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SIMPLE AND RAPID SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF URANIUM (VI) IN LOW GRADE URANIUM ORES USING ARSENAZO (III)

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Abstract. A simple and highly selective non-extractive spectrophotometric method is presented for the rapid determination of uranium in low grade uranium ores using arsenazo (III). The method is based on the complex formation of uranium (VI) with Arsenazo (III) at pH 2.0 ± 0.1 which showed maximum absorption at 651 nm. Uranium concentration of $10 \mu\text{g g}^{-1}$ with a molar absorptivity of $4.45 \cdot 10^4 \text{ mol}^{-1} \cdot \text{cm}^{-1}$ at $296 \pm 2 \text{ K}$ obeyed Beer's law. Interferences caused by various metallic ions, such as Mn, Fe, Zn, Mo, Cr, Cu, Co, Ni, Zr, Pb, Al and Na were effectively masked by diethylenetriaminepenta-acetic acid (DTPA) and tartaric acid. The proposed technique has been effectively applied to the determination of low levels of uranium in uranium leach liquors. The accuracy of the current method was checked by comparison with the results obtained by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Keywords: spectrophotometric method, uranium, arsenazo (III), low grade uranium ores.

1. Introduction

Uranium behaves in a different way from many other metals because of its unpredictable oxidation state and propensity to form a broad diversity of positive, neutral and negatively charged complexes, at approximately neutral pH. Unlike many other radioactive elements, its half life is equal to the age of the earth and due to this, small quantities of uranium are found approximately everywhere in the soil, rocks and ores [1].

Many techniques have previously been developed for determination of uranium. Recently, these methods have contained inductively coupled plasma atomic emission spectrometry (ICP-AES) [2], inductively coupled plasma-mass spectrometry (ICP-MS) [3, 4], ion

chromatography (IC) [5], capillary zone electrophoresis (CZE) [6], and flow injection analysis (FIA) [7]. However, as these instrumental analyses need rather valuable apparatus and higher running costs, they offer restricted accessibility.

Spectrophotometry is a comparatively easy substitute method, which has been applied to determination of uranium [8, 9]. Spectrophotometry is a satisfactory detection method, owing to its good precision and accuracy, associated with its lower cost compared with other methods. Several processes for the spectrophotometric determination of uranium base on the use of pyrocatechol violet, balmic acid, morin, sodium fluoride, *etc.*, have been reported [10-15] but most of them need a solvent-extraction step and involve numerous drawbacks regarding reproducibility, simplicity, rapidity and sensitivity.

The application of organic dyes for the spectrophotometric determination of actinides including uranium, in a variety of materials has been reported to be easy and selective, and have been broadly studied [16-20]. The bisazo derivatives of chromotropic acid are amongst the most sensitive reagents for determination of uranium and among these, arsenazo (III) has been described to be the most sensitive [21-24].

Arsenazo (III) (1,8-dihydroxynaphthalene-3,6-disulfonic acid-bis (azophenyl arsenic acid)) which is derived from chromotropic acid and *o*-aminophenylarsonic acid, is usually employed for determination of uranium (VI) [25]. The major benefit of this reagent lies in the high stability of its uranium complex which makes achievable its analytical exploitation in powerfully acidic media, where neither hydrolysis, nor the formation of poly nuclear species, takes place in the reaction [26, 27]. The usefulness of the reactivity of arsenazo-III demonstrates that metals, which complex formation relies on high pH; do not interfere with determination of other elements such as

Th, Zr, Pu and Np which give complexes in strongly acidic medium [23]. On the other hand, by specifying the pH it is probable to utilize arsenazo-III very selectively.

Despite the fact that there are many techniques for the analysis of uranium, spectrophotometry is extensively used for its simplicity, low cost and adaptability. Therefore, it is decided to develop this technique for evaluation of uranium in ore samples. The literature review expose that existing spectrophotometric methods are time consuming, employing numerous reagents to develop color and involving extraction of uranium complex into organic solvents. In this paper, a simple and accurate method to determine uranium (VI) in low grade uranium ores is described using arsenazo (III) as a spectrophotometric reagent. The development procedure authorizes routine analysis of a great number of samples without specialist equipment or skills. In the proposed method, DTPA and tartaric acid are used for increasing the sensitivity of the system and to eliminate most of the interfering ions [28, 29].

2. Experimental

2.1. Apparatus

A PG T80+ UV/Vis spectrometer equipped with a recording device was employed for measurement of optical density. Absorption measurements at fixed wavelength were performed with 1-cm quartz cells. A Metrohm pH meter (model 827) with a combined glass electrode was used for pH measurements.

