



Research Paper

## Spectrophotometric Determination of Thorium (IV) Ions In Acidic Solutions Using 2-(5-Bromo-2-Pyridylazo)-5-Diethyl Aminophenol Dye

El-Sayed A. Manaa<sup>\*</sup>, Marwa M. Rashad, Walaa A. Kassab, Mahmoud O. Abd El-Magied and Sameh H. Negm

Nuclear Materials Authority, P.O. Box 530, El Maadi, Cairo, Egypt

**ABSTRACT:** The present work describes a method for the determination of Th (IV) ions spectrophotometrically using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) as a sensitive chromogenic reagent. The method is based on the formation of a red-orange colored complex between Th (IV) species and the Br-PADAP dye in the acidic medium. In addition, factors affecting the sensitivity of the formed Th-Br-PADAP complex include pH, reaction time, and reaction temperature. In addition, the reagent and Th (IV) concentrations were studied and optimized. Based on the obtained results, the Th-Br-PADAP complex is formed at pH 3 after 20 min at room temperature, and the maximal absorbance is obtained at 590 nm. The effect of some water-miscible alcohols and acetone on the colorimetric determination of Th (IV) is studied and described to show their effects on Th-Br-PADAP complex color intensity. The results showed that the absorbance of the Th-Br-PADAP complex is enhanced by alcohol or acetone addition, and the maximum absorbance percent (33%) is obtained using 60% solvent content. The proposed method is applied to the determination of Th (IV) concentrations from 0.05 to 10  $\mu\text{gml}^{-1}$ , but the detection limit is decreased to 0.01  $\mu\text{gml}^{-1}$  by miscible alcohols or acetone addition. The influence of associated species on the optical density of Th-Br-PADAP was investigated and determined within its allowable limits. Finally, the proposed method was tested for the analysis of thorium ions in different international standards and some Egyptian rock samples.

**Keywords:** Thorium; Br-PADAP, Spectrophotometric; Determination and Rock Samples

Received 28 Nov, 2021; Revised 10 Dec, 2021; Accepted 12 Dec, 2021 © The author(s) 2021.

Published with open access at [www.questjournals.org](http://www.questjournals.org)

### I. INTRODUCTION

Thorium is spread naturally and connected mainly with lanthanides and it widely distributed in nature with an average concentration of 11  $\mu\text{g g}^{-1}$  in the upper earth's crust to be more than three times the amount of uranium. In general, thorium occurs in relatively small number in Th-enriched minerals: thorite [(Th, U).SiO<sub>4</sub>] thorianite [ThO<sub>2</sub>], monazite [(Ce, La, Y, Th).PO<sub>4</sub>], Thorbastnasite [ThCa(CO<sub>3</sub>)<sub>2</sub>F<sub>2</sub>·3H<sub>2</sub>O], and thorumite [(Th, U)(SiO<sub>4</sub>)<sub>1-x</sub>(OH)<sub>4x</sub>] ores. However, the main world resources of thorium are coupled with monazite [1]. Thorium compounds are used in many industries, especially its oxide (ThO<sub>2</sub>) that has an extremely high melting point, such as welding electrodes, laboratory crucibles, ceramic, catalytic, and lens applications. Furthermore, thorium alloys with manganese and tungsten are used in electric filaments, airframe construction, and inert gas welding beside in aircraft engines [2]. In addition of the previous applications; some Indian programs are applied for using thorium in nuclear reactors with plutonium. This kind of a closed fuel cycle reactors was designed to breed fuel and to minimize generation of nuclear waste. These applications produce many wastes containing thorium species that have acute toxicological effects on humans because thorium and its compounds are carcinogens that penetrate the human body and are absorbed readily by the lungs. Thus, WHO advises thorium must not exceed 0.246 mg L<sup>-1</sup> in the drinking waters [3]. These guidelines need regular thorium monitoring and hence quick, cost-effective, simple, and sensitive thorium measurement techniques. Several methods for thorium estimates, such as; titrimetry [4], potentiometry [5], gravimetry [6], fluorimetry [7], liquid chromatography [8], X-ray fluorescence [9], chromatography [10], and inductively coupled plasma mass spectrometry have been [11]. Many of these methods are sensitive but are highly expensive due to their high cost [8]. Thorium estimations spectrophotometrically using complexing reagents are simple, inexpensive, and rapid methods that have been used. Among of these reagents are; sodium 4,8-diamino-1,5-dihydroxy-anthraquinone-2,6-disulphonate [12], sodium 5-(4-diethyl-amino-2-hydroxyl phenyl azo), 4-triazole-3-

\*Corresponding Author: El-Sayed A. Manaa

carboxylate [13]. In addition to these reagents; Arsenazo I, Arsenazo III [14], 2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone [15], 8-quinolinol [16] rifampicin [17], bromocresol and xylenol orange [18], orange, methylthymol blue [19], 5,8-dihydroxy-1,4-naphthoquinone [20], 1-amino-4-hydroxyanthraquinone [21], 4-(2-triazolylazo) resatophenone [22], 1-(2-thiazolylazo)-2-naphthol are also used [23]. The main limitations of these agents for Th (IV) estimation are their low selectivity and the presence of significant interference from various ions then; many efforts are applied to create a direct, selective, and sensitive thorium (IV) estimation method [14]. This study aims to establish a simple, rapid and sensitive determination process of Th (IV) species mainly in aqueous solutions using 5-Br-PADAP as an analytical reagent.

## II. MATERIALS AND METHODS

### 2.1. Chemicals and Reagents

In this study, all the used chemicals were analytical-grade reagents, and double-distilled water was used throughout. The standard thorium (IV) solution ( $1000 \text{ g L}^{-1}$ ) is prepared by dissolving 2.46 g of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  (Merck) in 1000 ml of acidified ( $\text{HNO}_3$ ) water, and the diluted working standard solutions are made right before use. The solution of  $1.431 \times 10^{-3} \text{ M}$  Bromo-2-pyridylazo-5-diethylaminophenol (5-Br-PADAP) dye (Aldrich) is prepared by dissolving 0.05 g in 30 ml of pure ethanol (99%) (Misr Petroleum Co.), and then topped up to 100 ml with double distilled water and stored in an amber bottle for at least 2 months. Stock interfering ion solutions are prepared by dissolving appropriate amounts of their analytical grade salts in distilled water.

