

# Synthesis of 2-hydroxy-3-carboxyl-5-sulfonicarsenazo and its application to the spectrophotometric determination of thorium

Yepu Chen,<sup>\*a</sup> Zaijun Li,<sup>a</sup> Zhenzhong Zhu<sup>a</sup> and Jiaomai Pan<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Wuxi University of Light Industry, Wuxi 214036, China. E-mail: chend@wxuli.edu.cn

<sup>b</sup> Department of Chemistry, East China Normal University, Shanghai 200062, China

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A new highly selective and sensitive chromogenic reagent, 2-hydroxy-3-carboxyl-5-sulfonicarsenazo (ASA-HCS), was synthesized and studied for determination of trace thorium. In a high concentration nitric acid medium, thorium reacts with ASA-HCS to form a 1:2 green complex which has a sensitive absorption peak at 676 nm. A 0–0.6  $\mu\text{g ml}^{-1}$  concentration of thorium obeys Beer's law. The complex is formed instantly in nitric acid medium and remains stable for 48 h at least. The stability constant of the complex is  $9.76 \times 10^{21}$  at 25 °C, its molar absorptivity and Sandell's sensitivity are  $1.05 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.00223 \mu\text{g cm}^{-2}$ , respectively. Its limit of quantification, limit of detection and relative standard deviations were found to be 14.3  $\text{ng ml}^{-1}$ , 4.9  $\text{ng ml}^{-1}$  and 1.2%, respectively. Ca(II), Mg(II), Ag(I), Al(III), K(I), Fe(III), Co(II), Ni(II), Pb(II), Mn(II), W(VI), Cr(III), Zn(II), Cu(II), Y(III), Mo(VI), Ce(III) and U(VI) do not interfere with the determination of thorium, so the selectivity is advantageous compared with other published reagents. The stepwise dissociation constants of the reagent at  $\lambda = 554 \text{ nm}$  and  $\lambda = 650 \text{ nm}$  have been determined. The proposed method has been applied to the determination of thorium in waste water and rare earth–magnesium–silicon alloy with satisfactory results.

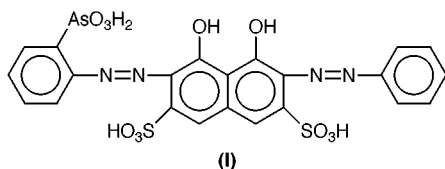
## 1 Introduction

Thorium and its compounds are seriously hazardous. Because of environmental pollution, the determination of thorium is becoming increasingly important. Although strong claims are made for the specificity and sensitivity of NAA, ICP-AES and ICP-MS, some of the interferences to which these methods are subject are poorly understood and continue to cause problems.<sup>1</sup> Therefore, spectrophotometric methods for thorium determination continue to be interesting.<sup>1</sup> Savvin<sup>2</sup> and Florence<sup>3</sup> recognized that arsenazo III is a good chromogenic reagent, but uranium(VI) and rare earths seriously interfere with thorium analysis. After that, a number of reagents were synthesized and studied for the determination of thorium, such as chlorophosphonazo III,<sup>4</sup> chlorophosphonazo-*m*-COOH,<sup>5</sup> chlorophosphonazo-*m*-SO<sub>3</sub>H,<sup>6,7</sup> *p*-methylchlorophosphonazo,<sup>8</sup> dibromo-*p*-nitroarsenazo,<sup>9</sup> chlorophosphonazo-*p*-amino-

hippuric acid,<sup>10</sup> *p*-arsenazo-COCH<sub>3</sub>,<sup>11</sup> tribromoarsenazo,<sup>12</sup> *p*-bromochlorophosphonazo<sup>13</sup> and *o*-nitrophosphonazo,<sup>14</sup> each reagent system having its advantages and disadvantages with respect to selectivity and sensitivity. Most of them require some previous separation before being applied to the determination of thorium in a complex sample so as to increase the selectivity (see Table 1). In order to continue the search for new sensitive and selective chromogenic reagents for the determination of thorium and studying the influence of the substituent group on the analytical characteristic of the reagents, we introduced three assisting functional groups, OH, COOH and SO<sub>3</sub>H to (I) to get a new chromogenic reagent, 2-hydroxy-3-carboxyl-5-sulfonicarsenazo (ASA-HCS)(II), an asymmetric bisazo derivative of chromotropic acid with one *o*-arsenic acid functional group. The –COOH group added to the phenyl has already been proved to increase the sensitivity of the chromogenic reactions.<sup>5</sup> Introducing –OH and –SO<sub>3</sub>H to the phenyl group can improve

