Flotation and Enhanced Spectrophotometric Determination of Uranium (VI) in Environmental Samples

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A GREEN and simple technique for the separation via flotation and spectrophotometric detection of U(VI) in water and real ore samples is presented in this research study in which the heterocyclic azo dye 4-(2pyridyl azo) resorcinol (NaPAR) is used to preconcentrate the uranyl(VI) ions to form a reddish complex in the aqueous solution in the pH range 5.0.-6.0. The oleic acid (HOL) surfactant was used to float the formed 1:1 U(VI):NaPAR complex successfully and completely to the scum layer. The physicochemical characteristics of the proposed analytical technique have been determined. Under optimum parameters, the following physicochemical characteristics were obtained. Beer's law was obeyed up to 300 $\mu g \ l^{-1}$, the correlation coefficient (R^2) was calculated to be $R^2 = 0.9995$. According to IUPAC recommendations, the limit of detection (LOD) and limit of quantification (LOQ) are 0.9 and 3.1 $\mu g \ l^{-1}$ (n = 5), respectively. The molar absorptivity (ε) is $0.63 \times 10^6 \ l \ mol^{-1} cm^{-1}$ in the scum layer with a preconcentration factor 100 and the RSD (n=5) is 2.5%. Excess amount of the chelating agent NaPAR was used to mask the effects of diverse ions on the flotation efficiency. The proposed procedure was applied to determine U(VI) in water samples as well as in U-Th and granite ore samples. The separation mechanism is explained.

Keywords: U(VI), Spectrophotometry, flotation, oleic acid, Surfactants-complex formation, U-Th and granite ores

Introduction

Uranium was the first radioactive element to be discovered and is one of the main natural nuclides in biogeochemical studies and environment monitoring [1]. The U-series nuclides are already traditionally used to judge biogeochemical procedures, including dynamic processes concerning sediments, vertical and horizontal diffusion procedures and submarine groundwater effluents [2]. The uranium concentration within the oceans is rather constant at about 3.3 mg/kg [3,4] and the average amount of uranium in river waters is approximately 1.3 nmol/kg [5].

Uranium content of land waters (Fresh water flowing over the land; flood water; the water of lakes, rivers, springs, etc., as opposed to sea-water) more than 1 ppb is considered abnormal. This extreme dilution in the existence of relatively high concentration of other ions causes it to be hard to determine directly and delicate analytical techniques have to be used to determine trace amounts [6].

Various techniques for the determination of total uranium are reported including voltammetry [7], polarography [8], fluorimetry [9, 10], X-ray fluorescence spectroscopy (XRF) [11], spectrophotometry [12-15], and ICP spectroscopy [16, 17]. Separation and preconcentration techniques tend to be employed just before analysis. Solvent extraction [18-20] and ion exchange [21, 22] are popular methods because of their applicability to both preconcentration and separation.

Various routes for the spectrophotometric determination of uranium depending on the utilization of balmic acid, morin, sodium fluoride, pyrogallol red, pyrogallic acid etc., are already reported [23], but a lot of them demands a liquid-liquid extraction step and entail many disadvantages regarding reproducibility, simplicity, rapidity and sensitivity.

The heterocyclic azo substances are sensitive important chromogenic and complexing agents. These dyes happen to be beneficial in the spectrophotometric determination because of

their good selectivity and sensitivity over a large range pH and since they›re not too difficult to synthesize and purify.

Flotation techniques are already extensively employed for determination of trace heavy metals in media of diverse origin. [24-36] Flotation has attracted significant attention as it simply matches the «Green Chemistry» principle, as the quantity of organic solvent is far small compared to that is used in the traditional liquid-liquid extraction.

Spectrophotometry is still considered as a good instrumental method of analysis for the determination of heavy metals in water samples because it is simple, of low-cost and is conveniently available [37].

The objective of the present study is to provide an easy, rapid and economical flotation- spectrophotometric method for microdetermination of uranyl (VI) in water and real ore samples using the heterocyclic azo dye 4-(2-pyridylazo)-resorcinol, (NaPAR) as a chelating reagent and the oleic acid (HOL) as a surfactant. Also, the effects of the foreign ions were studied.

Experimental

Instruments

The flotation cells used in this study have previously been described [24]. Flotation cell (a) is a cylindrically graduated glass tube of 16 mm inner diameter and 290mm length with a stopcock at the bottom. Such cell is used to study the different factors affecting the efficiency of flotation. Flotation cell (b) is a cylindrical tube of 6 cm inner diameter and 45 cm length with a stop cock at the bottom and a quick fit stopper at the top. This cell is used to separate cobalt from 1 liter of different water samples. Unicam UV/ Vis spectrometers were used to record the spectral data. Digital pH meters were used to measure the pH values of sample solutions.

