

Original Article

PRECONCENTRATION, SOLVENT SUBLATION AND SPECTROMETRIC DETERMINATION OF URANIUM(VI) IN WATER SAMPLES USING ARSENAZO III AND TRI N-OCTYL AMINE

RAGAA E. SHOHAIB¹, MAGDA A. AKL², NAGDY M. FARAG³, AYMAN A. GOUDA^{1,4*}, SAMEH R. ABDEL HAMID³

¹ Chemistry Department ⁴ Faculty of Science ⁴Zagazig University ⁴Zagazig, 44519, Egypt., ² Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt., ³Nuclear Material Authority, Cairo, Egypt., ⁴ Faculty of Public Health and Informatics, Umm AL-Qura University, Makkah, Saudi Arabia.
Email: aygangsouda77@gmail.com,

Received: 04 Apr 2014 Revised and Accepted: 10 May 2014

ABSTRACT

Objective: Preconcentration and solvent sublation has been studied for the separation and determination of trace uranium (VI) in various spiked water samples.

Methods: A strongly red colored anionic $[UO_2(Ar-III)]^{2-}$ complex was formed at pH 1.0 upon adding arsenazo III (Ar-III) to the sample solution. Tri n-octyl amine (TOA) was added in the solution to form the $(TOA)_2[UO_2(Ar-III)]$ ion pair, and an oleic acid (HOL) surfactant was added. Then, the $(TOA)_2[UO_2(Ar-III)]$ ion pairs were floated by vigorous shaking in the flotation cell and extracted into methyl isobutyl ketone (MIBK) on the surface of the aqueous solution. The uranium collected in the MIBK layer was measured directly by spectrophotometry. Different experimental variables that may affect the sublation efficiency were thoroughly investigated.

Results: The molar absorptivity of the $(TOA)_2[UO_2(Ar-III)]$ ion pair was 3.28×10^4 and 1.24×10^6 L mol⁻¹ cm⁻¹ in the aqueous and organic layers, respectively. Beer's law held up to 0.01-1.0 mgL⁻¹ of U(VI) in the aqueous as well as in the organic layers.

Conclusion: The adopted solvent sublation method was successfully applied for the determination of U(VI) in various kinds of water samples with a preconcentration factor of 250.

Keywords: Solvent sublation; Spectrometric determination; Uranium(VI); Arsenazo III; Water samples.

INTRODUCTION

Analysis and separation of the metallic species is still a most actual problem. In recent years, when the environment came to have a considerable impact upon us all, the identification and separation of the metallic ions became especially important.

Due to its chemical toxicity and radioactive nature, uranium (U) is one of the most hazardous heavy metals in the environment. U in trace amount is found almost everywhere in water, soil and rocks [1]. It is also known as responsible to cause toxicological effects in mammals and is potential occupational carcinogen [2]. Uranium assessment in trace quantity is important task to estimate the performance of different nuclear processes and thus its determination in environmental samples is a matter of concern for safety reasons [3].

A number of various methods have been developed for U determination in different samples. These various techniques are laser fluorimetry [4], gamma spectrometry [5], stripping voltammetry [6], fluorimetry [7], potentiometry [8], polarography [9], X-ray fluorescence [10], inductively coupled plasma mass spectrometry [11, 12], neutron activation analysis [13], and alpha spectrometry [4, 14]. Although all these techniques are sensitive and capable of fast measurement, but requires expensive instruments, perfect experimental conditions and complicated sample-pretreatment steps.

Because of its dynamic oxidation state, U has a unique nature as compared to many other metals. U has the capability to be a part of positive, neutral and negatively charged complexes, nearly at neutral pH. Due to the strong association of U with other elements, its determination needs selectivity. Because of simplicity and selectivity, different chromogenic agents and organic dyes have been widely investigated and reported for the spectrophotometric determination of U(VI) [15-27]. Among a variety of these organic reagents which are largely based on azo-dyes for U(VI) determination, sodium salt of Ar-III is reported as a responsive

chromogenic reagent. Because of U(VI)-(Ar-III) high stability its quantitative determination even in very low pH became possible, where neither hydrolysis, nor the formation of polynuclear species can take place.

Several methods for determination of uranium based on the preconcentration techniques have been reported. Solid phase extraction [28-41], cloud point extraction [42-47], liquid-liquid extraction [48, 49] and coprecipitation [50] have been reported for the enrichment of uranium(VI) from dilute solutions prior to determination by a variety of analytical techniques.

There are several possible strategies for enhancing the overall sensitivity for metal determination when using a metal-chelate technique. In an effort to develop a preconcentration technique for measuring U(VI) in ground water samples, investigations were conducted concerning the use of Ar-III as complexing agents for uranium [51, 52]. These techniques called solvent sublation. Solvent sublation is a very useful technique in which the precipitates, complexes, or ion-pair of analytical elements are floated and extracted into a light and immiscible solvent on the analytical solution by a gas bubbling in a flotation cell. This is a combined technique of solvent extraction and flotation. The sublation had a good advantage to pre-concentrate analytes with a big ratio from large volume sample to a small volume of solvent. Besides, some necessary fundamental studies were done for the effective sublation of elements by the solvent extraction to optimize sublation conditions and the recovery test was performed to evaluate the applicability to practical analysis of real samples. The extracted analytes in the solvent can be measured without further treatment. A desired element(s) can be selectively concentrated and determined in a sample solution(s) by adjusting the pH and using a proper ligand [53, 54].

