

## Floatation-spectrophotometric Determination of Thorium, Using Complex Formation with Eriochrome Cyanine R

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**Abstract:** A novel and sensitive floatation-spectrophotometric method is presented for determination of trace amounts of thorium in water samples. The method is based on the ion-associated formation between thorium, Eriochrome cyanine R and Brij-35 at pH = 4 media. The complex was floated in the interface of the aqueous phase and n-hexane by vigorous shaking. After removing the aqueous phase the floated particles were dissolved in methanol and the absorbance was measured at 607 nm. The influence of different important parameters such as Eriochrome cyanine R and surfactants concentration, pH, volume of n-hexane, standing time and interfering ions were evaluated. Under optimized conditions the calibration graph was linear in the range of 6–230 ng mL<sup>-1</sup> of thorium with a correlation coefficient of 0.9985. The limit of detections (LOD), based on signal to noise ratio (S/N) of 3 was 1.7 ng mL<sup>-1</sup>. The relative standard deviations for determination of 150 and 30 ng ml<sup>-1</sup> of thorium were 3.26 and 4.41%, respectively (n = 10). The method showed a good linearity, recoveries, as well as some advantages such as sensitivity, simplicity, affordability and a high feasibility. The method was successfully applied to determine thorium in different water and urine samples.

**Keywords:** floatation-spectrophotometric, thorium, Eriochrome cyanine R

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## Introductory Statement

Thorium has extensively been used in a variety of applications such as industrial, energy and environmental issues.<sup>1–3</sup> Due to negative impacts of thorium such as toxicity, radio toxicity and carcinogenic properties, such kind of applications generate a diversity of wastes which pollute waters.<sup>4–8</sup>

Many procedures have been developed for determination of thorium in water samples, including liquid–liquid extraction,<sup>9,10</sup> and solid phase extraction (SPE).<sup>11–14</sup> However, these traditional techniques are time consuming, less sensitive and require a large amount of toxic organic solvents.

Extracting a trace amount of thorium spectrophotometry has been introduced as a powerful technique due to its acceptable precision and accuracy, associated with its lower cost compared to the other techniques.<sup>4,15,16</sup>

In the present research, a fast and sensitive flotation-spectrophotometric method was developed for quantitative determination of thorium, based on its complex formation with Eriochrome cyanine R in buffer media. Using this method, a complex was formed between thorium and Eriochrome cyanine R, floated into the interface between aqueous and n-hexane phase and then extracted into methanol solvent with an absorbance measured at 607 nm.

## Materials and Methods

### Chemicals and solvents

All reagents were of analytical grade (Merck, Germany). Solutions were prepared with double distilled water. A  $1 \times 10^{-4}$  mol L<sup>-1</sup> of Brij-35 solution,  $1 \times 10^{-4}$  mol L<sup>-1</sup> of Eriochrome cyanine R, and  $10 \mu\text{g mL}^{-1}$  stock solution of thorium was prepared by dissolving thorium nitrate salt in freshly distilled water. Standard working solutions of various concentrations were obtained by an appropriate dilution of stock solution with water before use.

### Instrumentation

The spectrophotometer UV-Vis (model 1245, Shimadzu, Japan) was used for all the absorbance measurements with a 10 mm quartz cell. pH measurements were made with a 827 pH meter (Metrohm, Switzerland) equipped with a combine Ag/AgCl glass electrode.

## Flotation-spectrophotometric procedure

A 1 mL portion of the standard solution containing the thorium at concentration level of  $10 \mu\text{g mL}^{-1}$  was placed into a 100 mL volumetric flask. To this solution 15 mL of  $1 \times 10^{-4}$  mol L<sup>-1</sup> Eriochrome cyanine R, 5 mL of buffer with pH = 4, 10 mL of 1M NaCl, 1.5 mL of  $1 \times 10^{-4}$  mol L<sup>-1</sup> Brij-35 were added. This mixture was diluted to the mark with fresh water. After 8 min, the flask contents completely transferred into a 100 mL separating funnel containing 11 mL of n-hexane. The funnel is sealed and vigorously shaken for 65s and then allowed to stand for 4 min. After this time the aqueous phase was extracted and 2 mL of methanol was added to the organic phase. The complex was dissolved in methanol and the absorbance was read at 607 nm against a reagent blank.

