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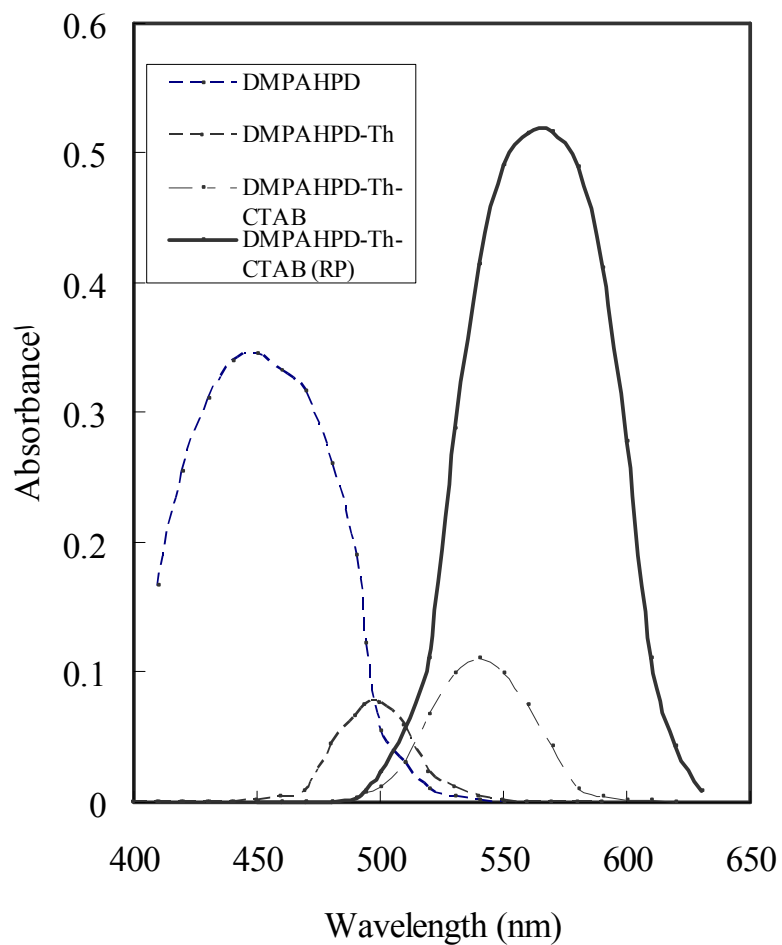


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Absorption spectra for  $0.5 \mu\text{g mL}^{-1}$  without CPE and  $5.0 \text{ ng mL}^{-1}$  complexed with DMPAHPD using CPE at pH 7.8

## Utilization of cloud-point extraction for colorimetric determination of trace amounts of thorium(IV) in real samples

Alaa S. Amin<sup>\*</sup>, Mohammed A. Kassem and Talaat Y. Mohammed

*Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*

A cloud point extraction process using mixed micelle of the cationic surfactant CTAB and non-ionic surfactant Triton X-100 to extract thorium(IV) from aqueous solutions was investigated. The method is based on the color reaction of thorium with 5-(2',4'-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione (DMPAHPD) in the presence of potassium iodide in hexamethylenetetramine buffer media and mixed micelle-mediated extraction of complex. The optimal extraction and reaction conditions (e.g. surfactant concentration, reagent concentration, effect of time) were studied and the analytical characteristics of the method (e.g. limit of detection, linear range, molar absorptivity, Sandell sensitivity, preconcentration, and improvement factors) were obtained. Linearity was obeyed in the range of 0.5–15 ng mL<sup>-1</sup> of thorium(IV) ion and the detection limit of the method is 0.16 ng mL<sup>-1</sup>. The interference effect of some anions and cations was also tested. The proposed method was successfully applied for the preconcentration of trace thorium in natural water samples as well as in plant material and soil samples prior to its determination by inductively coupled plasma atomic emission spectrometry (ICP-AES) with satisfactory results.

