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Micelle-Mediated Extraction for Direct Spectrophotometric Determination of Trace Uranium(VI) in Water Samples

Farzaneh Shemirani[a]; Reyhaneh Rahnama Kozani[a]; Mohammad Reza Jamali[a]; Yaghoub Assadi[b]; Seyyed Mohammad Reza Milani[b]
[a] Department of Chemistry, Faculty of Science, University of Tehran, Tehran, Iran [b] Department of Analytical Chemistry, Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran

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Farzaneh Shemirani, Reyhaneh Rahnama Kozani, and Mohammad Reza Jamali
Department of Chemistry, Faculty of Science, University of Tehran, Tehran, Iran

Yaghoub Assadi and Seyyed Mohammad Reza Milani
Department of Analytical Chemistry, Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran

Abstract: The possibility of using Dibenzoylmethane (DBM) for uranium(VI) concentrating by the way of micellar extraction at cloud point temperature and later spectrophotometric determination was investigated. Under the optimum conditions, preconcentration of 50 mL of water samples in the presence of 0.2% (w/v) octylphenoxypolyethoxy ethanol (Triton X-114), 2×10^{-4} mol L^{-1} DBM and 2×10^{-3} mol L^{-1} buffer solution (pH = 9) gave a limit of detection 11 ng mL^{-1}, and the calibration graph was linear in the range of 15–300 ng mL^{-1}. The recovery under optimum working conditions was higher than 98%.

The proposed method has been applied to the spectrophotometric determination of uranium(VI) in natural water samples after cloud point extraction with satisfactory results.

Keywords: Micellar extraction, spectrophotometric determination, natural water samples, uranium

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Address correspondence to Farzaneh Shemirani, Department of Chemistry, Faculty of Science, University of Tehran, Tehran, Iran. E-mail: shemiran@khayam.ut.ac.ir

INTRODUCTION

The toxicology of uranium is complicated by the dual nature of the biological effects of uranium on organisms. The initial biological effects produced by uranium are the result of its toxicity. The effects are due to the radioactivity of delayed uranium (1). The importance of the determination of uranium has grown manifold due to the increasing applications in nuclear industry.

Because uranium is a relatively mobile element in many surface or near-surface environments, its geochemical exploration methods require the measurement of the trace quantities of metal ion in water samples along with that in plants, soils, and rocks. The uranium concentration of seawater is about $3.3\,\mathrm{ng\,mL^{-1}}$ (2), in freshwater, even lower. Thus, highly sensitive methods are required for preconcentration and determination of uranium in water samples collected for prospecting purpose.

There are various techniques for the separation and/or preconcentration of uranium such as co-precipitation (3), chelating resin adsorption (4), solid phase extraction (5), and solvent extraction (6).

Cloud point extraction (CPE) (7, 8) is an attractive preconcentration technique that reduces the consumption of and exposure to solvents, disposal costs, and extraction time. This technique is based on the use of surfactants.

Nonionic surfactant molecules form self-aggregate structures called "micelles" in aqueous solutions above the critical micellar concentration (CMC). The hydrocarbon cores of the micelles give them the ability to solubilize hydrophobic organic compounds.

Aqueous solutions of almost all nonionic surfactants became turbid when heated to a temperature known as the cloud point temperature (CPT). Above this temperature the isotropic micellar solution separates into two transparent liquid phases: a surfactant-rich phase of very small volume, composed mostly of the surfactant plus small amounts of water, and an aqueous phase, in equilibrium with the former, which contains a surfactant concentration close to its CMC.

The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, speedy, and of lower toxicity to the environment than those extractions that use organic solvents.

Cloud point extraction and preconcentration was applied to determination of Cr(III) and Cr(VI) (9); Ag and Au (10); Ni and Zn (11); Cd, Pb, Cu, Cr(III); Zn and Fe(III) (12) by flame atomic absorption spectrometry; Bi (13) and As(III) and As(V) (14) by electrothermal atomic absorption spectrometry; and U (15), Er (16), Cd (17), Al (18) and Co, Ni (19) by spectrophotometric detection.

Although X-ray fluorescence spectroscopy (XRF) (20), α-spectrometry (21), and ICP spectroscopy (22) are the most commonly used techniques in determination of uranium, spectrophotometry continues to enjoy wide

popularity. The common availability of the instrumentation, the simplicity of procedures, speed, precision and accuracy of the technique still make spectrophotometric methods attractive.

In this work, an efficient method for the preconcentration of uranium(VI) from water samples with Dibenzoylmethane (DBM) as a chelating and chromogenic agent and direct spectrophotometric determination is proposed.

EXPERIMENTAL

Reagents and Solutions

All reagents used were of analytical grade. Stock solution of uranium(VI) ion was prepared by dissolving an appropriated amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in $0.5\,mol\,L^{-1}$ nitric acid. Working solutions were prepared from the stock solution by serial dilutions with doubly distilled water.

