

## Developed Method for Low Concentration Determination of Uranium

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*Received: 29 July 2008; Accepted: 13 September 2008*

### Abstract

An improved spectrophotometric method of determination of U(VI) with 4-(2-pyridylazo) resorcinol (PAR) in a mixed micellar medium (mixed cationic and nonionic surfactants) in presence of EDTA/NaF as masking agent has been carried out in normal and derivative modes. The molar absorption coefficient ( $\epsilon$ ) and Sandell's sensitivity ( $S$ ) of U(VI)-PAR complex at 541.0 nm are  $4.33 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $0.0055 \mu\text{g cm}^{-1}$ , respectively. The proposed method has been successfully applied to the determination of uranium in tap water, river water, seawater and synthetic sample.

### Keywords:

Uranium; Uv-Vis; Derivatives; Micells

### 1. Introduction

Spectrophotometric methods for the determination of uranium (VI) are numerous and have been used in the analysis of a large variety of materials over a wide range of uranium concentrations [1]. Thiocyanate and oxinate were usually used as chromogenic reagents for the determination of uranium, but their chromogenic reactions were neither highly sensitive nor selective [2]. In this concern, extractive-first derivative spectrophotometric determination of uranium (VI) method based on the extraction of its complex with TBP (tri-normal butyl phosphate) from kerosene and direct determination in organic phase was reported in [3]. Uranium (VI) was determined in aqueous solutions with Resorcinol in presence of EDTA and NaF as masking agent solution using first derivative spectrophotometry [4]. Where, it is a spectral technique in which the rate of change of absorbance with wavelength is measured as a function of wavelength. It is considered as an alternative approach to normal one because it is showing a good sensitivity and higher specificity. In the derivative spectrum the ability to detect and to measure minor spectral features is considerably enhanced hence increased sensitivity [5]. Surfactants were often introduced to increase the sensitivity and selectivity of determinations [6]. The effectiveness of coexisting surfactants; cationic or non-ionic surfactants, has also been recognized in the coloring reaction between many reagents and uranium[7]. Although the spectrophotometry of uranium with PAR (4-(2-pyridylaz) resorcinol) as a water-soluble azo dye has already been reported, [8,9] the systematic study based on the color formation reaction between PAR and U (VI) in the presence of mixed surfactants has not been investigated. In this study, an improved spectroscopic method for determination of U(VI) with PAR was proposed. This was carried out by an addition of mixed surfactants (cetylpyridinium chloride-TritonX-100) as cation and anionic ones to the reaction

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Moment Publication ©2009

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media that containing uranium ion and PAR which is widely used as analytical reagents for spectrophotometric determination despite is being nonselective [10,11,12].

## **2. Experimental**

### **2.1. Instruments**

For spectroscopic measurements, Shimadzu UV/Vis-160A spectrophotometer (Shimadzu, Tokyo, Japan) spectrophotometer with 1-cm quartz cells was used for measurement of the absorbance and its derivative spectra. A digital pH-meter of the type CG - 820, West Germany was used for pH measurements through connection to a single glass calomel electrode. For the equilibration experiments, the aqueous and organic phases were mixed together using a thermostated mechanical shaker of the type Julabo SW-20C, Germany, controlled within  $\pm 1$  °C and with stirring range from 20 to 2000 rpm.

### **2.2. Reagents**

#### **2.2.1. Uranium solution**

Uranium solution ( $1000 \mu\text{g}\cdot\text{mL}^{-1}$ ) was prepared by dissolving 2.1095 g of uranyl nitrate in bidistilled water containing 1.0 mL of conc.  $\text{HNO}_3$ . The solution was diluted with water to one liter in a volumetric flask. The aqueous stock solution (0.2%) of PAR 4-(2-pyridylazo)-resorcinol was prepared by dissolving a 0.2 gm in 100 mL of double distilled deionised water.

#### **2.2.2. Surfactants solutions**

Cetylpyridinium chloride (CPC), Triton X-100, Tween 20 and sodium dodecylsulphate (SDS) were prepared by dissolving appropriate weights in hot distilled water to give required concentrations.

