# Cloud Point Extraction for Preconcentration and Determination of Uranium in Water Samples by Spectrophotometry

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## Article Info

## Abstract

A cloud point extraction methodology for preconcentration and spectrophotometric determination of uranium in water samples is presented. The analyte was complexed with 2,7-bis(2-arseno-phenylazo)-1,8-dihydroxynaphtalane-3,6-disulfonic acid (arsenazo-III) and octylphenoxy polyethoxyethanol (Triton X-114) was added as surfactant. The effects of experimental conditions such as pH, concentration of chelating agent and surfactant, equilibration temperature and time on cloud point extraction were studied. Under the optimum conditions, enrichment factor for 40 mL of sample solution is 34. The method allows the determination of uranium with a detection limit of 1.55 ng mL$^{-1}$ a quantification limit of 5.16 ng mL$^{-1}$ and a precision expressed as relative standard deviation of 2.7% for uranium concentration of 25 ng mL$^{-1}$ ($n$ = 10). The method was applied to the determination of trace uranium in water samples with satisfactory results.

## INTRODUCTION

Uranium metal in its pure form is chemically active, anisotropic and has poor mechanical properties [1]. On the other hand, uranium alloys are useful in diluting enriched uranium liquid fuel meant for nuclear reactors and pure uranium coated with silicon and canned in aluminum tubes are used in production reactors. However, uranium and its compounds, like lead are highly toxic. Exposure to uranium can result in both chemical and radiological toxicity [2]. The main chemical effect associated with exposure to uranium and its compounds is kidney toxicity. This toxicity can be caused by breathing air containing uranium dusts or by eating substances containing uranium, which then enters the bloodstream. Once in the bloodstream, the uranium compounds are filtered by the kidneys, where they can cause damage to the kidney cells. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 µg/kg of body weight per day [3-5]. The WHO, Health Canada and Australian drinking water guidelines fixed the maximum uranium concentration in drinking waters to be less than 9, 20 and 20 µg L$^{-1}$ [3,4].

Several methods for determination of uranium based on the preconcentration techniques have been reported. Solid sorbents such as polymer-XAD resin series [6-9], modified activated carbon [10], polyurethane foam [11,12], textile dye based

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solid sorbent [13], octylsilane ($C_8$) [14], octadecyl silica membrane discs [15,16], ion imprinting polymers [17-19] have been used for the separation and/or preconcentration of uranium from dilute solutions prior to determination by various analytical methods.

Cloud point extraction (CPE), is an attractive preconcentration method that reduces the consumption of and exposure to solvents, disposal costs, and extraction time. The method is based on the property of most non-ionic surfactants in aqueous solutions to form micelles and become turbid when heated to a temperature known as the cloud point temperature (CPT). Above this temperature, the micellar solution separates in a surfactant rich phase of a small volume and in a dilute aqueous phase [20]. Any species present in the solution that interact with the micellar aggregates are thus extracted and may be preconcentrated in the small volume of the surfactant rich phase. Cloud point extraction has frequently been applied in methods for preconcentration and determination of metals in several samples [21-24].

The bisazo group reagents, such as arsenazo-III and other derivatives, have been found suitable for the spectrophotometric determination of uranium [25]. Arsenazo-III is an extremely sensitive colorimetric reagent in strongly acidic medium [26]. The main advantage of this reagent lies in the high stability of its uranium complex which makes possible its analytical utilization in strongly acidic media, where neither hydrolysis, nor the formation of polynuclear species occur in the reaction [27,28]. The usefulness of the reactivity of arsenazo-III lies in the fact that metals whose complex formation depends on high pH, do not interfere with the determination of other elements which give complexes in strongly acidic media [29]. In other words, by specifying the pH it is possible to use arsenazo-III very selectively. Hence, a simple, reproducible and sensitive cloud point extraction method for uranium was developed by the use of arsenazo-III as a complexing agent and Triton X-114 as a surfactant prior to spectrophotometric determination. The method was also applied to the determination of uranium in water sample and standard reference material.

## EXPERIMENTAL

### Reagents and Materials

All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.2 MΩ cm) obtained from a SG, Ultra Clear purification system. A 200 μg $mL^{-1}$ uranium standard solution was prepared by dissolving appropriate amounts of $UO_2(NO_3)_2 \cdot 6H_2O$ (Fisher Scientific Company) in deionized water. Working solutions were prepared from the stock solution by serial dilutions with deionized water. The non-ionic surfactant Triton X-114 (Sigma-Aldrich) was used without further purification. A 0.1% (w/v) arsenazo-III solution was prepared by dissolving appropriate amount of arsenazo-III obtained from Acros Organics in deionized water. Hydrochloric acid (Carlo Erba) and pure sodium hydroxide pellets (Merck) was used to adjust the sample pH. All laboratory glassware was kept overnight in 5% nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in dust free environment. SPS-SW2, Surface Water (LGC, UK) certified reference waters were used for method validation.