In the present paper, the determination of U(VI) by using Ar-III as a complexing agent, Tri n-octyl amine (TOA), oleic acid (HOL) surfactant and MIBK as an organic solvent is reported. Ar-III is more sensitive and specific than many of the previous reported reagents

for U(VI). A number of experimental variables was evaluated, e.g. the pH of sample solution, the concentration of metals and ligand *etc.*

MATERIALS AND METHODS

Apparatus

Two types of flotation cells were used throughout [55]. Flotation cell type 1 was a stoppered tube of 1.2 cm inner diameter and 29 cm length with a stopcock at the bottom. This cell was used to study the factors affecting the efficiency of flotation. The second type was a cylindrical tube of 6.0 cm inner diameter and 45 cm length with a stopcock at the bottom and a quick-fit stopper at the top. This cell was used to separate the investigated analytes from a relatively large volume. Spectrophotometric measurements were made using UV/VIS-1601 SHIMADZU spectrophotometer. The pH measurements were carried out using a HANA Instrument (Portugal) (HI: 9321) digital pH-meter.

Chemicals and solutions

All of the reagents and solvents were of analytical grade and were used without further treatment. Bidistilled water was used throughout this study.

- An U(VI) stock solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) was prepared by dissolving Uranyl acetate ($\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in concentrated HCl and up to 100 mL with water.
- Arsenazo-III (Ar-III) was purchased from Merck Chemicals Ltd. A stock solution of Ar-III ($1.0 \times 10^{-3} \text{ M}$) was prepared by dissolving an appropriate amount of the ligand in bidistilled water and up to 100 mL and stored in dark bottle.
- A solution of ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) tri n-octyl amine (TOA) (Fluka) was prepared by dissolving the reagent in bidistilled water.
- An oleic acid (HOL) stock solution ($6.3 \times 10^{-2} \text{ mol L}^{-1}$) was prepared by dispersing 20 mL of oleic acid (J. T. Baker Chemical) and completed to 1000 mL with Kerosene.
- Solutions of other foaming reagents (0.05%) were prepared by dissolving in appropriate solvents: Tween 80 in water, cetyltrimethylammonium bromide (CTAB) in 95% ethanol.
- Methyl isobutyl ketone (MIBK).

Analytical procedures

In an Erlenmeyer flask, 2.0 mL of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ Ar-III was introduced into 10 mL measuring flask containing 1.0 mL of 0.1 M HCl pH 1.0 and different concentration of U(VI) solution ranged between $0.25 \times 10^{-5} \text{ mol L}^{-1}$ to $1.0 \times 10^{-5} \text{ mol L}^{-1}$, then the solution was thoroughly mixed. A red colored anionic $[\text{UO}_2(\text{Ar-III})]^{2-}$ complex was developed instantaneously. After that 2.0 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ TOA solution was added. The mixture was shaken well for 2.0 min to allow complete development of the $(\text{TOA})_2[\text{UO}_2(\text{Ar-III})]$ ion pair. All contents were quantitatively transferred into a flotation cell (type 1) and the volume was diluted to 10 mL with bidistilled water. Then, 3.0 mL of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ HOL was added. The flotation cell was shaken upside down by hand for 5.0 min. Vigorous shaking of the flotation cell in the presence of a surfactant (HOL) created bubbles in the solution, which enhanced the floatability of the $(\text{TOA})_2[\text{UO}_2(\text{Ar-III})]$ ion pair. A 2.0 mL of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ MIBK was added to the solution surface and the flotation cell was shaken upside down by hand for 5.0 min to ensure complete flotation of the colored complex in room temperature. The $(\text{TOA})_2[\text{UO}_2(\text{Ar-III})]$ ion pair was quantitatively transferred into the organic layer on the solution surface. The aqueous phase was run off through the bottom of the cell. The concentration of U(VI) in the organic layer was determined spectrophotometrically using standard addition method by transferring a suitable volume to the quartz cell and measuring the absorbance at 655 nm against a reagent blank ($3.0 \times 10^{-5} \text{ mol L}^{-1}$ Ar-III).

The separation or solvent sublation efficiency ($S, \%$) of the U(VI) in the organic solvent was determined from the following relationship:

$$S = (C_o / C_i) \times 100\% \quad (1)$$

where, C_o and C_i denote the concentration of U(VI) in the organic and the initial aqueous layers, respectively.

Sample analysis

Natural water samples (recovery test)

To assess the applicability of the proposed procedure to real samples, it was applied to the extraction and determination of U(VI) in water samples. Three water samples taken from the springs near the uranium mines at Abu Tarturregion, Egypt were analyzed. The samples were first filtered through a Millipore $0.45 \mu\text{m}$ pore size membrane to remove any suspended particulate matter and immediately treated with a few milliliters of conc. HNO_3 and boiled for 10 min in order to oxidize any trace organic matter and to expel dissolved carbon dioxide. The sample stored in previously cleaned polyethylene bottles and treated according to the designed procedure. Different concentrations of U(VI) were introduced into a series of flotation cells, each containing 1.0 L of a water sample. Then, 5.0 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ Ar-III were added and each cell was shaken upside down vigorously by hand for 5.0 min to allow complexation. To each cell, 5.0 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ TOA was added and the mixture was shaken well. To this solution, 5.0 mL of an kerosene HOL solution ($2.0 \times 10^{-3} \text{ mol L}^{-1}$) was added and the cell was then inverted upside down many times by hand. After that, 4.0 mL of MIBK was introduced onto the surface of each cell and the cell was shaken well. The organic layer was separated to ensure a preconcentration factor of 250. This solution was then subjected directly to spectrophotometric determination.