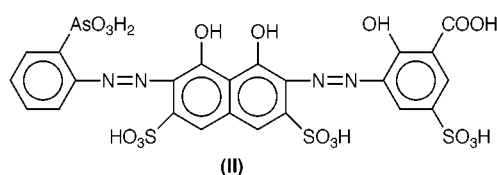
**Table 1** Review of some spectrophotometric methods for the determination of thorium

Reagent	$\epsilon \times 10^{-4}$	Tolerance limit of some metal ions (mg per 25 ml)	Ref.
Arsenazo III	5.12	Ti(IV)(0.1), Ce(IV)(0.5), La(III)(0.5), U(VI) (interfere seriously)	2
Chlorophosphonazo III	5.57	Y(III)(0.02), Ti(IV)(0.02), U(VI), Ce(IV), La(III) (interfere seriously)	4
<i>p</i> -Bromochlorophosphonazo	9.4	U(VI)(0.1), Ti(IV)(0.3), Ba(II)(0.35), Mg(II)(0.5), Cu(II)(1.0), Ce(IV), Y(III), (interfere seriously)	13
<i>p</i> -Methylchlorophosphonazo	9.7	U(VI), Ce(III), Y(III) (interfere seriously)	8
Arsenazo- <i>p</i> -COCH <sub>3</sub>	9.24	U(VI)(0.34), Ti(IV)(0.15), Ba(II)(2.0), La(III), Ce(IV) (interfere seriously)	11
Chlorophosphonazo- <i>p</i> -aminohippuric acid	9.63	K(I)(0.4), Zn(II)(0.2), Mn(II)(0.045), Ni(II)(0.04), Ca(II)(0.025), Al(III)(0.2), Cr(III)(0.025), Ce(IV), Ba(II), Cu(II), U(VI) (interfere seriously)	10
Chlorophosphonazo- <i>m</i> -COOH	10.3	Ba(II)(0.04), Bi(III)(0.3), Ca(II)(0.1), Cu(II)(0.5), Pb(II)(0.2), Ti(IV)(0.1), Zr(IV)(0.1), Ce(IV), La(III) (interfere seriously)	5
Chlorophosphonazo- <i>m</i> -SO <sub>3</sub> H	7.0	Ti(IV)(0.3), Zr(IV)(0.2), U(VI)(0.1), Y(III) (0.3)Ce(IV), La(III) (interfere seriously)	6,7
Tribromoarsenazo	10.1	Ca(II)(0.5), La(III), Ce(III), Y(III) (interfere seriously)	12
Dibromo- <i>p</i> -nitroarsenazo	9.0	Y(III)(0.5), La(III)(0.03), Ce(IV)(0.03) (interfere seriously)	9
<i>o</i> -Nitrophosphonazo	7.20	Y(III)(0.23), U(VI)(0.25), Ce(IV), La(III) (interfere seriously)	14
2-Hydroxy-3-carboxyl-5-sulfonicarsenazo	10.5	Ca(20), Mg(40), Fe(10), Zn(20), Mo(3.5), Ce(5), U(4), La(5)	Present work



the reagent's water solubility, which might be helpful in increasing its selectivity in strong acid medium. It was found that ASA-HCS is one of the most convenient and efficient chromogenic reagents which has high selectivity and only gives a sensitive reaction with thorium(IV) in a strongly acidic medium. Its selectivity is advantageous over all other reagent published.

In this paper, the synthesis, physical and chemical properties of ASA-HCS and the spectrophotometric method for determination of thorium in real samples are described in detail.



## 2 Experimental

### 2.1 Synthesis of ASA-HCS

**2.1.1a Synthesis of 3-amino-5-sulfonic-2-hydroxyphenyl-carbonic acid.** Add concentrated  $\text{H}_2\text{SO}_4$  (70 g) to a three-necked flask, drop in *o*-hydroxyphenylcarbonic acid with stirring, heat on a water bath at 95–96 °C for 30 min, cool to 20 °C, add concentrated  $\text{HNO}_3$  (11 g) and concentrated  $\text{H}_2\text{SO}_4$  (35 g), and hold the temperature between 40–50 °C for 10 min. A nitrate solution was obtained.