#### **2.2.2. Buffer solution**

The buffer solution of pH 8.6 was prepared by mixing 60 mL of  $0.1 \text{ mol L}^{-1}$  sodium hydroxide with 250 mL of  $0.1 \text{ mol L}^{-1}$  boric acid in  $0.1 \text{ mol L}^{-1}$  potassium chloride in a 500-mL volumetric flask and diluting to the mark with bidistilled water. This gives a solution of pH 8.6. For Buffer solution of pH 6.0, it was prepared by mixing 9.5 mL of  $2 \text{ mol L}^{-1}$  NaOAc with 0.5 mL of  $2 \text{ mol L}^{-1}$  acetic acid then diluted to 100 mL with distilled water .

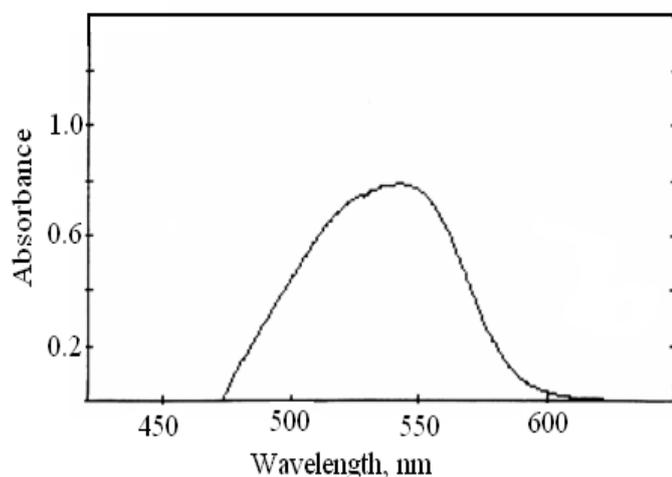
### **2.3. Procedures**

A final volume of 25.0 mL of mixed solution of appropriate amounts of U(VI) was introduced to a 25 mL measuring flask, 10.0 mL of buffer, 1.0 mL of masking agent solution (prepared from 1 g of EDTA and 1.25 g of NaF in 80 mL of distilled water, solution was adjusted to pH 8 and diluted to 100 mL), 2-mL of PAR solution, 1.5 mL of CPC solution and 1.5-mL of Triton X-100 solution were added and the pH was adjusted if necessary. Then the whole mixture is completed to the mark with water and the absorbance at 541nm is measured against the reagent blank. Third derivative spectrophotometric determination was recorded when the uranium concentration is in the range of 0.1 to  $5.0 \mu\text{g mL}^{-1}$ . In this case, the third derivative spectrum was obtained for (N) value of 9 nm and scan speed of  $1500 \text{ nm min}^{-1}$  in the range from 420 to 650 nm. The analytical response was obtained by a peak-to-peak method or by measuring the distance between the peak at 541 nm and the valley at 569 nm.

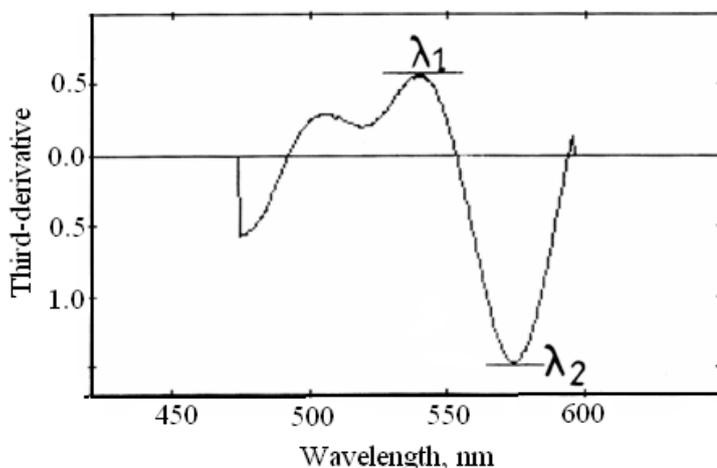
### 3. Results and Discussions

#### 3.1. Spectral Characteristics

Due to the anionic nature of the U(VI)-PAR complex [13], cationic surfactant like CPC (Cetylpyridinium chloride) was examined for their possible effect on the absorbance of the U(VI)-PAR complex. In the presence of CPC the absorbance increased and the wavelength of maximum absorbance was found to be 541 nm for the U (VI)-PAR-CPC, at pH of 8 compared with 530 nm for U (VI)-PAR systems in absence of CPC surfactant. This indicates a bathochromic shift as a result of the formation of a ternary metal ion complex with PAR and CPC with improved optical properties. These results are in agreement with the data reported earlier for U (VI) [12]. It was found that the absorbance of complex increased when the combination occurs between CPC and Triton (X-100) compared with presence of CPC only. Figs. 1, 2 show the ordinary and third-derivative spectrum of U(VI)-PAR complex in presence of mixed micellar medium. Derivatization of the spectrum leads to sharper peak than ordinary band and gives a higher signal in the resolved spectra. The analytical response was obtained by a peak-to-peak method between  $\lambda_1=541$  nm and  $\lambda_2=569$  nm or by measuring the distance between the peak at  $\lambda_1$  and the valley at  $\lambda_2$ . Its value was large compared with the ordinary absorption spectrum.