RESULTS AND DISCUSSION

Solvent sublation of U(VI)

Influence of pH

A series of experiments was carried out to study the effect of the hydrogen-ion concentration on the sublation efficiency of U(VI) in both absence and presence of Ar-III. The results are shown in Fig. 1. In the absence of Ar-III, the separation efficiency is not quantitative, in which the sublation efficiency ($S, \%$) does not exceed 20%. On the other hand, Figure 1, shows the effect of the pH on the sublation efficiency of U(VI) in the presence of Ar-III. The U(VI)-Ar-III complex was quantitatively sublated as an ion pair from an aqueous solution in the optimum pH 1.0, because above pH= 4.0 the solution start precipitation in presence of organic phase (HOL-TOA-MIBK). The effect of varying the pH from 1.0 to 10 on the sublation of $1.0 \times 10^{-5} \text{ mol L}^{-1}$ U(VI), 2.3 ppm, was investigated in the presence of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ Ar-III, $1.0 \times 10^{-3} \text{ mol L}^{-1}$ TOA, $2.0 \times 10^{-3} \text{ mol L}^{-1}$ HOL and $2.0 \times 10^{-3} \text{ mol L}^{-1}$ MIBK. The results are shown that the maximum sublation efficiency reach $S\%=100$ which was obtained in the pH 1.0 of 0.1 M HCl solution.

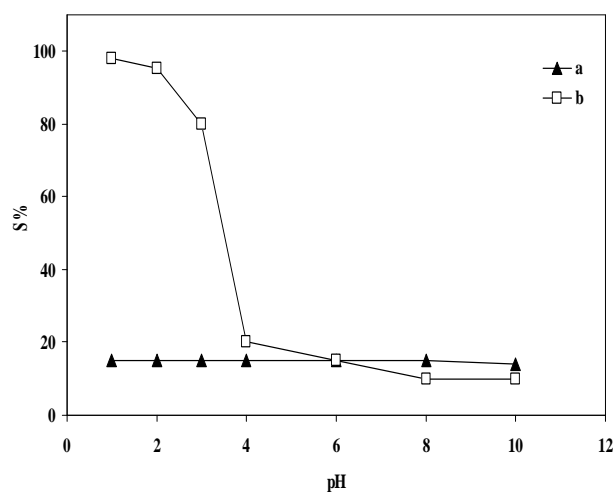


Fig. 1: Effect of pH on the Sublation efficiency ($S, \%$) of (a) U(VI) in the absence of Ar-III and (b) $(\text{TOA})_2[\text{UO}_2(\text{Ar-III})]$ ion pair. U(VI), $1.0 \times 10^{-5} \text{ mol L}^{-1}$; Ar-III, $1.0 \times 10^{-4} \text{ mol L}^{-1}$; TOA, $1.0 \times 10^{-3} \text{ mol L}^{-1}$; HOL, $2.0 \times 10^{-3} \text{ mol L}^{-1}$ and MIBK, $2.0 \times 10^{-3} \text{ mol L}^{-1}$.

Influence of Ar-III concentration

The effect of different concentrations of arsenazo III on the sublation efficiency of $1.0 \times 10^{-5} \text{ mol L}^{-1}$ U(VI) using $1.0 \times 10^{-3} \text{ mol L}^{-1}$ TOA, 3.0 mL of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ HOL and 2.0 mL of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ MIBK at pH 1.0 was investigated (Fig. 2). Complete sublation of U(VI) was achieved at Ar-III concentration $>4.0 \times 10^{-5} \text{ mol L}^{-1}$. The excess Ar-III concentration has no adverse effect on sublation, thus giving a good chance for applying the procedure for analysis of uranium on water samples. Different concentrations of Ar-III was examined ranged between $0.1-15 \times 10^{-5} \text{ mol L}^{-1}$ under the optimum condition. These results confirmed that quantitative sublation was obtained when $[\text{U(VI)}]:[\text{Ar-III}] \geq 1:4$. In most experiments in this investigation, the concentration of Ar-III was chosen to be more than 10-fold that of U(VI).

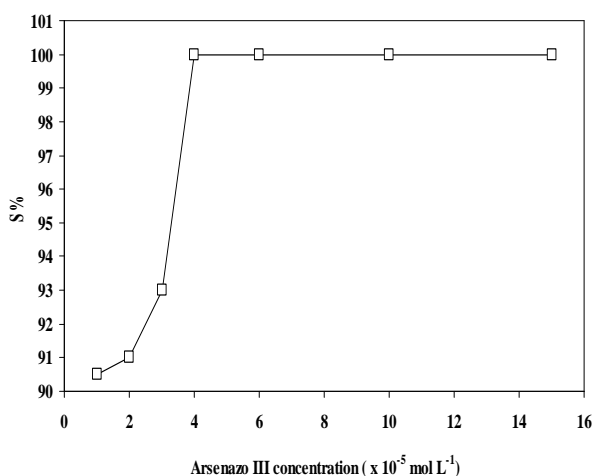


Fig. 2: Influence of the Ar-III concentration on the sublation efficiency (S, %) of U(VI), $1.0 \times 10^{-5} \text{ mol L}^{-1}$; TOA, $1.0 \times 10^{-3} \text{ mol L}^{-1}$; HOL, $2.0 \times 10^{-3} \text{ mol L}^{-1}$; MIBK, $2.0 \times 10^{-3} \text{ mol L}^{-1}$ and pH 1.0 at 25°C .