The nonionic surfactant Triton X-114 (Fluka chemie AG-Switzerland) was used without further purification.

A chelating-agent solution was prepared by dissolving 0.2242 g of DBM (Merck) in 100 mL of 96% ethanol.

A stock standard buffer solution, $0.1\,mol\,L^{-1}$ was prepared by dissolving appropriate amounts of $Na_2B_4O_7$, $10H_2O$.

The pipettes and vessels used for trace analysis were kept in solfochromic acid mixture for at least 1 h and subsequently washed four times with water.

Apparatus

A model UV-2550 spectrophotometer (Shimadzu) with 1.0 cm glass cell was used. A thermostated bath model (Stuart, Scientific) maintained at the desired temperature experiments and phase separation was assisted using a centrifuge (Centurion scientific Ltd Model: 1020D). The pH of the solutions was controlled with a Metrohm pH-meter model 713.

Recommended Procedure

For the cloud point extraction, an aliquot of 50 mL of a solution containing the analyte, 0.2% Triton X-114, $2 \times 10^{-4}\,mol\,L^{-1}$ DBM, and $2 \times 10^{-3}\,mol\,L^{-1}$ buffer (pH = 9) was kept for 10 min in the thermostatic bath at 50°C. Subsequently, separation of phases was achieved by centrifugation for 10 min at 3500 rpm. 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. The surfactant-rich phase in the tube was made up to 1.0 mL by adding methanol. The absorbance

was measured at the wavelength of maximum absorbance of complex, 400 nm, for uranium(VI).

RESULTS AND DISCUSSION

Effect of pH

The separation of metal ions by cloud point method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase; thus obtaining the desired preconcentration (23). pH plays a unique role on metal-chelates formation and subsequent extraction.

Figure 1 shows the influence of pH on the absorbance of the uranium(VI) complex at 400 nm. As can be seen, at pH = 9 maximum extraction efficiency was obtained. Hence, pH = 9 was chosen as the working pH.

Effect of DBM Concentration

The effect of concentration of DBM on analytical response is shown in Fig. 2. As it is seen for uranium(VI) complex, the signal increase up to a known concentration of DBM, reaching, plateau, which is considered as complete extraction. A concentration of 2×10^{-4} mol L^{-1} was chosen as the optimum.

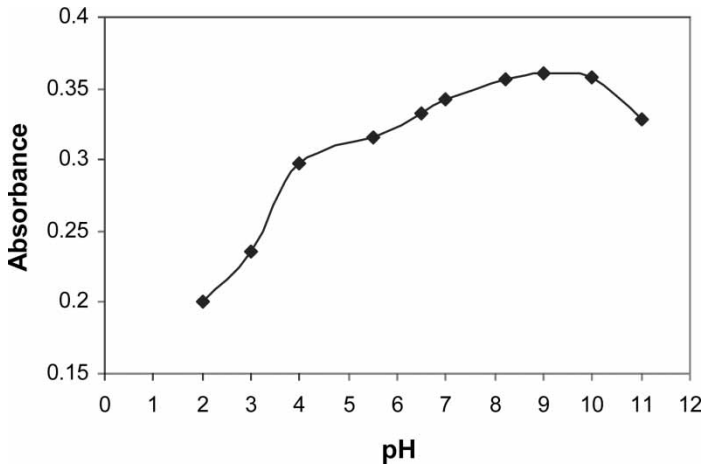

Figure 1. Effect of pH on the CPE-preconcentration performance: UO_2^{2+} 100 ng mL^{-1}; Triton X-114 0.2% (w/v); DBM 2×10^{-4} mol L^{-1}.

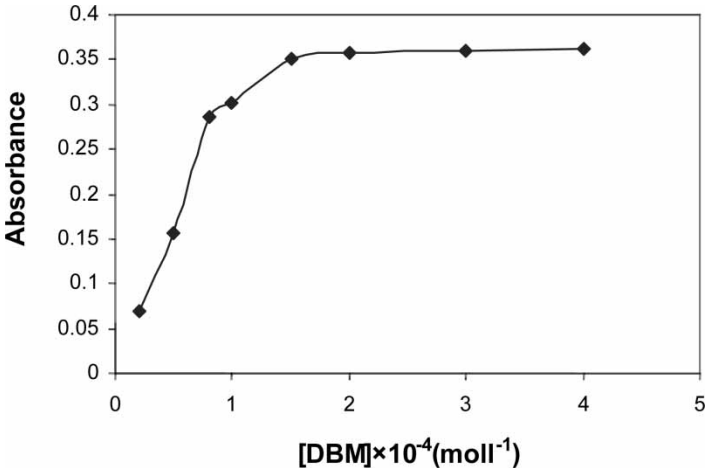

Figure 2. Effect of DBM concentration on the CPE-preconcentration performance: UO_2^{2+} 100 ng mL^{-1}; $Na_2B_4O_7$ 2 × 10^{-3} mol L^{-1}; Triton X-114 0.2% (w/v).

