



## Determination of U(VI) Using Sodium-Carbonate and Rhodamine-B as Ion-Associate by Flotation-Spectrofluorometric

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A simple and cost effective method for separation and preconcentration of U(VI) at the  $10^{-8}$  mol L<sup>-1</sup> level in the environmental and mineral sample has been developed. The method is based on the flotation of uranyl-carbonate complex as an ion-associate with rhodamine-B at pH of 6.5 from a large volume of an aqueous solution (100 mL) using *n*-hexane. The floated layer was then dissolved in methanol for the subsequent spectrofluorometric determination. The detection limit ( $n = 5$ ) was  $6.5 \times 10^{-8}$  mol L<sup>-1</sup> and RSD ( $n = 6$ ) obtained for  $7 \times 10^{-6}$  mol L<sup>-1</sup> of U(VI) was 1.44 %. The interference effects of number of elements was studied and not found any interference. The proposed method was applied to determine of U(VI) in a synthetic wastewater and geological sample.

**Key Words:** Flotation, Spectrofluorometric, Uranyl, Ion-associate.

### INTRODUCTION

Uranium is a toxic metal that can be absorbed by humans and other organism and its occurrence in the environment is very harmful for all living organism<sup>1,2</sup>. Uranyl (UO<sub>2</sub><sup>2+</sup>) ions, such as uranium trioxide or uranyl nitrate and other hexavalent uranium compounds, have been shown to cause birth defects and immune system damage in laboratory animals<sup>3</sup>. Uranyl is present in low quantities ( $10^{-5}$ - $10^{-3}$  M) in wash streams coming out from nuclear reactors both in aqueous and nonaqueous media<sup>4</sup>. The World Health Organization (WHO), Health Canada and Australian drinking water guidelines have fixed the maximum uranyl concentration in drinking waters to be less than 9, 20 and 20 µg/L, respectively<sup>5</sup>. Duo to the highly toxic nature of this element the determination of such low level in an aquatic environmental is of great importance. There are various techniques such as thin layer chromatography<sup>6</sup>, gravimetry<sup>7</sup>, titrimetry<sup>8</sup>, fluorimetry<sup>9,10</sup>, potentiometry<sup>11</sup>, polarography<sup>12</sup>, X-ray fluorescence<sup>13</sup>, inductively coupled plasma mass spectrometry<sup>14</sup> and spectrophotometry<sup>15-18</sup> for the determination of uranium.

Since the amount of uranium in the samples is very low, it is necessary to preconcentrate the low contents before its determination. Among the preconcentration procedures, such as liquid-liquid extraction<sup>19,20</sup>, ion-exchange<sup>21,22</sup>, sorption<sup>23</sup>, etc., flotation techniques have proven to be very efficient<sup>24,25</sup>. These techniques are very expensive and suffer from many complicated processing separation and are frequently recognized as time consuming with low reproducibility.

Recently, flotation-spectrometry is established as a preconcentration method in which trace amounts of elements in various complex materials can be enriched in a short time. In such treatment, when a sparingly soluble species containing the analyt is formed, by using a light organic solvent it is floated at the interference of aqueous/organic layers. These procedures are suitable especially in treatment with large volume of the solution sample and cause to achieve a high enrichment factor. In addition, the organic phase can be usually reused without any pretreatment process. Thus, in comparison with the conventional solvent extraction methods, these are not such environmental contamination problem. Flotation- spectrofluorometry probably provides the most sensitive, relatively simple and fast approach to trace metal analysis.

The aim of this work is to present a simple method for the separation and spectrofluorometric determination of U(VI) ions using carbonate and rhodamin B, as ion-associated complex, *via* the flotation process.

### EXPERIMENTAL

A Cary Eclipse 10A 250VAC spectrofluorometer with a 6-mm quartz cell was used for the fluorescence emission measurements solutions. A metrohm model 691 pH meter was used for pH adjustment.

All the reagents were of analytical grade, obtained from Merck and Fluka used without further purification.