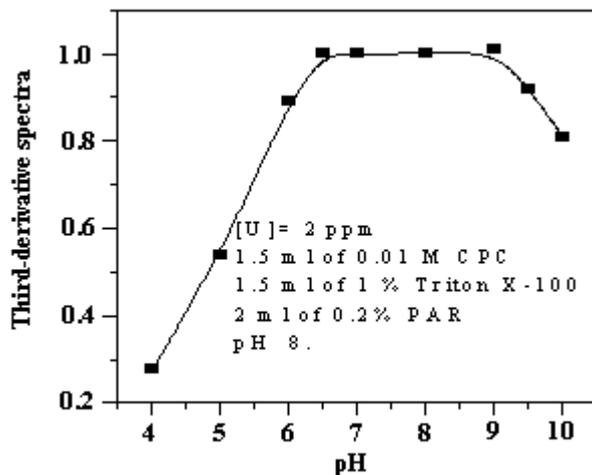
**Fig.1.** Absorption spectra of U (VI)-PAR complex at 541 nm in mixed micellar media, 1.5 ml of 0.02 M CPC, 1.5 ml of 1% Triton (X-100), [U] = 4 ppm, 2 ml of 0.2 % PAR at pH 8.



**Fig.2.** Third-derivative spectra of U (VI)-PAR complex in mixed micellar media, 1.5 ml of 0.02 M CPC, 1.5 ml of 1% Triton (X-100), [U]= 4 ppm, 2 ml of ml of 0.2 % PAR at pH 8

### 3.2. Effect of pH

The effect of variation of pH on the absorbance of U (VI)-PAR complex in mixed micellar media has been examined. It has been found that the absorbance of 3 ppm U (VI) in the presence of 1.5-mL of 0.01M CPC and 1.5-mL of 1% Triton X-100 has its maximum value over the pH range 7–9. Fig.3 shows the effect of pH on the third-derivative spectra of U (VI)-PAR complex in mixed micellar medium. It can be seen that the maximum and constant  $d^3A/d\lambda^3$  was obtained within ranges of pH 6.5-9.0. The pH 8 buffer solutions were selected for subsequent work. A borate buffer of pH 8 was chosen in all measurements.



**Fig.3.** Effect of pH on the third-derivative spectra of the U (VI)-PAR complex in mixed micellar media.

### 3.3. Effect of surfactants concentration

The reaction between PAR and U(VI) was studied in presence of different volumes of 0.01 mol L<sup>-1</sup> CPC surfactant solution alone. The effect of CPC concentration on the absorbance of 3 ppm U (VI) is shown in Fig.4. It was found that the absorbance of U (VI)-PAR complex reaches to its maximum value at the range from 1 to 2 mL of 0.01 mol L<sup>-1</sup> CPC solutions. Therefore, 1.5 mL of CPC was chosen in all measurements. The effect of combination of CPC with other surfactants such as Triton (X-100) or Tween-20 [poly (oxyethylene)-sorbitanmonolaurate] as nonionic surfactant and SDS (sodium dodecylsulphate) as anionic surfactant was studied. The effect of surfactant combination was examined in terms of sensitivity of the color reaction. The use of the surfactant-combination of Triton (X-100) as nonionic surfactant with CPC as cationic surfactant was found to be most effective, and the color development was stable and reproducible. The effect of concentration of Triton (X-100) solution on the signal of 3 ppm of uranium in presence of 1.5 mL of 0.01 M CPC is shown in Fig. 5. The optimum amounts of surfactants were 1.5-mL of 0.01 mol L<sup>-1</sup> of CPC solution and 1.5-mL of 1% Triton (X-100) (mixed micellar medium), which give high absorbance in comparison with that in presence of CPC only.