## Results and Discussion

In the present study the effects of several important parameters influencing the flotation step such as type of the organic phase, pH of the solution, concentration of Eriochrome cyanine R, surfactant, flotation, relaxation and complexation time were investigated.

### Effect of Eriochrome cyanine R concentration

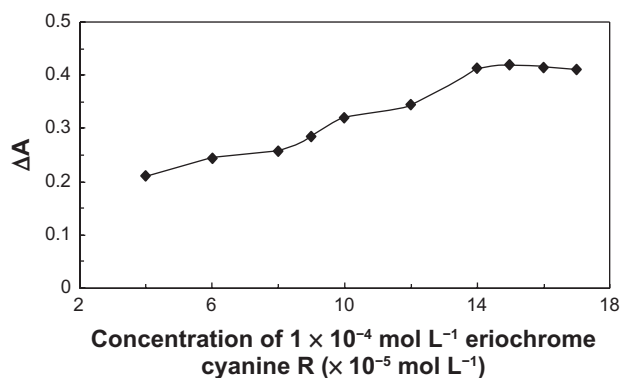
The selection of optimum concentration of Eriochrome cyanine R is one of the important parameter in the flotation method. The effect of Eriochrome cyanine R concentration used for the flotation of thorium was evaluated in the range from  $0.4 \times 10^{-5}$  mol L<sup>-1</sup> to  $1.7 \times 10^{-5}$  mol L<sup>-1</sup>. The maximum absorbance occurs to Eriochrome cyanine R concentration above  $1.5 \times 10^{-5}$  mol L<sup>-1</sup> therefore, a concentration value of  $1.5 \times 10^{-5}$  mol L<sup>-1</sup> was chosen for further investigation (Fig. 1).

### Effect of pH and volume of buffer

Figure 2 demonstrates the influence of pH and volume of buffer (mL) on the absorbance efficiency within the range of 1–10. An optimum volume of acetate buffer of 5 mL with pH = 4 was obtained.

### Effect of surfactants concentration

The effect of surfactant concentration is shown in Figure 3. The volume of surfactants (Brij-35, CTAB and CPC) with the concentration was investigated in

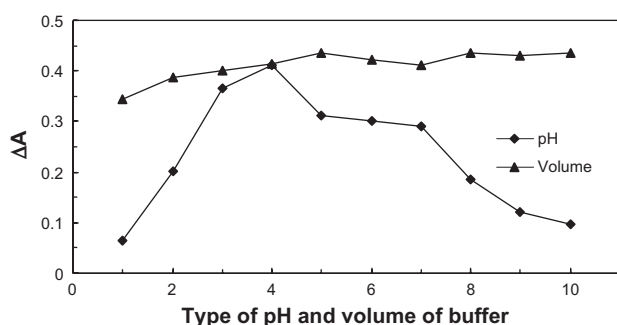


**Figure 1.** Effect of Eriochrome cyanine R concentration. Experimental condition: pH = 4, volume of buffer = 5 mL, concentration of surfactant =  $1.5 \times 10^{-6} \text{ mol L}^{-1}$ , volume of n-hexane = 11 mL, volume of methanol = 2 mL, standing time = 4 min.

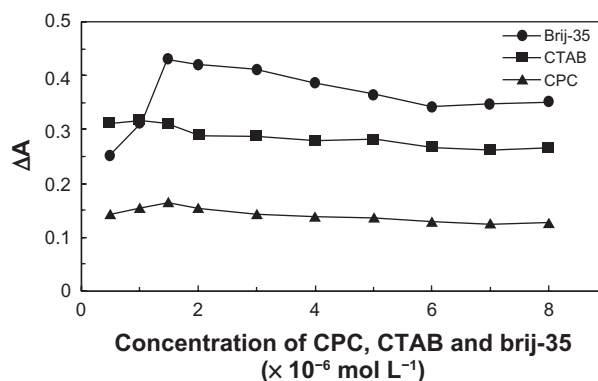
the range of  $1 \times 10^{-6}$  to  $8 \times 10^{-6} \text{ mol L}^{-1}$ . The differences observed in the signals at various surfactant concentrations are also exposed in Figure 3. At lower concentrations of surfactant, the efficiency was low probably due to the inadequacy of the assemblies to entrap the complex quantitatively. According to this result, all further experiments were carried out at the optimum concentration  $1.5 \times 10^{-6} \text{ mol L}^{-1}$  of Brij-35.

