



# Extraction of Th, Zr and Sc from rock matrix using silica modified with arsenazo-III and their determination by inductively coupled plasma atomic emission spectrometry

BINCY CYRIAC<sup>a,\*</sup> , MASTAN VALI<sup>b</sup>, NISHMA OJHA<sup>b</sup> and SMEER DURANI<sup>c</sup>

<sup>a</sup>Chemistry Laboratory, Atomic Minerals Directorate for Exploration and Research, Central Region, Civil Lines, Nagpur 440001, India

<sup>b</sup>Chemistry Laboratory, Atomic Minerals Directorate for Exploration and Research, Southern Region, Nagarbhavi, Bangalore 560072, India

<sup>c</sup>Chemistry Laboratory, Atomic Minerals Directorate for Exploration and Research, Northern Region, R.K. Puram, New Delhi 110066, India

E-mail: bincycyriacam@gmail.com

MS received 6 December 2019; revised 3 March 2020; accepted 3 March 2020

**Abstract.** A simple, selective and rapid determination procedure for Th, Zr and Sc in rock samples using adsorbent silica modified with arsenazo-III is described. Silica modified with arsenazo-III (SAR-III) was synthesised by a single step process in presence of cationic surfactant cetyltrimethylammonium bromide. Effect of pH, amount of adsorbent, contact time for adsorption and the optimum eluent for the quantitative recovery of Th, Zr and Sc were investigated. Optimum conditions selected for the selective extraction of these elements by SAR III are pH-3, 0.2 g adsorbent, contact time 30 minutes and 10 mL of 5 % ammonium oxalate as eluent. Adsorption capacities of SAR III for Th, Zr and Sc are 5.68, 23.9 and 4.42 mg g<sup>-1</sup>, respectively. Effect of major elements present in the rock on the pre-concentration of these elements was investigated. Interference of iron was eliminated by reducing ferric iron with hydroxylamine hydrochloride. The method was validated by applying the procedure to synthetic rock sample solutions and certified geological reference materials SY-2 (CCRMP, Canada), BCR-1 (USGS), GSN (ANRT, France) and AGV-1(USGS). Detection limits obtained for Th and Zr by this method are 1 µg g<sup>-1</sup> and that of Sc is 0.1 µg g<sup>-1</sup>. The relative standard deviation of the method at 1 µg g<sup>-1</sup> was in the range of 1.0–2.5%.

**Keywords.** Silica modified with arsenazo-III; thorium, zirconium, and scandium determination; inductively coupled plasma-atomic emission spectrometry; rock sample.

## 1. Introduction

Thorium, zirconium and scandium are strategically important elements which find application in diverse fields. Major use of thorium is in nuclear industry as it can be converted to nuclear fuel. Thorium (Th-232), after absorbing a neutron is converted to U-233 which is an excellent fissile material.<sup>1</sup> Thorium-232 on absorbing a neutron is converted into thorium-233 which has a half-life of 22 minutes. Thorium-233 decays into protactinium-233 through β decay. Protactinium-233 has a half-life of 27 days and beta decays into uranium-233. Zirconium, due to its very low thermal neutron capture cross section finds application as cladding material in nuclear reactors.<sup>2</sup>

Scandium and its compounds are widely used in the fields of aeronautics, optics, electronics and transportation due to its very low density and high melting point.<sup>3</sup> In addition, zirconium and scandium are geochemically significant elements and their signatures in the rock reflect petro genesis.<sup>4</sup> In normal rocks, these elements are present at microgram levels and the crustal abundance of Th, Zr and Sc are 8, 165 and 22 µg g<sup>-1</sup> respectively.<sup>5</sup> Determination of these elements in rock sample at their abundance level requires the use of sensitive instruments like ICP-AES or ICP-MS.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is currently recognized as one of the well-established, cost-effective, multi-element technique for the determination of trace elements in

\*For correspondence

mineral exploration programmes due to its good sensitivity and simplicity.<sup>6</sup> However, the major disadvantage of this technique is the spectral interference caused by matrix elements.<sup>7</sup> Hence it is imperative to pre-concentrate and separate trace elements from matrix elements prior to their determination by ICP-AES.

Solvent extraction methods are routinely adopted for the separation and pre-concentration of Th, Sc and Zr in geological matrices.<sup>8–11</sup> Lately solid phase extraction (SPE) methods have replaced solvent extraction methods as it reduces usage, exposure and disposal of solvents, extraction time and increases the enrichment factor and sample throughput.<sup>12–15</sup> Modified activated carbon, carbon nanotubes and oxidised multi-walled carbon nanotubes are used as solid phase extractants for the pre-concentration of scandium.<sup>16–18</sup> Modified polymers,<sup>19, 20</sup> ion imprinted polymers<sup>7</sup> and chelating resins<sup>21</sup> have been employed for the pre-concentration of Th. Charcoal and alginate gel polymers were used as adsorbents for Zr pre-concentration.<sup>22, 23</sup>

Present method describes the use of silica modified with arsenazo-III (SAR III) as an extractant for the pre-concentration of Th, Zr and Sc. Selectivity of solid phase extraction methods is improved by modifying the adsorbents with element specific chelating agents. In the present study, arsenazo III [3,6-bis((2-arsenophenyl)-azo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid] was selected to modify silica as it is a sensitive chelating reagent for Th, Sc, U and Zr.<sup>24–27</sup> Single stage modification of silica by arsenazo-III was carried out in presence of cationic surfactant cetyltrimethylammonium bromide (CTAB). The synthesised adsorbent was used for the pre-concentration of Zr, Th and Sc. Further, the study has been applied to the determination of these elements in rock samples.

## 2. Materials and methods

### 2.1 Instrumentation

ICP-AES: A sequential Jobin Yvon (France) model Jobin Yvon Horiba JY 2000(2) spectrometer was used for all ICP-AES measurements. Optimum instrumental parameters and operating conditions are given in Table 1.

### 2.2 Reagents

Silica gel (CDH make): 100-200 mesh, chromatographic grade, pH 7 for 100g/L slurry.