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\* Corresponding author: Tel; 00201205225223; Fax: 0020133222578;

e-mail: asamin2005@hotmail.com

**Keywords:** Cloud point extraction; Spectrophotometry; Mixed micelle; Thorium(IV) determination; Water, plant and soil samples

## Introduction

Thorium is the most abundant radioactive element in nature and has widespread application in variable areas, such as aeronautics and aerospace, metallurgy, optics, radio, chemical industry, and material fields extensively.<sup>1</sup> Unfortunately, thorium not only has chemical toxicity like other heavy metals do, but also has radioactivity which can cause a large scale permanent damage of bone, kidney and liver.<sup>2,3</sup> For the sake of health, safety and extensive usage, precise determination of thorium in geological materials and environmental is of utmost importance. However, the direct determination of thorium is still a barrier because of the very trace content and the presence of complex matrix.<sup>3</sup> Therefore, preconcentration and selective separation of thorium from real samples are very important and need much more attention.

Currently, the most widely used techniques for preconcentration of thorium include liquid–liquid extraction,<sup>4,5</sup> ion exchange,<sup>6</sup> extraction chromatography,<sup>7,8</sup> electrodeposition<sup>9</sup> and solid-phase extraction (SPE),<sup>10–12</sup> of all these preconcentration methods, the SPE is most popular one because of flexible working conditions and simple procedures. The main basic principle of SPE is the concentration and purification of analytes from solution by sorption on a solid sorbent.<sup>13</sup> Therefore, the choice of the solid sorbent is the most crucial factor and for a sorbent to be useful it must enable selective extractions to be achieved.

To carry out the separation and preconcentration of the analyte, mixed micelle-mediated extraction (mixed-MME) system was used in this study. MME is

becoming an important and practical application of the use of surfactants in analytical chemistry.<sup>14-16</sup> Such an extraction offers a convenient alternative to more conventional extraction systems. Cloud point (CP) phenomenon is generally observed in nonionic surfactant micellar solutions when the temperature of the system is raised to a certain value. It was reported that the CP of Triton X-114 increased on adding small amounts of either cationic surfactant cetyltrimethylammonium bromide (CTAB) or anionic surfactant sodium dodecyl sulfate (SDS).<sup>17</sup> Mixed surfactants of different charges in order to accomplish both ideal hydrophobic and non-ideal electrostatic interactions within the same extraction system. The use of cationic surfactants in combination with non-ionic surfactant has been documented with an increase in the extraction efficiency of polar organic compounds.<sup>18,19</sup> Moreover, the CP of a mixed solution of Triton X-114 and ionic surfactants decreased when small amounts of inorganic salts were added. The decreasing effect depended on the nature and concentration of the salt and salting out effect.<sup>20,21</sup> Mixed-MME was used to the preconcentration of organic compounds<sup>20,22</sup> and metal cations.<sup>23,24</sup>

To the best of our knowledge, there is no report on the preconcentration of thorium using mixed-MME. 5-(2',4'-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione (DMPAHPD) dye has been used for spectrophotometric determination of samarium(III) and others.<sup>25-29</sup> The goal of the present work is to develop a colorimetric method to determine of thorium based on cloud point extraction (CPE) of the complex of thorium(IV) with DMPAHPD complex in mixed surfactant media.

## Experimental

### Apparatus

A Perkin-Elmer Lambda 12 UV/Vis spectrometer was used for recording absorbance spectra with 1.0-mm quartz cell. A Perkin Elmer model 5300 DV; ICP-AES (Waltham, MA, USA) was used for all ICP-AES measurements. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A water bath with good temperature control and a centrifuge with 10-mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process. Tabletop Low Speed Large Capacity Centrifuge model L-550 was used

### Reagents

Unless otherwise stated, reagents of analytical purity were used for all experiments and doubly distilled water (DDW) was used throughout. The surfactants, Triton X-100 and cetyltrimethylammonium bromide (CTAB) (obtained from Sigma company) were used without further purification. Stock solution of thorium at a concentration of 0.025 M thorium(IV) solution is prepared by dissolving 3.675 g of thorium nitrate [ $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ ] in distilled water containing a few drops of nitric acid. The solution is made upto 250 mL and standardized gravimetrically by employing the iodide method. 0.1 M. working standard solutions were obtained by appropriate dilution of the stock. 5-(2',4'-Dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione (DMPAHPD) was prepared using conventional diazotization and coupling methods.<sup>25</sup> A solution of  $1.0 \times 10^{-3}$  M of DMPAHPD was prepared by dissolving appropriate amounts of this reagent in bidistilled water. The solution pH  $7.8 \pm 0.2$  was adjusted with hexamethylenetetramine (HTM)/ hydrochloric acid buffer. N,N-dimethyl formamide (DMF) solvent and potassium iodide salt were purchased from Merck.