### Effect of volume of the n-hexane

The effect of volume of the n-hexane on the flotation process was examined in the range of 4–17 mL. By increasing the n-hexane, the volume of the absorbance of extracted content increased up to 11 mL. For thorium, a similar pattern was observed in the volume ranged between 10–17 mL. Therefore 11 mL



**Figure 2.** Effect of pH and volume of buffer. Experimental condition: Eriochrome cyanine R concentration =  $1.5 \times 10^{-5} \text{ mol L}^{-1}$ , concentration of surfactant =  $1.5 \times 10^{-6} \text{ mol L}^{-1}$ , volume of n-hexane = 11 mL, volume of methanol = 2 mL, standing time = 4 min.



**Figure 3.** Effect of surfactants concentration. Experimental condition: Eriochrome cyanine R concentration =  $1.5 \times 10^{-5} \text{ mol L}^{-1}$ , pH = 4, volume of buffer = 5 mL, volume of n-hexane = 11 mL, volume of methanol = 2 mL, standing time = 4 min.

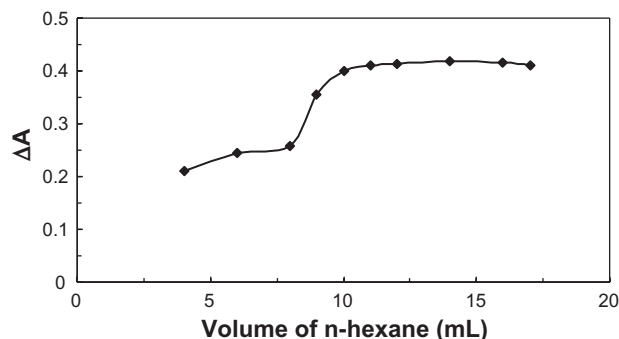
of n-hexane was selected for subsequent experiments (Fig. 4).

### Effect of type and volume of organic solvent

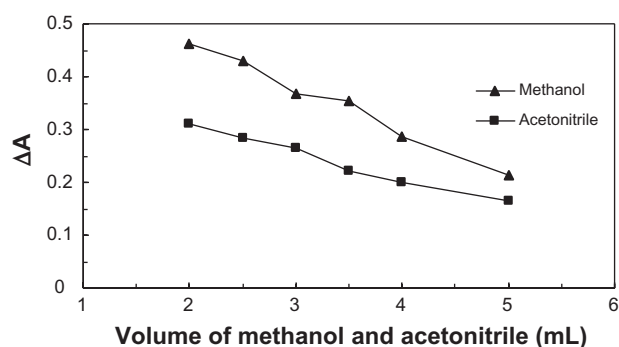
The effect of type and volume of organic solvent (methanol and acetonitrile) on absorbance was also investigated. A volume of 2.5 mL of methanol provided better results compared to acetonitrile (Fig. 5).