Chemicals

The chemicals used in this study are all of analytical reagent grade. Double distilled water (DDW) was used. To prepare uranium stock solution (1000 mg/L), 0.89095 g of $UO_2(CH_3COO)_2.H_2O$ was dissolved in 100 milliliters of water in the presence of 2 milliliters of concentrated HCl and is diluted to 0.5 L with DDW. Oleic acid was obtained from Sigma. Oleic acid (HOL) stock solution; 6.03×10^{-2} moll^{-1}, has been prepared [24]. Stock solution of NaPAR,

0.01 moll^{-1} was prepared by dissolving 0.255 gm of 4-(2-pyridyl azo)-resorcinol monosodium salt in 100 ml of DDW. Five certified ore samples, known as U-Th ore (206 ADL 1A), U-Th ore (206 ADH 1A), U ore (206 ABL 2A), granite (I) (MALI MINTEK GRANITE: NIM. G.) and granite(II) (83 MALS MINTEK LUJAVRITE NJM.I.) were obtained from the National Institute of Metallurgy, South Africa and were used to conduct this study.

Analytical procedure

Defined amount (specified for each investigation) of both the analyte U(VI) and the reagent (NaPAR) were mixed. Acetate buffer was used to adjust the pH of mixture to 6. The mixture was then taken totally to the flotation cell (type a) and completed to 20 ml with DDW. The cell was shaken well for few seconds. 3 ml of 2×10^{-4} mol l^{-1} HOL, were added, to this solution. The flotation cell was then inverted upside down for few minutes by hand. After 5 min, to ascertain that flotation is completed, the concentration of the U(VI) ion in the scum layer was determined spectrophotometrically at λ_{max} 530.

The floatability (F, %), of U(VI) was determined using the relation:

$$F = \{C_S/C_i\} \times 100\% \quad [24]$$

Where C_i and C_s are the initial and scum concentrations of the analyte, respectively.

Results and Discussion

Absorption spectra

The absorption spectra of the reagent NaPAR, the U(VI)-NaPAR complex formed in water solution and in the surfactant layer are provided in Fig. 1. The reagent NaPAR has a maximum absorption spectrum at 400 nm, (Fig.1 a). On the other hand, the U(VI)-NaPAR complex formed in aqueous solution, (Fig. 1 b), had a maximum absorption spectrum at 530 nm that is completely different from that of the ligand NaPAR. Moreover, the absorbance of U(VI)-NaPAR complex formed in the HOL layer, (Fig.1 c), is much greater than that formed in the aqueous solution. These findings provide a good evidence of the role of the surfactant HOL in concentrating the U(VI)-NaPAR complex in the scum layer.

Flotation of U(VI)
Influence of hydrogen ion concentration
A number of experiments were performed

to float U(VI) in the existence of HOL alone. A proper amount of U(VI), (2×10^{-5} moll⁻¹), was taken into the flotation cell along with an adequate amount of oleic acid surfactant (2×10^{-4} moll⁻¹) to float U(VI) over a wide pH range. The final results represented in Fig. 2 curve a, denotes how the flotation percentage is below 20% throughout the pH values used wherein the uranyl ions float as U(VI)-oleate towards the scum layer. Precisely the same experiments were performed in the existence of 2×10^{-4} moll⁻¹ NaPAR being a complexing agent. The results, Fig. 2 graph b, revealed that maximum and complete flotation ($\approx$ 100%) of U(VI) was gained within the 5-6 pH range.

Influence of ligand and metal concentration
The Influence of ligand and metal concentration is presented in Fig. 3 and 4, respectively.

From Fig. 3, it had been found out that the flotation % of U(VI) increases progressively with the increase in the ligand concentration until it reaches its maximum at 2×10^{-5} moll⁻¹ at which U(VI) forms 1:1 complex with NaPAR. The flotation % remains constant upon further increase in ligand concentration. This finding allows an easy procedure to separate and determine U(IV) particularly in samples that contain unknown amounts of U(VI).