**Table 1.** Instrumental parameters used for the ICP-AES determination of Th, Zr and Sc.

Parameter	Value
RF Generator	40.68 MHz
Forward power	1000 W
Reflected power	<5 W
Gas flow	12 lit min <sup>-1</sup> (coolant) 0.6 lit min <sup>-1</sup> (sample)
Monochromator	Modified Czerny-turner
Focal Length	640 mm
Diffraction grating	4320 grooves mm <sup>-1</sup>
Wavelength range	170-440 nm
Nebulizer	Burgener Peek Mira Mist
Solution uptake rate	1.0 mL min <sup>-1</sup>
Slits	21 $\mu$ m entrance, and 22 $\mu$ m exit
Detector	Photomultipliers R-106
Observation height	11 mm above load coil
Element	Wavelength
Th	401.913 nm
Zr	348.800 nm
Sc	361.542 nm

pH meter: pH measurements were carried out using Elico digital pH meter LI-122.

Cetyltrimethylammonium bromide (CTAB) (Rolex, India): 0.1% (w/V) solution in water.

Arsenazo III (Aldrich, USA) 0.1% (w/V) solution was prepared by dissolving 0.1g of the reagent in 100 mL of deionized water.

Thorium stock solution (1 mg mL<sup>-1</sup>) was prepared by dissolving spec pure ThO<sub>2</sub> (Johnson Matthey, Germany) in 0.1 M HF - conc. HCl. The fluoride ion was removed after repeated evaporation with concentrated HCl. The residue was dissolved in 100 mL of 3% HCl solution.

1 mg mL<sup>-1</sup> Zr solution: Zr stock solution was prepared by the direct dissolution of ZrOCl<sub>2</sub>·8H<sub>2</sub>O (99.5%) (HIMEDIA) in 100 mL deionised water.

1 mg mL<sup>-1</sup> Sc solution was prepared by dissolving Sc<sub>2</sub>O<sub>3</sub> oxide (99.99%) (Johnson Matthey) in 10 mL of 1:1 HCl solution and diluting to 100 mL with deionised water.

1 mg mL<sup>-1</sup> solutions of Al, Fe, Ca, Mg, Mn, Na and K were prepared from spec pure Al wire (99.99%), Fe<sub>2</sub>O<sub>3</sub> (99.99%), CaCO<sub>3</sub>(99.99%), MgO (99.99%), MnO (99.99%), NaCl (99.99%) and KCl (99.99%) (Johnson Matthey), London

Working standard solutions were prepared by serial dilutions of the stock solution prior to analysis.

Analytical grade oxalic acid, citric acid, tartaric acid, ethylenediaminetetraacetic acid (EDTA), trans-1,

2-cyclohexanediaminetetraacetic acid (CyDTA), diethylenetriaminepentaacetic acid (DTPA), trisodium citrate, ammonium oxalate, hydroxylamine hydrochloride and ascorbic acid were procured from Merck and used without further purification.

### 2.3 Preparation of adsorbent, modification of silica gel

Silica gel was activated by successively immersing it in 1:1 HNO<sub>3</sub> and 1:1 HCl. It was filtered and washed with deionized water until free from acid and then dried in air oven. 50 g of silica was taken in 1.0 litre beaker. 500 mL of de-ionised water was added to it. This solution was mixed with 25 mL of 0.1% (w/V) cetyltrimethylammonium bromide and 25 mL of 0.1% (w/v) arsenazo-III (A III). The solution was kept overnight with occasional stirring. Silica gel coated with arsenazo-III (SAR III) formed was filtered and washed thoroughly to remove un-adsorbed reagent. The adsorbent formed was dried in an air oven at 80 °C. It was stored in plastic vial.

### 2.4 Characterisation of SAR III

Fourier transform infrared spectra were recorded using Bruker FT-IR spectrometer.

### 2.5 Optimisation of parameters for pre-concentration Th, Zr and Sc using SAR III

Batch experiments were carried out to optimise pH, contact time and amount of adsorbent required for adsorption of Th, Zr and Sc to SAR III. The conditions for desorption of these elements from SAR III were also optimised using batch experiments. Solution containing 100 µg each of Th, Zr and Sc was taken in 100 mL beakers and pH of the solutions were adjusted to 0-9 and kept in contact with 0.1 - 5g of SAR III for time durations of 10 minutes to 6 hours. The solutions were filtered and the un-adsorbed elements in the filtrate were determined by ICP-AES. Desorption of these elements from the adsorbent was carried out with different acids and complexing agents like, EDTA, CyDTA, DTPA, trisodium citrate, citric acid, tartaric acid, oxalic acid and ammonium oxalate at different concentrations. Recovered elements in the leach solutions were estimated by ICP-AES.

### 2.6 Column experiments

In column experiments, 1g of SAR III was loaded into column and a solution containing Th, Zr and Sc, adjusted to the suitable pH, was percolated at 1 mL min<sup>-1</sup> flow rate. These elements were eluted with a suitable eluent and determined by ICP-AES.

### 2.7 Adsorption equilibrium (Effect of initial concentration)

Batch experiments were carried out by contacting 200 mg adsorbent with 50 mL solution at pH-3 containing different initial concentrations of Th, Zr and Sc (20 - 100 mg L<sup>-1</sup>) with occasional stirring for 30 minutes. Solutions were filtered and the concentration of the elements remaining in the filtrate was determined by ICP-AES. Adsorption percentage and adsorption capacity (q<sub>e</sub> in mg g<sup>-1</sup>) were calculated using the Equations (1) and (2).

$$\% \text{ Adsorption} = (C_0 - C_e)/C_0 * 100 \quad (1)$$

$$\text{Adsorption capacity } q_e = (C_0 - C_e) * (V/m) \text{ (mg g}^{-1}\text{)} \quad (2)$$

where C<sub>0</sub> is the initial metal ion concentration (mg L<sup>-1</sup>), C<sub>e</sub> is the concentration of metal in the solution at equilibrium (mg L<sup>-1</sup>), V is the volume of the contact solution in litre and 'm' is the dry weight of sample (g). The adsorption isotherms were investigated by varying the elemental concentrations between 20 mg L<sup>-1</sup> and 100 mg L<sup>-1</sup>.