### Standing time

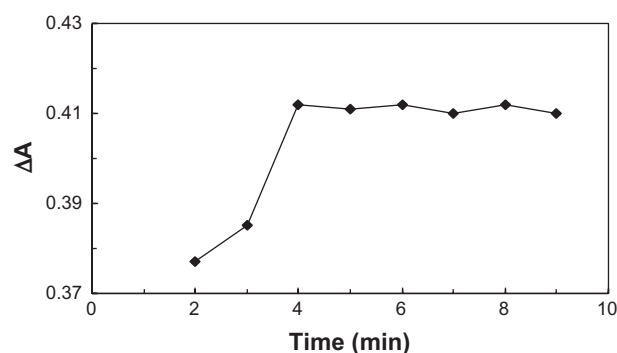
For enhancing the repeatability and efficiency, it is necessary to choose a time in which equilibrium is reached between the organic phase and the aqueous sample. The influence of standing time on the complex formation was studied over a time period



**Figure 4.** Effect of volume of the n-hexane. Experimental condition: Eriochrome cyanine R concentration =  $1.5 \times 10^{-5} \text{ mol L}^{-1}$ , pH = 4, volume of buffer = 5 mL, concentration of surfactant =  $1.5 \times 10^{-6} \text{ mol L}^{-1}$ , volume of methanol = 2 mL, standing time = 4 min.



**Figure 5.** Effect of type and volume of organic solvent. Experimental condition: Eriochrome cyanine R concentration =  $1.5 \times 10^{-5} \text{ mol L}^{-1}$ , pH = 4, volume of buffer = 5 mL, concentration of surfactant =  $1.5 \times 10^{-6} \text{ mol L}^{-1}$ , volume of n-hexane = 11 mL, standing time = 4 min.



**Figure 6.** Standing time. Experimental condition: Eriochrome cyanine R concentration =  $1.5 \times 10^{-5} \text{ mol L}^{-1}$ , pH = 4, volume of buffer = 5 mL, concentration of surfactant =  $1.5 \times 10^{-6} \text{ mol L}^{-1}$ , volume of n-hexane = 11 mL, volume of methanol = 2 mL.

of 2–9 min. A standing time of 4 min was needed in order to obtain maximum absorbance (Fig. 6).

### Conformity with Beers law and figure of merit

Under mentioned optimized conditions, linearity, precision, and limit of detection (LOD) were used for validation of method. The calibration curve was constructed for thorium over the concentration range of between 6–230  $\text{ng mL}^{-1}$ . The correlation coefficient ( $R^2$ ) was 0.998 ( $n = 7$ ), showing the plot was linear for target compound. In order to determine the precision of the analytical procedure, 10 consecutive analyses were performed at about 150 and 30  $\text{ng mL}^{-1}$  level. The relative standard deviation for 150 and 30  $\text{ng mL}^{-1}$  of thorium were determined to be 3.26% and 4.41%, respectively.

The limit of detection for thorium was defined as the concentration of analyte which gave a signal of  $3\sigma$  above the mean blank signal (where  $\sigma$  is the standard deviation of the blank signal). The LOD for thorium was found to be 1.71  $\text{ng mL}^{-1}$ .

### Effect of foreign ions

The influences of some cations and anions on the determination of thorium were investigated in detail. A relative error of not greater than  $\pm 5\%$  in the recovery at a concentration of 30  $\text{ng mL}^{-1}$  thorium was observed. The tolerance limits of a foreign species were as follows: 1000-fold excess of  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{SCN}^-$ , and  $\text{NO}_3^-$ ; 500-fold excess of  $\text{Mn}^{2+}$ ,  $\text{ClO}_4^-$  and  $\text{HPO}_4^{2-}$ ; 400-fold excess of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$ ; 200-fold excess of  $\text{CO}_3^{2-}$ ; and 100-fold excess of  $\text{Hg}^{2+}$ ,  $\text{MoO}_4^{2-}$  and  $\text{WO}_4^{2-}$  did not interfere with the determination of thorium in this method.

### Application of real samples

The proposed method was applied to determine thorium in the natural water and urine samples. Table 1 summarizes the average recovery of thorium in the fortified river waters and urine samples. The water samples were spiked with 20, 30 and 100  $\text{ng mL}^{-1}$  of standard solution of thorium. The recoveries of from the spiked water samples varied in the range of 93.8%–100.3%.