### General procedure

An aliquot of a thorium(IV) standard solution was transferred to a 10 mL centrifuge tube, 1.5 mL of the  $1.0 \times 10^{-3}$  M DMPAHPD solution and 1.0 mL HTM buffer solution were added. This was followed by the addition of 1.5 mL of  $1.0 \times 10^{-3}$  M surfactant CTAB solution, 1.0 mL of 0.2 % (v/v) of Triton X-100 solution and 0.5 mL of 0.1 M of KI solution. The solution was taken up to the mark with bidistilled water. Separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 5.0 min at 3800 rpm. Then, the aqueous phase could be separated by inverting the tube, later 0.1 mL of DMF was added to the surfactant-rich phase and the solution was transferred to 1.0-mm quartz cell for measurement of absorbance at 566 nm.

### **Procedure for waste water samples**

Different water samples from cities with potential thorium pollution were collected in polyethylene containers, filtered and adjusted to the optimum pH values by HCl or NaOH. An appropriate aliquot of the sample was placed in a 25-mL calibrated flask and then the above-described general procedure was followed for the determination of the Th(IV) ions.

### **Sample preparation**

Balsam pear leaves, Lotus leaf and soil samples were obtained from Enshas City, Egypt. Sample preparation was followed as described in refs.<sup>30,31</sup> All samples were dried in an oven at 80 °C to constant weight. 0.5–1.0 g of samples was weighted and transferred to Teflon beakers, and then 5.0 mL of concentrated HNO<sub>3</sub> was added into it. The samples were left at room temperature for one night and slowly evaporated (<165 °C) to dryness. They were cooled down to ambient temperature. 5.0 mL of concentrated HF and 1.3 mL HClO<sub>4</sub> were added and the beakers stood cold for 4.0 h.

After evaporation to dryness, fresh HF was added and they were placed on a plate heater to ensure complete digestion. Following this, samples were again dried at moderate heat, redissolved in 5.0 mL of 6.0 M HCl, and heated strongly (>140 °C) to dryness. A second high temperature evaporation step was carried out after addition of 2.0 mL of 6.0 M HCl. The samples were then dissolved in 5.0 mL of 1.0 M HCl and heated overnight in closed beakers to ensure a complete solution. The solution was adjusted to pH 3 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution, transferred into a 100 mL calibrated flask, and diluted to volume with  $\text{NH}_4\text{Cl}$  buffer solution of pH 3.0.

## Results and discussion

Complex of thorium with DMPAHPD illustrates an absorption spectrum with maximum absorbance at 499 nm, whereas in the presence of CTAB the ternary complex Th(IV)–DMPAHPD–CTAB shows a red shift of the absorption maximum to 536 nm, with considerable increase in absorbance. We observed that addition of the neutral surfactant Triton X-100 and iodide ion and heating makes the solution turbid. Therefore the ternary complex of Th(IV)–DMPAHPD–CTAB can be extracted by CPE method. The absorption spectrum of the ternary complex in surfactant-rich phase illustrates a maximum absorbance at 566 nm. After separation of surfactant-rich phase, the absorbance was measured in 566 nm against a reagent blank similarly prepared (Fig. 1).

### Optimization of the system

The effect of pH on the absorbance of the Th(IV)–DMPAHPD–CTAB system at 536 nm in aqueous media was studied against the reagent blank. Maximum absorbance was obtained at pH 7.5–8.2. In acidic or more alkaline solutions, absorbance decreased because of incomplete complex formation and hydrolysis of the complex.



From this we concluded that the optimum pH to carry out all experiments ranged from 7.6 to 8.0.

Effect of CTAB concentration on the extraction and determination of thorium was investigated in the range  $0.05\text{--}3.0 \times 10^{-4}$  M. The results are shown in Fig. 2. The amount of the absorbance for sample increased by increasing CTAB concentration up to  $1.5 \times 10^{-4}$  M and remained nearly constant at higher concentrations. The blank absorbance also increased by increasing CTAB concentration. This is due to more extraction of DMPAHPD by increasing CTAB concentration, but the difference between the sample and blank absorbance ( $\Delta A$ ) increased by increasing CTAB concentration up to  $1.5 \times 10^{-4}$  M and decreased at higher concentrations. Therefore,  $1.5 \times 10^{-4}$  M CTAB was chosen as the optimum.