### Apparatus

Shimadzu UV mini-1240 model UV-visible spectrophotometer with 1.0 cm quartz cell was used for uranium measurements in both surfactant-rich and poor phase. A Fisher Scientific Accumet Model 15 pH meter was used to measure pH values. A

Clifton Model NE1-22 thermostatic bath, maintained at the desired temperature, was used for cloud point temperature experiments. A Hettich, EBA 21 model centrifuge was used to accelerate the phase separation.

**Procedure**

For the cloud point extraction, aliquots of 40 mL of the standard or sample solution containing the analyte (5 - 250 ng mL$^{-1}$), 5 mL of 2 mol L$^{-1}$ HCl, 1 mL of 0.1% (w/v) arsenazo-III solution and 1 mL of 0.1% (v/v) Triton X-114 solution were placed in a Falcon tube with 50 mL. This solution was kept at 70°C for 20 min in the thermostatic bath for equilibration and then separation of two phases was achieved by centrifugation for 5 min at 6000 rpm. The mixture was cooled in an ice bath to increase the viscosity of the surfactant-rich phase, and the supernatant aqueous phase was carefully removed with a pipette. The surfactant-rich phase in the tube was made up to 1.5 mL by adding methanol solution in order to reduce its viscosity and facilitate sample handling. The absorbances of standard and sample solutions were measured at the wavelength of maximum absorbance of the complex (650 nm). The blank solution was submitted to the same procedure.

**RESULTS AND DISCUSSION**

**Effect of pH**

The separation of metal ions by the cloud point method involves the prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase, thus obtaining the desired preconcentration [30]. It is known that the formation of the arsenazo-III-lanthanide complex is strongly pH dependent [31]. Thus, extraction recovery also depends on the pH at which complex formation occurs. The effect of pH on the extraction efficiency of the system for U(VI)

ions was examined over a pH range of 2-10. 40 mL of 25 ng mL$^{-1}$ U(VI) standard solution was extracted by procedure mentioned above after pH adjustment with HCl and NaOH. The results are depicted in Figure 1. As can be seen from this figure, a pH value between 2.0 and 3.0 found to be the optimum for the quantitative extraction of U(VI)-arsenazo-III complex and a around pH 2 was selected for further studies. These results are in agreement with the values reported by other researchers [25-27].
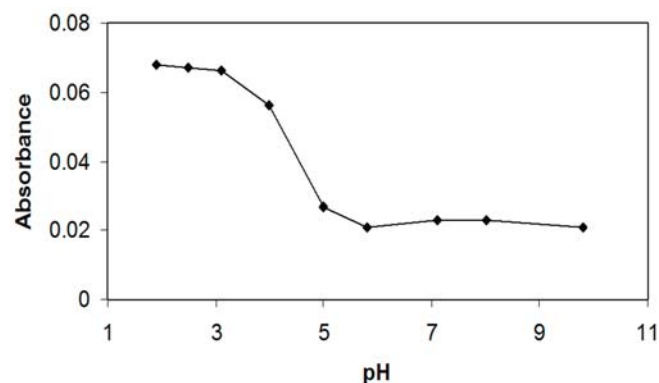


Figure 1. Effect of pH on the absorbance of the U(VI)-arsenazo-III complex. Conditions: 25 ng mL$^{-1}$ U(VI), 0.1% (w/v) arsenazo-III, 0.1% (v/v) Triton X-114, Temperature: 70°C .

**Effect of Arsenazo-III Concentration**

In order to study the influence of concentration of arsenazo-III on analytical response the concentration of arsenazo-III was evaluated over the range 0.005 to 0.5% (w/v). The CPE efficiency increased rapidly as the concentration of arsenazo-III increased from 0.005 to 0.05% (w/v), then kept almost constant with further increase in the arsenazo-III concentration up to 0.5% (w/v). Therefore, in order to prevent the reduction of extraction efficiency in the presence of interferences, arsenazo-III concentration of 0.1% (w/v) was chosen for subsequent experiments.