2.2. Reagents

All chemicals in this experiment were of analytically pure grade and double-distilled water was used.

Standard uranium solution ($1000 \mu\text{g}\cdot\text{ml}^{-1}$). Prepared by dissolving 0.2110 g of uranyl nitrate hexahydrate (Fluka) in 3 ml concentrated sulfuric acid and diluting to volume with deionized water in a 100 ml volumetric flask.

Arsenazo-III. Prepared by dissolving 0.25 g Arsenazo-III (Merck) in 0.5 N NaOH and diluting to volume with deionized water in a 100 ml volumetric flask.

DTPA solution (2.5 %). Prepared by dissolving 25 g diethylenetriaminepenta-acetic acid (DTPA) (Merck) in 1000 ml deionized water and dropwise addition of 0.5 N NaOH.

Tartaric acid (10 %). Prepared by dissolving 10 g of tartaric acid (Merck) in 100 ml deionized water.

2.3. Procedure

1 g of ore (minus 200 mesh) was weighted in a breaker and 10 ml of 4 N HNO_3 were added. The mixture

was evaporated to near dryness on a hot plate. This was followed by the addition of 2 ml concentrated H_2SO_4 and evaporation to dryness on a hot plate. Then 50 ml deionized water were added to the dried sample. It was heated to a boiling point for five minutes. After cooling, the solution was filtered through a small paper into a 100 ml volumetric flask. The solution was taken up to the mark with deionized water.

An aliquot of sample solution containing less than 200 μg of uranium was transferred into a 50 ml volumetric flask. 2 ml of DTPA, 1 ml of tartaric acid and 1 ml of arsenazo-III reagent solution were added. The solution was taken up to the mark with dilute H_2SO_4 (pH 2.0). After 5 min, the absorbance of the pink-violet complex at 651 nm in a 1-cm cell was determined against a reagent blank as the reference.

3. Results and Discussion

3.1. Spectral Characteristics

The absorbance of the solution at 550–750 nm was measured against a reagent blank as the reference. The absorption spectra of the uranium (VI)–arsenazo-III complex and reagent blank are shown in Fig. 1. As shown, the maximum absorption of the pink-violet complex occurred at 651 nm. At this wavelength, arsenazo-III did not demonstrate any respected absorption. A pink-violet complex was obtained with λ_{max} at 651 nm due to the interaction of uranyl ion with arsenazo-III while arsenazo-III showed negligible absorbance at 651 nm.

The reaction was carried out at 296 ± 2 K and the absorbance of the colored complex was measured after 5 min at 651 nm. Therefore the absorbance measurement as a function of initial concentration of uranyl ion was utilized to develop a spectrophotometric method for determination of uranium (VI).

Fig. 2 reveals the relationship between concentration of uranium ions and absorbance at $\lambda_{max} = 651$ nm, as determined formerly. The value of molar absorptivity (ϵ) of uranium (VI)–arsenazo-III complex was calculated from the standard curve and was established to be $4.45 \cdot 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$. The concentration range $0.1\text{--}10 \mu\text{g}\cdot\text{g}^{-1}$ obeyed Beer's law and the detection limit was $0.025 \mu\text{g}\cdot\text{g}^{-1}$.

3.2. Optimization of Experimental Conditions

For finding the optimum conditions, the effect of pH values on the absorbance of uranium (VI) and arsenazo-III

complex at a constant concentration at 651 nm was studied against the reagent blank. As it is shown in Fig. 3, maximum absorption was obtained at pH 2–2.1. The complex concentration formed was not significant between uranium and arsenazo-III below pH 1.5 or above 2.5.

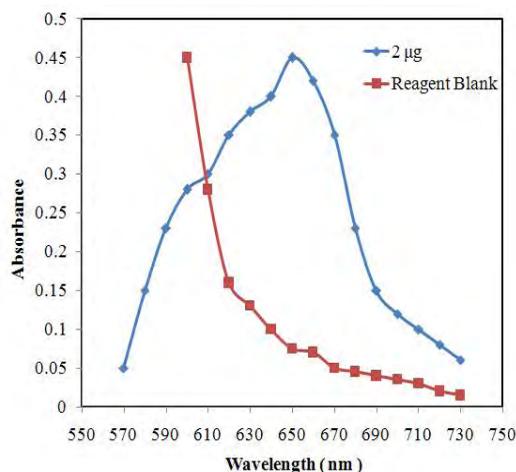


Fig. 1. Absorption spectra of Uranium (VI)-arsenazo-III complex

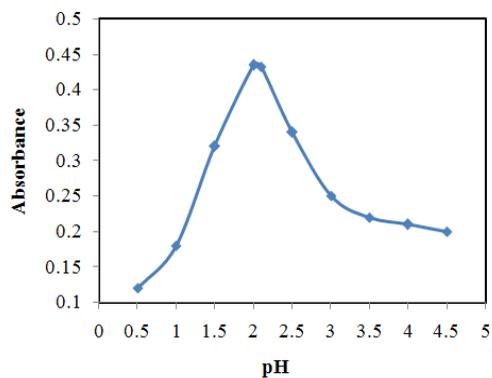


Fig. 3. Effect of pH on development of color of Uranium (VI)-arsenazo-III complex