We observed that Triton X-100 concentration as a non-ionic surfactant can affect the extraction of complex and sensitivity of the method, therefore the effect of Triton X-100 concentration on the absorbance of the extracted phase was investigated. The absorbance of the surfactant-rich phase increased by increasing Triton X-100 concentration between 0.02% and 0.5% (v/v) and remained nearly constant at higher concentrations. Therefore, 0.2% (v/v) Triton X-100 was used as optimum concentration.

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency.<sup>32</sup> Several inorganic salts, including NaCl, NaF, KNO<sub>3</sub>, KBr and KI, was tested and KI was found as the best. It was observed that the addition of KI within the interval of  $3.0 \times 10^{-3}$  to  $1.5 \times 10^{-2}$  M had a

good effect on the cloud point extraction efficiency, therefore  $5.0 \times 10^{-3}$  M KI was used.

Optimal incubation time and equilibration temperature are necessary to complete reaction, and to achieve easy phase separation and preconcentration as efficient as possible. The greatest analyte preconcentration factors are thus expected under conditions where the CPE is conducted using equilibration temperatures that are well above the cloud point temperature of the surfactant. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. It was found that a temperature of 60 °C is adequate for nearly complete recovery of thorium. The dependence of absorbance upon equilibration was studied within the range of 1.0–15 min. Times of 5.0 min were chosen as optimal times for equilibration and incubation.

In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same sense as in conventional separations of a precipitate from its original aqueous environment.<sup>33</sup> Therefore, a centrifugation time of 5.0 min at 3800 rpm was selected as optimum, since complete separation observed for long time.

Because the surfactant-rich phase was very viscous, DMF was added to the surfactant-rich phase after CPE to facilitate its transfer into spectrophotometric cell. The amount of 0.1 mL DMF was chosen to have an appropriate amount of sample for transferring and measuring the sample absorbance.

### **Stoichiometric ratio**

The nature of the complex was established at the optimized conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of DMPAHPD to Th(IV), obtained by varying the

DMPAHPD concentration, showed inflection at molar ratio 2.0, indicating presence of two DMPAHPD molecules in the formed complex. Moreover, the Job method showed a ratio of DMPAHPD to Th(IV) = 2.0. Consequently, the results indicated that the stoichiometric ratio was (2 : 1) [DMPAHPD : Th(IV)]. The structure of which is probably as follows:



The conditional formation constant ( $\log K$ ), calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 7.57, whereas the true constant was 7.75.

### **Interference study**

The effect of different cations and anions on the determination of 5.0 ng mL<sup>-1</sup> thorium ion by the proposed method was studied. An ion was considered to be an interfering when it caused a variation greater than  $\pm 5.0\%$  in the absorbance of the sample. For the determination of 5.0 ng mL<sup>-1</sup> Th(IV) by this method, the foreign ions can be tolerated at the levels given in Table 1. DMPAHPD forms stable complexes with various metal ions, including transition metal ions. Most of the cations and anions examined do not interfere with the extraction and determination of thorium, and many of them are tolerated at very high levels. However, some of the species tried such as Al<sup>3+</sup>, Fe<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup> and Zr<sup>4+</sup>, interfered on the determination of thorium ion at 5.0 ng mL<sup>-1</sup> levels. The interfering effect of these ions was completely removed up to 500 ng mL<sup>-1</sup> in the presence 0.5 mL of 0.1 % of EDTA as a proper masking agent.

### **Analytical characteristics**

Table 2 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, and limit of detection, reproducibility, and preconcentration and improvement factors. Calibration curve is represented as shown in Fig. 3. The limit of detection, defined as  $CL = 3SB/m$  (where CL, SB, and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively), was  $0.16 \text{ ng mL}^{-1}$ . Because the amount of thorium in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of 0.3 mL (0.2 mL surfactant-rich phase + 0.1 mL DMF), the solution is concentrated by a factor of 33.3. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that the calibration graph in micellar media without preconcentration, was 464. The relative standard deviation (RSD) for five replicate measurements of  $5.0 \text{ ng mL}^{-1}$  of thorium was 1.56 %.