### 2.8 Effect of major elements in the rock on the adsorption of Th, Zr and Sc onto SAR III

Batch experiments were carried out to find the effect of major elements present in rock samples on the adsorption of Th, Zr and Sc onto SAR III. 50 mL water containing 100 µg each of Th, Zr and Sc was doped with different concentrations of elements like Al, Fe, Ca, Mg, Ti, Na and K. pH of the solutions was adjusted to 3 and kept in contact with 200 mg of the adsorbent for 30 minutes. The adsorbent was filtered and washed thoroughly with water to remove salts. The elements adsorbed on SAR III were recovered by leaching with 10 mL of 5% (w/V) ammonium oxalate solution. Recovered elements were estimated using ICP-AES.

### 2.9 Recommended procedure for the determination of Th, Zr and Sc in rock samples

0.5 g powdered rock sample (-200#), was digested with hydrochloric acid and hydrofluoric acid and few drops of sulphuric acid in a platinum dish or Teflon (PTFE) beaker. The digested residue was taken in 200 mL of 3% HCl solution. The insoluble residue, if any, was ignited and fused with 0.5g flux (mixture of 3g  $\text{KHF}_2$  and 1g NaF), heated with concentrated sulphuric acid to remove the fluoride and mixed with the original solution. 10 mL of 5% (w/V) hydroxylamine hydrochloride was added to this solution. pH of the solution was adjusted to 3 with 10% (v/v) Ammonium hydroxide solution and 10% (v/v) HCl. The solution was percolated through a column loaded with 1 g of SAR III at a rate of 1 mL  $\text{min}^{-1}$ . The column was washed free of unabsorbed elements with distilled water. The adsorbed elements in the column was eluted with 10 mL of 5% (w/V) ammonium oxalate solution and recovered Th, Zr and Sc were determined by ICP-AES.

## 3. Results and discussions

### 3.1 Silica modification with arsenazo-III

The reagent arsenazo III (A III) was selected for the modification of silica since it is a well-known complexing agent for thorium,<sup>25, 28–30</sup> zirconium<sup>31, 32</sup> and scandium.<sup>33</sup> SAR III was synthesised by adsorbing the reagent on silica surface in presence of a cationic surfactant cetyl trimethylammonium bromide (CTAB). It was observed that in the absence of surfactant, A III was completely removed from the silica surface during washing. The surfactant Cetyltrimethylammonium bromide (CTAB) acts as a bridge between silica and A III molecule. The cationic surfactant CTAB gets adsorbed onto the silica surface due to the electrostatic attraction between positively charged head group of surfactant  $[(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{15}(\text{CH}_3)]$  and negatively charged silanol ( $\text{SiO}^-$ ) group on the silica.<sup>34</sup> CTAB forms a bi-layer on silica surface where the upper layer of surfactants have hydrophilic groups exposed to bulk water and their hydrophobic tail remains entangled with the tail group of surfactant molecule adsorbed onto silica gel.<sup>35</sup> A III molecule gets embedded into these bilayer. A III molecule, thus, coated on the silica surface can form chelating complexes with metal ions. This property of the adsorbent is used for the pre-concentration of Th, Zr and Sc from the solution (Figure 1).

### 3.2 Characterisation of SAR III

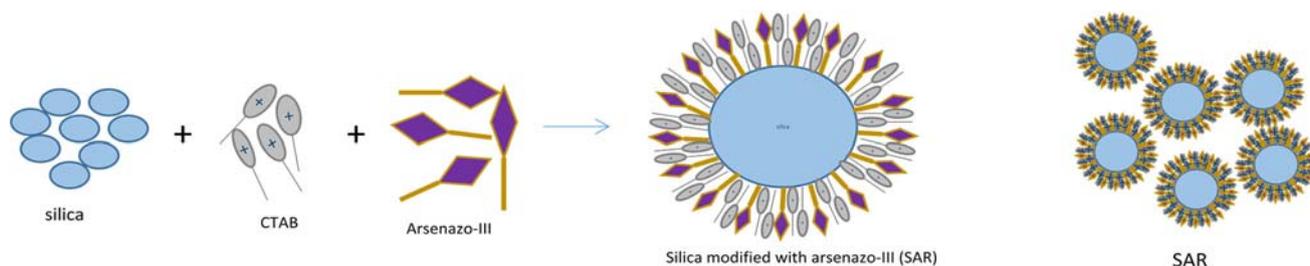
The FT-IR analysis is a very useful technology in identifying the immobilization process by comparing the precursor and modified surfaces. An intense band at  $1057\text{cm}^{-1}$  corresponding to Si–O–Si stretching vibration was present in the IR spectrum of silica gel. The same was observed in the spectra of SAR III. This confirms that the functionalization of silica gel with A III was outside the silica core and has no effect on the Si–O–Si structural framework. On the other hand, IR spectra of silica gel showed a characteristic Si–OH stretching band at  $956\text{cm}^{-1}$ . The peak was shifted to  $945\text{cm}^{-1}$  in case of SAR III. These shifts confirm the adsorption of SAR III on silica gel as Si–O–A III. Weak broad band in the region of  $3300\text{--}3500\text{cm}^{-1}$  was due to intra molecular hydrogen bonding of hydroxyl groups present on silica gel. The disappearance of the same band in SAR III infers that hydroxyl groups are not free, which is due to the adsorption of A III. This further confirms the adsorption of A III onto silica gel. Also, the presence of peaks at  $1237\text{cm}^{-1}$  and  $1210\text{cm}^{-1}$  in SAR III corresponds to aromatic hydroxyl and aromatic ketonic group further support the presence of A III on silica surface (Figure 2).