### 3.4. Effect of PAR concentration

The effect of PAR concentration on the absorbance of 3 ppm uranium (VI) -PAR complex in mixed micellar media at pH of 8.0 was examined. The maximum absorbance was obtained at 1.5-mL of 0.2 % PAR solution and remained almost constant with increasing of 0.2 % PAR solution up to 3-mL as shown in Fig.6. Therefore, 2-mL of 0.2 % PAR solution was chosen for all measurements.

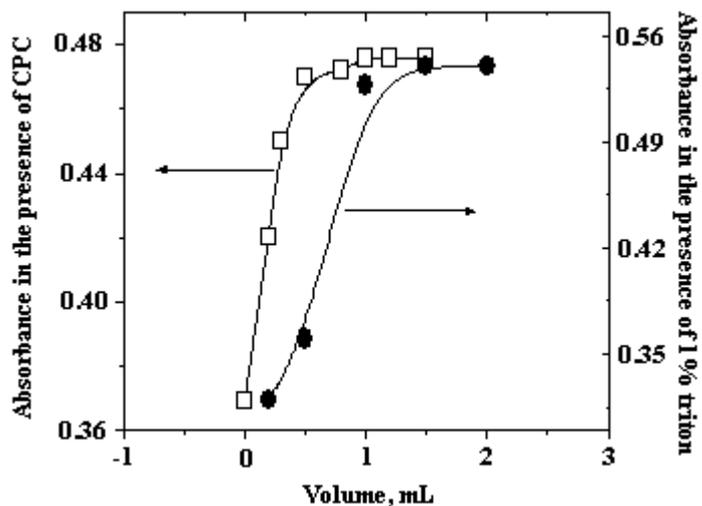


Fig.4. Effect of volume of CPC solution on the absorbance of U(VI)-PAR complex

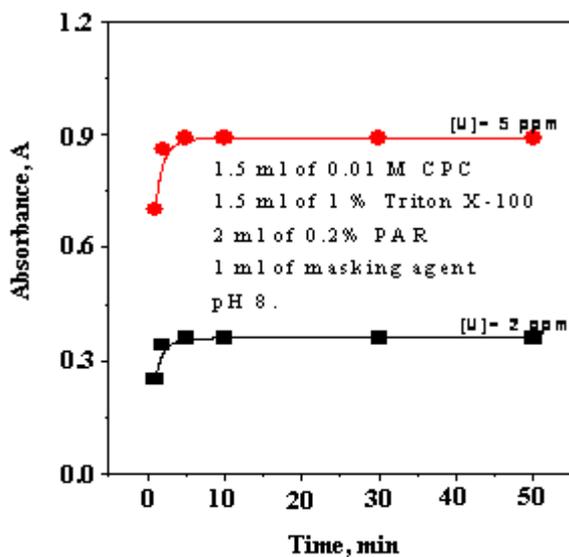


Fig.5. Effect of Triton (X-100) concentration on the absorbance of U (VI)-(PAR)-complex

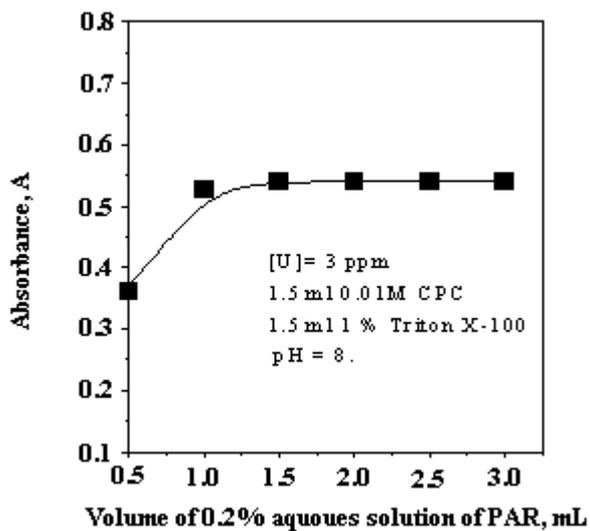
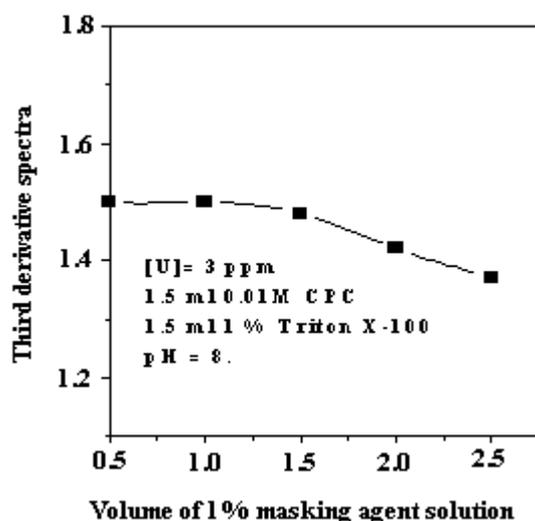