On the other hand, another number of experimental work was completed using a fixed amount of NaPAR, 2×10^{-5} moll⁻¹, and changing the U(VI) concentration The results (Fig. 4) demonstrated that complete flotation was obtained at 2×10^{-5} moll⁻¹ of U(VI) . At that concentration U(VI) forms a 1:1 U(VI): NaPAR complex. When the U(VI) concentration was increased above such a ratio, the flotation % was decreased. This finding demonstrated that an adequate amount of the reagent NaPAR should be present to ensure complete complexation and hence subsequent flotation of U(VI) ions.
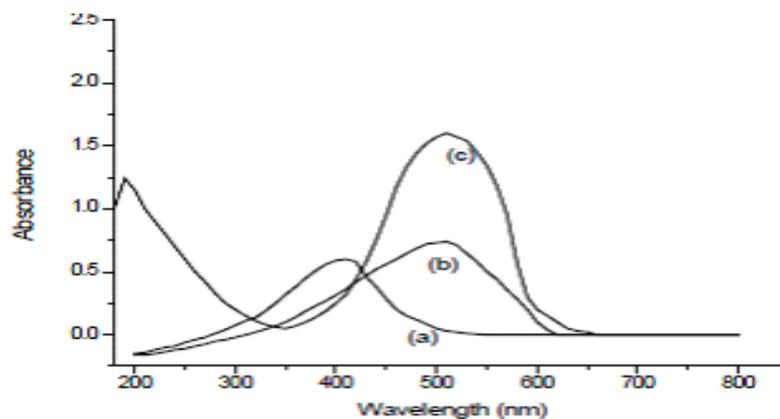

Fig. 1. Absorption spectra of: (a) The reagent NaPAR, (b) U*NaPAR system and (c) U*NaPAR-HOL system.
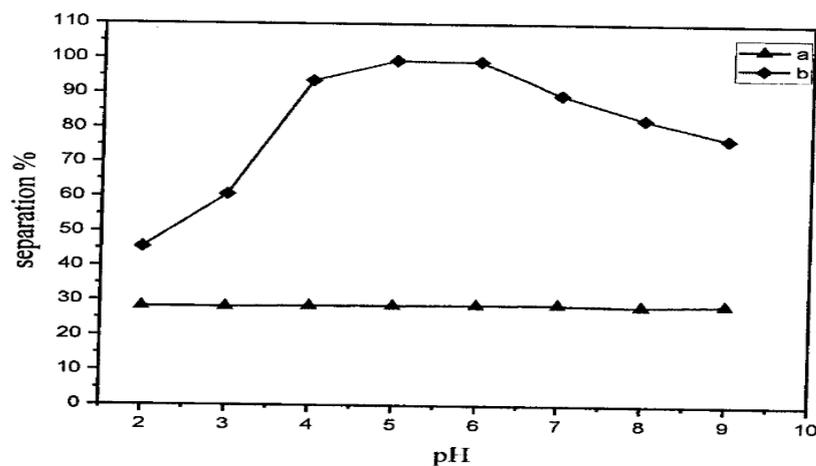

Fig. 2. The variation of separation % of 2×10^{-5} moll⁻¹ U(VI) with the pH values (a) in the absence of NaPAR (b) in the presence of 2×10^{-4} moll⁻¹ NaPAR using 2×10^{-4} moll⁻¹ HOL.
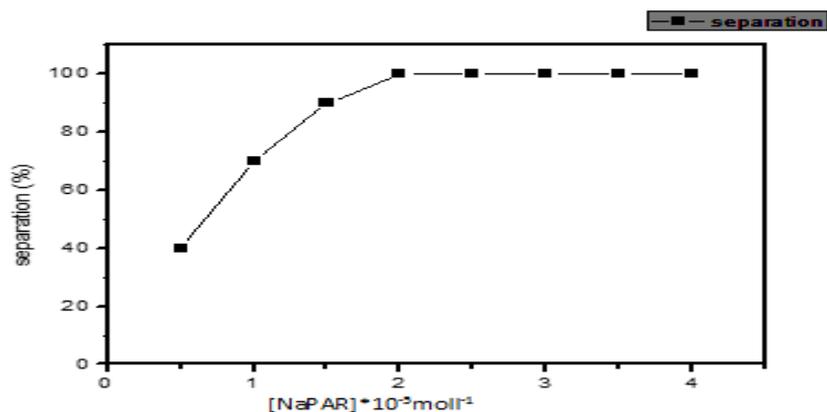
Fig. 3. The variation of separation % of 2×10^{-5} moll^{-1} U(VI) with ligand concentration in the presence of 2×10^{-4} moll^{-1} HOL a pH 6.
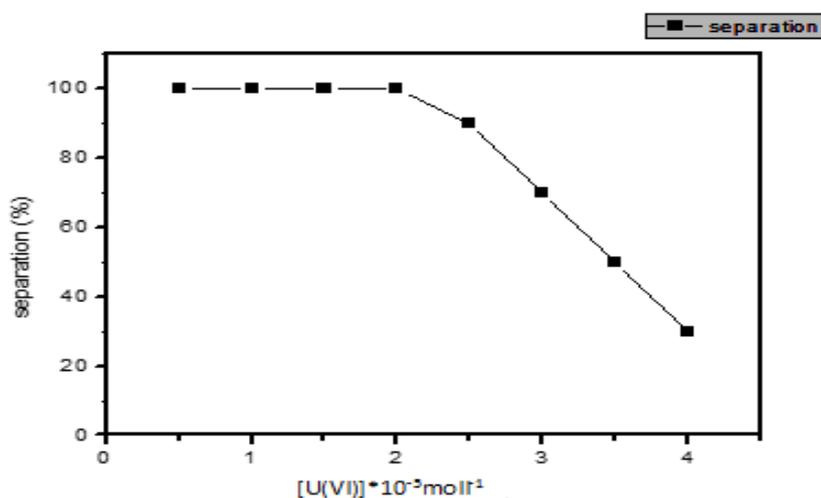