Deionized water was used in all experiments. A stock U(VI) solution ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup>) was made by suitable

dilution of the standard solution and used for preparing the working solution. The stock solution was stored in PTFE bottles. Solution of rhodamine-B ( $1 \times 10^{-3} \text{ mol L}^{-1}$ ) was made by sequential dissolving of the appropriate amounts of the rhodamine-B. The solution of sodium carbonate ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ) was made by dissolving the appropriate amounts of sodium carbonate.

**Procedure:** To aliquot of U(VI) (100 mL) with a maximum concentration of  $1 \times 10^{-5} \text{ mol L}^{-1}$ , which was placed in a suitable flask, 0.1 mL  $5 \times 10^{-5} \text{ mol L}^{-1}$  sodium carbonate was added and its pH was adjusted to a 6.5 by addition of hydrochloric acid ( $1 \text{ mol L}^{-1}$ ) and ammonia ( $4 \text{ mol L}^{-1}$ ).

The solution was transferred to a 250 mL separating funnel and then 5 mL of *n*-hexane, 0.1 mL rhodamin B ( $10^{-5} \text{ mol L}^{-1}$ ) were added, sequentially. The funnel was stoppered and vigorously shaken for 10 min, the left for few minutes.

When the ion-associate was perfectly floated at the aqueous/organic interface, the upper organic and lower aqueous layers were discarded slowly by opening the stop cock of the funnel. The floated layer, which was completely separated by adhering to the inner walls of the funnel, was then dissolved in 5 mL of methanol for the subsequent spectrofluorometric determination. The emission measurements were carried out against a reagent blank prepared in the same manners.

## RESULTS AND DISCUSSION

**Optimization:** The optimum conditions for precise determination of U(VI) were achieved by studying certain experimental parameters, which influenced on the stability of the ion- associate and characterized the flotation process. At first it is essential condition to select an excitation and emission appropriate wavelength in which excitation and emission spectra are mirror image of each other. The excitation and emission wavelength were become 546 and 568 nm, sequentially.

The effect of pH examined by varying the pH of the solution in the range of  $5.00-7.50 \pm 0.1$ , just before the organic phase addition. As shown in Fig. 1, intensity of emission is maximum at pH of 6.5. Hence, this pH was chosen for future studies. Evidently, the intensity of emission decreasing at pH less and more than 6.5 may be due to a structural dependence of rhodamine-B on the pH.

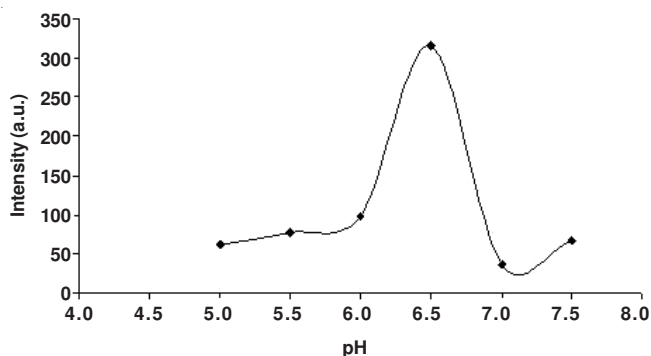


Fig. 1. Effect of pH on ion-associate formation in the flotation process at the condition, where:  $C_{\text{Carbonate}} = 5 \times 10^{-5} \text{ mol L}^{-1}$ ,  $C_{\text{Uranyl}} = 1 \times 10^{-5} \text{ mol L}^{-1}$  and  $C_{\text{Rhodamine-B}} = 1 \times 10^{-5} \text{ mol L}^{-1}$

It was reported that the reactivity of rhodamine-B in an interesting manner is dependent on the pH variations. The

carboxyl group, which belongs to the structure, is completely protonated in acidic media, but dissociates in an alkaline solution<sup>26</sup>.