The sensitivity expressed as molar absorptivity, as well as the detection limits of the proposed method is compared with those of published spectrophotometric methods (Table 3). The higher sensitivity of the proposed method is notable, greater even than that of other methods,<sup>27,34-48</sup> that based on spectrophotometry. Although the measurable concentration range is from approximately  $0.5\text{--}150 \text{ ng L}^{-1}$  with graphite furnace atomic absorption spectrometry, the proposed method was very simple and accurate.

### **Analytical applications**

Aiming to demonstrate the usefulness of the proposed system a set of samples comprising several water and plant materials was analyzed. The proposed method was applied successfully to the determination of thorium ion in tap, well, and wastewater samples as well as in plant material samples. The results are shown in

Table 4. The recoveries are close to 100 % and indicate that the proposed method was helpful for the determination of thorium in the real samples.

The performance of the proposed method was assessed by calculation of the t-value (for accuracy) and F-test (for precision) compared with ICP-AES method.<sup>48</sup> The mean values were obtained in a Student's t- and F-tests at 95% confidence limits for five degrees of freedom.<sup>49</sup> The results showed that the calculated values (Table 4) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other method.

## Conclusion

The proposed procedure gives a simple, very sensitive and low-cost colorimetric procedure for determination of thorium ion that can be applied to real samples. The surfactant has been used for preconcentration of thorium in water, and thus toxic solvent extraction, has been avoided. A comparison of the proposed method with the previously reported methods for preconcentration and spectrophotometric determination of thorium (Table 3) indicates that the proposed method is faster and simpler than the existing methods and that it provides a lower limit of detection. To the best of our knowledge this is the first report in the mixed-MME of thorium.

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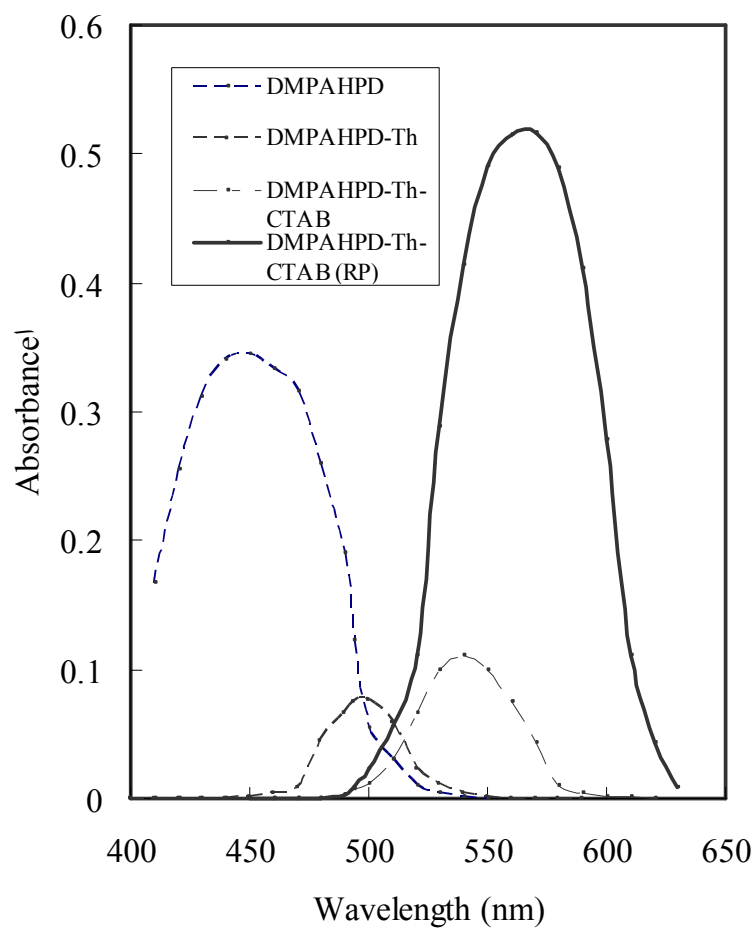


Fig. 1 Absorption spectra for  $0.5 \mu\text{g mL}^{-1}$  without CPE and  $5.0 \text{ ng mL}^{-1}$  complexed with DMPAHPD using CPE at pH 7.8