Transfer 200 ml of KCl solution (20 g of KCl dissolved in 200 ml of water) to another three-necked flask and add the above nitrate solution dropwise with stirring. After that, heat on a water bath, keeping the temperature at 80 °C for 30 min. Then collect the precipitate on a filter and dry the precipitate at 80 °C; 3-amino-5-sulfonic-2-hydroxyphenyl carbonic salt is obtained.

Dissolve 15 g of 3-amino-5-sulfonic-2-hydroxyphenylcarbonic salt in 90 ml of water, adjust to pH = 11 by dropping in 10% NaOH and add  $\text{Na}_2\text{S}_2\text{O}_4$  (2 g) slowly. After that, heat on a water bath, keeping the temperature between 70–80 °C, stand overnight, acidify the solution by adding concentrated HCl (to pH < 1), filter, wash and dry at 80 °C. 3-Amino-5-sulfonic-2-hydroxyphenylcarbonic acid is obtained with a productive rate of 72%.

**2.1.1b Synthesis of 2-hydroxy-3-carboxy-5-sulfonazo.** 3-Amino-5-sulfonic-2-hydroxyphenylcarbonic acid (5.0 g) is dissolved in 45 ml of water, and 2.0 g of  $\text{NaNO}_2$  is added and mixed in well. The mixture is then added dropwise to 30 ml of 1:1 cold HCl to diazotize, keeping the reaction temperature below 50 °C. Dissolve chromotropic acid (8 g) in 50 ml of 40% NaAC solution, keep the temperature below 50 °C, drop the acid into the above diazotized solution and stand for 4 h. After that, acidify the solution (pH < 1) to obtain precipitate, stand for 12 h, filter and dry the precipitate at 80 °C. 2-Hydroxy-3-carboxy-5-sulfonazo is obtained with a productive rate of 89%.

**2.1.1c Synthesis of ASA-HCS.** Dissolve 2-aminophenylarsenic acid (1.8 g) in 20 ml of 1:1 HCl, add  $\text{NaNO}_2$  solution

dropwise (0.4 g of  $\text{NaNO}_2$  dissolved in 4 ml of water), maintain the reaction temperature below 50 °C. Add 3 g of 2-hydroxy-3-carboxy-5-sulfonazo and 6.0 g of LiOH to a three-necked flask, controlling the temperature below 50 °C, and drop in the above diazotized solution slowly. After that, stand the solution overnight, acidify the solution to pH < 1 by adding concentrated HCl, filter and dry the precipitate at 80 °C. The crude ASA-HCS was obtained with a productive rate of 58.7%.

### 2.1.2 Purification of crude ASA-HCS

Dissolve 1 g of crude ASA-HCS in 50 ml of water, add 5% NaOH solution dropwise until the solution is blue and extract six times with *n*-butanol (50 ml for each extraction). Then add 10 ml of 1:1 HCl to the aqueous phase and re-extract with 100 ml of *n*-butanol. Wash the organic phase with 10 ml of water and add 100 ml of 5% NaOH solution for back-extraction. Next add 10 ml of 1:1 HCl to the aqueous phase to precipitate ASA-HCS and, after standing overnight, collect the precipitate on a filter, wash with 1 mol  $\text{l}^{-1}$  HCl and dry at 80 °C. The product contains 5 moles of water, estimated by thermogravimetry.

The purity of ASA-HCS was checked by paper chromatography with a (5 + 2) mixture of sodium citrate and 25% ammonia solution as eluent; a single blue band was obtained for the pure product. The results of elemental analysis corresponded with the composition of ASA-HCS.

## 2.2 Apparatus

Absorption spectra and absorbance were recorded and measured with a Beckman DU-7HS spectrophotometer, using a 2 cm cell.

## 2.3 Reagents

Unless otherwise stated, all reagents used were of analytical grade and all solutions were prepared with distilled water.

**2.3.1 Standard thorium solution.** The standard stock solution of thorium was prepared by dissolving thorium nitrate in a given volume of water and the solution was standardized by titration with EDTA. The working standard solution (10  $\mu\text{g ml}^{-1}$ ) was prepared by dilution.

**2.3.2 0.08% ASA-HCS solution.** 0.08% ASA-HCS solution was prepared by dissolving 0.08 g of ASA-HCS in 100 ml of water.

## 2.4 General procedure

Transfer an aliquot of standard or sample solution containing not more than 15  $\mu\text{g}$  of thorium, add 12 ml of 10 mol  $\text{l}^{-1}$  nitric acid and 5 ml of 0.08% ASA-HCS solution successively, dilute to the mark with water and measure the absorbance at 676 nm in a 2 cm cell against a reagent blank.