Fig. 4. The variation of separation % with different U(VI) concentration at pH 6.0 in the presence of 2×10^{-5} moll^{-1} NaPAR using 2×10^{-4} moll^{-1} HOL at pH 6.0.
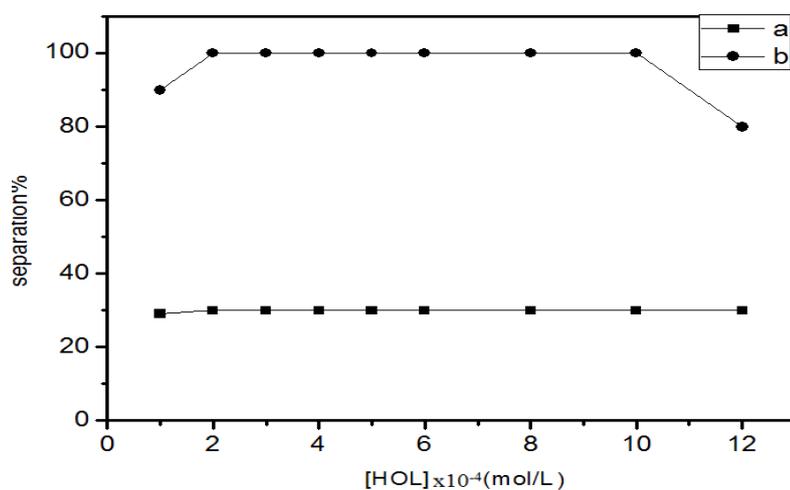

Fig. 5. The variation of separation % of 2×10^{-5} moll^{-1} U(VI) with different HOL concentrations at pH 6.0 (a) in the absence of NaPAR (b) in the presence of 2×10^{-4} moll^{-1} NaPAR.

Influence of HOL concentration.

The flotation efficiency of U(VI) in the absence of NaPAR using different concentrations of HOL is demonstrated in Fig. 5, a. The Flotation % doesn't exceed 20%. On the other hand, maximum flotation % of U(VI) 100% was successfully obtained over large scale of HOL concentration (2×10^{-4} -1×10^{-3} mol l^{-1} in the use of 2×10^{-4} mol l^{-1} of NaPAR, (Fig. 5, b). This finding clearly demonstrates the beneficial role of the ligand in the complexation and successful flotation of U(VI). An appropriate concentration of HOL (2×10^{-4} mol l^{-1}) was utilized for subsequent experiments.

Influence of temperature

The proposed flotation technique was performed over 20-80 °C. The results in Fig. 6, demonstrated that the maximum flotation of U(VI)-NaPAR complex wasn't markedly changed within the 20-80°C. Subsequent experiments were performed at 25°C.