The effect of sodium carbonate concentration was studied over the range of  $1 \times 10^{-6}-5 \times 10^{-3} \text{ mol L}^{-1}$  indicates a maximum intensity of emission occurs at  $5 \times 10^{-5} \text{ mol L}^{-1}$  (Fig. 2).

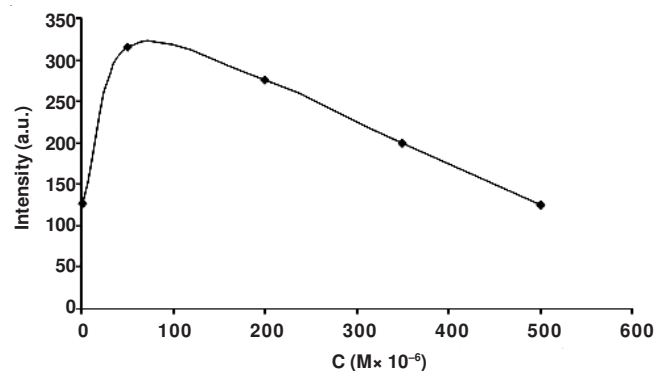


Fig. 2. Effect of concentration of sodium carbonate on the ion-associate formation in the flotation process at condition, where: pH = 6.5,  $C_{\text{Uranyl}} = 1 \times 10^{-5} \text{ mol L}^{-1}$ ,  $C_{\text{Rhodamine-B}} = 1 \times 10^{-5} \text{ mol L}^{-1}$

The effect of rhodamine-B concentration on flotation of the ion-associate was also studied over the range of  $1 \times 10^{-7}-1 \times 10^{-4} \text{ mol L}^{-1}$ . As shown in Fig. 3, a maximum intensity of emission was obtained at the concentration of  $1 \times 10^{-5} \text{ mol L}^{-1}$ , which was used for further examination. Decreasing the intensity of emission at the lower concentration of rhodamine-B was probably due to the increasing tendency to form an ion-pair between sodium carbonate and rhodamine-B in the blank. On the other hand, the addition of an excess amount of rhodamine-B caused to a delay of the flotation process in the sample solution.

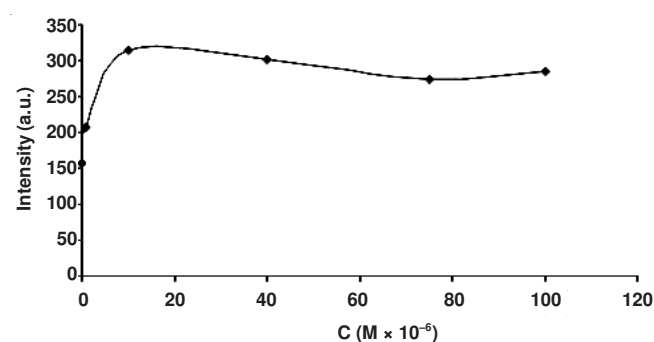


Fig. 3. Effect of rhodamine-B concentration on the ion-associate formation in the flotation process at condition, where: pH = 6.5,  $C_{\text{Uranyl}} = 1 \times 10^{-5} \text{ mol L}^{-1}$ ,  $C_{\text{Carbonate}} = 5 \times 10^{-5} \text{ mol L}^{-1}$

The flotation process was also examined by using several organic solvents including *n*-heptane, cyclohexane, *n*-hexane and acetonitrile. It was found that the intensity of emission depends on type of organic phase (Table-1). For example, at the optimum conditions the emission values for the flotation of  $1 \times 10^{-6} \text{ mol L}^{-1}$  U(VI) using *n*-heptane, cyclohexane, acetonitrile and *n*-hexane were 208.110, 281.637, 157.057 and 402.540, respectively. By considering that separation between the phases was also achieved more quickly using *n*-hexane, it was chosen as organic phase for the future examinations. In

TABLE-1  
CHOICE OF ORGANIC PHASE FOR THE FLOTATION PROCESS  
( $1 \times 10^{-6}$  mol L<sup>-1</sup> UO<sub>2</sub>(II) AT OPTIMUM CONDITIONS