Effect of Triton X-114 Concentration

Triton X-114 was chosen for the formation of the surfactant-rich phase due to its commercial availability in a high purified homogeneous form, low toxicological properties, the lack of electro-active groups in its molecule and cost. Also, its low cloud point temperature and high density of surfactant-rich phase, which facilitates phase separation by centrifugation.

The variation in the extraction efficiency upon surfactant concentration was examined with the following range: $C_{\text{Triton X-114}}$ 0.05–0.5% (w/v). The results are shown in Fig. 3, it was proved that Triton X-114 effectively extracts uranium(VI) from liquid samples at a concentration of 0.2% (w/v). The optimum surfactant concentration used for the uranium(VI) was 0.2% (w/v) Triton X-114, in order to achieve the optimal analytical signal in conjunction with the highest possible extraction efficiency. Using more than 0.2% (w/v) of surfactant, the analytical sensitivity decreased due to dilution of the sample by additional surfactant solution.

Effect of Buffer Concentration and Ionic Strength

The influence of buffer concentration prior to cloud point extraction process on absorbance of uranium(VI) complex was investigated. The results are shown in Fig. 4. A 2 × 10^{-3} mol L^{-1} buffer solution was chosen as the optimal.

Ionic strength had no appreciable effect upon extraction efficiency and sensitivity up to 0.5 mol L^{-1}.

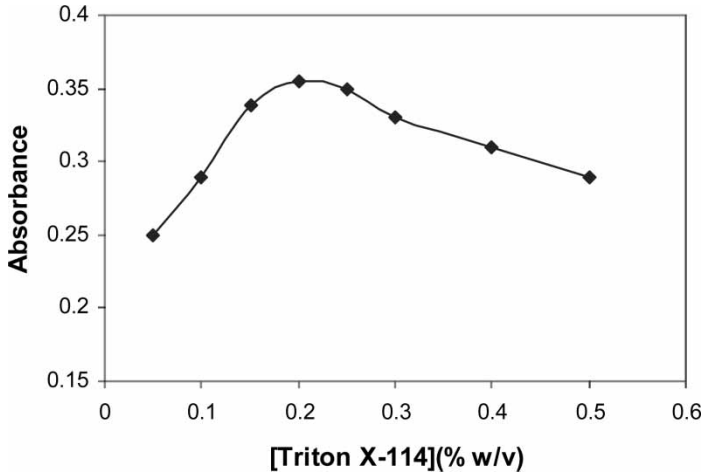

Figure 3. Effect of Triton X-114 concentration on the CPE-preconcentration performance: UO_2^{2+} 100 ng mL^{-1}; $Na_2B_4O_7$ 2 × 10^{-3} mol L^{-1}; DBM 2 × 10^{-4} mol L^{-1}.

Effect of Equilibration Temperature and Time

The greatest analyte preconcentration factor is achieved when the CPE process is conducted with equilibration temperatures that are well above the cloud point temperature of the surfactant (24).

Therefore, this parameter was studied within the ranges 25–70°C. It was found that a temperature of 50°C was adequate.

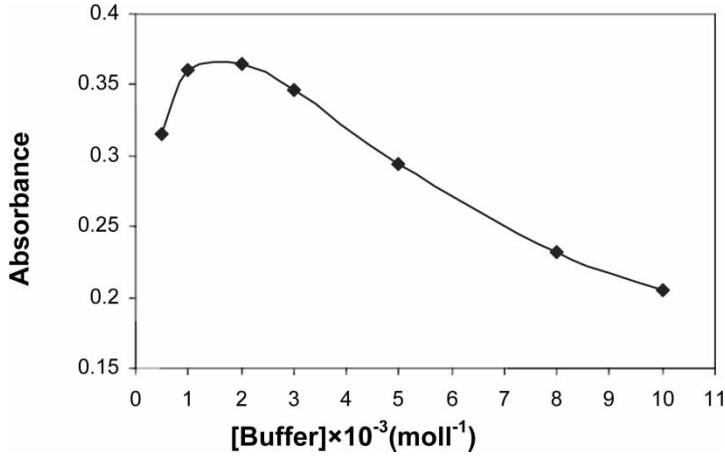

Figure 4. Effect of buffer concentration on the CPE-preconcentration performance: UO_2^{2+} 100 ng mL^{-1}; DBM 2 × 10^{-4} mol L^{-1}; Triton X-114 0.2% (w/v).