### 2.2. Apparatus

A UV-Visible-100 double-beam spectrophotometer (Labomed, INC, USA) using quartz cells with a 10 mm optical path length was used for scanning the colored complexes, while a digital pH meter (Digimed DM-21, Japan) was used for measuring the solution pH values (within a resolution of 0.01 and an accuracy of  $\pm 0.01$ ). In some experiments, a water bath shaker (LabortechnikmbH, 1083, Germany) was used while the solid samples were weighed using a digital analytical balance (Sartorius TE 214S, Germany).

### 2.3. Thorium Determination

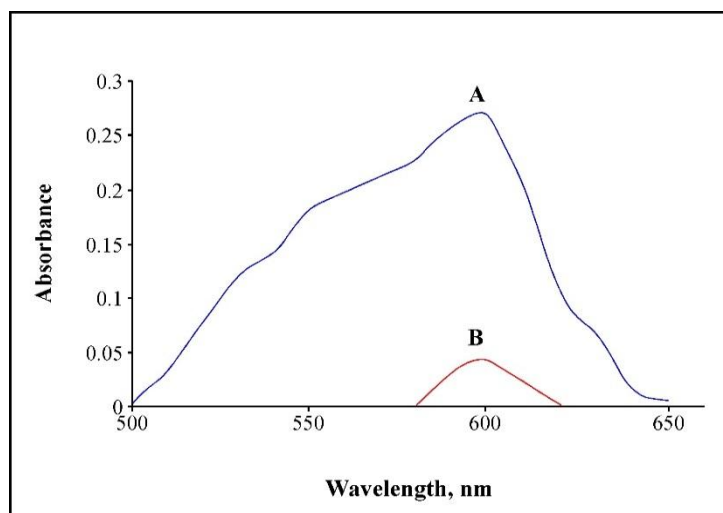
In the first step, before any experiments, the Thoron I reagent is used for determination of thorium (IV) in the prepared standard solutions. This method is based on the reaction of Th (IV) ions with Thoron I in an HCl medium in the presence of ascorbic and tartaric acids. The resulting red Thoron-Th (IV) complex is then calorimetrically measured at 540 nm against a blank solution [24]. On the other hand; during the study of the affecting factors, the thorium content is spectrophotometrically determined using the Br-PADAP dye.

## III. RESULTS AND DISCUSSION

In this work, during the study of the complex formation of Th (IV) with Br-PADAP dye in the acidic medium; many parameters were studied and optimized.

### 3.1. Absorption Spectra

The optimum wavelength value was determined by scanning the absorption spectra of 5-Br-PADAP dye and Th(IV)-Br-PADAP complex in an acidic medium. The obtained results in Figure (1) show that both the dye and Th-Br-PADAP complex are maximally absorbed at 590 nm. The absorbances of 5-Br-PADAP dye alone and with a  $2 \mu\text{g ml}^{-1}$  are 0.04 and 0.25, respectively, as shown in Figure (1A, B). The molar absorptivity is  $3.13 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ , which increases to  $3.95 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  when a 60% methanol solvent is added.

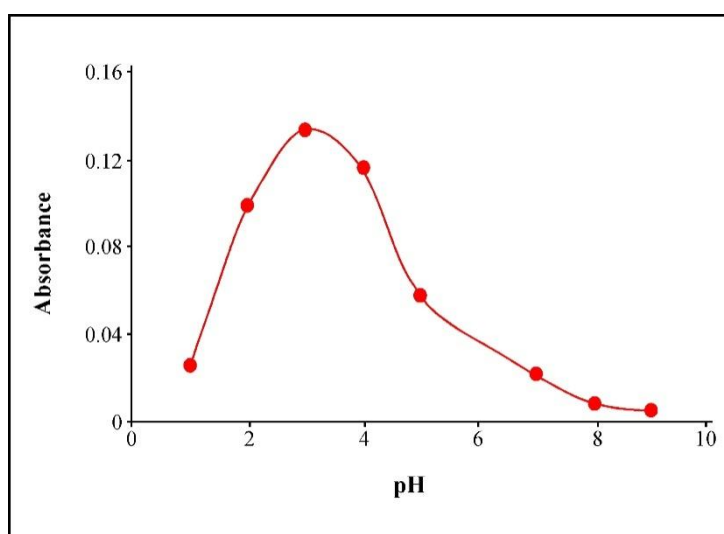


**Figure (1):** Visible absorption spectra of the formed complex of  $2 \mu\text{g ml}^{-1}$  Th (IV) at pH3 after 20 min using  $5.72 \times 10^{-5}$  M 5-Br-PADAP (A) Th (IV)-Br-PADAP (B) 5-Br-PADAP

