

A Developed Spectrophotometric Method for Thorium Determination using Alizarin Red S Dye in Different Types of its Bearing Rocks

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Abstract: *The spectrophotometric determination of thorium from its different bearing rock types such as Thorite, Trachyte, and Ring complexes using the well known chromogenic alizarin red S (ARS) dye was proposed in the present work. Optimization of the formed thorium-alizarin red S complex was performed by studying several parameters such as different acid media, suitable buffer pH, dye concentration, duration time of the formed complex, and thorium concentration (calibration curve). The optimized method was applied to different rock types bearing thorium as well as standard phosphate (2). Interference due to major oxides was treated by partial decomposition of rock samples, which minimized their concentrations together with complete leaching of thorium facilitated the accurate determination of thorium in those samples. On the other hand, interference due to high uranium concentrations was overcome by its selective extraction using trioctylamine in xylene. Beer's law was obeyed from a concentration of 1 $\mu\text{g ml}^{-1}$ till 80 $\mu\text{g ml}^{-1}$ with a molar absorptivity value of $0.42 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. The percentage relative standard deviation (%RSD) for 10 replicate measurements of 10 $\mu\text{g ml}^{-1}$ thorium was 2.23%.*

Keywords: Spectrophotometric, determination, thorium, alizarin, rocks

1. Introduction

Spectrophotometry is always an acceptable alternative method for total element determination (e.g. either total-uranium or total-thorium determination), due to its robustness and acceptable precision and accuracy, associated with its lower cost compared with other techniques. The critical point against the use of spectrophotometry for determination of uranium and thorium is generally associated with low sensitivity and selectivity of the spectrophotometric determinations. These limitations can be solved by using selective extraction materials. [1] In the proposed methods spectrophotometric detection was chosen to the development of simple and inexpensive systems easily adaptable to field measurements.

Many types of reagents were applied for spectrophotometric analysis of thorium, these include; arsenazo III [2], 2-(4-sulphophenylazo)chromotropic acid (SPADNS) [3], β -hydronaphth hazarin [4], Quercetin [5], Morin [6], α -benzoin oxime [7] and thoron [8] that showed great performance for thorium analysis in most samples.

A selective anion-exchange separation and spectrophotometric method was developed for the determination of uranium and thorium in phosphate rocks. Uranium and thorium were adsorbed by anion-exchange on an Amberlite CG 400 (NO_3^-) column from the sample solution then eluted consecutively with 6.6M nitric acid and 0.1M nitric acid, respectively. Uranium and thorium in the respective effluents are determined spectrophotometrically with Arsenazo III. [9]

Among the anthraquinone dyes, alizarin and its derivatives (1,2-dihydroxy-3-anthraquinone sulphonic acid) has found application in the micro determination of a number of metals [10]. The presence of quinoid oxygen, with two hydroxyl groups at α - and β - positions makes it very suitable for chelation. Coordination bonding of metal to dye molecule occurs when phenolic group of dye is partly oxidized and partly ionized and metal gets bound. Oxidized quinonic oxygen begins to form a coordination with the same metal and thus chelate is formed which facilitates the charge transfer (CT) from ligand to metal ion, which is responsible for its chromophoric properties. This property has been exploited in the detection and determination of a number of transition metals [11]. The presence of sulphonate group in the molecule adds further reactivity to the molecule.

The electrochemical behavior of ARS has been also studied in connection with voltametric determination of metals like Ca, Sc and Al [12-14]. The staining of gel with ARS has been reported in which stained gel was washed and washing was monitored using spectrophotometry [15].

The spectrophotometric determination of metal ions using ARS and other anthraquinone derivatives continued to hold interest to scientists [16, 17]. It is well known that the ease of formation of a complex with dye, thus stability of the complex decides its applicatory importance. The dyes of hydroxyl phenyl group in alizarin red S gave colored chelates with metal ions in solution and the pronounced chelating properties of these dyes must be due to the presence of donor groups like $-\text{COOH}$, $-\text{OH}$ and $-\text{O}$.