Influence of TOA concentration

Although the anionic complex, $[\text{UO}_2(\text{Ar-III})]^{2-}$, is sublated by the bulky organic cation, TOA⁺, sublation is not quantitative. However, by the addition of the surfactant, HOL, the complex could be quantitatively floated and extracted easily into MIBK. The solvent sublation efficiency reached 100% at pH 1.0. The effect of the TOA concentration on the sublation efficiency of the complex in the presence of HOL was investigated using $1.0 \times 10^{-5} \text{ mol L}^{-1}$ (2.3 ppm) U(VI) at pH 1.0. Fig. 3 shows that the maximum sublation efficiency of $[\text{UO}_2(\text{Ar-III})]^{2-}$ was attained when the concentration of TOA was $\geq 1.0 \times 10^{-3} \text{ mol L}^{-1}$. Thus, $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of TOA was chosen in the present study.

Type and amount of surfactant

The flotation and extraction of complexes into MIBK on the surface of aqueous solution in a flotation cell is enhanced by changing the complexes from hydrophilic to hydrophobic properties. The change can be done by using a surfactant. Such an enhancement can be explained as follows.

The ion-pair or metal-ligand complexes are adsorbed with a surfactant and easily floated to the top of the solution by bubbling nitrogen gas or vigorous shaking. The complexes adsorbed are desorbed in an organic phase if the complexes are floated to the phase [57]. A neutral TOA ion pair of complexes can be floated and extracted into MIBK, but a surfactant has been used to improve the flotation. This is due to the fact that a surfactant not only supports an ion pair by forming foams, but can also make the surface of the ion pair hydrophobic, and hence can easily be attached to air bubbles [58–60].

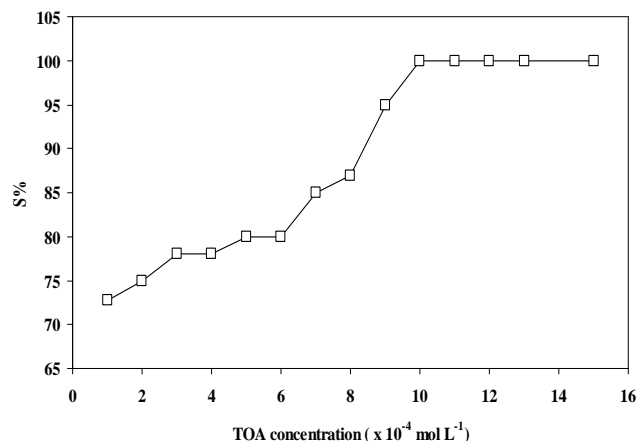


Fig.3: Influence of the TOA concentration on the sublation efficiency (S, %) of U(VI), $1.0 \times 10^{-5} \text{ mol L}^{-1}$; Ar-III, $1.0 \times 10^{-4} \text{ mol L}^{-1}$; HOL, $2.0 \times 10^{-3} \text{ mol L}^{-1}$; MIBK, $2.0 \times 10^{-3} \text{ mol L}^{-1}$ and pH 1.0 at 25°C .

The effect of the type of surfactant on the efficiency of sublation was studied using anionic (HOL), non-ionic (Tween 80) and cationic (CTAB) surfactants. The $(\text{TOA})_2[\text{UO}_2(\text{Ar-III})]$ ion pair was not sublated at all upon using cationic or non-ionic surfactants. On the other hand, the anionic surfactant HOL strongly increased the sublation efficiency. Such a phenomenon can be interpreted to mean that excess TOA around the $[\text{UO}_2(\text{Ar-III})]^{2-}$ complex creates ion pairs of positive charge. Therefore, the addition of an anionic surfactant improves the efficiency of sublation.

Influence of oleic acid (HOL) concentration

The concentration of HOL is an important parameter to improve the limit of the separation percentage. Sublation is not quantitative. However, by the addition of the surfactant (TOA) and HOL, the complex could be quantitatively floated and extracted easily into MIBK. Fig. 4 shows that the sublation efficiency of the $(\text{TOA})_2[\text{UO}_2(\text{Ar III})]$ ion pair reaches its maximum (100%) over a wide range of HOL concentrations ($1.0-6.0 \times 10^{-3} \text{ mol L}^{-1}$). A suitable concentration ($2.0 \times 10^{-3} \text{ mol L}^{-1}$) of HOL and 3.0 mL volume were selected throughout this work.

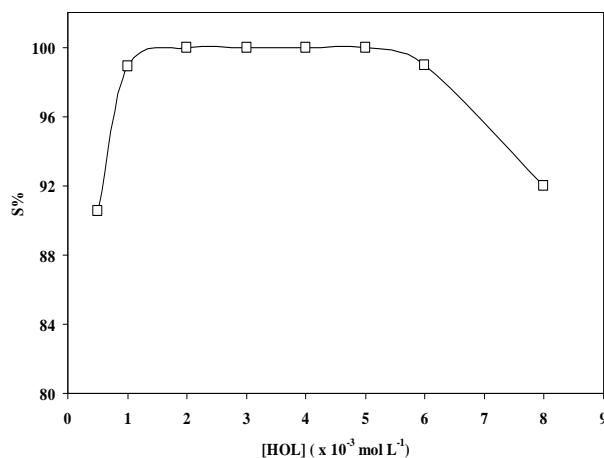


Fig. 4: Solvent sublation of the $(\text{TOA})_2[\text{UO}_2(\text{Ar III})]$ ion pair vs HOL concentration. U(VI), $1.0 \times 10^{-5} \text{ mol L}^{-1}$; arsenazo III, $1.0 \times 10^{-4} \text{ mol L}^{-1}$; TOA, $1.0 \times 10^{-3} \text{ mol L}^{-1}$; MIBK, $2.0 \times 10^{-3} \text{ mol L}^{-1}$ and pH 1.0 at 25°C .