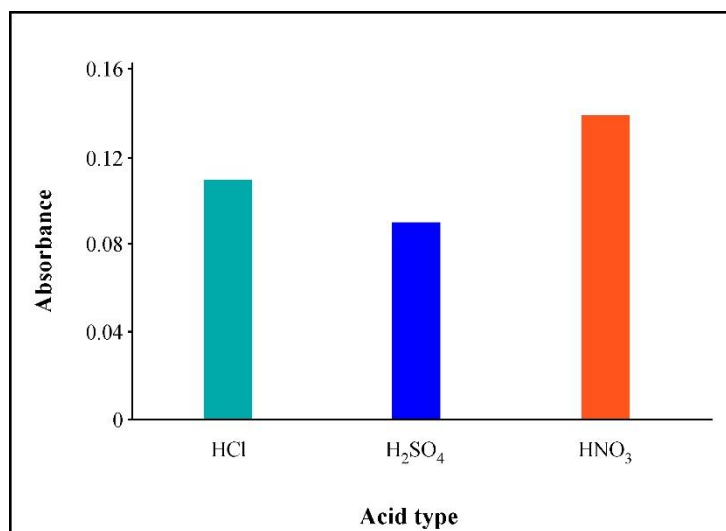
### 3.2. Effect of pH

The effect of the solution pH on the Th-Br-PADAP complex formation was studied. The studied solutions containing  $1 \mu\text{g ml}^{-1}$  Th (IV) were adjusted at variable pH values ranging from 1 to 9 using dilute HCl and NaOH solutions. To the prepared solutions, 1 ml of 5-Br-PADAP (0.05%) reagent is added and steaded for 30 min. The obtained results in Figure (2) show that the absorbance of the formed complex is highly dependent upon the solution's pH. The absorbance value in highly acidic mediums is very low (0.03), and increasing the solution pH to 3 increased in absorbance intensity of 0.1347. As the solution pH increased to 9, the absorbance intensity decreased again to 0.005, and pH 3 was chosen as the optimum value. The low absorbance at pH 2 could be attributed to the high acidic medium (excess hydrogen ions) causing strong competition between  $\text{H}^+$  and Th(IV) ions on the dye-binding sites, resulting in a decrease in Th(IV) chelation with the Br-PADAP reagent. Increasing the pH of the solution to 3 resulted in precipitation and hydrolysis of Th(IV) species such as  $\text{Th}(\text{OH})_2^{2+}$  and  $\text{Th}(\text{OH})_3^+$  [25, 26].

In an additional trial, the type of acid effect on Th(IV)-Br-PADAP complex formation was studied using different acids, including nitric, sulfuric, and hydrochloric acid for pH adjustments (pH 3). The results in Figure (3) show that; nitric acid is the most dependable acid that can be used in pH adjustment as well as rock sample preparation. However; the absorbance of the formed complex is remarkably reduced by using sulfuric or hydrochloric acids. Then  $\text{HNO}_3$  acid and NaOH solutions are used for pH adjustment.



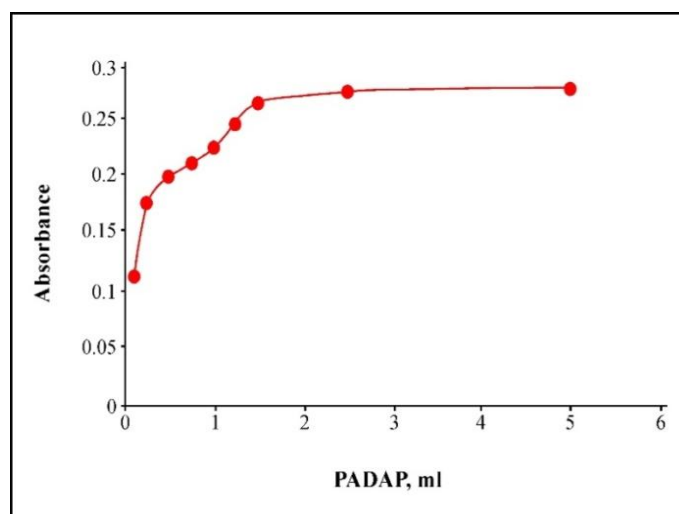
**Figure (2):** Effect of pH on the color development of the Th(IV)-Br-PADAP complex



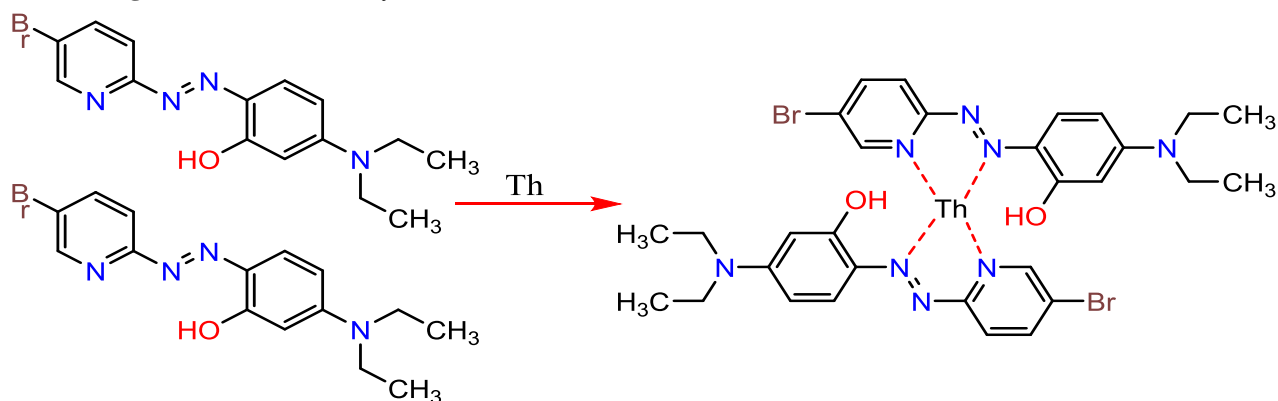
**Figure (3):** Effect of the acid type on the absorbance of Th-Br-PADAP complex at 590 nm

### 3.3. Effect of 5-Br-PADAP Dye Concentration

The effect of varying concentrations of 5-Br-PADAP dye on the color intensity of the Th-Br-PADAP complex is studied using different thorium amounts ranging from 0.1 to 5 ml of a  $1.431 \times 10^{-3}$  M Br-PADAP dye solution (0.05% w/v). The formed complexes between Br-PADAP solutions and  $2 \mu\text{g ml}^{-1}$  were measured at  $\lambda_{\text{max}}$  590 nm. The results in Figure (4) show that; the maximum absorbance takes place at 1.5 ml of ( $8.586 \times 10^{-5}$  M) 5-Br-PADAP solution. The molar ratio of Th (IV)-Br-PADAP complex is established using the molar ratio and Job's methods and is found at 2:1 or in some times at 3:2 of Br-PADAP: Th (IV), (Scheme 1).



