed method

The limits of detection of uranium achieved (Table 4) are superior to reported procedures.^{10,32–39} This method allows the determination of low levels of uranium (VI) using molecular absorption spectrometry. It was successfully applied for the determination of uranium in various water samples.

Acknowledgements. We would like to thank the research council at the Razi University for their cooperation and support of this work.

REFERENCES

1. M. L. Zamora, B. L. Tracy, J. M. Zielinski, D. P. Meyerhof, and M. A. Moss, *Toxicol. Sci.* **43** (1998) 68–77.
2. D. E. McClain, K. A. Benson, T. K. Dalton, J. Ejnik, C. A. Emond, S. J. Hodge, J. F. Kalinich, M. A. Landauer, A. C. Miller, T. C. Pellmar, M. D. Stewart, and V. Villa, *J. Xu, Sci. Total Environ.* **274** (2001) 115–118.
3. A. Kimaro, L. A. Kelly, and G. M. Murray, *Separ. Sci. Technol.* **40** (2005) 2035–2052.
4. K. Oguma, T. Suzuki, and K. Saito, *Talanta* **84** (2011) 1209–1214.
5. A. Milliard, M. D. Jézéquel, and D. Larivière, *Anal. Chim. Acta* **684** (2011) 40–46.
6. B. Welz and M. Sperling, *Atomic Absorption Spectrometry*, Wiley-VCH, New York, 1999.
7. A. Montaser, D. W. Golightly, *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd edn. VCH, New York, 1992.
8. D. M. Goltz, D. C. Gregoire, J. P. Byrne, and C. L. Chakrabarti, *Spectrochim. Acta Part B* **50** (1995) 803–814.
9. Z. F. Liu and S. P. Liu, *Analyst* **116** (1991) 95–98.
10. P. Metilda, K. Sanghamitra, J. M. Gladis, G. R. K. Naidu, and T. P. Rao, *Talanta* **65** (2005) 192–200.
11. J. M. Gladis and T. P. Rao, *Anal. Bioanal. Chem.* **373** (2002) 867–872.
12. P. Taechangam, J. F. Scamehorn, S. Osuwan, and T. Rirksomboon, *Colloids Surf. A* **347** (2009) 200–209.
13. J. Chen, J. Mao, X. Mo, J. Hang, and M. Yang, *Colloids Surf. A* **345** (2009) 231–236.
14. D. Citak and M. Tuzen, *Food Chem. Toxicol.* **48** (2010) 1399–1404.
15. P. Liang and J. Yang, *J. Food. Compos. Anal.* **23** (2010) 95–99.
16. P. Liang, J. Li, and X. Yang, *Microchim. Acta* **152** (2005) 47–51.
17. D. L. G. Borges, M. A. M. S. Veiga, V. L. A. Frescura, B. Welz, and A. J. Curtius, *J. Anal. At. Spectrom.* **18** (2003) 501–507.
18. T. D. Maranhao, D. L. G. M. Borges, A. M. S. Veiga, and A. J. Curtius, *Spectrochim. Acta Part B* **60** (2005) 667–672.
19. M. A. M. Silva, V. L. A. Frescura, and A. J. Curtius, *Spectrochim. Acta Part B* **56** (2001) 1941–1949.
20. M. D. Pereira and M. A. Z. Arruda, *Microchim. Acta* **141** (2003) 115–131.
21. M. A. Bezerra, M. A. Z. Arruda, and S. L. C. Ferreira, *Appl. Spectroscopy Rev.* **40** (2005) 269–299.
22. J. Chen and T. K. Chuan, *Anal. Chim. Acta* **434** (2000) 325–330.
23. A. Afkhami, T. Madrakian, and A. Maleki, *Anal. Biochem.* **347** (2005) 162–164.
24. E. J. Kim and D. O. Shah, *Langmuir* **18** (2002) 10105–10108.
25. B. S. Valaulikar and C. J. Manohar, *J. Colloids Interf. Sci.* **108** (1985) 403–406.
26. J. W. Kang, G. De Reymaeker, A. Van Schepdael, E. Roets, and J. Hoogmartens, *Electrophoresis* **22** (2001) 1356–1362.
27. E. K. Paleologos, A. G. Vlessidis, M. I. Karayannis, and N. P. Evmiridis, *Anal. Chim. Acta* **477** (2003) 223–231.
28. D. L. Giokas, J. Antelo, E. K. Paleologos, F. Arce, and M. I. Karayannis, *J. Environ. Monitor.* **4** (2002) 505–504.
29. M. B. Gholivand, A. Babakhanian, and E. Rafiee, *Talanta* **76** (2008) 503–508.
30. O. Braun, C. Contino, M. H. Henge-Napoli, E. Ansoborlo, and B. Pucci, *Analisis* **27** (1999) 65–68.
31. R. P. Frankewich and W. L. Hinze, *Anal. Chem.* **66** (1994) 944–954.
32. T. Madrakian, A. Afkhami, and A. Mousavi, *Talanta* **71** (2007) 610–614.
33. F. Shemirani, R. R. Kozani, and M. R. Jamali, *Sep. Sci. Technol.* **40** (2005) 2527–2537.
34. S. R. Yousefi, S. J. Ahmadi, F. Shemirani, M. R. Jamali, and M. S. Niasari, *Talanta* **80** (2009) 212–217.
35. S. Shariati, Y. Yamini, and M. K. Zanjani, *J. Hazard. Mater.* **156** (2008) 583–590.
36. S. Sadeghi and E. Sheikhzadeh, *J. Hazard. Mater.* **163** (2009) 861–868.
37. J. M. Joshi, P. N. Pathak, A. K. Pandey, and V. K. Manchand, *Talanta* **76** (2008) 60–65.
38. Y. Kalyan, A. K. Pandey, G. R. K. Naidu, and A. V. R. Reddy, *Spectrochim. Acta Part A* **74** (2009) 1235–1241.
39. J. B. Ghasemi and E. Zolfonoun, *Talanta* **80** (2010) 1191–1197.