Solvent	Intensity (a.u.)	Dielectric constant (ε)
<i>n</i> -Hexane	402.5	1.8865
Acetonitrile	157.1	36.6400
<i>n</i> -Heptane	208.1	1.9209
Cyclohexane	281.6	2.2176

order to investigate the volume of the aqueous phase, a number of the experiments were carried out in which the volume of the aqueous phase containing  $1 \times 10^{-6}$  mol L<sup>-1</sup> U(VI) was varied over the range of 25-125 mL. It was seen the flotation process can be carried out quantitatively, irrespective of the aqueous volume. However the reproducibility was better by increasing the volume up to 100 mL.

**Analytical figures of merit:** Under the optimum conditions, a linear calibration curve was constructed for the spectrofluorometric determination of U(VI), over the range of  $5 \times 10^{-7}$ - $1 \times 10^{-5}$  mol L<sup>-1</sup> with a correlation coefficient ( $R^2$ ) of 0.9813. The RSD obtained for  $7 \times 10^{-6}$  mol L<sup>-1</sup> of U(VI) was 1.44 % ( $n = 6$ ) and detection limit defined as the sample concentration giving a signal equal to the blank average signal ( $n = 5$ ) plus three times the standard deviation of the blanks was found to be  $6.5 \times 10^{-8}$  mol L<sup>-1</sup>.

**Effect of foreign ions:** The flotation process was carried out on aliquot of 100 mL of solution containing U(VI) with concentration of  $1 \times 10^{-5}$  mol L<sup>-1</sup> and various amounts of foreign ions. Since the determination of U(VI) in real samples was proposed, the interference effects of various ions, which are probably found in the uranium content environmental samples, were investigated. These ions were introduced into a solution containing  $1 \times 10^{-5}$  mol L<sup>-1</sup> of U(VI), where the concentration of each of them was 100 times more than the U(VI) contents. It was found that number of ions, such as, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, W<sup>6+</sup>, Mo<sup>6+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were not interfered (Table-2).

TABLE-2  
EFFECTS OF  $1 \times 10^{-3}$  mol L<sup>-1</sup> OF INTERFERING IONS ON THE  
FLOTATION OF  $1 \times 10^{-5}$  mol L<sup>-1</sup> UO<sub>2</sub>(II) IN THE SOLUTION

Added ion	Recovery (%)	Added ion	Recovery (%)
Mg <sup>2+</sup>	95	Cl <sup>-</sup>	88
Ca <sup>2+</sup>	99	SO <sub>4</sub> <sup>2-</sup>	81
Na <sup>+</sup>	102	Mo <sup>6+</sup>	105.5
K <sup>+</sup>	80	W <sup>6+</sup>	105

**Real sample analysis:** The applicability of the proposed method was tested with two different concentrations of U(VI) ions which were spiked into the waters (stations 1 and 2; Behabad spring and Mashhad, Iran, respectively) adjusted with hydrochloric acid and ammonia at pH 6.5. The concentration of the uranyl ions were measured using the proposed method. Table-3 shows good agreement between the added and found amounts of uranyl ions implied that the present method can be used for determination of uranyl ion in water samples.

### Conclusion

Although many separation techniques have been reported for the determination of uranium ions, this method presents the appropriate sensitivity and selectivity for the determination

TABLE-3  
RESULTS OF THE URANYL DETERMINATION  
IN SAMPLES BY THE PROPOSED METHOD

Sample	Added (μM)	Found (μM)	Recovery (%)
Station 1	0	–	ND
Station 1	3	2.83	94
Station 1	5	4.35	86
Station 2	0	–	ND
Station 2	3	2.89	96
Station 2	5	4.33	86

ND: No detection.

of trace amount of uranium. This method is useful owing to the sufficient capability for the determination of uranium in various wastewater samples. Apart from the high sensitivity, the procedure is very simple, fast and gains a low detection limit without any complicated equipment.

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