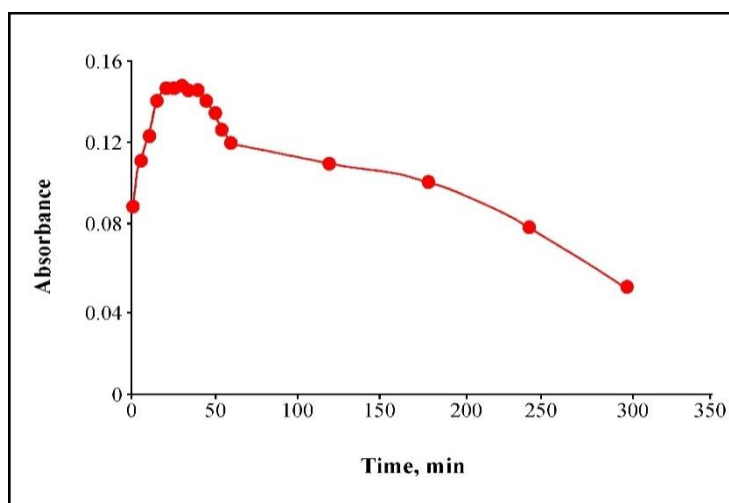
**Figure(4):** Effect of the dye concentration on the absorbance of the Th-Br-PADAP at 590 nm



**Scheme (1):** The suggested mechanism of the Th-Br-PADAP complex formation

### 3.4. Effect of Time

In general, during the colorimetric studies; the complex formation may be slow and, in some cases the color development requires several minutes or may hours. Then the colorimetric measurement time was studied and optimized. To study the effect of time on the formation and stability of the formed Th-Br-PADAP intensity complexes between 2  $\mu\text{g ml}^{-1}$  Th (IV) and 1 ml 5-Br-PADAP (0.05%) at pH values of 3, after certain time intervals from 5 to 300 min, measured colorimetrically at 590 nm. The results plotted in Figure (5) indicate that the complex of Th (IV) with 5-Br-PADAP is instantaneously formed and the color intensity reaches its maximum value after 20 min and remains nearly constant for at least 180 min. The complex formed is stable for a long time, which verifies the stability of the proposed method for the determination of Th (IV) ions. An additional experiment was carried out to study the effect of temperature, from room temperature to 80 °C, on the Th (IV)-Br-PADAP complex time formation. The results showed that; indirect heating (in a water bath to avoid the complex destruction) at 50 °C increased the maximum colored complex Th(IV)-Br-PADAP intensity after only 5 minutes instead of 20 minutes under normal conditions (room temperature). A prolonged heating time than 20 minutes resulted in the form complex breaking up.



**Figure (5):** Effect of time on the formation and stability of the Th (IV)-Br-PADAP complex

### 3.5. Effect of Solvents

The effect of miscible solvents on the absorption spectra of the formed Th-Br-PADAP complexes is studied using variable amounts of ethanol, methanol, and acetone solvents ranging from 0 to 70%. In addition to aiding in the enhancement of colored complexes intensity, miscible solvents are also used to avoid metal species precipitation. The absorbances of the formed complexes are then scanned against a blank solution at 590 nm. The obtained results show that; the absorbance intensity, especially at low thorium concentrations, is increased by the miscible solvents' addition, and as the percent of the used solvent increases, the intensity of the formed complexes increase according to the solvent type and its percent. In general, the maximum color enhancement is obtained by adding 60% solvent, and, at this ratio, the color intensities remain constant. Nearly all the used solvents examined exhibit the same pattern, but methanol gives the best results, followed by ethanol and acetone. Data in Figure (6) shown that; the color intensity of the formed complexes varies depending on the polarity of the used solvent and increases as the polarity of the solvent increases. In this study, ethanol or acetone was used instead of methanol due to its poisonous effects. This phenomenon might be due to the interaction between polar solvents and polar chromophore groups in Br-PADAP dye. Another interpretation is the low solvation of the complex in water compared to miscible organic solvents [27].

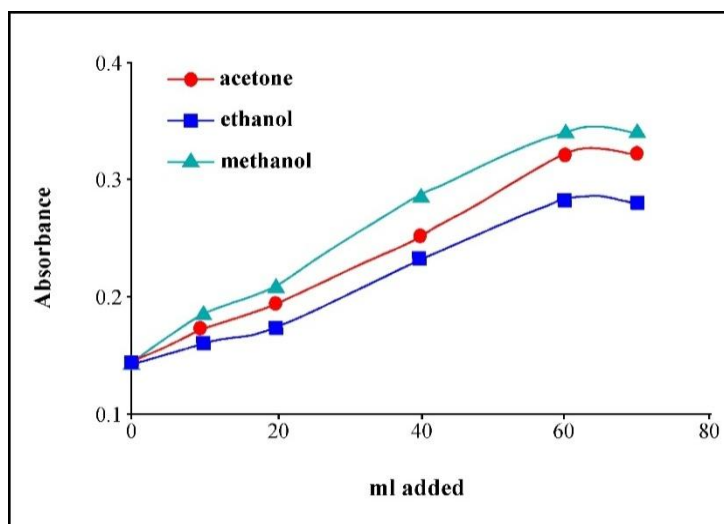


Figure (6): Effect of miscible solvents on absorbance of the Th-Br-PADAP complex at 590 nm

### 3.6. Beer's Law Validity

In general, the detection limit is defined as the minimum concentration of the examined element that can be detected with good sensitivity by the proposed analytical procedure. The calibration graph is built under ideal conditions, and as the detection limit value decreases, so does the method's sensitivity increase. The calibration graph is constructed in this work by detecting various standard Th (IV) concentrations ranging from 0.005 to 20  $\mu\text{g ml}^{-1}$ . The obtained results show that the calibration graph is linear and passes through the origin with a wide range of Th (IV) concentrations and Beer's law is obeyed from 0.05 to 8  $\mu\text{g ml}^{-1}$  of Th (IV). The relative standard deviation (RSD) is < 0.35% and the reproducibility of the method is determined by running 2  $\mu\text{g ml}^{-1}$  Th (IV) five replicates. Using organic solvents as; ethanol, acetone, or methanol reduces the detection limit of the proposed method to 0.01g  $\text{ml}^{-1}$ , while the maximum Th(IV) concentration remains at 8  $\mu\text{g ml}^{-1}$ ; Figure (7).