**Effect of Triton X-114 concentration**

The amount of Triton X-114 not only affected the extraction efficiency, but also the volume of surfactant-rich phase [32]. There is a narrow range within which easy separation, maximum extraction

efficiency and analytical signal are accomplished. The variation of the analytical signal of U(VI)-arsenazo-III complex within the Triton X-114 concentration range of 0.05 to 1% (v/v) was examined and the results can be seen in Figure 2. Quantitative extraction was observed when the Triton X-114 concentration was higher than 0.1% (v/v). At lower concentrations, the extraction efficiency of complex is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. With increase of Triton X-114 concentration above 0.20% (v/v) the signals decrease because of the increment in the volumes and the viscosity of the surfactant phase. So, a concentration of 0.1% (v/v) was chosen as the optimum Triton X-114 concentration in order to achieve the highest possible extraction efficiency.
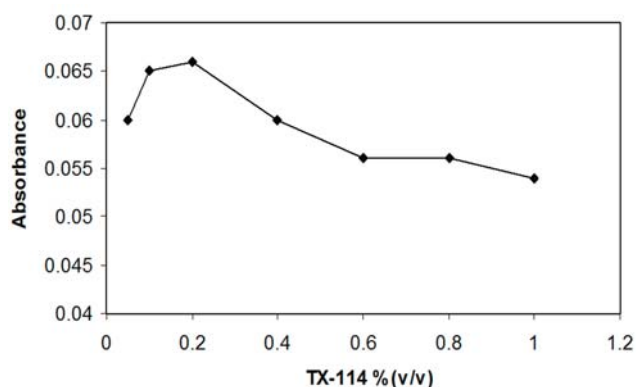


Figure 2. Effect of Triton X-114 concentration on the absorbance of the U(VI)-arsenazo-III complex. Conditions: 25 ng mL$^{-1}$ U(VI), pH = 2, 0.1% (w/v) arsenazo-III, Temperature: 70°C .

## Effects of the equilibrium temperature, time and centrifugation time

When temperature increases, the system is further away from the cloud point, causing the nonionic surfactant to be less water soluble. To achieve easy phase separation, optimal equilibration temperature and incubation time are necessary to complete extraction. The effect of the equilibration temperature and time was studied with a range of 25-80°C and 5-60 min respectively. It was found that an equilibration temperature of 70°C and a time of 20 min were adequate to achieve quantitative

extraction. A centrifugation time of 5 min at 6000 rpm was selected as optimum, because complete separation occurred in this time and no more improvements were obtained for longer time.

## Effect of viscosity

Because the surfactant-rich phase was very viscous, methanol solution was added to the surfactant-rich phase after CPE to facilitate its transfer into spectrophotometric cell. The amount of methanol was chosen to have 1.5 mL of surfactant-rich phase for transferring and measuring the sample absorbance.

## Effect of ionic strength

For the investigating the influence of ionic strength on performance of CPE, various experiments were performed by adding different amount of NaCl (0-0.5 mol L$^{-1}$). Other experimental conditions were kept constant. The results showed that ionic strength has no significant effect on the enrichment factor. This result is in agreement with the literature results which demonstrated than an increase in ionic strength in micelle systems does not seriously alter the extraction efficiency of the analytes [33]. The optimized conditions of CPE are summarized in Table 1.

Table 1. The optimized conditions for cloud point extraction of U(VI).

| Optimum conditions for CPE | |
|---|---|
| Concentration of chelating agent | 0.1% (w/v) |
| Concentration of surfactant | 0.1% (v/v) |
| pH range | 1.0-3.0 |
| Equilibrium temperature (°C) | 70 |
| Equilibrium time (min) | 20 |
| Centrifugation rate (rpm) | 6000 |
| Centrifugation time (min) | 5 |
| Diluent | methanol |

## Interferences

The effect of foreign ions on the determination of 25 ng mL$^{-1}$ U(VI) by the proposed method was studied. An ion was considered to interfere when its presence causes a variation in the absorbance of the sample of more than 5%. The results of the interference study are summarized in Table 2. As seen from the table uranium recoveries were nearly quantitative in the presence of other ions.