### 3.3 Effect of pH on the adsorption

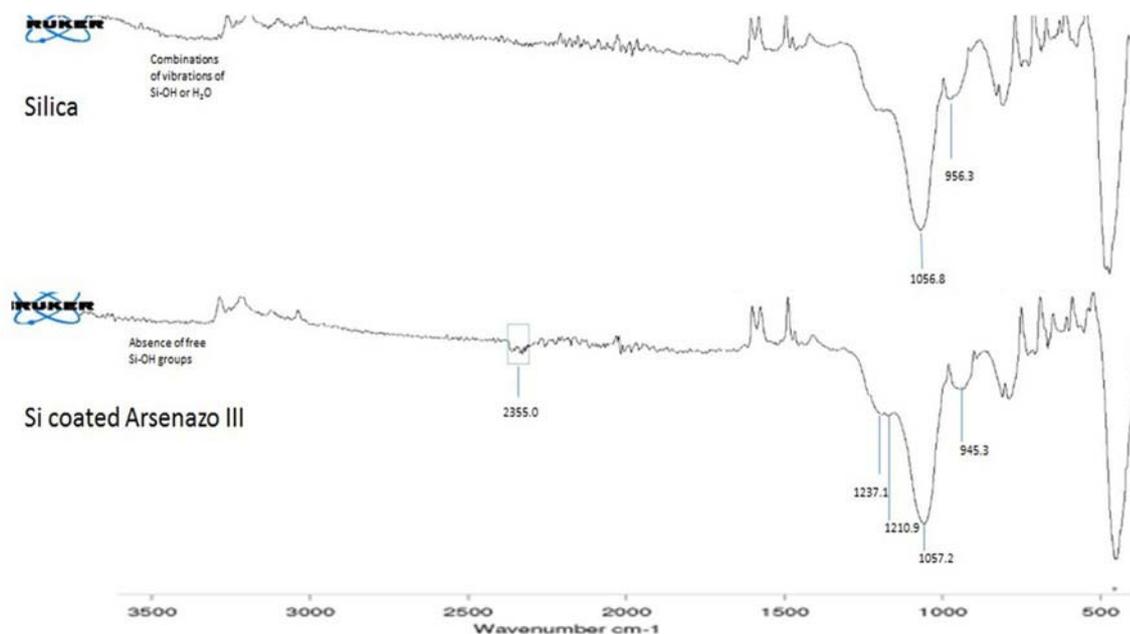
The effect of the initial solution pH is a very important parameter for adsorption of a metal ion onto an adsorbent. The effect of pH on adsorption is based on the ionic state of metal ions and the chelating agent in the solution. The influence of pH was investigated by keeping 50 mL of  $1\text{ }\mu\text{g mL}^{-1}$  Th, Zr and Sc in contact with 500 mg of SAR III by varying pH (Figure 3). On increasing the pH from 0 to 3, adsorption of Th and Sc increased sharply. In the case of Zr, 85% adsorption was observed even at pH-2. With increase in pH from 0-3, ionisation of hydroxyl groups on the A III molecule takes place which results in increased adsorption. Optimum pH for the adsorption of these elements on SAR III was selected as pH 3 for further studies.

### 3.4 Effect of adsorbent weight on adsorption

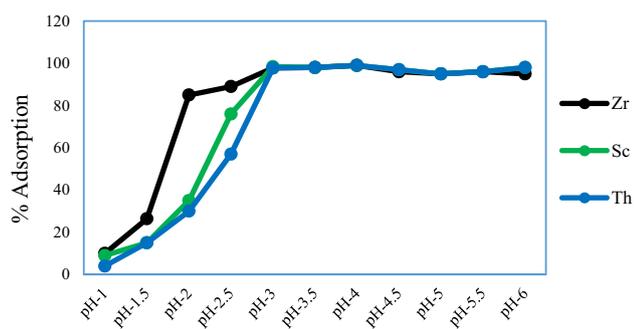
From Figure 4, it is evident that quantitative adsorption occurs from 200 mg of adsorbent and there is no change in adsorption above this amount. Hence, 200 mg of adsorbent was selected as optimum weight for the adsorption of  $1\text{ }\mu\text{g mL}^{-1}$  Th, Zr and Sc at pH-3 for 50 mL sample volume.



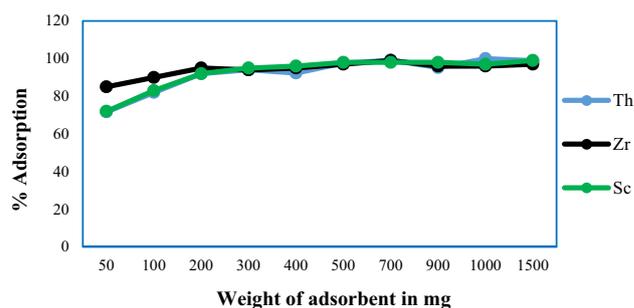
**Figure 1.** Schematic representation of formation of silica modified with arsenazo-III.



**Figure 2.** IR spectrum of silica and SAR III.



**Figure 3.** Variation of % adsorption of Th, Zr and Sc onto SAR III with pH of the solution.



**Figure 4.** Variation of % adsorption of Zr, Th and Sc onto SAR III with quantity of adsorbent.

### 3.5 Effect of contact time on adsorption

The time dependence of adsorption of Th, Zr and Sc is given in Figure 5. The percentage adsorption was more than 95% from 30 min onwards. After that, the adsorption efficiency became constant.

### 3.6 Adsorption capacity

Adsorption capacity was investigated by studying the adsorption at different initial concentrations of Th, Zr and Sc. Elemental concentrations in the range of 20-100 mg L<sup>-1</sup> were used for this study. Adsorption capacity ( $q_e$ ) was calculated from equation (2).