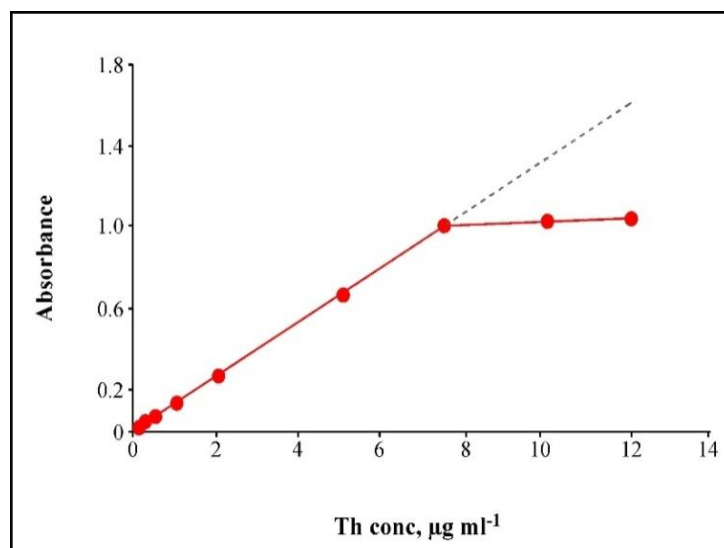


Figure (7): Calibration curve of Th(IV)-Br-PADAP complex in an aqueous medium at 590 nm

### 3.7. Effect of Associated Ions

The effect of the foreign ions interference which is mostly present in the analyzed solutions on the determination of 5  $\mu\text{g ml}^{-1}$  Th (IV) using Br-PADAP dye under the optimized conditions has been checked and optimized. The results summarized in Table (1) show that; silicate, nitrate, phosphate in addition carbonate anions under 4000  $\mu\text{g ml}^{-1}$  and acetate up to 1000  $\mu\text{g ml}^{-1}$  have a low positive interfering effect ranging from 5.5 to 12.8% while the sulfate and chloride anions have a negative effect of 18.2 and 16.6 respectively. On the other hand; 750  $\mu\text{g ml}^{-1}$  concentrations of  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$  species have low positive effects with RSD ranging from 4.2 to 8.2% while 200  $\text{Mn}^{2+}$   $\mu\text{g ml}^{-1}$  has a negative effect with an RSD of 8.4%. On the other hand, 20  $\mu\text{g ml}^{-1}$  of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$ , 200  $\mu\text{g ml}^{-1}$   $\text{Al}^{3+}$  in addition 5  $\mu\text{g ml}^{-1}$  of  $\text{U}^{6+}$ , 10  $\mu\text{g ml}^{-1}$  of  $\text{La}^{3+}$ , and 10

$\mu\text{g ml}^{-1}$  of  $\text{Ce}^{3+}$  (rare earth) are also tolerated with RSD from 2.1 to 12.6% while rare earth as;  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Ce}^{3+}$  do not affect Th(IV) because they form complexes with 5-Br-PADAP dye only at alkaline medium ( $\text{pH} > 10$ ). The most serious positive interference effect results from  $5 \mu\text{g ml}^{-1}$  of  $\text{Cr}^{6+}$ ,  $5 \mu\text{g ml}^{-1}$   $\text{V}^{5+}$ ,  $\text{Zr}^{3+}$  and  $\text{V}^{5+}$ ,  $25 \mu\text{g ml}^{-1}$   $\text{Ti}^{4+}$ ,  $7 \mu\text{g ml}^{-1}$   $\text{Fe}^{3+}$  and  $15 \mu\text{g ml}^{-1}$   $\text{Mo}^{4+}$  species with RSD values ranging from 24.4 to 32.4% while  $10 \mu\text{g ml}^{-1}$   $\text{Co}^{2+}$  ions caused a negative effect with RSD 18.2%. Most of the checked ions are likely to be removed by using an encounter dissolution procedure during sample preparation, separation method, or using masking agents.

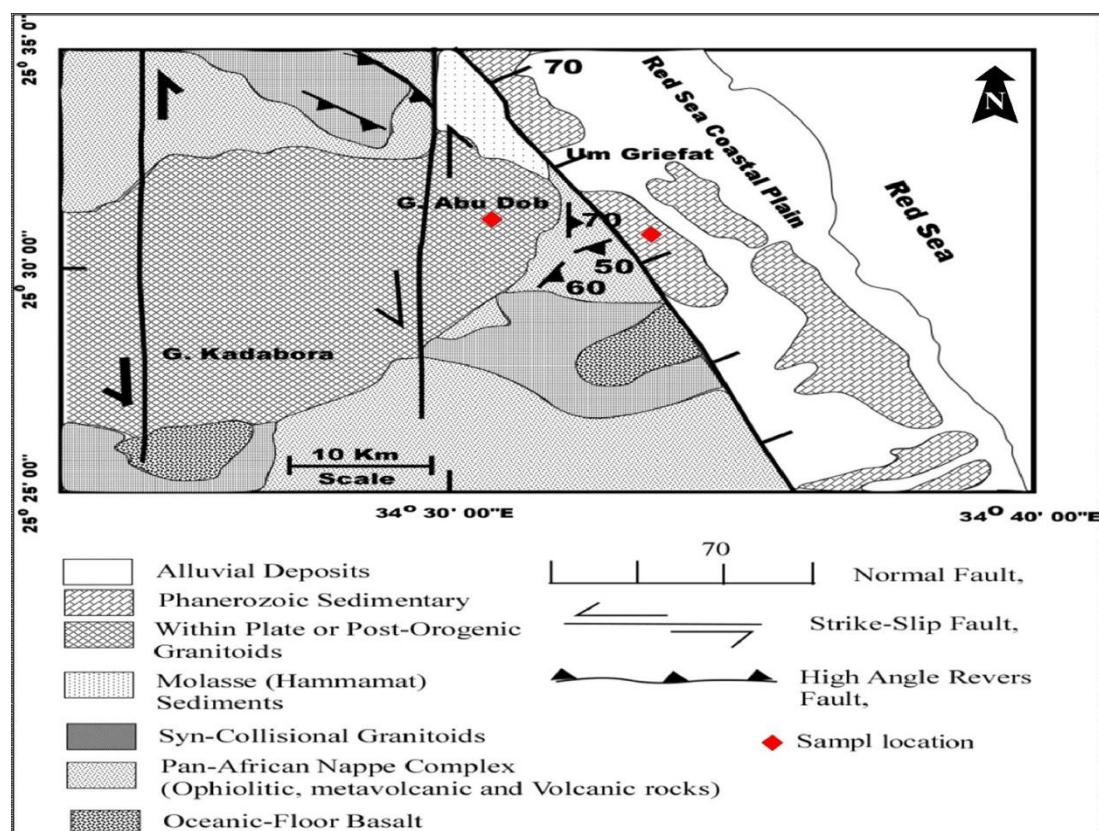
**Table (1):** Effect of other ions on determination of  $5 \mu\text{g ml}^{-1}$  of Th (IV) using Br-PADAP dye