Table 2. Tolerance limits of interfering ions in the determination of 25 ng mL$^{-1}$ U(VI).

| Ions | Interferent to U(VI) ratio |
|---|---|
| Na$^+$, K$^+$, Cl$^-$, SCN$^-$ | 10000 |
| Ca$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, CO$_3$$^{2-}$ | 1000 |
| Al$^{3+}$, NO$_3$$^-$ | 500 |
| Co$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Cr$^{3+}$ | 100 |

## Analytical characteristics

Using the optimized condition for preconcentration of uranium, calibration graph is linear from 5 to 500 ng mL$^{-1}$. The linear equation for uranium was A = 1.8 × 10$^{-3}$ C + 2.7 × 10$^{-2}$ ($R^2$ = 0.999), here A is the absorbance and C is the uranium concentration in solution (ng mL$^{-1}$). The equation obtained without preconcentration (500-20,000 ng mL$^{-1}$) was A = 5.3 × 10$^{-5}$ C - 3.7 × 10$^{-2}$ ($R^2$ = 0.994). Enrichment factor (EF) was calculated as the ratio of the slopes of the calibration graphs obtained with and without preconcentration [34]. The precision of the method, calculated as the relative standard deviations for sample solutions containing 25 ng mL$^{-1}$ uranium. The limit of detection is defined as the concentration equivalent to three times the standard deviation of 10 measurements of the blank [35] and is the lowest analyte concentration that produces a response detectable above the noise level of the system. The limit of quantification (10$s$), ($n$ = 10) is the lowest level of analyte that can be accurately and precisely measured. Table 3 gives the analytical features of the method.

Table 3. Analytical characteristics of the method.

| Parameter | Analytical Feature |
|---|---|
| Enrichment factor | 34 |
| Sample volume, mL | 40 |
| Surfactant rich phase volume, mL | 1.5 |
| Limit of detection, ng mL$^{-1}$ ($n$ = 10) | 1.55 |
| Limit of quantification, ng mL$^{-1}$ ($n$ = 10) | 5.16 |
| Precision (U(VI), 25 ng mL$^{-1}$, $n$ = 10) RSD (%) | 2.7 |
| Linear range, ng mL$^{-1}$ | 5 - 500 |

## Determination of uranium in real and spiked water samples

In order to validate the proposed method, recovery experiments were also carried out by spiking the water sample. For this purpose, different amount of uranium was added to 40 mL of tap water (Ankara, Turkey). The results are shown in Table 4. The recovery values calculated for the added standards were always higher than 95%, and these results confirm the validity of the proposed method.

The CPE method was also applied to certified reference material SPS-SW2 (Surface Water) for the determination of contents of U(VI) ions. The certified and observed values are given in Table 4. Results are the average of three replicates. As Table 4 indicates there is a good agreement between the obtained results and the known values. The recoveries are close to 100% and indicate that the proposed system was helpful for the determination of uranium in the real samples.

Table 4. Determination of U(VI) in tap water and certified reference material samples ($n$ = 3).

| Sample | Certified value (ng mL$^{-1}$) | Added (ng mL$^{-1}$) | Found (ng mL$^{-1}$) | Recovery (%) |
|---|---|---|---|---|
| Tap water | - | - | nd[a] | - |
| | | 10 | 9.78 ± 0.11 | 97.8 |
| | | 25 | 24.82 ± 0.38 | 99.3 |
| | | 50 | 50.80 ± 0.51 | 101.6 |
| | | 100 | 100.43 ± 0.68 | 100.4 |
| SPS-SW2 | 2.5 | - | nd[a] | - |
| | | 10 | 12.29 ± 0.18 | 98.3 |
| | | 25 | 27.20 ± 0.29 | 98.9 |
| | | 50 | 51.08 ± 0.45 | 97.3 |
| | | 100 | 102.09 ± 0.58 | 99.6 |

[a] nd, not detected.

## CONCLUSIONS

Cloud point extraction is an easy, safe, rapid and inexpensive methodology for preconcentration and separation of trace metals in aqueous solutions. The methodology also offers an eco-friendly alternative to other separation preconcentration systems. Arsenazo-III has already been used as complexing agent for determination of uranium spectrophotometrically. But the novelty of presented study is originated from the low detection limit and high enrichment factor values for spectrophotometric uranium determination. With the usual spectrophotometric method for uranium-arsenazo-III complex the detectable concentration is in $\mu$g mL$^{-1}$ levels, while the detectable concentration is in ng mL$^{-1}$ levels with proposed cloud point extraction procedure. In this way the determination of ng mL$^{-1}$ levels of uranium in water samples was successfully performed by using cloud point extraction and arsenazo-III reagent spectrophotometrically. The method gives a very low detection limit and good RSD value. Arsenazo-III is a very stable and by specifying the pH it is possible to use arsenazo-III very selectively. The proposed method can be applied to the determination of trace metals in various water samples.

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