Langmuir equation for monolayer adsorption onto a surface with a finite number of identical sites can be expressed as:

$$C_e/q_e = C_e/q_m + 1/K_L * q_m \quad (3)$$

where  $C_e$  is the concentration of metal in the solution at equilibrium ( $\text{mg mL}^{-1}$ ),  $q_m$  is the maximum monolayer adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_L$  is the Langmuir constant related to the free energy of adsorption ( $1/\text{mg}$ ). A plot of  $C_e/q_e$  versus  $C_e$  yields a straight line with slope  $1/q_m$  and intercepts  $1/q_m K_L$ . Adsorption capacity is calculated from slope of the curve.

Figure 6(a–c) shows the adsorption isotherms of Th, Zr and Sc on SAR III. Maximum adsorption capacity calculated was  $5.68 \text{ mg g}^{-1}$  for Th,  $23.9 \text{ mg g}^{-1}$  for Zr and  $4.42 \text{ mg g}^{-1}$  for Sc. Adsorption capacities for selected adsorbents are given in Table 2. Adsorption capacity of Zr for SAR-III is more compared to other adsorbents.

### 3.7 Desorption of elements from the adsorbent

Desorption of Th, Zr and Sc was studied with different concentration of various complexing agents. Result obtained is given in Figure 7. Quantitative recovery of Sc was observed with HCl,  $\text{HNO}_3$ , citric acid, tartaric acid and ammonium oxalate. However, only ammonium oxalate was able to quantitatively recover of Th from adsorbent. Even though oxalic acid was able to recover Zr quantitatively, recovery of Th was not quantitative and that of Sc was very less. Ammonium oxalate was selected as eluting reagent for these elements since it was able to elute all elements quantitatively. Quantitative recovery observed with ammonium oxalate in comparison with other reagents is due to the formation of soluble complexes of these elements with ammonium oxalate. Zirconium gave quantitative recovery in presence of oxalic acid and ammonium oxalate because it forms oxalate complex

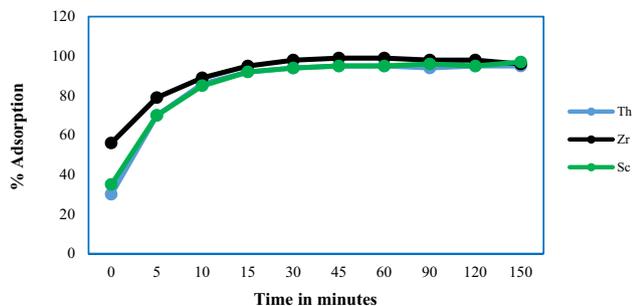


Figure 5. Variation of % adsorption with time.

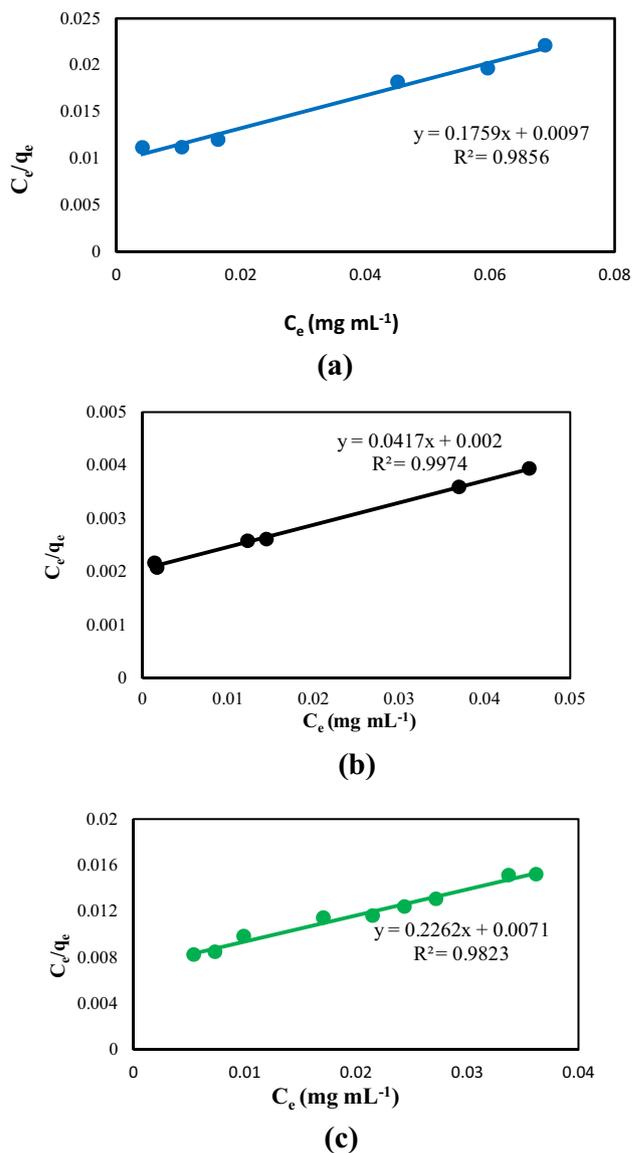


Figure 6. Langmuir plots for adsorption of (a) Th, (b) Zr and (c) Sc by SAR III

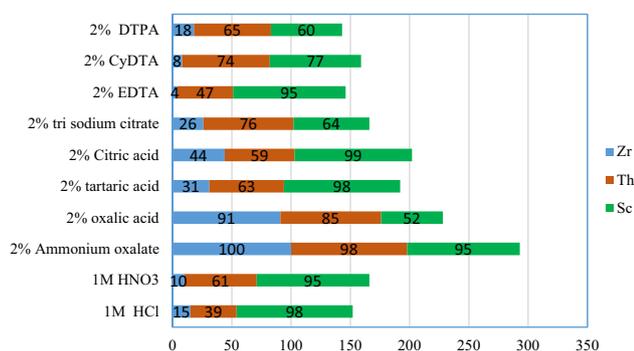
at acidic and neutral pHs.<sup>40</sup> Recovery of thorium was less in presence of oxalic acid as it forms insoluble oxalate complexes at lower pHs.<sup>41</sup> Sc is also known to form soluble oxalates in neutral or slightly acidic pHs.<sup>42</sup>

### 3.8 Column studies

Studies were carried out to find the feasibility of above method for column experiments. Solution containing Th, Zr and Sc at pH 3 was passed through a column of 1g adsorbent at a flow rate of  $1 \text{ mL min}^{-1}$ . Adsorbed elements were eluted with 10 mL of 5 % ammonium oxalate solution. Quantitative recoveries were obtained.