Species	Conc. ( $\mu\text{g ml}^{-1}$ )	RSD	Species	Conc. ( $\mu\text{g ml}^{-1}$ )	RSD
Sulfate	4000	-18.2	$\text{Ti}^{4+}$	20	+24.4
Phosphate	4000	+8.6	$\text{Ni}^{2+}$	20	+9.4
Carbonate	4000	+5.6	$\text{Cu}^{2+}$	20	+12.6
Silicate	4000	+12.8	$\text{Ba}^{2+}$	20	+10.2
Chloride	4000	- 16.6	$\text{Pb}^{2+}$	20	+8.4
Nitrate	4000	+10.2	$\text{Mo}^{4+}$	15	+32.4
Acetate	1000	+9.8	$\text{Co}^{2+}$	10	-18.4
$\text{K}^{+}$	750	+8.2	$\text{La}^{3+}$	10	+2.1
$\text{Na}^{+}$	750	+5.8	$\text{Ce}^{3+}$	10	+4.1
$\text{Ca}^{2+}$	750	+4.2	$\text{Fe}^{3+}$	7	+27.6
$\text{Mg}^{2+}$	750	+6.2	$\text{U}^{6+}$	6	+11.2
$\text{Mn}^{2+}$	750	-8.4	$\text{Cr}^{6+}$	5	+27.2
$\text{Al}^{3+}$	200	+10.6	$\text{V}^{5+}$	4	+25.8
$\text{Zn}^{2+}$	25	+7.6	$\text{Zr}^{3+}$	4	+26.5

#### IV. APPLICATION

Although the good results were obtained from the above-described experiments, we have to consider that these experiments were applied to synthetic solutions, so there is a need to test the quality of thorium measured with Br-PADAP dye using different natural geological samples. In this regard, two categories of geological samples will be employed. The first category includes two internationally certified samples named **G2** (*Granite*) and **JG2** (*Granodiorite*). These standard materials will provide us with the accuracy level of the used method. On the other hand, the second category will include two geological samples of the different matrices (granite and sandstone). The granitic one was sampled and collected from the Abu-Dob area precisely from the mineralized zone, while the sandstone one was sampled from the Um-greifat area from a barren zone; both areas are located within the central eastern desert, Egypt along the red sea coast between latitudes  $25^{\circ} 33'$  and  $25^{\circ} 34'$  N and longitudes  $34^{\circ} 31'$  and  $34^{\circ} 35'$  E Figure (8).





**Figure (8):** Geological map of Abu-Dob and Um-Greifat areas, Central Eastern Desert

#### 4.1. Chemical Composition of the Studied Samples

For this part, the chemical composition of the studied natural samples is a matter of interest, particularly for their Th-content as well as the type and concentration of the other elemental. While the chemical composition of the international geological samples is available as published certified data, the other two collected samples are of unknown chemical composition, so they are exposed to complete quantitative analysis to determine their components. Both Abu-Dob granite and Um-Greifat sandstone samples were chemically analyzed for their major composition as indicated in Table (2) [28, 29], while their trace components were obtained using the XRF technique in Table (3). The Th-contents the samples were investigated by the radiometric technique as well as the wet chemistry using Arzenaso III dye method and the resultants were shown in Table (4) [30]. It is worth mentioning that for the precision calculation, each granite and sandstone sample was carefully divided into three portions by the quartering method, and each part was separately analyzed for the Th content. The obtained data pointed to comparable results from both the radiometric and chemical analysis, which means the thorium element was incorporated into each investigated sample in a one-time span. Also, the data reflected two levels of Th concentrations, one relatively high level ( $161 \mu\text{g ml}^{-1}$ ) in the granitic sample and the other a low level ( $30 \mu\text{g ml}^{-1}$ ) in the sandstone one. This variation will allow us to assess the efficiency and accuracy of the Br-PADAP method for determining Th at different concentration levels. Also, the conducted thorium concentration, particularly in the granite sample, attracted us to investigate the source mineral (s) in the employed samples.

**Table (2):** The major components composition (%) of Abu-Dob and Um-Greifat samples

Oxide Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	LOI *	Total
Granite	72.35	0.02	14.03	2.78	0.96	1.24	4.12	3.78	0.03	0.92	100.23
Sandstone	81.37	0.09	1.55	13.1	0.19	0.32	1.23	0.22	0.04	2.09	99.98

\*LOI: loss of ignition at 950 °C

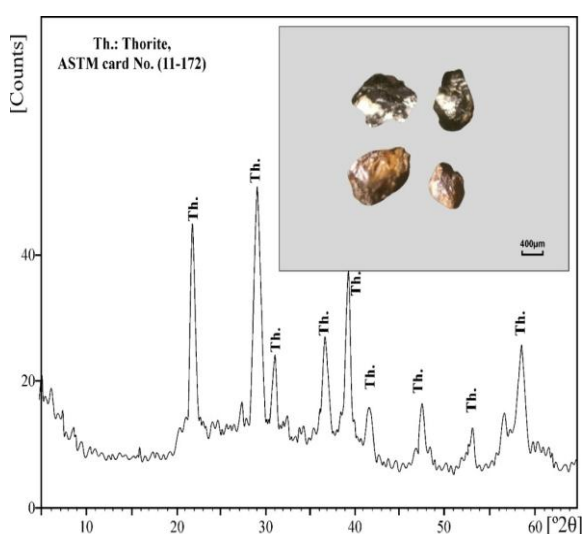
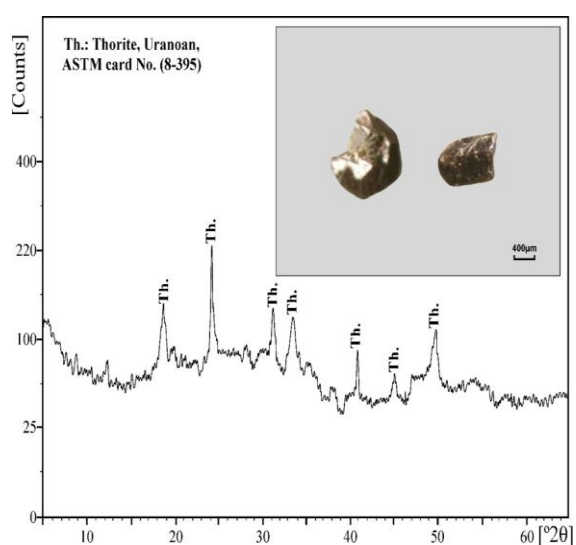