The analytical chemistry department of the Nuclear Materials Authority was concerned with the determination of thorium in high and low concentrations as in monazite

sand and different rock types bearing thorium concerning geochemical studies. Therefore, an effort was made to develop a selective, reproducible and sensitive method for thorium (IV) determination using the well known alizarin red S dye in different types of rocks bearing thorium.

2. Experimental

Chemicals and reagents

Analytical grade and chemical pure reagents were used in all experiments, such as thorium nitrate (Stream chemicals, USA), alizarin red S (BDH, England), perchloric acid, nitric acid, hydrochloric acid (Panreac, Spain), hydrofluoric acid, sulphuric acid (Riedel De Haën, Germany), glacial acetic acid (Fisher, Switzerland), sodium acetate, hydrogen peroxide and trioctyl amine (Merck, Germany).

Apparatus

A double beam UV – Visible spectrophotometer model Labomade (UVD 2950), USA, was used for measuring the absorbance of thorium - dye complex. All measurements were carried out at room temperature (about 25° C, ± 5°C). A Jenway pH meter was used for recording the pH of different solutions. It was calibrated regularly with two successive buffer solutions (4 and 7 or 7 and 10).

Decomposition Procedure

A decomposition procedure was proposed by authors, [18] which facilitated partial decomposition of major oxides together with total leaching of thorium, an advantage for minimizing the concentration of accompanying elements hence lowering their interference effect during thorium determination. All rock samples applied for thorium determination were partially decomposed using the following procedure to facilitate total leaching of thorium for accurate determination. The decomposition method was given as follows:

- 1) In a teflon beaker, 20 ml HF were added to a weight of 0.2g from each ground sample.
- 2) Heat till dryness then add 15 ml of dilute HF (1:1) and filter.
- 3) The precipitate was treated with 10 ml concentrated HClO₄ and 5 ml concentrated HNO₃ (15.55 N) then heated again till dryness.
- 4) An aliquot of 15 ml HCl (6 N) was added to the residue and the whole dissolved content was completed in a 250 ml volumetric flask.

3. Results and Discussion

All the obtained results concerning thorium determination using alizarin red S dye were discussed. Several factors were studied to optimize the formation of thorium-alizarin complex. This included the effect of different acid media, choice of the suitable buffer pH, optimum concentration of alizarin red S dye, the duration time of the complex as well as the optimum concentration of thorium (calibration curve). Finally, the optimum molar ratio between metal and dye was studied.

Effect of acid medium

The effect of perchloric acid, hydrochloric acid, nitric acid and sulfuric acid with different concentrations (pH) on complex formation were studied. To determine the optimum concentration of acidic medium, a constant volume of 1 ml from each of the thorium stock solution (10⁻³ M), and alizarin red S dye (10⁻³ M) were taken, while several aliquots from different acids (0.1ml to 5ml) from 1N, 10⁻²N and 10⁻⁴N were added to a series of 10 ml volumetric flasks. The absorbance of each acid concentration was measured in the range from 450- 600 nm. The obtained data illustrated in Figures (1a,b,c,d) illustrated the effect of the studied acids on thorium- alizarin red S complex formation. The maximum absorbance value of the complex was found at withdrawing of 0.2 ml from 10⁻² N perchloric acid (0.2 x 10⁻³ N, pH 3.7) at λ_{max} 530 nm. Perchloric acid was selected for optimum complex formation where it has the advantage since either nitric or hydrochloric acid can be converted easily to perchlorate medium.

