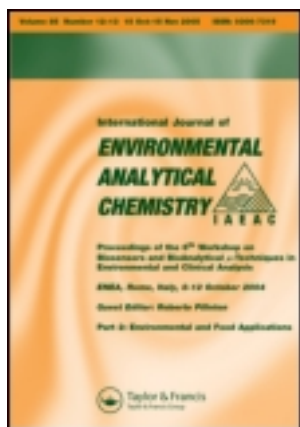


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Selective preconcentration of trace thorium from aqueous solutions with Th(IV)-imprinted polymers prepared by a surface-grafted technique

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A novel ion-imprinted adsorbent for selective solid phase extraction of thorium(IV) based on the surface of silica gel was prepared by a surface-grafted technique with methacrylic acid (MAA) as a functional monomer. After removal of Th(IV) ions with 3 mol L⁻¹ HCl solution, the obtained imprinted particles for Th(IV) exhibited specific recognition and relatively rapid kinetic process. The maximum static and total dynamic adsorption capacity of the ion-imprinted polymers (IIPs) for Th(IV) was 33.2 and 17.3 mg g⁻¹, respectively. A comparison of the selectivity coefficient of the imprinted polymers with that of non-imprinted polymers showed that the imprinted matrix for Th(IV)/U(VI), Th(IV)/Ce(III), Th(IV)/La(III) and Th(IV)/Zr(IV) was 58.8, 107, 106.4 and 151.7 times greater than non-imprinted matrix, respectively. With a series of samples loading flow rate of 3 mL min⁻¹ for preconcentration, an enrichment factor of 14.6 and the detection limit of 0.59 µg L⁻¹ were obtained. The relative standard deviation of the method under optimum conditions was 2.1% (*n* = 7). The developed method was successfully applied to the determination of trace Th(IV) in real water samples with satisfactory results.

Keywords: ion-imprinted polymers; solid phase extraction (SPE); thorium(IV); silica grafting; spectrophotometric determination

1. Introduction

Thorium is a naturally occurring radioactive element widely distributed over the earth's crust and has extensive application in industry, e.g. optics, radio, aeronautics and aerospace, metallurgy and chemical industry, and material fields [1]. And more importantly, it can act as nuclear energy for generating electricity [2]. Unfortunately, thorium, which is a toxic heavy metal, is not only known to cause acute toxicological effects for humans and its compounds are potential occupational carcinogens, but it also has radioactivity, which in acute cases may lead to kidney and liver failure and death [3]. Additionally, thorium and its compounds are hazardous, causing environmental problems. Because of its extensive usage, health and safety, the development of reliable methods for the separation and recovery, and determination of thorium in environmental and geological samples, are of a particular significance [4]. Thorium and rare-earth elements, zirconium, and uranium often coexist in their minerals, products, and even in wastewater.

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However, the separation of thorium from these elements is difficult and limited because their compounds show similar properties to thorium [5]. As a result, preconcentration or sample clean-up step to facilitate selective extraction and sequential separation of analytes prior to its detection is required [6].

Several separation techniques have been developed in the past for this purpose, including liquid-liquid extraction (LLE) [7,8], solid phase extraction (SPE) [9,10], ion exchange, and flotation, etc. Of all the preconcentration methods, the SPE method is currently being used as a preconcentration or separation technique whenever there are complex matrices or low concentration, owing to its flexible working conditions and simple procedures. In SPE, the choice of adsorbent is a key point because it can control the analytical parameters, such as selectivity, affinity and capacity [11]. Ion imprinted polymers as adsorbents of SPE are a recent innovation, which offer higher selectivity and retention capacity.

Ion imprinting is a versatile technique for preparing polymeric materials that are capable of high ionic recognition and a way of making selective binding sites in synthetic polymers by using ion template. During the imprinting procedure, the template forms a complex with the constituent monomers. By removing the template, it leaves construction, which is selective for the template and not any other structurally related compounds. Due to the specific recognition sites offered by IIPs these materials have attracted widespread attention as highly selective adsorbents for SPE [12–15]. Surface imprinting is one of the important types of imprinting methods. Surface-based imprinted polymer is simple and convenient to prepare. Moreover, surface ion imprinted polymers not only possess high selectivity but also avoid problems with mass transfer [16]. More recently several studies have reported ion-imprinted materials based on surface imprinting [17–19].

Methacrylic acid (MAA) has been reported as a complexing monomer for many metal ions in ion imprinting [20,21]. However, to the best of our knowledge, its complexing with Th(IV) has not yet been explored. Thus, in this study, we proposed a new approach with MAA as a monomer for the preparation of surface-grafted ion-imprinted polymers specific for Th(IV). Polymerisable double bond was introduced to the surface of silica gel by reaction between $-OH$ and maleic anhydride rather than by amidation reaction [19]. In the ion-imprinting process, thorium(IV) was complexed with MAA, then imprinted in the polymers grafted to the surface of silica gel. After removal of Th(IV) ions, the characterisation of this imprinted adsorbent and its applicability to selective solid-phase extraction of Th(IV) coupled with UV-Vis spectrophotometry are described and discussed in detail.