Influence of organic solvents

A proper choice of the solvent is very important to dissolve and extract the floated ion pairs into the solvent. The solvent should be lighter than an aqueous solution, *i.e.*, with a specific gravity less than 1.0 g mL⁻¹, separated clearly from the aqueous phase and does not turn turbid by mixing with water. In the present study, the sublation efficiency was investigated with such solvents as benzene, MIBK, xylene and hexane. MIBK was chosen as a solvent in the present study because of the maximum absorbance and the lowest background for the investigated analyte.

Influence of temperature

In order to study the optimum temperature required for quantitative sublation of uranium- Ar-III complex, a series of experiments was conducted over a wide temperature range (20-70°C). The temperature effect on the sublation efficiency is depicted in Fig. 5. The sublation of (TOA)₂[UO₂(Ar-III)] ion pair is not affected by raising the temperature up to 40 °C, above which the sublation efficiency starts to decrease. This decrease may be attributed to an instability of the ion pairs (TOA)₂[UO₂(Ar-III)] as well as weak binding between the HOL surfactant and the ion pair species. Thus, all work was carried out at room temperature (25 °C).

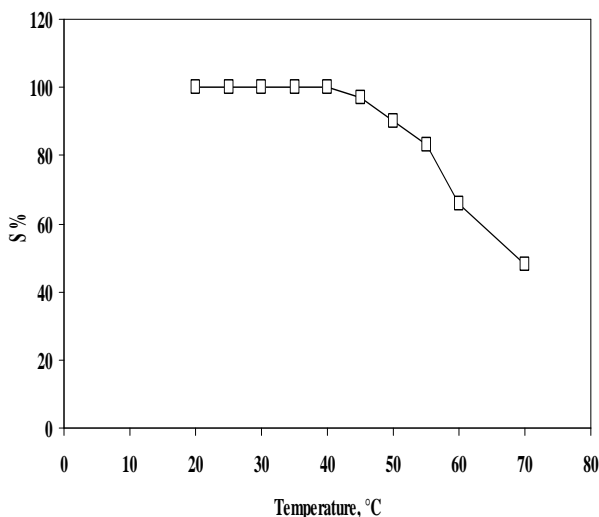


Fig. 5: Influence of the temperature on the sublation efficiency (S, %) of the (TOA)₂[UO₂(Ar III)] ion pair. U(VI), 1.0 × 10⁻⁵ mol L⁻¹; Ar-III, 1.0 × 10⁻⁴ mol L⁻¹, TOA, 1.0 × 10⁻³ mol L⁻¹; HOL, 2.0 × 10⁻³ mol L⁻¹; MIBK, 2.0 × 10⁻³ mol L⁻¹ and pH 1.0.

Influence of foreign ions

The possible interference of various ions, which are thought to account for the major constituent of water samples, especially the ions that interfere with the spectrophotometric method, was examined by introducing them into the solutions containing 1.0 × 10⁻⁵ mol L⁻¹ of U(VI) and treating as described in the procedure.

The tolerance limit was fixed as the maximum amount of an ion causing an error no greater than 3.0% in the absorbance of the consequent solution. The results are given in Tables 1. It was observed that almost all of the cations and anions except for Th⁴⁺ and Zr⁴⁺ were tolerated at high concentration ratios. Synthetic mixture of studied cations and anions which are thought to account for the major constituent of water.

Analytical parameters

Calibration graph was constructed from spectrophotometric measurements performed under the optimum conditions described

above. The calibration graph was linear in the range 10–1000 ng mL⁻¹ (Fig. 6). The calibration equation is $A = 0.3889x + 0.0047$ with a correlation coefficient of 0.9990 ($n = 6$), where A is the absorbance of the complex at 655 nm and C is the concentration of U(VI) in original sample solution in ng mL⁻¹. The effective molar absorptivity of the (TOA)₂[UO₂(Ar-III)] ion pair was 3.28 × 10⁴ L mol⁻¹ cm⁻¹ in the aqueous layer. That of organic phase, with respect to the initial U(VI) concentration in aqueous phase, was 1.24 × 10⁶ L mol⁻¹ cm⁻¹. The limit of detection, defined as $C_L = 3S_b/m$ [56], where C_L, S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was 1.10 × 10⁻⁸ mol L⁻¹ (2.6 ng mL⁻¹) of U(VI).

Table 1: Tolerance limits of the foreign ions in the determination of 1.0 × 10⁻⁵ mol L⁻¹ U(VI).