Flotation time and stability of U(VI)-NaPAR complex within the scum layer

Flotation time could be defined as the interval time relating to the introducing of all reagents (U(VI), NaPAR, HOL and buffer) inside the flotation cell and the start of flotation. The effects of flotation time for the flotation efficiency of U(VI) was examined over a time period range of 0-60 min whilst the other parameters were kept constant. It had been found out that maximum flotation (F» 100%) could possibly be obtained within 2 min, (Fig. 7). A time period of 5 min was chosen for additional experiments as the flotation time. Because of this, the flotation separation procedure isn't time consuming. As a way to confirm the stability of U(VI)-NaPAR complex after 5 min, additional tests had been performed from 5 minutes to 72 hours. It had been demonstrated that the colour of floated U(VI)-NaPAR complex in the scum layer as well as the separation efficiency % didn't change approximately for 72 hr.
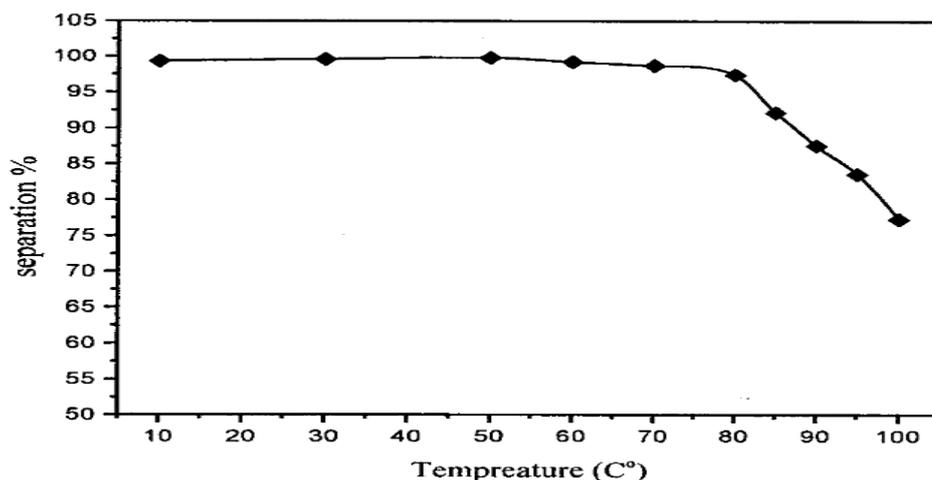

Fig. 6. The variation of separation % of 2×10^{-5} moll^{-1} U(VI) with different temperature values using 2 x 10^{-4} moll^{-1} NaPAR in the presence of 2×10^{-4} moll^{-1} HOL at pH 6.0.
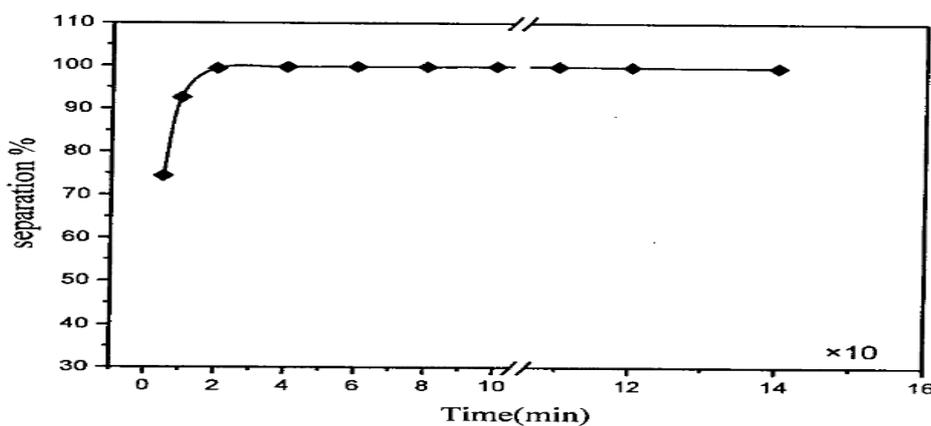

Fig.7.The variation of separation % of 2×10^{-5} moll^{-1} U(VI) with the flotation time using 2 x 10^{-4} moll^{-1} NaPAR in the presence of 2×10^{-4} moll^{-1} HOL at pH 6.0.

Influence of solution volume.

Suitable large flotation cells have been used to float different concentrations of U(VI) from various aqueous volumes using the proposed technique. The results, Fig. 8, demonstrated that, as much as 100 ppm of U(VI) could possibly be completely separated into the HOL layer from 1000 ml of sample solution into 10 ml of HOL. The preconcentration factor was calculated to be 100**.**