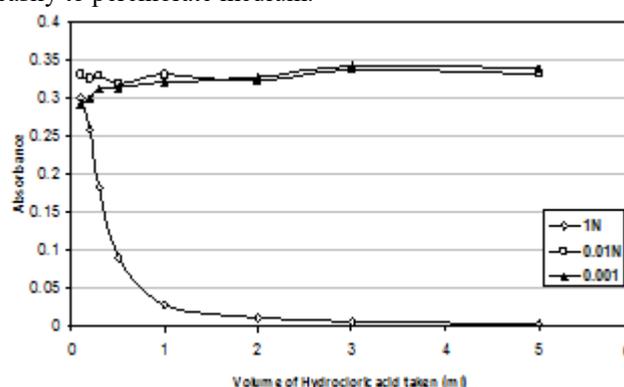


Figure 1(a)

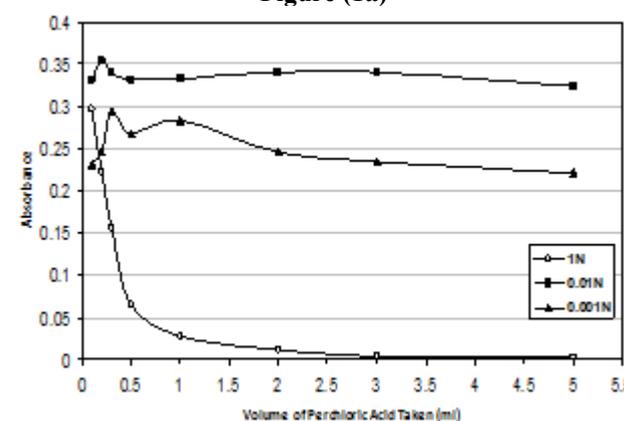


Figure 1(b)

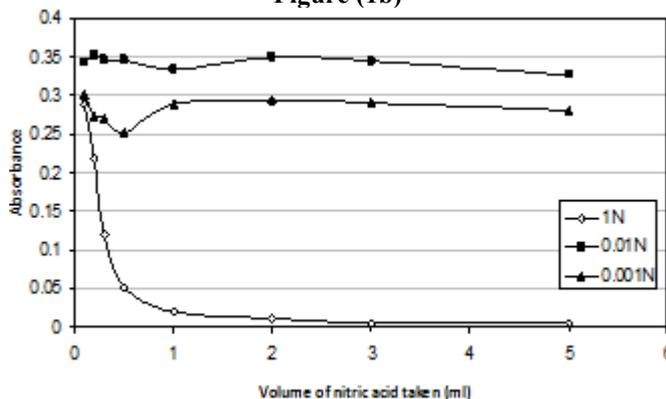


Figure 1(c)

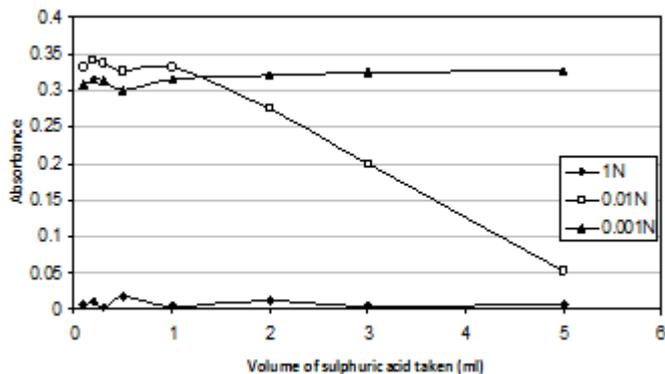


Figure 1d)

Figures (1a, 1b, 1c, 1d): Effect of different acids and their pH on the formation of Th-alizarin complex

Choice of the suitable buffer pH

A buffer solution was used in this study to fix the optimum acid concentration value of complex formation. Sodium acetate (2M) and acetic acid (2M) buffer solution was prepared to give variable pH values 3.4, 3.7 and 4. Each buffer solution was added to different solutions containing 1ml from 10^{-3} M thorium, 0.2ml from 10^{-2} N perchloric acid and 1ml from 10^{-3} M alizarin red S dye where the final volumes of these solutions were completed to 10ml. The absorbance of the formed complex was measured in the wavelength range 450- 600 nm. Table (2) summarized the effect of buffer pH variation on the absorbance of thorium-alizarin red S complex. It was clearly evident that the maximum absorption of the complex at λ_{max} 530 nm was by addition of 0.5 ml from buffer pH 3.4.