**Table 1.** Determination of thorium in 60 mL of water samples and in 5 ml of urine sample ( $n = 5$ ).

Sample	Test no.	Standard volume spiked with $2 \mu\text{g mL}^{-1}$ thorium	Measured ( $\text{ng mL}^{-1} \pm \text{SD}$ )	Final concentration ( $\text{ng mL}^{-1}$ )	Recovery (%)
Water	1	0.0	0.00 ( $\pm 0.05$ )	0	0.0
	2	1.0	18.76 ( $\pm 0.38$ )	20	93.8
	3	1.5	29.63 ( $\pm 0.43$ )	30	98.8
	4	5.0	100.29 ( $\pm 0.28$ )	100	100.3
Urine	1	0.0	0.00 ( $\pm 0.03$ )	0	0.0
	2	1	19.21 ( $\pm 0.47$ )	20	96.1
	3	1.5	30.08 ( $\pm 0.61$ )	30	100.3
	4	5.0	102.76 ( $\pm 3.2$ )	100	102.8

**Table 2.** Comparison of different methods for the determination of thorium.

Parameter	Value and remark	
	Reported methods	Present method
LOD	$1.85 \times 10^{-6} \text{ mol L}^{-1a}$ , $>1 \mu\text{g L}^{-1b}$	$1.7 \text{ ng mL}^{-1}$
LR	$6.48 \times 10^{-6}$ – $9.91 \times 10^{-5} \text{ mol L}^{-1a}$ , $0.5$ – $5 \text{ mol L}^{-1b}$ , $0.22$ – $2.51 \mu\text{g mL}^{-1c}$ , $0.1$ – $1 \mu\text{g mL}^{-1d}$	$6$ – $230 \text{ ng mL}^{-1}$
RSD%	$<2.71^a$ , $25.00^b$ , $<1.50^c$ , $4.76^d$	$<4.41\%$
Time (min)	$<20 \text{ s}^a$ , $5 \text{ min}^b$ , $5 \text{ min}^c$ , $>20 \text{ min}^d$	65 S
Recovery%	$>98^a$ , $>90^b$ , $>97.5^c$ , $98^d$	$>93.8$
Matrix	water <sup>a</sup> , Soil <sup>b</sup> , waste water <sup>c</sup> , tissue paper <sup>d</sup>	water

Notes: <sup>a</sup>Reference [2], <sup>b</sup>Reference [4], <sup>c</sup>Reference [17], <sup>d</sup>Reference [18].

Urine samples were kindly donated by volunteers. Urine was filtered using Whatman No. 42 filter paper and centrifuged. Into a set of 100 mL volumetric flasks, separate aliquots of urine (5 mL) were spiked with varying amounts of thorium (20, 30 and 100 ng mL<sup>-1</sup>). Finally, the extraction was carried out under the most appropriate conditions. The recoveries of from the spiked urine samples varied in the range of 96.1%–102.8%. The result indicated that the proposed method was applicable for quantitative determination of thorium in water and urine samples.

The characteristics of the proposed method were compared with other methods used for determination of thorium. Table 2 compares the limit of detection (LOD), relative standard deviation (RSD), linear range (LR), extraction time, recovery and matrix using optical chemical sensor,<sup>2</sup> ICP-MS and spectrophotometric detection,<sup>4</sup> spectrophotometric determination with pyrimidine azo dyes and cetylpyridinium chloride<sup>17</sup> and Supercritical fluid extraction.<sup>18</sup> The proposed method provided similar quantification extraction efficiency, with advantages of being faster than many other mentioned techniques.

## Conclusions

In this study, a fast, simple, sensitive and selective method was proposed for determination of thorium in several water samples in the range of 6–230 ng mL<sup>-1</sup>. This method provided an efficient and affordable extraction procedure to determinate trace amounts of thorium in real samples. In the case of working with large sample volume solutions of about 100 mL and also small extracting solvent volume (methanol) of 2 mL, a fifty fold preconcentration factor was achieved. The limit of detection in the proposed method was excellent compared to the other reported method.

## Disclosure

This manuscript has been read and approved by all authors. This paper is unique and is not under consideration by any other publication and has not been published elsewhere. The authors and peer reviewers of this paper report no conflicts of interest. The authors confirm that they have permission to reproduce any copyrighted material.

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