**Table (3):** Some trace elements ( $\mu\text{g g}^{-1}$ ) content in Abu-Dob and Um-Greifat samples

Element Sample	Ni	Ba	Cr	Pb	Zn	V	Y	Zr	Ga
Granite	12	185	22	38	134	11	482	1397	18
Sandstone	18	197	31	99	2152	22	9	140	3

**Table (4):** Radiometric and chemical Th-content ( $\mu\text{g g}^{-1}$ ) in Abu-Dob and Um-Greifat samples

Thorium Sample		Th (rad.)	Av.	RSD	Th (chem.)	Av.	RSD
Granite	A	162	166.7	2.49	158	161	1.64
	B	170			162		
	C	168			163		
Sandstone	A	30	29.3	7.1	29	30	8.82
	B	27			33		
	C	31			28		

**Figure (9):** The XRD chart of thorite minerals.**Figure (10):** XRD chart of uranothorite mineral

#### 4.2. Mineralogical Investigation

For the mineralogical study of the studied samples, one kilogram of each rock type (*granite and sandstone*) was crushed, disintegrated and sieved to obtain the portion of the desired grain size. Then each portion was treated with bromoform solvent (*Sp. gr.* 2.86). Consequently, two parts were obtained; the heavy part (*Sp. gr.* > 2.86) and the light part (*Sp. gr.* < 2.86). After separation of the two parts using filter papers, repeated washing with acetone, and drying, the heavy part was microscopically investigated, and some minerals were handily picked. The separated minerals were examined by the XRD technique, which identified both thorite and uranothorite minerals in Um-Greifat sandstone and Abu-Dob granite, respectively (Figures 9, and 10).

#### 4.3. Thorium determination using Br-PADAP Dye

In addition to the Abu-Dob granite and Um-Greifat sandstone samples, two international reference sample named; G2 and JG2, were subjected to thorium determination using the Br-PADAP dye. For this purpose, 5 ml of conc.  $\text{H}_2\text{SO}_4$  acid (97%) was added to 0.5 g of each ground sample (- 0.063 mm) in a glass beaker. The mixture was heated at 250 °C till complete dryness. The solidified cake was agitated with 5 ml of double-distilled water for 10 min. at 100 °C, then 10 ml of  $\text{HNO}_3$  acid (30%) was added with agitation for another 45 min. at the same temperature (100 °C). After cooling, the mixture was filtered and the filtrate was taken for Th-determination using the Br-PADAP dye. The results in Table (5) showed that the validity of the suggested method for Th-determination recorded acceptable analytical accuracy as obtained from the international standard samples (G2 & JG2). Also, the relative standard deviation (RSD), which was calculated from the analytical data of both Abu-Dob granite and Um-Greifat sandstone, appeared in the acceptable range,

reflecting the validity of the Br-PADAP dye method to measure Th-element in both low and relatively high concentrations with a narrow deviation value.

**Table (5):** Th-determination in all investigated samples using the Br-PADAP dye

	Sample type	Th-content ( $\mu\text{g g}^{-1}$ )	Th-content using Br-PADAP dye	Accuracy
International samples	G2 (Granite)	25.2 (certified value) (certified value)	30.7	21.8
	JG2 (Granodiorite)	31.6 (certified value) (certified value)	37.8	19.6
Investigated geological samples	Abu-Dob (Granite)	161; (measured value)	181.3	RSD 5.52
	Um-Greifaf (Sandstone)	30.1; (measured value)	33.6	RSD 15.25

## V. CONCLUSION

In this study, a simple and accurate method for the determination of Th (IV) species in an acidic medium was proposed 5-Br-PADAP dye. The method has many advantages, such as having a low detection limit ( $0.01 \mu\text{g ml}^{-1}$ ) and a low cost for thorium analysis. This method is mainly based on the chelation of Th (IV) ion with 5-Br-PADAP dye, showing the involvement of one reagent only in the acidic medium. The obtained red-orange complex is stable for at least 120 min due to the good selectivity of the dye toward Th (IV) species under the studied and optimized conditions. The studied method was examined for Th (IV) determination in different standard rock samples. In addition, the method can be used for the routine analysis of Th (IV) in real aqueous and rock samples with high accuracy and good precision.