Influence of diverse ions

The influence of diverse ions on the separation

via flotation of U(IV) using NaPAR and HOL continues to be examined in details. Cations such as sodium(I), potassium(I), silver(I), calcium(II), magnesium(II), Sr(II), lead(II), cadmium(II) and Nickel(II) and anions like chlorides, sulphates or nitrates don't have any effect. Other cations like aluminum (III), mercury(II), iron(III), and vanadium(V) didn't have much interfering effects (~1%), Table 1. Most of these effects were totally eliminated with the addition of excess of the chelating agent NaPAR (2×10^{-3} mol l^{-1}).
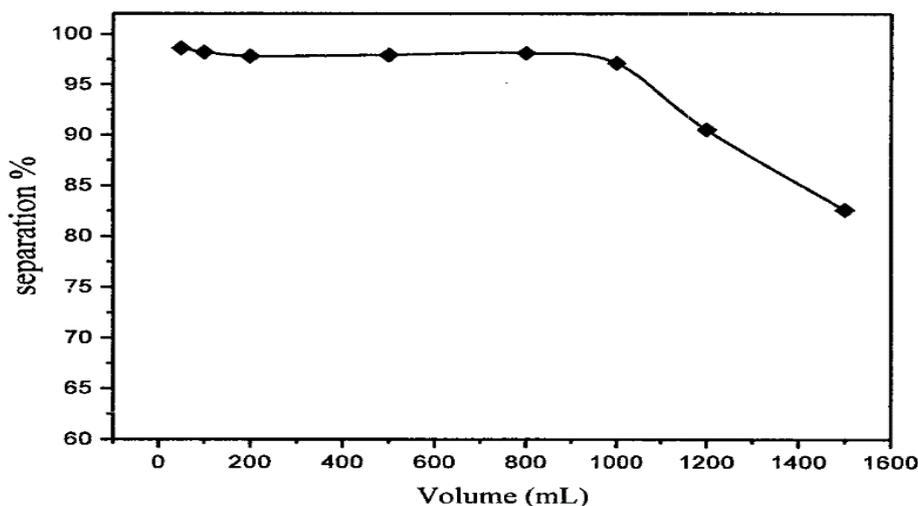

Fig. 8. The variation of separation % of 2×10^{-5} moll^{-1} U(VI) with different solution volumes using 2 x 10^{-4} moll^{-1} NaPAR in the presence of 2×10^{-4} moll^{-1} HOL at pH 6.0.

TABLE 1 . Effect of concentration of foreign ions on the recovery of 2.0 x 10^{-5} moll^{-1} of U(VI) using 2.0 x 10^{-4} moll^{-1} of NaPAR, 2.0 x 10^{-4} moll^{-1} HOL at pH 6 (n= 5).

Foreign ion	Concentration (mg/L)	Recovery% U(VI)
Hg^{2+}	50	99.6
Fe^{3+}	50	96.8
Cd^{2+}	50	99.8
Cu^{2+}	50	98.8
Co^{2+}	50	87.2
Cr^{3+}	50	99.4
Bi^{3+}	50	82.6
Zn^{2+}	50	99.8
Pb^{2+}	50	99.6
Ni^{2+}	50	99
Th^{3+}	50	99
Mn^{2+}	50	85
EDTA	01.0	46
Na_2CO_3	0.5	85
$Na_2S_2O_3$	0.5	98.2
$NaNO_2$	0.5	99.8

Influence ionic strength

The effect of ionic strength on the floatability of 2.0×10^{-5} moll^{-1} of U(VI) using 2.0×10^{-4} moll^{-1} of NaPAR and 2.0×10^{-4} moll^{-1} HOL at pH 6 is shown in Table 2. Different salts have been used for adjusting the ionic strength. As it can be noticed a marked flotation % could be obtained up to 010 moll^{-1} of the used ionic strength adjustors.

Physicochemical characteristics

Various physicochemical characteristics are represented in Table 3 including the linear range, limits of detection as well as the limit of quantification, the relative standard deviation (RSD), the correlation coefficient (R2) and the preconcentration factor. Under optimum parameters, the proposed flotation procedures of U(VI), the following physicochemical characteristics were obtained. Beer's law was obeyed over 3.0-300 µg l^{-1} concentration range, the correlation coefficient (R^2) was calculated to be R^2 = 0.9995. According to IUPAC recommendations, the limit of detection (LOD) and limit of quantification (LOQ) were calculated to be 0.9 and 3.1 µg l^{-1} ($n = 5$), respectively. The molar absorptivity (ε) is 0.63×10^6 l mol^{-1}cm^{-1} with a preconcentration factor 100 and the RSD (n=5) is 2.5%. The precision of the flotation method for uranium(VI) was determined by repeatability (intra-day) and intermediate precision (inter-day). Intra-day precision was evaluated by assaying samples at the same concentration and on the same day. Five sample solutions (100 µg ml^{-1}) were prepared and examined. The intermediate precision was studied by comparing the assays on different days (three days). The inter day and intra-day precision were calculated and showed a RSD of 0.58 and 0.98%, respectively.