**Table 2.** Adsorption capacities for Th, Zr and Sc using other adsorbents.

Ion	Adsorbent used	Adsorption capacity			References
		Th mg g <sup>-1</sup>	Zr mg g <sup>-1</sup>	Sc mg g <sup>-1</sup>	
Th	UiO-66-OH zirconium metal-organic framework	47.5			36
Th	mesoporous silica (MCM-41) modified using 5-nitro-2-furaldehyde (fural)	49.0			37
Th	Thorium imprinted N-propylmaleamic acid—functionalized silica gel (PMASG)	35.9			7
Sc	Carbon nanotubes			42.0	17
Sc	Silica gel modified with 1-(2-aminoethyl)-3-phenylurea			32.5	38
Sc	4-(2-morinyldiazenyl)-N-(3-(trimethylsilyl)propyl)benzamide modified silica gel (SG-MTPB)			27.0	39
Zr	Charcoal in nitric acid medium		17.5		22



**Figure 7.** Extraction percentage of Th, Zr and Sc with different solutions.

### 3.9 Validation of the method

The present pre-concentration method was validated by applying the procedure using standard solutions of Th, Zr and Sc. Eight standard solutions were simultaneously processed by the proposed procedure and reproducibility of the method was accessed. Relative standard deviation obtained was in the range 1-2.5% which indicated very good precision of the method for the determination of Th, Zr and Sc. Detection limit of the method for Th, Zr and Sc were calculated as three times the standard deviation obtained by applying the

proposed method in ten blank solutions. The detection limit obtained for this procedure is 1.0 µg mL<sup>-1</sup> for Th and Zr and 0.1 µg mL<sup>-1</sup> for Sc.

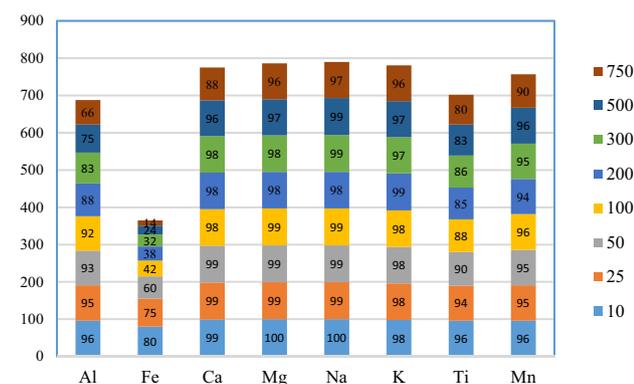
### 3.10 Effect of major elements in the rock on the adsorption of Th, Zr and Sc on SAR III

Batch experiments were carried out to find the effect of different major elements on the adsorption of Th, Zr and Sc on to SAR III and the results are given in Figure 8(a-c). Presence of Na, K, Ca and Mg did not interfere on the adsorption of these elements on SAR III. 20% suppression in recovery was observed when aluminium was present above 200 mg L<sup>-1</sup>. Maximum suppression was observed in presence of iron. 60% suppression was observed for iron concentration above 50 mg L<sup>-1</sup>. Slight suppression in recovery was observed at higher Ti<sup>4+</sup> concentration. Suppression in presence of Fe<sup>3+</sup>, Al<sup>3+</sup> and Ti<sup>4+</sup> can be ascribed to the preferential formation of arsenazo III complexes of these elements when they are present at very high concentration.

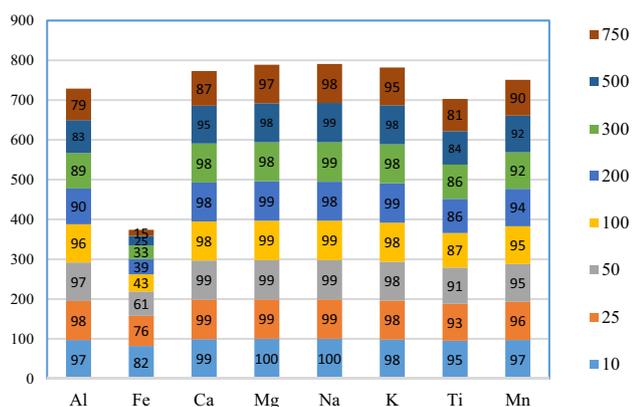
It is reported that Fe<sup>2+</sup> ion does not form complex with arsenazo III.<sup>43</sup> Hence, the adsorption was studied with 250 mg L<sup>-1</sup> of Fe in presence of reducing agents like ascorbic acid, hydroxylamine hydrochloride and

**Table 3.** Comparative result of Th, Zr and Sc from certified reference materials.

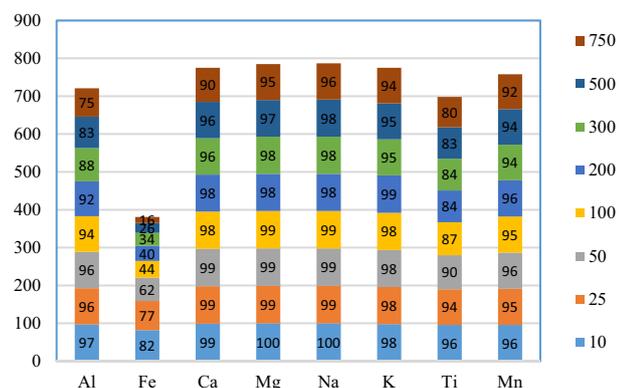
CRM ↓	Present method µg/mL			Certified values µg/mL		
	Th	Zr	Sc	Th	Zr	Sc
SY-2	380	280	7	398	285	7.5
BCR-1	6	190	33	5.6	201	30
GS-N	41	235	7.3	35	245	6.9
AGV	12	370	2.1	11	372	1.8