Ions	Maximum tolerated ratio of coexisting ion to U(VI), m/m
Na ⁺ , K ⁺ , Cl ⁻ , SCN ⁻	5000
Mg ²⁺ , Ca ²⁺ , Hg ²⁺ , Pb ²⁺ , Cd ²⁺ , CO ₃ ²⁻ , PO ₄ ³⁻	1000
Fe ³⁺ , Al ³⁺ , Cr ³⁺ , Cu ²⁺ , Zn ²⁺ , Mn ²⁺ , Ni ²⁺	500
Th ⁴⁺ , Zr ⁴⁺	100

Also, concerning this matter, a fixed quantity of U(VI) was taken and added to different volumes of aqueous solutions. It was found that of 4.3 × 10⁻⁷ mol L⁻¹ U(VI) was quantitatively separated and determined from different volumes up to 1.0 L. This means that 102 ng mL⁻¹ of U(VI) can be safely separated and determined by such a procedure from 1.0 L solution into 4.0 mL of the organic layer, so, the preconcentration factor of 250 was achieved in this method.

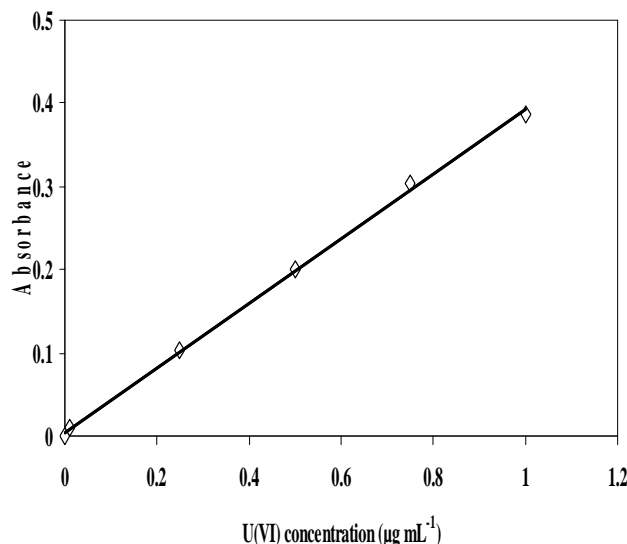


Fig. 6: Calibration graph for of the "U(VI)-Ar-III" complex.

Applications

Recovery yields of U(VI) in natural water samples

The developed procedure for the determination of U(VI) using a sublation methodology and spectrophotometry was examined for three water samples (Table 2). The good recoveries of spiked known additions to different water samples were in the ranges of 97 – 104%.

Table 2: Analytical results of water samples by the solvent sublation

Sample	Spiked U(VI) (ng mL ⁻¹)	Found U(VI) (ng mL ⁻¹)	Recovery (%)	RSD (%)
Tap water	50	49.50	99.00	1.90
	100	98.8	98.80	2.10
	200	194	97.00	1.40
Waste water	50	50.10	100.2	1.80
	100	99.40	99.40	1.65
	200	199.0	99.50	2.30
Well water	50	49.8	99.60	2.40
	100	104	104	1.90
	200	202	101	2.50

CONCLUSIONS

Solvent sublation, compared with ion flotation, has an advantage in that it allows analysis of the organic phase directly, and it is not necessary to destroy the foam (which is not always a very easy task). In the present study, traces of U(VI) in media of diverse origin were determined by a solvent sublation methodology using an ion pair of [U(VI)-Ar-III] anion and TOA for the utilization of a synergistic effect. The hydrophobic ion pairs, created by the addition of oleic acid surfactant, were floated and extracted into MIBK by vigorous shaking of the flotation cell. The U(VI) concentrated in the organic layer was subjected directly to spectral determination without preliminary elution. This procedure was successfully applied to the analysis of various kinds of water samples spiked with known amounts of U(VI) with a preconcentration factor of 250. This method is free from some limitations, such as using harmful solvents, less amount of reagents, and also considered from economically feasible. The process is relatively simple, fast, and utilized from the organic phase so that there is not so much toxicity. Furthermore, the organic phase can be used repeatedly without any purification; hence, this method has no problem in view of the environmental pollution.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests with the company name used in the paper.