## 3 Results and discussion

### 3.1 Physical and chemical properties of ASA-HCS

ASA-HCS is a violet solid and easily soluble in water. The absorption spectra of ASA-HCS at different pH values are shown in Fig 1. According to the absorbance of the reagent at

554 nm and 650 nm, the reagent's dissociation constants were calculated by following formula:<sup>14-16</sup>

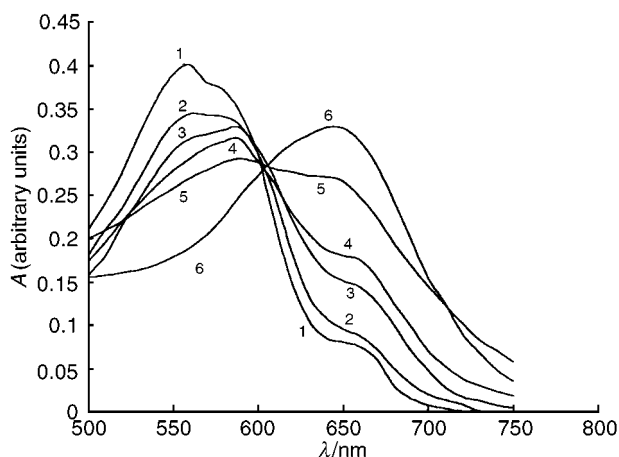
$$k_n = \frac{(A_i h_i - A_p h_p)(h_i - h_m) - (A_{i h_i} - A_m h_m)(h_i - h_p)}{(A_i - A_m)(h_i - h_p) - (A_i - A_p)(h_i - h_m)}$$

in which  $k_n$  is the stepwise dissociation constant of the reagent,  $A_i$ ,  $A_p$ ,  $A_m$  and  $h_i$ ,  $h_p$ ,  $h_m$  are absorbance and hydroxyl ion's concentration at various times, respectively. The results are shown in Table 2.

The results show that the reagent has 9 dissociation steps and each dissociation constant is close every other at 554 nm and 650 nm. According to the structure and the dissociation constants of the reagent, the probably dissociation process was proposed and listed in Table 3.

### 3.2 Absorption spectra

In nitric acid medium, ASA-HCS exhibits a maximum absorption at 554 nm, whereas the Th-ASA-HCS complex gave one absorption peak at 676 nm (see Fig. 2). Therefore, a wavelength of 676 nm was chosen for the spectrophotometric determination of thorium.



**Fig. 1** Absorption spectra of the reagent at various pH values [ASA-HCS]  $1.25 \times 10^{-5}$  mol l<sup>-1</sup>. **1**, 1.0 mol l<sup>-1</sup> HCl; **2**, pH = 3.00; **3**, pH = 7.00; **4**, pH = 9.00; **5**, pH = 11.00; **6**, pH = 12.88.

**Table 2** Calculated results of stepwise dissociation constants of ASA-HCS

$k_n$	$\lambda = 554$ nm	$\lambda = 650$ nm
$k_1$	$(2.034 \pm 1.100) \times 10^{-1}$	$(2.51 \pm 1.300) \times 10^{-1}$
$k_2$	$(2.38 \pm 0.900) \times 10^{-2}$	$(1.63 \pm 0.800) \times 10^{-2}$
$k_3$	$(1.00 \pm 0.700) \times 10^{-3}$	$(1.60 \pm 0.900) \times 10^{-3}$
$k_4$	$(1.79 \pm 0.750) \times 10^{-6}$	$(1.39 \pm 0.500) \times 10^{-6}$
$k_5$	$(3.79 \pm 0.650) \times 10^{-7}$	$(3.30 \pm 0.450) \times 10^{-7}$
$k_6$	$(2.06 \pm 0.200) \times 10^{-9}$	$(1.40 \pm 0.150) \times 10^{-9}$
$k_7$	$(3.61 \pm 0.300) \times 10^{-10}$	$(3.38 \pm 0.250) \times 10^{-10}$
$k_8$	$(2.09 \pm 0.100) \times 10^{-11}$	$(2.88 \pm 0.120) \times 10^{-11}$
$k_9$	$(9.14 \pm 0.120) \times 10^{-14}$	$(8.53 \pm 0.100) \times 10^{-14}$