Fig.6. Effect of concentration of PAR on the absorbance of U (VI)-PAR complex in mixed micelle media

### 3.5. Effect of masking agent on the color development

The PAR is known to form colored complexes with many metal ions that contribute to the absorbance in the region of maximum absorbance of uranium. Therefore, a masking reagent is usually used to increase the selectivity of PAR toward the analyte [10,11]. In this concern the masking agent solution (solution contains 1g of EDTA, 1.25 g of NaF in 80 mL of distilled water adjusted to pH 8 and diluted to 100 mL) was tried. By addition of 1 mL of masking agent solution the absorbance of uranium was found to be very slightly decreased. The effect of masking agent solution on the third-derivative spectra of U (VI)-PAR complex in mixed micellar medium is shown in Fig. 7. It can be seen that 1mL of masking agent solution is the optimum volume which shows slight decrease in the signal.



**Fig.7.** Effect of masking agent solution on the third derivative spectra of U(VI)-PAR complex in micelle.

### 3.6. Effect of standing time

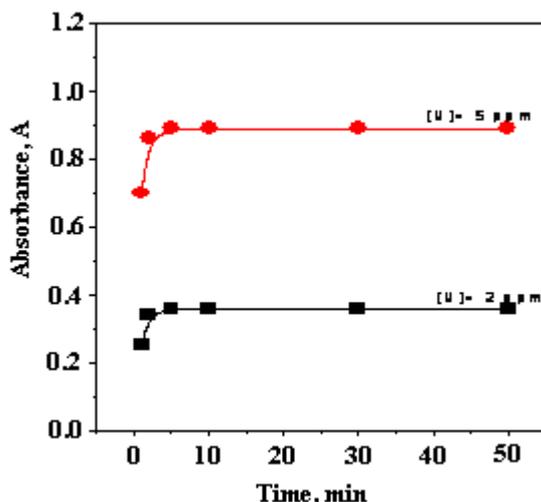
The minimum time required for completion of the color development of uranium (VI)-PAR complex in mixed micellar medium was found to be 5 min. The effect of time on color development of U (VI) complex in the presence of mixed micellar medium and 1mL of masking agent solution is shown in Fig.8. It was found that the time required for complete complexation and to reach to maximum absorbance is 5 min. Therefore, for all measurements, a 5 min standing time was selected. The presence of masking agent solution does not affect the stability of the uranium-PAR system, the Absorbance and third-derivative spectra of the uranium (VI)- complex remained almost constant for 20 h.

### 3.7. Calibration graph, precision and sensitivity

The calibration curve was constructed for the determination of uranium in standard solutions of uranium (VI). The standard solutions were prepared according to the general procedure under the optimum conditions developed above. In zero-order spectrophotometer method, Beer's law was obeyed in the uranium (VI) concentration in the range from 1 to 6 ppm and the graph passed through the origin. The data fitting the equation:

$$A = 0.181 [U] \quad (r=0.999)$$

The Sandell sensitivity ( $S$ ) and the molar absorptivity ( $\epsilon$ ) at  $\lambda_{\max} = 541 \text{ nm}$  were  $0.0055 \mu\text{g} / \text{cm}^2$  and  $4.33 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively.