TABLE 2. Effect of different ionic strengths on the recovery of 2.0×10^{-5} moll^{-1} of U(VI) using 2.0×10^{-4} moll^{-1} of NaPAR, 2.0×10^{-4} moll^{-1} HOL at pH 6.

Ionic strength (moll^{-1})	Adjuster	Recovery %
0. 10	NaCl	99.7
	Na$_2$SO$_4$	95.0
	NaNO$_3$	90.6
0.01	NaCl	94
	Na$_2$SO$_4$	85.4
	NaNO$_3$	95
0.05	NaCl	92.4
	Na$_2$SO$_4$	95.8
	NaNO$_3$	93.4
0.001	NaCl	99.6
	Na$_2$SO$_4$	98.0
	NaNO$_3$	98.3

TABLE 3. Physicochemical characteristics of U(VI)-NaPAR complex.

Characteristic	UO$_2$(II)-NaPAR complex
λ_{max}, nm	530
pH range	5.0-6.0
Linear range, µg l^{-1}	3.0-300
Sandell's sensitivity, µg cm^{-2}	0.0125
Molar absorptivity (ε), l mol^{-1}cm^{-1}	0.63×10^6
Composition (M:L) by Job's method	1 : 1
Limits of detection, µg l^{-1}	0.80
Limits of quantification, µg l^{-1}	2.70
Relative standard deviation (RSD),%	2.50
Correlation coefficient (R^2)	0.9995
Preconcentration factor	100
RSD, %	2.5

Applications

The proposed flotation technique had been used to determine U(VI) in various real ore, granite and waters samples. The results for natural water samples are given in Table 4. As it can be seen, the recovery of the added U(VI) reached about 95% in all samples. On the other hand, the results for U Th ore and granite ore samples presented in Table 5, provide good evidence for the suitability and applicability of the proposed methodology for preconcentration and spectrophotometric determination of uranyl ion from real samples, depending on the good agreement between the determined and assigned standard composition of the examined ores. The calculated $|t|$ values are below the hypothetical $|t|_1$ value (2.78) for P = 0.05 and n = 5 (4 degree of freedom). Statistical analysis of the results in Table 5 indicates that the preconcentrated samples are not subject to any systematic error i.e. accurate.

Flotation Mechanism

The mechanism of flotation of U(VI) using the NaPAR chelating agent and the HOL surfactant might be attributed to the formation of a hydrogen bonding between the hydrophilic part of HOL and the active sites in the U(VI)-NaPAR chelate. This proposal has been concluded from the following findings: 1) the complex formed in scum layer has the same red color as the complex formed in the aqueous solution; 2) The colour intensity and absorbance of the scum layer were not affected by heating up to 80°C, 3) The infrared spectra of the U(VI)NaPAR complex formed in the DDW is completely different from the U(VI) NaPAR complex formed in presence of oleic acid surfactant (Fig. 9).

TABLE 4. Recovery of U(VI) spiked in natural water samples after flotation using 2x10-4 moll-1 NaPAR and 2.0 x 10-4 moll-1 HOL at pH ~6 at 25 ºC.

Type of water (location)	U(VI) added (mgl⁻¹)	Recovery %	RSD %
Distilled water	1.00	98.6	0.42
	3.00	98.5	0.56
	5.00	99.7	0.78
Tap water	1.00	97.4	0.62
	3.00	98.9	1.12
(our lab)	5.00	99.3	1.41
Nile water	1.00	95.6	0.38
	3.00	94.9	0.74
(EL-Mahalla city)	5.00	93.8	1.18
Sea water	1.00	99	1.05
	3.00	99.2	1.35
(Alexandria city)	5.00	99.9	1.74
Well water	1.00	99.5	1.48
	3.00	99.3	0.94
Anter city) Meet)	5.00	99.1	1.14

TABLE 5. Statistical evaluation for analysis of U(VI) in some certified ore samples using the proposed flotation technique(n=5). Comparison of experimental mean ($\overline{X}$) with true value () by $|t|_1$ test

Ore Sample	X (Exp. Value)	(Standard value)	$|t|_1$
U-Th ore (206 ADL 1A) *	0.008 0.03	0.012 %	2.23
U-Th ore (206 ADH 1A)*	0.268 0.02	0.263 %	2.1
U ore (206 ABL 2A) *	0.430 0.05	0.426 %	1.12
Granite (I) (MALI MINTEK GRANITE: NIM. G.)	14.5 1.3	15 ppm	1.90
Granite (II)(83 MALS MINTEK LUJAVRITE NJM. I.)	13.7 0.8	14 ppm	2.5