Table 2: Effect of buffer pH on the absorbance of thorium-alizarin red S complex

Volume of buffer ml	pH 3.4		pH 3.7		pH 4	
	λ nm	Abs.	λ nm	Abs.	λ nm	Abs.
0.1	530	0.351	530	0.351	530	0.353
0.2	530	0.355	530	0.342	530	0.345
0.3	530	0.350	530	0.340	528	0.343
0.5	530	0.359	530	0.340	528	0.338
1	522	0.346	528	0.337	522	0.331
1.5	524	0.331	528	0.335	522	0.326
2	522	0.331	528	0.327	520	0.324
2.5	520	0.328	522	0.325	520	0.320
3	518	0.324	522	0.320	520	0.318

Effect of alizarin red S dye concentration on the absorbance of thorium complex by molar ratio method

It was evidently known that the dye concentration should be optimized since any variation in its concentration may cause deviation from Beer's law. In this experiment different volumes from 10^{-3} M alizarin red S dye solution were added in a series of 10 ml volumetric flasks with fixed concentration of thorium (1ml from 10^{-3} M), 0.2ml from 10^{-2} N perchloric acid and 0.5 ml from acetate buffer pH 3.4. The final volume was completed to 10 ml with double distilled water. The absorbance of each solution was measured at λ_{max} 530 nm. The molar ratio method showed that the concentration of the dye required to form stable thorium-alizarin red S complex with high absorbance at λ_{max} 530 nm was at 4×10^{-4} M of the dye (4ml from 10^{-3} M) and the ratio

between thorium [M] and alizarin red S dye [L] at high absorbance was [L]:[M] = 4:1 as shown in Figure (2).

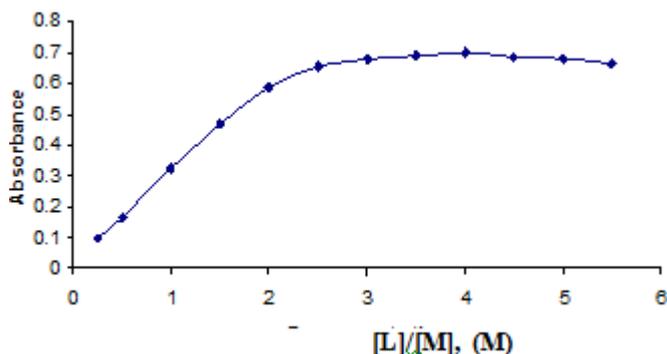


Figure 2: Effect of alizarin red S dye concentration on the absorbance of thorium complex

Effect of duration time on the stability of thorium complex

The stability of thorium – alizarin red S complex was tested over a period of time, where the absorbance was measured periodically every 5 minutes. It was found that the complex was stable for 25 minutes after which it began to dissociate slowly as shown in Table (3).

Table 3: Effect of duration time on the stability of thorium – alizarin red S complex

Time (minutes)	Abs. at λ_{max} 530 nm
Zero	0.775
5	0.778
10	0.779
15	0.779
20	0.779
25	0.775
30	0.768
35	0.767
40	0.766
45	0.760
50	0.754
55	0.748
60	0.543

Construction of calibration curve

According to Beer's law it was necessary to determine the maximum and minimum thorium detectable concentrations, for this purpose a series of thorium concentrations were prepared while fixing the concentration of perchloric acid 0.2 ml from 10^{-2} N, 0.5 ml from buffer pH 3.4 and 4 ml from 10^{-3} M alizarin red S dye. The absorbance of each complex was measured at the recommended λ_{max} 530nm against a proper blank solution. Beer's law was obeyed from a minimum detectable thorium concentration of 1 ppm till a maximum concentration of 80 ppm after which a plateau was formed. Figure (3) indicated the working calibration curve for thorium determination.