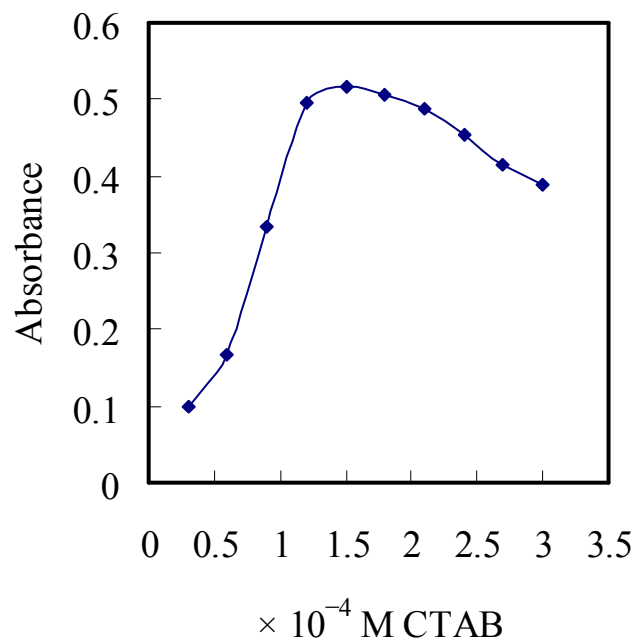


Fig. 2 Effect of CTAB on the complex formation of  $5.0 \text{ ng mL}^{-1} \text{ Th}^{4+}$  immobilized DMPAHPD

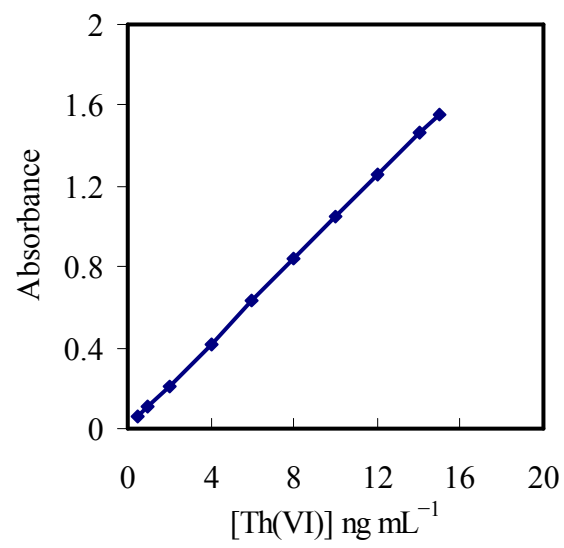


Fig. 3 Calibration curve for Th(VI) determination under optimum conditions

**Table 1**

Influence of interfering ions on the determination of  
5.0 ng mL<sup>-1</sup> thorium

Foreign ion	Tolerance limit/ng mL <sup>-1</sup>	Foreign ion	Tolerance limit/ ng mL <sup>-1</sup>
Ca(II)	10000	Tartrate	3000
Na(I)	7500	Oxalate	1750
K(I)	5000	Mo(VI)	1500
Mg(II)	7500	Cr(III)	1000
Bi(III)	5000	Al(III) <sup>a</sup>	500
Mn(II)	4000	W(VI)	5000
Ni(II)	3500	V(V)	3000
Zn(II)	250	Cl <sub>2</sub>	20000
Pb(II)	2500	Ti(IV)	1000
La(III)	1750	I <sub>2</sub>	750
Co(II)	1500	NO <sub>3</sub> <sup>-</sup>	4000
Ce(III)	1250	CH <sub>3</sub> COO <sup>-</sup>	7500
Cu(II)	1000	SO <sub>4</sub> <sup>2-</sup>	1000
Fe(III) <sup>a</sup>	500	SiO <sub>3</sub> <sup>2-</sup>	1500
Cd(II)	750	PO <sub>4</sub> <sup>3-</sup>	3000
UO <sub>2</sub> (II) <sup>a</sup>	500	Co <sub>3</sub> <sup>2-</sup>	2500
Zr(IV) <sup>a</sup>	500	Citrate	2250

<sup>a</sup> 0.5 mL of 0.1 % EDTA solution was used to mask this interference

**Table 2**  
Analytical parameters.

Parameter	Value	Parameter	Value
Beer's law limit (ng mL <sup>-1</sup> )	0.5–15	Regression equation <sup>a</sup>	
Ringbom optimum range (ng mL <sup>-1</sup> )	0.1–13.6	Slope (b)	0.105
Molar absorptivity (L mol <sup>-1</sup> cm <sup>-1</sup> )	7.18×10 <sup>5</sup>	Intercept (a)	- 0.04
Sandell sensitivity (ng cm <sup>-2</sup> )	2.42	Correlation coefficient (r)	0.9997
Detection limit (ng mL <sup>-1</sup> )	0.097	RSD (%)	1.56
Quantification limit (ng mL <sup>-1</sup> )	0.52	Preconcentration factor	33.33
Stoichiometric ratio (L:M)	2:1	Improvement factor	464

<sup>a</sup>  $A = a + bC$ , where C is the concentration of iron in ng mL<sup>-1</sup>.