It was desirable to employ the short equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. The dependence of absorbance upon equilibration time was studied within a range of 2–30 min. Time of 10 min was chosen as optimal time.

Effect of Centrifugation Time

A centrifugation time of 10 min at 3500 rpm was selected as optimum, since complete separation occurred for this time and no appreciable improvements were observed for longer time.

Figures of Merit

The figures of merit of the proposed procedure are shown in Table 1. The enrichment factor was defined as the ratio of the slopes of the calibration curves with and without preconcentration. The calibration curve without preconcentration was obtained by measuring analytical solutions that were matched to the surfactant-rich phase.

As shown in Table 1, good enrichment factor was obtained which was favored with adapted complexation. The range of calibration curve was $15-300\,ng\,mL^{-1}$.

The correlation coefficient (R^2) of the calibration curve was 0.9996. The detection limit (defined as the concentration equivalent to three times the standard derivation of 10 measurements of the blank) is also shown in Table1.

The relative standard deviation (RSD), obtained by preconcentrating 10 analytical solutions, was below 3.7%, demonstrating a good precision for such low concentration.

Table 1. Analytical characteristics of the method

Parameter	Analytical feature
Preconcentration factor	62
LOD ($ng\,mL^{-1}$)	11
RSD% ($n = 10$)[a]	3.7
Correlation coefficient (R^2)	0.9996
Linear range ($ng\,mL^{-1}$)	15–300

[a]Uranium concentration was $100\,ng\,mL^{-1}$ for which RSD was obtained.

Table 2. Effect of foreign ions on the preconcentration and determination of uranium

Ion	Ion/U(VI) (w/v)	Recovery (%)
Li^{+}	1000	101
K^{+}	1000	100.5
Na^{+}	1000	100
Bi^{3+}	1000	99.5
Cd^{2+}	50	98
Pb^{2+}	50	99.5
Mg^{2+}	50	102
Mo^{6+}	50	99
Ag^{+}	50	99.5
Cr^{3+}	25	101
Ni^{2+}	25	98
Cu^{2+}	10	102
Mn^{2+}	10	99
Co^{2+}	10	102
Zn^{2+}	10	98
Cr^{6+}	5	102
Th^{4+}	5	98.5

Interference Effects

The influence of several cations on the adsorption and determination of uranium(VI) ion ($100\,ng\,mL^{-1}$) was studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample of more than 5%. The results are summarized in Table 2. Most of

Table 3. Analytical determination of uranium(VI) in water samples

Water sample	α-spectrometry	U(VI) added ($ng\,mL^{-1}$)	Found ($ng\,mL^{-1}$)[a]	RSD%
Tashk[b]	2.3	0.0	nd[d]	—
	—	20.0	21.6	3.7
	—	30.0	32.0	3.9
Anarak[c]	33.3	0.0	33.2	3.7
	—	20.0	52.7	3.8
	—	30.0	61.9	3.6

[a]Results Certified by Atomic Energy Organization of Iran.
[b]Springer water near the uranium mine (Tashk, bandar abbass, Iran).
[c]Springer water near the uranium mine (Anarak,Yazd, Iran).
[d]Not detected.

Table 4. Analytical determination of uranium(VI) in reference material

Sample	Certified (ng mL^{-1})	U(VI) added (ng mL^{-1})	Found (ng mL^{-1})
CASS-4	3.0	—	nd[a]
		20.0	22.8 ± 0.8[b]
NASS-5	2.6	—	nd
		20.0	22.4 ± 0.7

[a]Not detected.
[b]Mean of three extraction $\pm$ SD.

the cations examined interfere with the extraction and determination of uranium(VI). However, we eliminated or reduced considerably these interferences in the presence of EDTA as proper masking reagent (25). This reagent forms a stable complex with most metal ions, but doesn't interfere with the reaction between uranium(VI) and DBM.

Application to Samples

The proposed method was applied to the determination of uranium(VI) in water samples. As shown in Table 3, satisfactory agreement exists between the results obtained by proposed method and those reported by α-spectrometry (26). Therefore the proposed method could be successfully applied for preconcentration of trace amounts of uranium(VI) in water samples and spiked water samples.

Validation of the method was performed using certified reference materials. The agreement of the certified values with those obtained using the proposed method is acceptable, as can be seen from Table 4.

CONCLUSION

Cloud point extraction is an easy, safe, rapid, and inexpensive methodology for the preconcentration and separation of metals from various samples.

This method allows the determination of ppb levels of uranium(VI) by spectrophotometry. The main advantage of the method is use of DBM as chelating and chromogenic reagent for direct determination of uranium(VI) in water samples in almost every laboratory.

The method gives a very low limit of detection and good RSD value. The proposed method was successfully applied to the determination of trace uranium(VI) spectrophotometrically in various water samples.

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