REFERENCES

1. Yemalyanov VS, Yevstyukhin AI. The Metallurgy of Nuclear Fuel. Atomizdat, Moscow, 1969.
2. Agency for Toxic Substances and Disease Registry (ATSDR), US public health service, Chapman and Hall, New York, 2000. Toxicological profile for arsenic: health effects chapter; cited 2006 April.
3. Suresh A, Patre DK, Srinivasan TG, Rao PRV. A new procedure for the spectrophotometric determination of uranium(VI) in the presence of a large excess of thorium(IV). Spectrochim. Acta A 2002; 58:341-347.
4. Rathore DPS. Advances in technologies for the measurement of uranium in diverse matrices. Talanta2008; 77:9-20.
5. Sundar U, Ramamurthy V, Buche V, Rao DN, Sivadasan PC, Yadav RB. Rapid measurements of concentrations of natural uranium in process stream samples via gamma spectrometry at an extraction facility. Talanta2007; 73:476-482.
6. Piech R, Bas B, Kubiak WW. The cyclic renewable mercury film silver based electrode for determination of uranium(VI) traces using adsorptive stripping voltammetry. Electroanalysis2007; 19:2343-2350.
7. Nivens DA, Zhang Y, Angel SM. Detection of uranyl ion via fluorescence quenching and photochemical oxidation of calcein. J Photochem Photobiol A Chem2002; 152:167-173.
8. Anwar M, Mohammad D. Potentiometric determination of free acidity and uranium in uranyl nitrate solutions. J RadioanalNuclChem 1989; 134:45-51.
9. Lakar MM, Branica M. Stripping voltammetric determination of trace levels of uranium by synergic adsorption. Anal ChimActa 1989; 221:279-287.
10. McMahon AW. Application of analytical methods based on X-ray spectroscopy to the determination of radio nuclides. Sci Total Environ 1993; 130:285-295.
11. Aydin FA, Soylak M. Solid phase extraction and preconcentration of uranium(VI) and thorium(IV) on Duolite XAD761 prior to their inductively coupled plasma mass spectrometric determination. Talanta2007; 72:192-197.
12. Rozmaric M, Ivšic AG, Grahek Z. Determination of uranium and thorium in complex samples using chromatographic separation, ICP-MS and spectrophotometric detection. Talanta2007; 80:352-362.
13. Shinotsuka K, Ebihara M. Precise determination of rare earth elements, thorium and uranium in chondritic meteorites by inductively coupled plasma mass spectrometry a comparative study with radiochemical neutron activation analysis. Anal ChimActa 1997; 338:237-246.
14. Benedik L, Vasile M, Spasova Y, Wařtjen U. Sequential determination of 210 Po and uranium radioisotopes in drinking water by alpha-particle spectrometry. ApplRadiatIsot2009; 67:770-775.
15. Khan MH, Warwick P, Evans N. Spectrophotometric determination of uranium with arsenazo-III in perchloric acid. Chemosphere 2006; 63:1165-1169.
16. Hosseini MS, Raissi H, Yavari HR. Synergistic flotation of U(VI)-alizarin complex with some diamines followed by spectrophotometric determination of U(VI) using 4,4-diaminophenylmethane. Anal ChimActa2006; 559:181-185.
17. Ru Y, Yan L, Guilan S, Tao W, Jiaomai P. Spectrophotometric determination of uranium in natural water with the new chromogenic reagent p-carboxychlorophosphonazo. Anal ChimActa1995; 314:95-99.
18. Leong CL, Florence TM, Farrar Y. Spectrophotometric determination of uranium(VI) with chromazurol S and cetylpyridinium bromide. Anal Chem1973; 45:201-203.
19. Florence TM, Farrar YJ. Spectrophotometric determination of uranium with 4-(2-pyridylazo) resorcinol. Anal Chem1963; 35:1613-1616.
20. LutfullahAlam MN, Rahman N, Azmi SNH. Optimized and validated spectrophotometric method for the determination of uranium(VI) via complexation with meloxicam. J Hazard Mater 2008; 155:261-268.
21. Jie C, Zajun L, Ming L. Spectrophotometric determination of ultra-trace uranium(VI) in seawater after extractive preconcentration with ionic liquid and dimethylphenylazosalicylfluorone. Int J Environ Anal Chem2008; 88:583-590.
22. Motojima K, Yoshida H, Izawa K. Spectrophotometric determination of small amounts of uranium with 8-quinolinol. Anal Chem1960; 32:1083-1085.
23. Ramakrishna TV, Murthy RSS. Spectrophotometric determination of uranium with anthranilic acid and rhodamine 6G. Talanta 1980; 27:442-444
24. Madrakian T, Afkhami A, Mousavi A (2007) Spectrophotometric determination of trace amounts of uranium(VI) in water samples after mixed micelle-mediated extraction. Talanta 71:610-614
25. Das SK, Kedari CS, Tripathi SC. Spectrophotometric determination of trace amount of uranium (VI) in different aqueous and organic streams of nuclear fuel processing using 2-(5-bromo-2-pyridylazo-5-diethylaminophenol). J RadioanalNuclChem2010; 285:675-681.
26. Shemirani F, Kozani RR, Jamali MR, Assadi Y, Milani SMR. Micelle-mediated extraction for direct spectrophotometric