**Table 3**

Comparison of the present method with other spectrophotometric methods for the determination of thorium(IV).

Reagent	$\lambda_{(\max)}$	$\varepsilon \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$	DL $\text{ng mL}^{-1}$	Ref.
1-(2-thiazolylazo)-2-naphthol	555	0.314	150	34
Calixarene hydroxamic acid (CPCHA)	450	0.220	100	35
2-hydroxy-1,4-naphthaquinone Lawsone (LAS)	440	0.027	1300	36
Mepazine hydrochloride				
2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone.	390	0.220	100	37
Disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naptylazo)-benzene arsenic acid	544	0.169	1500	38
4-chloro-N-(2,6-dimethylphenyl)-2-hydroxy-5-sulfamoylbenzamide	445	0.622	35	39
2,3,4-trihydroxyacetophenoneoxime	325	0.3179	1200	40
xylenol orange-CTAB	568	~10	1.4	41
Arsenazo III	655	4.20	25	42
Bromocresol orange	560	0.928	150	43
Pyrocatecol violet	660	0.62	40	44
2-Hydroxy-3-carboxyl-5-sulfonicarsenazo	676	1.05	200	45
Chromazurol	620	0.520	50	46
Arsenazo III	684	0.625	33	47
Pyrimidine azo dyes	563	2.03	25	27
DMPAHPD	566	7.18	~ 0.1	This work

**Table 4**

Determination of thorium in real samples by the proposed method

Sample	Th(IV) (ng mL <sup>-1</sup> )		T- test <sup>b</sup>	F- value <sup>b</sup>	ICP-AES (ng/mL)
	Added	Found <sup>a</sup>			
Potable water	--	3.4 ± 2.1		--	3.5 ± 1.2
	4.0	7.5 ± 1.9	1.83	3.26	
	8.0	11.3 ± 2.1	1.62	2.93	
Well water -	--	7.3 ± 2.1			7.2 ± 2.5
	3.0	10.2 ± 1.4	1.55	2.93	
	6.0	13.4 ± 0.8	1.47	2.77	
River Nile water	--	4.5 ± 1.4			4.6 ± 2.2
	5.0	9.4 ± 1.1	1.81	3.47	
	10	14.6 ± 1.5	1.39	2.78	
Rain water	--	2.7 ± 1.3			2.8 ± 2.1
	6.0	8.8 ± 1.1	1.64	3.03	
	12.0	14.6 ± 0.8	1.28	2.52	
Mineral water	--	3.0 ± 1.4			3.1 ± 1.7
	7.0	10.1 ± 1.3	1.88	3.63	
	12	13.2 ± 2.6	1.80	3.23	
Tap water	--	6.5 ± 1.6			6.4 ± 2.1
	4.0	10.4 ± 1.0	1.33	2.69	
	8.0	12.4 ± 1.3	2.12	3.80	
Sea water	--	10.3 ± 0.7			10.5 ± 1.8
	2.0	12.3 ± 0.9	1.22	2.51	
	4.0	14.4 ± 1.0	1.68	3.11	
Balsam pear leaves	--	0.26 ± 2.0			0.27 ± 2.7
	0.10	0.36 ± 1.7	1.94	3.85	
	0.20	0.47 ± 1.2	1.76	3.23	
Lotus leaves	--	0.05 ± 1.8			
	0.15	0.145 ± 1.3	1.48	2.82	
	0.30	0.253 ± 1.6	1.17	2.45	
Soil sample	--	2.15 ± 1.4			2.22 ± 2.1
	0.25	2.41 ± 1.8	1.59	3.04	

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0.50	2.66 ± 1.3	1.15	2.38
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<sup>a</sup> Average of four determinations ± standard deviation

<sup>b</sup> Theoretical values for t and F at 95% confidence limit (n = 5) were 2.57 and 5.05, respectively.