(a)



(b)



(c)

**Figure 8.** Variation of % adsorption of (a) Th, (b) Zr and (c) Sc onto SAR III with different concentration of major elements in  $\text{mg L}^{-1}$ .

sodium sulphite. Out of the three reducing agents studied, quantitative recovery was obtained with 5% (w/V) solution of hydroxylamine hydrochloride. Further studies have shown that 4 mL of 5% (w/V) solution of hydroxylamine hydrochloride was enough for suppressing interference of  $250 \text{ mg L}^{-1}$  of  $\text{Fe}^{3+}$ . Hence, an optimum amount of 10 mL of 5% (w/v)

hydroxylamine hydrochloride was selected to complex iron concentrations up to 25%. The suppression in recovery of Th, Zr and Sc was observed when concentration of Al and Ti in the solutions was above  $500 \text{ mg L}^{-1}$  and  $100 \text{ mg L}^{-1}$  respectively in the solution. Hence, this method can be applied to rock samples with  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  content below 30 % and 4 %, respectively. Most of the rock samples, unless mineralised, Al and Ti contents are well below this level.

### 3.11 Application of method to certified reference samples

Accuracy of the proposed method was tested by analysing two certified reference materials (CCRMP, Canada) SY-2, BCR-1(USGS), GSN (ANRT, France) and AGV-1(USGS). The values obtained are given in Table 3. These are in good agreement with the certified values.

## 4. Conclusion

A novel single step synthesis procedure for silica modified with arsenazo III has been developed. The synthesized adsorbent has been applied for the pre-concentration, separation and determination of Th, Zr and Sc in rock samples. Adsorption capacities of Th, Zr and Sc for SAR III are  $5.68$ ,  $23.9$  and  $4.42 \text{ mg g}^{-1}$  respectively, which is much higher than that of other common adsorbents. This adsorbent has a good potential to separate these elements from high concentration of alkali, alkaline earth and other elements present in rock samples. Iron interference on the adsorption was eliminated by reducing ferric iron to ferrous iron with hydroxylamine hydrochloride. The results obtained by applying the method on certified reference samples are in good agreement with certified values.

## Acknowledgement

Authors are thankful to the Director, AMD, Additional Director (OP-I), AMD, Regional Director, AMD/SR and Head Chemistry Group, AMD for providing the technical support to carry out the present work. Authors wish to thank chemistry department, Bangalore University, India for FT-IR data.

## References

- Kaynar U H, Ayvacikli M, Hicsonmez U and Kaynar S C 2015 Removal of thorium ions from aqueous solutions by nano porous ZnO; isotherm, kinetics and