- determination of trace uranium(VI) in water samples. *Sep Sci Technol* 2005; 40:2527–2537
27. Currah JE, Beamish FE. Colorimetric determination of uranium with thiocyanate. *Anal Chem* 1947; 19:609–612
 28. Kazeraninejad M, Haji Shabani AM, Dadfarnia S, Ahmadi SH. Solid phase extraction of trace amounts of uranium(VI) from water samples using 8-Hydroxyquinoline immobilized on surfactant-coated alumina. *J Anal Chem* 2011; 66:11–15.
 29. Ghasemija B, Zolfonoun E. Simultaneous spectrophotometric determination of trace amounts of uranium, thorium, and zirconium using the partial least squares method after their preconcentration by α -benzoin oxime modified Amberlite XAD-2000 resin. *Talanta* 2010; 80:1191–1197.
 30. Sadeghi S, Sheikhzadeh E. Solid phase extraction using silica gel functionalized with Sulfasalazine for preconcentration of uranium(VI) ions from water samples. *Microchim Acta* 2008; 163:313–320.
 31. Ozdemir S, Kilinc E. Geobacillus thermoleovorans immobilized on Amberlite XAD-4 resin as a biosorbent for solid phase extraction of uranium(VI) prior to its spectrophotometric determination. *Microchim Acta* 2012; 178:389–397.
 32. Shahida S, Ali A, Khan MH, Saeed MM. Flow injection online spectrophotometric determination of uranium after preconcentration on XAD-4 resin impregnated with nalidixic acid. *Environ Monit Assess* 2013; 185:1613–1626.
 33. Totur D, Bozkurt SS, Merdivan M. Use of pyrocatechol violet modified sodium dodecyl sulfate coated on alumina for separation and preconcentration of uranium(VI). *J Radioanal Nucl Chem* 2012; 292:321–327.
 34. Maheswari MA, Subramanian MS. AXAD-16-3,4-dihydroxy benzoyl methyl phosphonic acid: a selective preconcentrator for U and Th from acidic waste streams and environmental samples. *React Funct Polym* 2005; 62, 105–114.
 35. Praveen RS, Metilda P, Daniel S, Rao TP. Solid phase extractive preconcentration of uranium(VI) using quinoline-8-ol anchored chloromethylated polymeric resin beads. *Talanta* 2005; 67, 960–967.
 36. Sadeghi S, Sheikhzadeh E. Solid phase extraction using silica gel functionalized with Sulfasalazine for preconcentration of uranium(VI) ions from water samples. *Microchim Acta* 2008; 163:313–320.
 37. Metilda P, Sanghamitra K, Gladis JM, Naidu GRK, Rao TP. Amberlite XAD-4 functionalized with succinic acid for the solid phase extractive preconcentration and separation of uranium(VI). *Talanta* 2005; 65:192–200.
 38. Sadeghi S, Sheikhzadeh E. Solid phase extraction using silica gel modified with murexide for preconcentration of uranium(VI) ions from water samples. *J Hazard Mater* 2009; 163: 861–868.
 39. Prabhakaran D, Subramanian MS. Selective extraction of U(VI), Th(IV), and La(III) from acidic matrix solutions and environmental samples using chemically modified Amberlite XAD-16 resin. *Anal Bioanal Chem* 2004; 379:519–525.
 40. Fafous II, Dawoud JN. Uranium(VI) Sorption by multiwalled carbon nanotubes from aqueous solution. *Appl Surf Sci* 2012; 259:433–440.
 41. Shah F, Soylak M, Kazi TG, Afridi HI. Development of an extractive spectrophotometric method for uranium using MWCNTs as solid phase and arsenazo(III) as chromophore. *J Radioanal Nucl Chem* 2013; 296:1239–1245.
 42. Ghasemi JB, Hashemi B, Shamsipur M. Simultaneous spectrophotometric determination of uranium and zirconium using cloud point extraction and multivariate methods. *J Iran Chem Soc.* 2012; 9:257–262.
 43. Madrakian T, Afkhami A, Mousavi A. Spectrophotometric determination of trace amounts of uranium(VI) in water samples after mixed micelle-mediated extraction. *Talanta* 2007; 71:610–614.
 44. Gholivand MB, Omidi M, Khodadadian M. Cloud point extraction and spectrophotometric determination of uranium(VI) in water samples after mixed micelle-mediated extraction using chromotrope 2R as complexing agent. *Croat Chem Acta* 2012; 85:289–295.
 45. Shemirani F, Kozani RR, Jamali MR, Assadi Y, Milani SMR. Micelle mediated extraction for direct spectrophotometric determination of trace uranium(VI) in water samples. *Sep Sci Tech* 2005; 40: 2527–2537.
 46. Shariati S, Yamini Y, Zanjani MK. Simultaneous preconcentration and determination of U(VI), Th(IV), Zr(IV) and Hf(IV) ions in aqueous samples using micelle-mediated extraction coupled to inductively coupled plasma-optical emission spectrometry. *J Hazard Mat.* 2008; 156 583–590.
 47. Şahin CA, Şatıroğlu N, Bektaş S. Cloud Point Extraction for Preconcentration and Determination of Uranium in Water Samples by Spectrophotometry. *Hacettepe J Biol&Chem* 2009; 37:241–247.
 48. Hu P, Qian L, He Y, Wang H, Wu W. Solvent extraction of uranium(VI) and thorium(IV) by N,N'-di-polylypyridine-2,6-dicarboxamide from nitric acid solution. *J Radioanal Nucl Chem* 2013; 297:133–137.
 49. Raileanu M, Grigoriu GE. Separation through liquid-liquid extraction and spectrophotometric determination of U(VI) with the ortho-aminophenol reagent. *J Radioanal Nucl Chem* 2012; 292:493–499.
 50. Kuznetsov VV, Zemyatova SV, Kornev KA. Automated determination of uranium(VI) in seawater using on-line preconcentration by coprecipitation. *J Anal Chem*, 2014; 69:105–110.
 51. Güell R, Fontàs C, Salvadó V, Anticó E. Modelling of liquid-liquid extraction and liquid membrane separation of arsenic species in environmental matrices. *Sep Pur Technology* 2010; 72: 319–325.
 52. Akl MA, Ismael DS, El-Asmy AA. Precipitate flotation-separation, speciation and hydride generation atomic absorption spectrometric determination of selenium (IV) in food stuffs. *Microchem J* 2006; 38: 61–69.
 53. Rao TP, Metilda P, Gladis JM. Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination—an overview. *Talanta* 2006; 68: 1047–1064.
 54. Khalifa, ME. Selective separation of uranium using alizarin red S (ARS)-modified anion-exchange resin or by flotation of U-ARS chelate. *Sep Sci Technol* 1998; 33:2123–2141.
 55. Akl MA, Khalifa ME, Ghazy SE, Hassanein MM. Selective flotation-separation and spectrophotometric determination of cadmium using phenanthraquinonemonophenylthiosemicarbazone. *Anal Sci* 2002; 18: 1235–1240.
 56. Miller JN, Miller JC. "Statistics and chemometrics for analytical chemistry" 5th ed., Prentice Hall, England, 2005.