The effect of complexing agents (DTPA and tartaric acid) on the formation of uranium-arsenazo-III complex was also studied with variable concentrations of DTPA and tartaric acid. The results indicated that the concentration of the complexing agent did not influence considerably the formation of a colored complex. The minimum concentrations of DTPA and tartaric acid for development of uranium-arsenazo-III complex were 2 ml and 1 ml, respectively.

The minimum time required for completion of the colored development of uranium-arsenazo-III was found to be 5 min. The results in Table 1 reveal that the color of the complex can be stable for more than 8 h.

The effect of diverse concentration of arsenazo-III reagent solution on the formation of uranium (VI)-arsenazo-III complex was also investigated. The results are shown in Fig. 4. It can be seen from the figure that 1 ml of arsenazo-III was adequate to complete the formation of the colored complex.

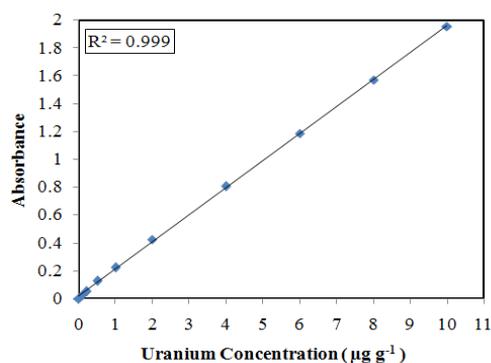


Fig. 2. Calibration curve for spectrophotometric determination of uranium. Color intensity was determined at 651 nm

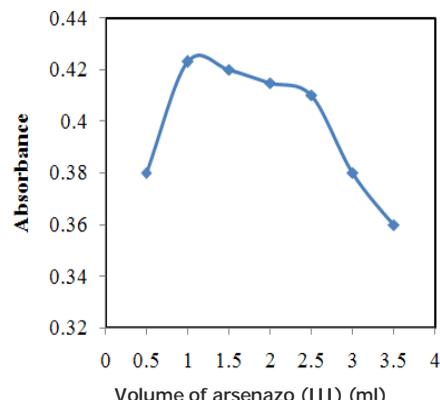


Fig. 4. Effect of concentration of arsenazo-III on color production with uranium

3.3. Interference Study

To study the effect of different metals on determination of uranium with arsenazo-III, a solution containing both uranium and the foreign metal was treated in accordance with the procedure. The results attained are given in Table 2. These data demonstrate that uranium could be determined in the presence of many heavy metals which commonly interfere with uranium in other spectrophotometric methods for uranium evaluation. Metal ions like Fe (III), Mn (II), Mo (VI), Ni (II), Co (II), Cu (II), Na (II) and Zr (IV) were found not to interfere significantly up to $150 \mu\text{g}\cdot\text{g}^{-1}$ concentrations. The pre-

sence of Ca (II), Al (III) and Pb (II) up to 30 $\mu\text{g}\cdot\text{g}^{-1}$ was successfully masked by DTPA and tartaric acid.

Table 1

Effect of reaction time on development of color of uranium (VI)–arsenazo-III complex*

Time	Absorbance
1 min	0.345
2 min	0.415
5 min	0.432
10 min	0.432
20 min	0.431
30 min	0.430
1 h	0.428
2 h	0.428
4 h	0.427
6 h	0.426
8 h	0.425
24 h	0.424
48 h	0.423

* pH = 2; uranium concentration is 2 $\mu\text{g}\cdot\text{g}^{-1}$; DTPA = 2 ml and tartaric acid = 1 ml

Table 2

Influence of interfering ions in the determination of uranium with arsenazo (III) after adding DTPA and tartaric acid*

Metallic ion	Concentrations of ions added, $\mu\text{g}\cdot\text{g}^{-1}$	Absorbance
None	-	0.432
Al (III)	150	0.422
Ca(II)	30	0.425
Co (II)	150	0.427
Cr (III)	30	0.439
Cu (II)	150	0.430
Fe (III)	150	0.424
Mn (II)	150	0.435
Mo (VI)	150	0.420
Na (II)	150	0.433
Ni (II)	150	0.438
Pb (II)	30	0.441
Zn (II)	30	0.436
Zr (IV)	150	0.439