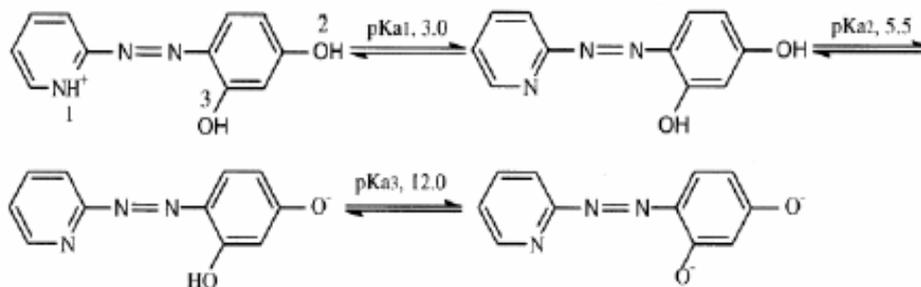


**Fig.8.** Effect of standing time on formation of U(VI)-PAR complex in mixed micellar media.

In the third derivative mode, the calibration graph was constructed by plotting the third-derivative value against uranium concentration. The third derivative value was obtained by measuring the distance between the peak at  $\lambda_1$  (541 nm) and the valley at  $\lambda_2$  (569 nm) against uranium concentration. The graph was found to be linear in the range from 0.1 to 5.0 ppm uranium. The data fitting the equation:

$$D^3 = 0.51 [U] + 0.016 \quad (r = 0.9996)$$

Where A is absorbance of U (VI)-PAR complex at 541 nm and  $D^3$  is the third derivative value and [U] the concentration of uranium in ppm. Precision of the method was tested with solutions of 3 ppm U (VI). The relative standard deviation was found to be 0.68%.



**Scheme 1**

In aqueous solutions, PAR exists with four species, including neutral, protonized and other two anionic species (as shown in Scheme 1). The pH was found to have a great effect on the speciation of PAR which might also decrease its ability to form metal complexes. This is because, in general, PAR acts as a tridentate ligand that chelates with metal ions through the pyridine nitrogen atom, the azo-nitrogen atom and the o-hydroxyl group. To form a stable PAR-metal complex, the oxygen atom must be involved. The monovalent PAR anion (PAR) species is the dominant species in pH 5.5 – 12. While the different species of uranium will be At pH > 7.5, occur as anionic species such as  $(\text{UO}_2)_3(\text{OH})^+$  and  $\text{UO}_2(\text{OH})_3^-$ . Therefore, PAR can form a complex species with through the chelating uranium ion to form anionic complex which can be neutralized using the CPC cationic surfactant [13].



### 3.8. Effect of foreign ions

Under the optimum conditions given in Table 1, the effects of various foreign ions on the determination of U (VI) with PAR in mixed micellar medium and presence of masking agent solution has been investigated. Table 1 shows the tolerable amounts of the examined ions in the determination of  $3.0 \mu\text{g mL}^{-1}$  U (VI) by ordinary and third-derivative spectrophotometry. The influence of foreign ions on the third-derivative method was compared with ordinary spectrophotometry. Third-derivative spectrophotometry shows better selectivity than ordinary spectrophotometry. Thus, third-derivative spectrophotometry is more suitable for direct determination of uranium using PAR in mixed micellar medium.

**Table 1.** Determination of tolerable levels for some foreign ions on the determination of uranium (VI) using PAR in mixed micellar medium

Interfering ion	Tolerated concentration ( $\mu\text{g mL}^{-1}$ )	
	Normal spectrum	Third-order erivative
K (I), Na(1)	80	140
Al (III)	10	20
Ba (II)	15	25
Ca (II)	30	60
Cu (II)	25	40
Cd (II)	10	18
Cr (III)	10	15
Co (II)	8	15
Ce (IV)	10	18
Gd (III)	10	20
Fe (III)	6	14
Pb (II)	15	25
Zn (II)	20	30
Mg (II)	15	25
Mn (II)	10	16
Mo (VI)	9	18
Nb (V)	10	15
Nd (III)	14	18
Ni (II)	6	15
V (IV)	5	8
Ti (IV)	5	12
Th (IV)	6	15
Zr (IV)	10	21
PO <sub>4</sub> <sup>3-</sup>	25	40
CO <sub>3</sub> <sup>2-</sup>	45	6

A repeated time 3 of each experiment

(0.2%) PAR, ml

(0.01M) CPC, ml

(1 %) Triton X-100

(1 %) masking solution, ml

#### 4. Application

The proposed method was successfully applied to the determination of uranium. Several spiked samples were prepared by adding uranium to real water matrices using River Nile water, tap water, seawater and synthetic mixture. The result in Table 2, shows good selectivity of determination of uranium (VI) in different matrix media.

#### 5. Conclusion

A comparative evaluation of the proposed method with some of the reported ones for the determination of uranium is given in Table 3. It is observed that in case of the present method using PAR in mixed micellar medium not only the sensitivity is better but also the selectivity is better than the widely used methods.

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