**Table 3** Dissociation process of the reagent H<sub>9</sub>R (probably)

pH	Reaction	Remarks
0.00–3.00	H <sub>9</sub> R = H <sub>6</sub> R <sup>3-</sup> + 3H <sup>+</sup>	$k_1, k_2, k_3$ : the dissociation of –SO <sub>3</sub> H group
5.50–6.50	H <sub>6</sub> R <sup>3-</sup> = H <sub>4</sub> R <sup>5-</sup> + 2H <sup>+</sup>	$k_4, k_5$ : the dissociation of –AsO <sub>3</sub> H <sub>2</sub> group
6.60–9.10	H <sub>4</sub> R <sup>5-</sup> = H <sub>3</sub> R <sup>6-</sup> + H <sup>+</sup>	$k_6$ : the dissociation of –COOH group
8.50–9.50	H <sub>3</sub> R <sup>6-</sup> = H <sub>2</sub> R <sup>7-</sup> + H <sup>+</sup>	$k_7$ : the dissociation of –OH group of phenyl
10.50–14.00	H <sub>2</sub> R <sup>7-</sup> = R <sup>9-</sup> + 2H <sup>+</sup>	$k_8, k_9$ : the dissociation of –OH groups of phenone

### 3.3 Effects of reaction media

The absorbance of the Th-ASA-HCS complex was almost unchanged when H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> were chosen as the reaction media. Owing to the fact that nitric salts' solubility is very good, we chose HNO<sub>3</sub> as the reaction medium. In the 25 ml of solution, the presence of 1–15 ml of 10 mol l<sup>-1</sup> HNO<sub>3</sub> gave a maximum and constant absorbance; over 15 ml of nitric acid caused the reagent to precipitate. Therefore, an optimum amount of 12 ml of 10 mol l<sup>-1</sup> HNO<sub>3</sub> is recommended.

### 3.4 Effect of ASA-HCS concentration

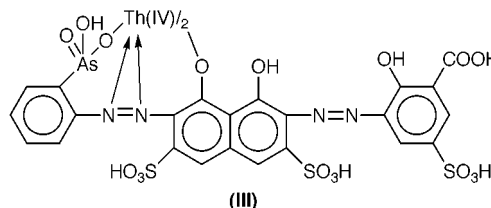
For up to 15 µg of thorium(vi), the addition of more than 5 ml of 0.08% ASA-HCS solution is sufficient to complete the reaction. Therefore, 5 ml of 0.08% ASA-HCS was subsequently used.

### 3.5 Stability of the chromogenic system

It was found that the absorbance of ASA-HCS-Th(vi) reaches a maximum value instantly at room temperature and remains stable for 48 h at least.

### 3.6 Composition of the complex

The composition and apparent stability constant were evaluated by the continuous variation and molar ratio methods. Both showed that the molar ratio of thorium(vi) to ASA-HCS is 1:2, which suggests has the structure **III**. The apparent stability constant of the complex is  $9.76 \times 10^{21}$  at 25 °C.



### 3.7 Analytical characteristics

The calibration graph was constructed according to the general procedure; Beer's law was obeyed over the 0–15 µg of thorium in 25 ml of solution, the molar absorptivity and Sandell's sensitivity were calculated from the slope of the calibration graph to be  $1.05 \times 10^5$  and  $0.00223$  µg cm<sup>-2</sup>; the limit of detection as defined by IUPAC<sup>17</sup> and the limit of quantification<sup>18,19</sup> were found to be 4.9 ng ml<sup>-1</sup> and 14.3 ng ml<sup>-1</sup>; ten replicate analyses of a test solution containing 10 µg of thorium by the general procedure gave a relative standard deviation of 1.2%.

### 3.8 Effect of foreign ions

Solution containing 10 µg of thorium and various amounts of foreign ions were prepared and determined by the general

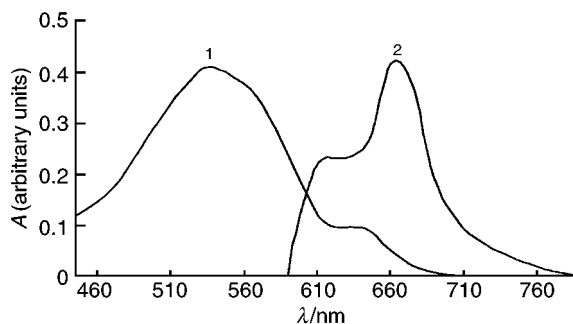


Fig. 2 Absorption spectra. 1, absorption spectrum of the reagent against water; 2, absorption spectrum of the complex against the reagent blank.