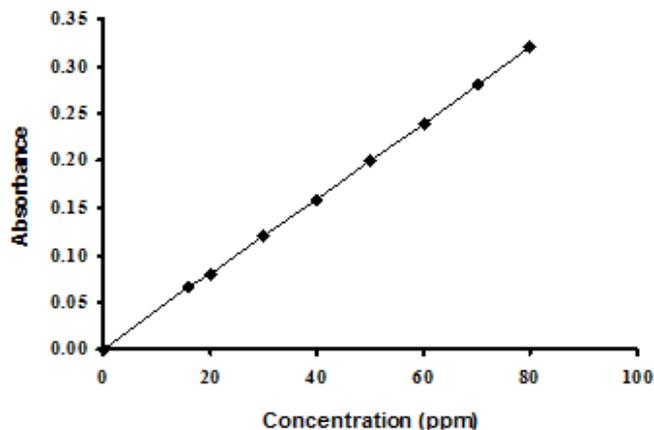


Figure 3: Calibration curve of thorium using alizarin red S dye

The interference effect on spectrophotometric determination of thorium using alizarin red S

It was necessary to study the interference effect of some associated elements with thorium in different rock types which may react similarly under the same conditions. The effect of different concentrations of anions and cations on thorium ($2.5 \mu\text{gml}^{-1}$) determination using alizarin red S were studied using the previously optimized additions (0.2ml from 10^{-2}N perchloric acid, 0.5ml of acetate buffer solution pH 3.4 and 4ml from 10^{-3}N alizarin red S dye). Table (4) summarized the tolerance limits of interfering ions on thorium determination by alizarin red S dye.

Table 4: Influence of interfering ions on the determination of thorium

Interfering ion	Tolerance limit ($\mu\text{g ml}^{-1}$)
PO_4^{3-}	1000
$\text{Al}^{3+}, \text{Co}^{3+}, \text{Cu}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Ba}^{2+}, \text{Zn}^{2+}$	1000
Cd^{2+}	500
$\text{Fe}^{3+}, \text{VO}^{2+}$	100
UO_2^{2+}	18

Application of the studied method on different rock types bearing thorium

After optimization of the developed spectrophotometric method for thorium determination using alizarin red S dye, several rock types bearing thorium were selected with different matrices namely; thorite, trachyte, ring complex, basmatic gneiss together with standard phosphate (2) [19] for thorium determination using the present studied alizarin red S dye. Thorite, a thorium uranium silicate from igneous pegmatite and volcanic rocks, hydrothermal veins and contact metamorphic rocks, it is also known to occur as small grains in detrital sands. Trachyte, from East Basin Kom Ombo – Aswan, is an igneous volcanic rock equivalent to syenite. The mineral assemblage consists of essential

alkali feldspar; relatively minor plagioclase and quartz. Ring complex from North El Atshan, Eastern Desert, Egypt is a circular 2 km in diameter igneous ring complex that intrudes upper Palaeozoic volcanics and granites, its outer ring consists of feldspathoidal igneous rocks. These rocks consist of orthoclase, albite, aegirine-augite, sodic amphibole, biotite, zeolites, pyrochlore and apatite. Basmatic gneiss from Abo Rusheid, Eastern Desert was formed by the metamorphism of arenaceous sediments.

The major oxides in the selected rock samples bearing thorium were analyzed [20] and thorium was analyzed using a well known analytical method for determination [21], Table (5).

Table 5: Complete analysis of selected applied samples for thorium determination

Sample ID / Oxides (%)	Trachyte	Ring complex	Basmatic gneiss	Thorite	Standard phosphate 2
SiO_2	63.4	54.94	71.98	83.3	8.74
Al_2O_3	15.49	13.69	13.18	6.66	1.62
Fe_2O_3 (total)	4.75	9.75	1.49	0.22	1.34
MgO	1.86	8.5	2.93	0.06	4.98
CaO	2.6	8.41	3.69	0.62	37.99
Na_2O	6.39	2.43	3.76	0.34	0.78
K_2O	4.08	0.93	2.97	0.17	0.18
TiO_2	0.069	0.049	0.035	0.43	0.07
P_2O_5	0.08	0.07	0.05	1.2	20.6
Th (ppm)	21.50	20.50	19.00	1330	21.40
U (ppm)	1400	1298	837	320	2.09

From Table (5) it was clearly evident that there were several points to be mentioned; first, the severe interference effect due to the high concentration values of the interfering accompanying major oxides (as studied in Table 4) which are present in percentage in all samples with respect to thorium concentration found in $\mu\text{g/ml}$. Second, the interference due to presence of high uranium concentration in some samples, as Trachyte, Ring complex and Basmatic gneiss, which interfered due to its concentration ratio to thorium was more than six ($\text{U} : \text{Th} > 6:1$) [21].