($\overline{X}$): experimental value, () true value. $|t|_1$: for P = 0.05 and n = 5 (4 degree of freedom) = 2.78
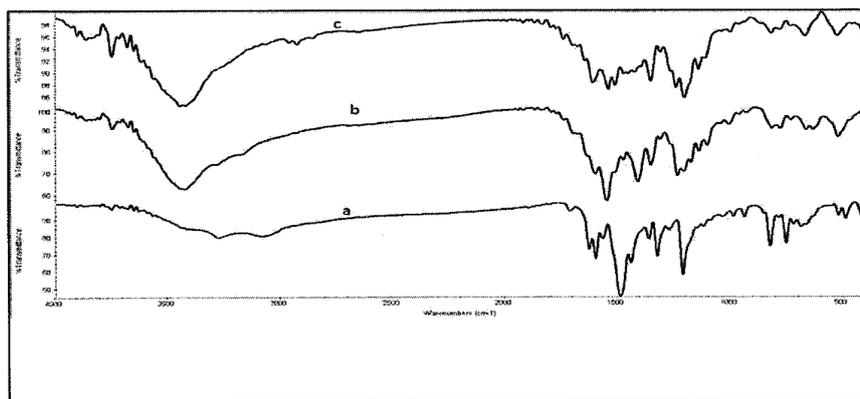* Concentration of uranium, %.
 Concentration of uranium, ppm.

Fig. 9. Infrared spectra of a) NaPAR, b) U(VI)·NaPAR complex isolated in aqueous solution and c) U(Vl)·NaPAR complex isolated in oleic acid.

Conclusion

The proposed flotation is a simple technique using a simple flotation cell. The method is advantageous to many of the separation techniques previously reported for the spectrophotometric determination of U(VI). The method has increased molar absorptivity value and law detection limit. It is sensitive, accurate, and can accommodate different foreign ions. The use of large flotation cells allowed the determination of U(VI) from water samples having large volume with a high preconcentration factor. The sensitivities of various spectrophotometric reagents known for U(VI) are given in Table 6. As it can be noticed the present combined flotation – spectrophotometric methodology has a good sensitivity for the micro determination of U(VI) compared to the previously reported procedures. Thus, the present study introduces a simple and low cost instrumental method like UV-Vis spectrophotometer to analysis of environmental and certified ore samples containing trace amounts of U(VI)

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التعويم وتحسين التقدير الطيفي لليورانيوم السداسي في العينات البيئية

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تم عرض تقنية خضراء وبسيطة للفصل عن طريق التعويم والتحليل الطيفي لليورانيوم السداسي في عينات المياه والخامات الحقيقية في هذه الدراسة البحثية التي تستخدم فيها صبغة الآزو غير المتجانسة 4- (2pyridyl أزو) ريسورسنول (NaPAR) للتركيز المسبق لأيونات اليورانيل (السادس) لتشكيل متراكب محمر في محلول مائي في نطاق درجة الحموضة 5.0-6.0. ، وقد تم استخدام حامض الأوليك (HOL) السطحي لتعويم المتراكب المتكون بنجاح وبشكل كامل للطبقة العضوية. وقد تم تحديد الخصائص الفيزيائية والكيميائية للتقنية التحليلية المقترحة. تحت المعلمات المثلى، تم الحصول على الخصائص الفيزيائية -الكيميائية التالية. تم اطاعة قانون بير حتى 300 ميكروغرام /لتر، وتم حساب معامل الارتباط (R^2) ليكون $R^2 = 0.9995$. وفقا لتوصيات IUPAC، والحد من الكشف (LOD) والحد من الكمي (LOQ) هي 0.9 و 3.1 ميكروغرام /لتر (ن = 5)، على التوالي. والامتصاصية المولارية (٤) هو $0.63*10^6$ لتر/ مول/ سم في الطبقة العضوية مع عامل تركيزمسبق 100 وRSD (ن = 5) هو 2.5٪. تم استخدام كمية زائدة من عامل مخلب NaPAR لإخفاء آثار الأيونات المختلفة على كفاءة التعويم. تم تطبيق الإجراء المقترح لتقدير اليورانيوم U السداسي في عينات المياه وكذلك في خامات اليورانيوم وعينات من خام الجرانيت. كما تم شرح آلية الفصل.