Table 4 Effect of foreign ions

Foreign ions	Amount added/mg	Found Th(iv)/μg	Recovery (%)
K(I)	100	10.0	100
Na(I)	100	10.0	100
NH <sub>4</sub> (I)	100	10.0	100
Ca(II)	200	10.1	101
Sr(II)	20	10.0	100
Ba(II)	20	10.2	102
Mg(II)	40	10.0	100
Fe(III)	10	10.3	103
Co(II)	40	10.0	100
Ni(II)	40	10.0	100
Cr(III)	40	10.0	100
Ag(I)	40	10.0	100
Al(III)	40	10.0	100
Pb(II)	40	10.1	100
Mn(II)	20	10.0	100
W(VI)*	10	10.0	100
Zn(II)	20	10.0	100
Mo(VI)	3.5	10.4	104
Cu(II)	1	10.2	102
Bi(III)	1	10.3	103
Ce(III)	5	10.1	100
Ti(IV)	1.0	10.2	102
Zr(IV)	0.5	10.4	104
U(VI)	4	10.1	101
Y(III)	12	10.0	100
La(III)	5	10.2	102
Cl <sup>-</sup>	100	10.0	100
NO <sub>3</sub> <sup>-</sup>	100	10.0	100
SO <sub>4</sub> <sup>2-</sup>	100	10.0	100
CO <sub>3</sub> <sup>2-</sup>	100	10.0	100
F <sup>-</sup>	100	10.0	100
Br <sup>-</sup>	100	10.0	100
I <sup>-</sup>	100	10.0	100
Citric acid	500	10.0	100

<sup>a</sup> In presence of 5 ml of 5% citric acid.

procedure. The tolerated limits (5% error maximum) are listed in Table 4. No foreign ions studied interfere significantly with the determination of thorium, which is an advantage over the published methods. This new method can be applied directly to determine thorium in various samples without previous separation.

### 3.9 Determination of thorium in rare earth–magnesium–silicon alloy and waste water

Weigh 0.1–0.2 g of powdered sample (rare earth–silicon–magnesium alloy) in a dried Pt crucible, heat for 30 min, cool, add 1–2 ml of HF and dissolve the samples completely, add 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub>, heat the solution to almost dry, dissolve the residue by adding 5 ml of 2 mol l<sup>-1</sup> HCl, transfer the sample solution to a 100 ml calibrated flask and finally dilute to the mark with water.

Table 5 Results of determination in samples<sup>a</sup>

Samples	Results by proposed method	Results by extraction method <sup>b</sup>
Rare earth-silicon-	88-4 0.023 ± 0.0002(%)	0.023 ± 0.0005(%)
magnesium alloy	88-5 0.031 ± 0.0001(%)	0.031 ± 0.0002(%)
	88-6 0.034 ± 0.0003(%)	0.033 ± 0.0007(%)
	88-8 0.196 ± 0.001(%)	0.195 ± 0.007(%)
		0.55 ± 0.01
Waster water sample 1	0.56 ± 0.03 (μg ml <sup>-1</sup> )	(μg ml <sup>-1</sup> )
	0.088 ± 0.001	0.088 ± 0.002
Waster water sample 2	(μg ml <sup>-1</sup> )	(μg ml <sup>-1</sup> )

$$^a \bar{x} \pm \frac{st}{\sqrt{n}} (n = 5)$$

<sup>b</sup> After extraction by PMBP–acetobutyric ester, spectrophotometric determination with arsenazo III.

Transfer the sample solution (not more than 15 μg of thorium) to a 25 ml calibrated flask, then follow the general procedure for the determination absorbance at 676 nm against reagent blank. Results are shown in Table 5.

### 3.10 Conclusions

The proposed method is very simple and rapid. The chromogenic reaction completes instantly and the complex is stable for at least 48 h at room temperature. It is also sensitive. Its molar absorptivity is much better than those given in the literature.

The proposed method has very high selectivity. From Table 1, we can clearly see that ASA-HCS selectivity is much better than that of any other reagent reported for the determination of thorium. All of the ions that we studied that can avoid previous separation cannot interfere with the chromogenic reactions.

Thus the proposed method can be used routinely for the determination of thorium in various samples, such as alloys, ore and waste water.

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