The high major oxides concentration was overcome by proposing a developed decomposition method [18] for all samples which minimized their concentration values as shown in Table (6). The high uranium concentration in some samples was treated by using trioctylamine as a selective solvent for uranium [21]. After separation of uranium, thorium was analyzed in the aqueous solution using the developed alizarin dye with good accuracy, Table (7). After those treatments the thorium concentration analyzed by the present developed alizarin red S dye was very close to the true values which referred that it has overcome successfully the interference effect during thorium determination.

Table 6: Comparative study between the complete and developed decomposition for Th determination in different rocks

Sample Oxide (%)	Thorite		Trachyte		Ring complex		Basmatic gneiss		Standard phosphate (2)	
	C.D	Developed	C.D	Developed	C.D	Developed	C.D	Developed	C.D	Developed
SiO ₂	83.3	1.65	63.4	1.31	54.94	1.07	71.98	1.97	8.74	0.37
Al ₂ O ₃	6.66	0.64	15.49	1.82	13.69	1.61	13.18	1.43	1.62	0.08
Fe ₂ O ₃ (total)	0.22	0.04	4.75	0.74	9.75	0.98	1.49	0.081	1.34	0.07
MgO	0.06	0.02	1.86	0.05	8.5	1.65	2.93	0.075	4.98	0.27
CaO	0.62	0.07	2.6	0.09	8.41	1.31	3.69	0.067	37.99	0.86
Na ₂ O	0.34	0.04	6.39	0.7	2.43	0.053	3.76	0.074	0.78	0.08
K ₂ O	0.17	0.02	4.08	0.82	0.93	0.04	2.97	0.039	0.18	0.02
TiO ₂	0.43	0.06	0.069	0.02	0.049	0.01	0.035	0.013	0.07	0.03
P ₂ O ₅	1.2	0.06	0.08	0.04	0.07	0.03	0.05	0.021	20.6	0.53
Th ppm	40000	1325	647	20.63	957	19.20	1143	17.47	591	18.5
U ppm	320		1400		1298		837		2.09	

C.D means complete decomposition

From results gathered in Table (6), it was clear that only partial decomposition of accompanying major oxides together with nearly total leaching percentage of thorium were reached which facilitated for an accurate determination of thorium in different rock types.

Table 7: Determination of thorium in different rock samples using alizarin red S dye method after uranium separation

Sample	Concentration of thorium using Alizarin red S dye method ($\mu\text{g ml}^{-1}$)	Thorium concentration using TOPO method ($\mu\text{g ml}^{-1}$)
Thorite	1325	1330
Trachyte	20.63	21.5
Ring Complex	19.2	20.5
Basmatic Gneiss	17.47	19.0
Standard phosphate 2	18.5	21.4

4. Conclusion

A developed spectrophotometric analysis for thorium using a well known chromogenic dye, alizarin red S, was used. Several parameters were studied for the optimization of the formed thorium-alizarin red S complex namely; effect of different acid media (pH), optimum buffer pH, dye concentration, duration of the stability of the complex and thorium concentration (calibration curve). The optimized method was applied to different rock types bearing thorium with different thorium concentrations and matrices. Interference due to high uranium concentration in some samples such as Trachyte, ring complex and basmatic gneiss was overcome by the selective extraction of uranium, whereas the interference due to some major oxides was treated using a developed method for decomposition which minimized greatly their concentrations and treated the drastic effect of the accompanying interfering major oxides without further separation methods. The method was proved to be accurate with a percentage relative standard deviation value of 2.32%.

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