- thermodynamic studies, *J. Environ. Radioactivity* 150 145
2. Linnen R L, Samson I M, Williams-Jones A E and Chakhmouradian A R 2014 *Geochemistry of the rare earth elements, Nb, Ta, Hf, and Zr Deposits*, Elsevier, Amsterdam
  3. Hedrick J B 2010 *Mineral Commodity Summaries* U.S. Geol. Surv. 1 196
  4. Srivastava R K 2006 Geochemistry and petrogenesis of neo-archaeon high-Mg low-Ti mafic igneous rocks in an intracratonic setting, Central India craton: Evidence for boninite magmatism. *Geochem. J.* 40 15
  5. Taylor S R 1964 Abundance of chemical elements in continental crust – a new table *Geochem. Cosmochim. Acta* 28 1275
  6. Jarvis I and Jarvis E 1992 Inductively coupled plasma-atomic emission spectrometry in exploration geochemistry *J. Geochem. Explor.* 44(1–3) 139
  7. He Q, Chang X, Wu Q, Huang X, Hu Z and Zhai Y 2007 Synthesis and application of surface grafted Th (IV) imprinted polymers for selective solid phase extraction of thorium *Anal. Chim. Acta* 605 92
  8. Fujino O, Umetani S, Ueno E, Shigeta K and Matsuda T 2000 Determination of uranium and thorium in apatite minerals by inductively coupled plasma- atomic emission spectrometry with solvent extraction separation into isobutyl ketone *Anal. Chim. Acta* 420 (1) 65
  9. Cyriac B and Durani S 2013 Determination of rare earth elements and yttrium in zircons by plasma emission spectrometry after solvent extraction separation of zirconium with di (2-ethyl hexyl)phosphoric acid *J. Indian. Chem. Soc.* 90(11) 2099.
  10. Fukuma H T, Fernandes E A N, Nascimento M R L and Quinelato A L 2000 Separation and spectrophotometric determination of thorium contained in uranium concentrate *J. Radioanal. Nucl. Chem.* 248 (3) 549
  11. Tran Q T, Le V T and Nguyen V C 2016 Solvent extraction of thorium using 5,11,17,23-Tetra[(2-ethyl-aceto-ethoxyphenyl)(azo)phenyl]calix[4]arene *J. Chem.* article id No 5078462,
  12. Sani A R, Bandegharai A H, Hosseini S H, Kharghani K, Zarei H and Rastegar A 2015 Kinetic, equilibrium and thermodynamic studies on sorption of uranium and thorium from aqueous solutions by a selective impregnated resin containing carminic acid *J. Hazard. Mater.* 286 152
  13. Trujillo I S, Alonso E V, Torres A G and Cano Pavón J M 2012 Development of a solid phase extraction method for the multielement determination of trace metals in natural waters including sea-water by FI–ICP–MS *Microchem. J.* 101 87–94
  14. Thuman E M and Mills M S 1998 *Solid phase Extraction- Principles and Practice*, Wiley, New York.
  15. Simpson J K 2000 *Solid Phase Extraction: Principles, Strategies and Applications*. Marcel Dekker, New York.
  16. Burakova I V, Burakov A E, Tkachev A G, Troshkina I D, Veselova O A, Babkin A V, Aung W M and Ali I 2018 Kinetics of the adsorption of scandium and cerium ions in sulfuric acid solutions on a nano modified activated carbon *J. Mol. Liq.* 253 277
  17. Pęgiel M, Kilian K and Pyrżyńska K 2018 Enrichment of scandium by carbon nanotubes in the presence of calcium matrix *Microchem. J* 137 371
  18. Jerez J, Isaguirre A C, Bazán C, Martínez L D and Cerutti S 2014 Determination of scandium in acid mine drainage by ICP-OES with flow injection on-line pre-concentration using oxidized multi-walled carbon nano tubes *Talanta* 124 89
  19. Jain V K, Handa A, Sait S S, Shrivastav P and Agrawal Y K 2002 Pre-concentration, separation and trace determination of lanthanum (III), cerium (III), thorium (IV) and uranium (VI) on polymer supported o-vanillin semicarbazone *Anal. Chim. Acta* 429 (2) 237
  20. Jain V K, Pandya R A, Pillai S G and Shrivastav P S 2006 Simultaneous pre-concentration of uranium (VI) and thorium(IV) from aqueous solutions using a chelating calix[4]arene anchored chloromethylated polystyrene solid phase *Talanta* 70 257
  21. Aydin F A and Soylak M 2006 Solid phase extraction and preconcentration of uranium (VI) and thorium (IV) on Duolite XAD761 prior to their inductively coupled plasma mass spectrometric determination. *Talanta* 72 187
  22. Hamed M M, Rizk H E and Ahmed I M 2018 Adsorption behavior of zirconium and molybdenum from nitric acid medium using low-cost adsorbent *J. Mol. Liq.* 249 361
  23. Onishi T, Koyama S and Mimura H 2015 Removal of zirconium from spent fuel solution by alginate gel polymer *Prog. Nucl. Energy* 82 69
  24. Savvin S B 1961 Analytical use of arsenazo III- Determination of thorium, zirconium, uranium and rare earth elements. *Talanta* 8 673
  25. Ku S, Obarsky N and Marczenk Z 1992 Determination of thorium, uranium and zirconium with arsenazo III using third order derivative spectroscopy *Anal. Sci.* 8 213
  26. Jauberty L, Drogat N, Decossas J L, Delpech V, Gloaguen V and Sol V 2013 Optimization of the arsenazo-III method for the determination of uranium in water and plant samples *Talanta* 115 751
  27. Matharu K, Mittal S K, Ashok Kumar S K and Sahoo S K 2015 Selectivity enhancement of Arsenazo(III) reagent towards heavier lanthanides using polyaminocarboxylic acids: A spectrophotometric study *Spectro. Chim. Acta Part A* 145 165
  28. Rohwer H, Rheeder N and Hosten E 1997 Interactions of uranium and thorium with arsenazo III in an aqueous medium *Anal. Chim. Acta* 341 263.
  29. Shevoeva O P, Dedkova V P and Savvin S B 2007 Sorption and complexation of uranium (VI) and thorium (IV) with arsenazo III and arsenazo M fibrous filled sorbents, *J. Anal. Chem.* 62(10) 935
  30. Khan M H, Ali A and Khan N N 2001 Spectrophotometric determination of thorium with disodium salt of arsenazo III in perchloric acid medium *J. Radioanal. Nucl. Chem.* 250 (23) 353
  31. Tikhomirova T I and Ivanov A V 2016 Surface modification of zirconia by Arsenazo III *Mendeleev Commun.* 26 259
  32. Zhai Q Z 2008 Determination of trace amount of oxalic acid with zirconium (IV)–(DBS-arsenazo) by spectrophotometry *Spectro. Chim. Acta Part A* 71 332
  33. Onishi H and Banks C V 1963 Spectrophotometric determination of scandium with arsenazo III *Anal. Chim. Acta* 29 240

34. Israclachvilli N and Pashely R M 1984 Measurement of hydrophobic interaction between two hydrophobic surfaces in aqueous electrolyte solution *J. Col. Inter Sci* 98 500
35. Rennie R, Lee E M, Simister E A and Thomas R K 1990 Structure of cationic surfactant layer at the silica water inter phase *Langmuir* 6 1031
36. Moghaddam Z S, Kaykhaii M, Khajeh M and Oveisi A R 2018 Synthesis of UiO-66-OH zirconium metal-organic framework and its application for selective extraction and trace determination of thorium in water samples by spectrophotometry *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 194 76
37. Yousefia S R, Ahmadib S J, Shemirania F, Jamalic M R and Salavati-Niasari M 2009 Simultaneous extraction and preconcentration of uranium and thorium in aqueous samples by new modified mesoporous silica prior to inductively coupled plasma optical emission spectrometry *Talanta* 80 212
38. Tu Z, Hu Z, Chang X, Zhang L, He Q, Shi J and Gao R 2010 Silica gel modified with 1-(2-aminoethyl)-3-phenylurea for selective solid-phase extraction and preconcentration of Sc(III) from environmental samples *Talanta* 80 1205
39. Zhang L, Chang X, Zhai Y, He Q, Huang X, Hu Z and Jiang N 2008 Selective solid phase extraction of trace Sc(III) from environmental samples using silica gel modified with 4-(2-morinyldiazenyl)-N-(3-(trimethylsilyl)propyl)benzamide *Analytica Chimica Acta* 629(1-2) 84
40. Hummel W 2005 *Chemical thermodynamics of compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands* Editors. Mompean. J, Illemassene. M, Perrone. J, OECD Nuclear agency, France
41. Kobayashi T, Sasaki T, Takagi and Moriyama I H 2012 Solubility of thorium (IV) in the presence of oxalic and malonic acids *J. Nucl. Sci. Technol.* 46 (11) 1085
42. Li D and Wang C 1998 Solvent Extraction of Scandium-III/ by Cyanex 923 and Cyanex 925 *Hydrometallurgy* 48 301
43. Sekin K 1976 Separation and spectrophotometric determination of uranium (VI) by extraction with arsenazo-III and zephiramine *Microchimica Acta* 66(5-6) 559