## REFERENCES

- [1]. Prasetyo E., and Toyoda K., Solid phase extraction of thorium and uranium and their separation from lanthanides using humic acid silica gel as a low-cost adsorbent, *Journal of Engineering and Technological Sciences* (2017), 49, (4), 508-519, DOI.org/10.5614/j.eng. Technol sci.2017.49.
- [2]. International Atomic Energy Agency (IAEA), N. E. S. Role of thorium to supplement fuel cycles of future nuclear energy systems, IAEA-tecdoc-1540, (2012).
- [3]. Sahoo K., Fujimoto K., Celikovic I., Ujic P. and Zunic S., Distribution of uranium, thorium, and isotopic composition of uranium in soil samples of south Serbia: Evidence of depleted uranium, *Nuclear Technology and Radiation Protection* (2004), (19), 26-30 doi.org/10.2298/NTRP0401026S.
- [4]. Maiwal U., and Srinivasula K., *Journal of the Indian Chemical Society*; (1982), 59(3); p. 395-396, ISSN 0019-4522.
- [5]. Baumann E., Complexometric titration of thorium with potentiometric end-point indication, *Analytical Chemical Acta*, (1982), 138, 391-396, doi.org/10.1016/S0003-2670(01)85328-9.
- [6]. Arora H., and Rao, G., Gravimetric determination of U(VI) and Th(IV) with substituted pyrazolones, *Indian Journal of Chemistry. Section A: Inorganic, Physical, Theoretical and Analytical*; (1981), 20(5); 539-540, ISSN; 0376-4710.
- [7]. Cano-Pavón J., García de Torres A., Ureña-Pozo F M., Sanchez-Rojas F., Cristofol Alcaraz E., Spectrofluorimetric determination of trace amounts of thorium, *Analytical Chimica Acta*, (1989), 224, 153-158, doi.org/10.1016/S0003-2670(00)83456-X.
- [8]. Hao F., Paull B., Had-Dad P., Determination of trace levels of Th(IV) and uranyl by reversed-phase chromatography with on-line pre-concentration and ligand exchange, *Journal of Chromatography A*, (1996), (18), 103-113, doi.org/10.1016/0021-9673(96)00450-5.
- [9]. Golson D.A., Atkin B.P. and Harvey, P.K., (1983), *Chem. Geol.* 38, 225-237.
- [10]. Soran M., Curtui M. and Rutoiu C., Separation of U(VI) and Th(IV) from some rare earths by thin layer chromatography with di-(2-ethylhexyl)-dithiophosphoric acid on silica gel, *Journal of Liquid Chromatography & Related Technologies* (2005), (28), 16, doi.org/10.1080/10826070500189653.
- [11]. Aydin F., and Soylak, M., Solid-phase extraction and pre-concentration of U(VI) and Th(IV) on Duolite XAD761 prior to their inductively coupled plasma mass spectrometric determination, *Talanta*, (2007), 72 (1), 187-197, doi.org/10.1016/j.talanta.2006.10.013
- [12]. Navas A., and Garcia-Sanchez F., Determination espectrofotométrica de Th (IV) 4,8-diamino-1,5-dihidroxiantraquinona-2,6-disulfonato sodico. *An. Quim.* (1979), 75, 511-513 (1979).
- [13]. Thimmaiah K., Chandrappa G. And Gowda A., Rapid spectrophotometric determination of traces of thorium (IV), *Curr. Sci.* (1984), 53, 645-646.
- [14]. Khan M., Ali A. and Niaz Khan N. Spectrophotometric determination of thorium with disodium salt of Arsenazo III in perchloric acid, *Journal of Radioanalytical and Nuclear Chemistry*, (2001), 250 (2), 353-357, DOI:10.1023/A:1017968217578.
- [15]. Kavlentis E., Spectrophotometric determination of Th(IV) and U(VI) in the presence of each other with 2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone (2-HNIH), *Micro chemical Journal*, (1988) 38(2), 188-190, doi.org/10.1016/0026-265X(88)90020-3.
- [16]. Goto K., Russell D. and Berman S., Extraction and spectrophotometric determination of thorium with 8-quinolinol, *Analytical Chemistry*, (1966), 38 (3), 493-495, doi.org/ 10.1021/ac60235a032.
- [17]. Lutfullah S., Sharma Rahman N., and Azmi S., Determination of Th(IV) with rifampicin in synthetic mixture and soil samples by spectrophotometry, *Arabian Journal of Chemistry*, (2016), 9(2), S1163-S1169, doi.org/10.1016/j.arabj.2011.12.001.
- [18]. Khalifa M., and Hafez M., Spectrophotometric and complexometric methods for the determination of thorium and fluoride using bromocresol orange, *Talanta*, (1998), 47, (3), 547-559, doi.org/10.1016/S0039-9140(98)00078-2.

- [19]. Adam J., and Pribil R. (1969), Colorimetric determination of thorium with Methyl thymol Blue, *Talanta*, 16(12), 1596-1601, doi:10.1016/0039-9140(69)80224-9.
- [20]. Agnihotri N., Singh V. and Singh H., Simultaneous derivative spectrophotometric determination of thorium and uranium in a micellar medium, *Talanta*, (1993), 40(12):1851-9, doi:10.1016/0039-9140(93)80107-3.
- [21]. Abu-Bakr MS., Sedaira H., and Hashem Y., Complexation equilibria and spectrophotometric determination of iron (III) with 1-amino-4-hydroxyanthraquinone. *Talanta*, (1994), 41(10):1669-1674, doi.org/10.1016/0039-9140(94)E0098-C.
- [22]. Ramesh A., Krishnamacharyulu J., Ravindranath LK, Brahjami SR., *J Radioanal Nucl. Chem* (1993), 170:181–187.
- [23]. Sharma CD. and Eshwar MC., *J Radioanal Nucl Chem.*, (1985), 91:323-328
- [24]. Cornelis, R.; Crews, H.; Caruso, J., and Heumann, G., *Handbook of elemental speciation II: species in the environment, food, medicine & occupational health*, John Wiley & Sons, Ltd (2005).
- [25]. Khan H., Bukhari S., Hafeez M., and Ali A., Spectrophotometric determination of micro amounts of thorium with thoria in the presence of cetylpyridinium chloride as surfactant in perchloric acid, *J Radioanal Nucl. Chem.*, (2014), (301), 703-709, DOI: 10.1007/s10967-014-3201-3.
- [26]. Cotton, S., *Lanthanide and actinide chemistry*, John Wiley & Sons Ltd (2006).
- [27]. Lasheen T., Hashad A., Ghonaim A. and Manaa. E, *Journal of Analytical Chemistry*, (2008), (17), 63-72.
- [28]. Hashad M., Soliman F., Saleh G., Negm S., Badran M. and Mohamaden T., *Geochemistry of the miocene sandstone and shale at Um-Greifat area, Central Eastern Desert, Egypt: Implications to provenance, tectonic setting and rare earth elements potentiality; Nuclear Sciences Scientific Journal*, (2020), 9A, 43- 61.
- [29]. Soliman F., Hashad M, Saleh G., Sameh H. Negm, Badran M., and Mohammaden T., *Mineralogical and radioactivity characteristics of Abu-Dobgranite and associated pegmatite, Central Eastern Desert, Egypt; Nuclear Sciences Scientific Journal*, (2020), 9, 119-140.
- [30]. Kuroda R., Kurosaki M., Hayashibe Y., Ishimaru S. Simultaneous determination of uranium and thorium with Arsenazo III by second-derivative spectrophotometry; *Talanta* (1990), 37, 619-624.