* uranium concentration is 2 $\mu\text{g}\cdot\text{g}^{-1}$; time of color development is 5 min; DTPA = 2 ml and tartaric acid = 1 ml

3.4. Application

The proposed method was applied successfully to the determination of uranium ion in low grade uranium ore. The results obtained were compared with those obtained by ICP-OES method. The results are shown in Table 3. On average between three determinations of the four samples there is no significant difference at the 95 % confidence level between both methods. The method

described herein has also been applied to the certified reference material DL-1a for uranium determination. The certificated value for the concentration of uranium in this reference material was $0.0116\pm 0.0003\%$. The obtained data, based on the average of triplicate determinations was 0.0114 ± 0.0003 and the relative standard deviation was 1.7% which shows that result was in good agreement with the certified value. By reason of precision of uranium from CRM, this method was shown to be reliable and accurate, and will be useful in the routine analysis of uranium at $\mu\text{g}\cdot\text{g}^{-1}$ level in ores.

Table 3

Uranium determination in low grade uranium ores^a

Sample	ICP-OES ^b , $\text{mg}\cdot\text{g}^{-1}$	Present method
1	5.72 ± 0.28	5.65 ± 0.31
2	1.27 ± 0.14	1.30 ± 0.12
3	0.72 ± 0.05	0.74 ± 0.06
4	1.75 ± 0.24	1.72 ± 0.21

^a Uranium ores used in this study was prepared from Bandar Abbas mines in Iran

^b Measurements are based on the mean of three determinations

3.5. Comparison with other Methods

Park *et al.* [19] developed a spectrophotometric method using Pyrocatechol Violet for determination of uranium in sand. Their method obeyed Beer's law over the concentration range of 0.2–2 $\text{mg}\cdot\text{g}^{-1}$. The detection limit ($S/N = 3$) was 0.15 $\text{mg}\cdot\text{g}^{-1}$ and the relative standard deviation at 0.5 $\text{mg}\cdot\text{g}^{-1}$. U (VI) level was 3.4 %.

The spectrophotometric method we described here obeyed Beer's law over the concentration range 0.1–10 $\text{mg}\cdot\text{g}^{-1}$. The detection limit ($S/N = 3$) was 0.025 $\text{mg}\cdot\text{g}^{-1}$ and the relative standard was 1.7 %. Compared with the work of Park *et al.* our model has 1) better accuracy; 2) more extensive concentration level and 3) lower detection limit.

4. Conclusions

The proposed method gives a simple, very sensitive and inexpensive spectrophotometric procedure for determination of uranium. No extraction step is required and therefore the employment of organic solvents, which are commonly toxic pollutants, is avoided. DTPA and tartaric acid were found to mask successfully the interferences caused by metal ion such as Ca, Fe, Ni, Cu, Mo, Na and Zr. This method was successfully applied to determine uranium in low grade uranium ores and the

results showed good agreement with ICP-OES methods, and the method involves less complicated instrumentation.

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ПРОСТИЙ І ШВИДКИЙ СПЕКТРОФОТОМЕТРИЧНИЙ МЕТОД З ВИКОРИСТАННЯМ АРСЕНАЗО (III) ДЛЯ ВИЗНАЧЕННЯ УРАНУ (VI) В НИЗЬКОСОРТНИХ УРАНОВИХ РУДАХ

Анотація. Приведено простий і високоселективний спектрофотометричний метод для швидкого визначення урану в низькосортних уранових рудах з використанням арсеназо (III). Метод базується на утворенні комплексу урану (VI) з арсеназо (III) за $pH = 2,0 \pm 0,1$ з максимумом поглинання при 651 нм. Концентрації урану порядку 10 мкг^{-1} і молярний коефіцієнт поглинання $4,45 \times 10^4 \text{ моль}^{-1} \cdot \text{см}^{-1}$ при $296 \pm 2 \text{ K}$ підкоряються закону Бера. Вплив різних іонів металів, таких як Mn, Fe, Zn, Mo, Cr, Si, Co, Ni, Zr, Pb, Al і Na ефективно нейтралізується діетилентриамінопентаоцтовою і винної кислотами. Запропонований метод був ефективно використаний для визначення низьких концентрацій урану в лугах після вилуговування. Точність запропонованого методу була перевірена порівнянням з результатами, отриманими за допомогою індуктивно-зв'язаної плазми-оптичної емісійної спектроскопії.

Ключові слова: спектрофотометричний метод, уран, арсеназо (III), низькосортні уранові руди.