2. Experimental

2.1 Instruments and apparatus

A Perkin-Elmer Lambda 45 UV/Vis spectrometer (Perkin Elmer, USA) and 10-mm quartz cells were used for the determination of metal ions concentrations. IR Spectra ($4000-400\text{ cm}^{-1}$) in KBr pellets were recorded using IRPrestige-21 (Shimadzu, Japan) Elemental analysis was performed on CE-440 VarioEL element analyser (Perkin Elmer, USA). The specific surface area and pore size of the adsorbent were measured using the Brunauer-Emmett-Teller (BET) model on ASAP2020M specific surface area analyzer (Micromeritics, USA). A peristaltic pump, Longfang Instrument Fitting Factory (Wenzhou, China), was applied to the preconcentration process. A pHs-10C digital pH meter, Pengshun Scientific Instruments Research (Shanghai, China), was used for the

pH adjustments. A variable speed reciprocal shaker and lab-made glass microcolumn were employed for static and dynamic studies, respectively.

2.2 Reagents and materials

Unless otherwise stated, reagents of analytical purity were used for all experiments and doubly distilled water (DDW) was used throughout.

Silica gel (40–60 μm) (SIL), maleic anhydride (MAH), azobisisobutyronitrile (AIBN) (98%), sodium chloroacetate, chloroacetic acid and methacrylic acid (MAA) were supplied from Aladdin (Shanghai, China). Ethylene glycol dimethacrylate (EGDMA) was purchased from EHSY (Shanghai, China). 3-Glycidoxypolytrimeth oxysilane (WD-60) was obtained from Wuhan University Silicone New Material Co. (Hubei, China). $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (SP) and other chemicals were purchased from Hengrui New Materials (Chengdu, Sichuan, China).

Standard stock solution of Th(IV) (1 mg mL^{-1}) was carefully prepared by dissolving spectral pure grade chemicals and made up in 1 mol L^{-1} HNO_3 . Standard stock solutions of other ions (1 mg mL^{-1}) were prepared according to standard method and further diluting daily prior to use as well. The buffer solution of pH 3 was prepared with mixing 0.1 mol L^{-1} NH_4Cl (100 mL) and 0.1 mol L^{-1} HCl (0.9 mL). EGDMA and MAA were distilled under reduced pressure. AIBN was recrystallised from ethanol three times before use. Toluene was freshly distilled over sodium.

2.3 Synthesis of SPE polymers

2.3.1 Preparation of carboxylic acid-functionalised silica gel (SIL-COOH)

Silica gel (SIL) was first activated by dipping in $\text{HNO}_3/\text{H}_2\text{O}$ solution (50 mL/50 mL) for 24 h, then it was filtered off, washed repeatedly with DDW until neutral and acetone, and dried in a vacuum at 110°C for 12 h.

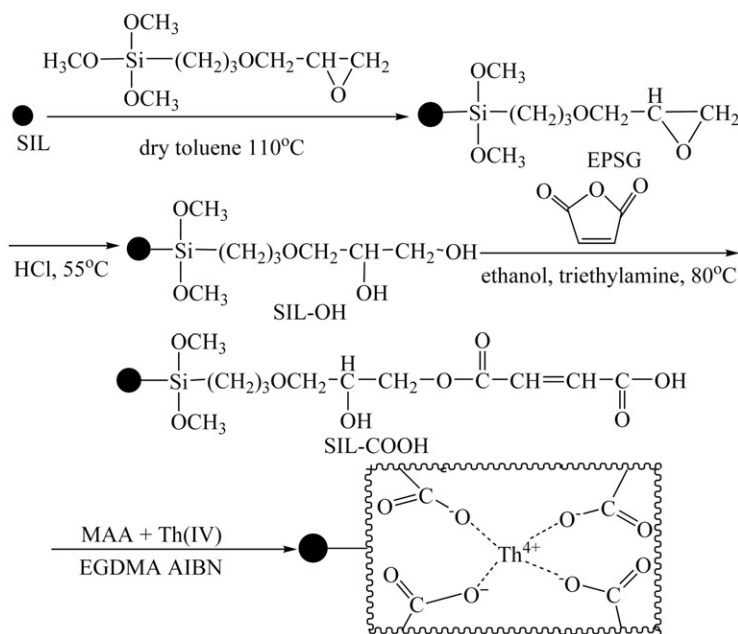
Synthesis procedure of epoxypropyl silica gel (EPSG) was given as follows: A mixture of activated SIL (10 g) and WD-60 (4 mL) in dry toluene (150 mL) was refluxed for 10 h under nitrogen atmosphere. The obtained product was filtered off, washed carefully with toluene and acetone, and dried in a vacuum at room temperature for 24 h.

SIL-OH was synthesised using the following procedure: EPSG (10 g) was added in a three-necked flask containing 0.05 mol L^{-1} HCl solution (100 mL). After refluxing the mixture for 2 h under nitrogen atmosphere, the particles (SIL-OH) were filtered off, washed with acetone and dried in a vacuum at room temperature for 24 h.

Carboxylic acid-functionalised silica gel (SIL-COOH) was prepared according to the following procedure: SIL-OH (10 g) was suspended in ethanol (50 mL). Then a solution of maleic anhydride (MAH) (4.9 g) and triethylamine (1.4 mL) in ethanol (50 mL) was added. After the mixture was stirred and heated at 80°C for 8 h, the resulting products were washed with ethanol and DDW, and dried in a vacuum at 80°C for 12 h.

2.3.2 Synthesis of the Th(IV)-imprinted and non-imprinted polymers

A solution of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (2 mmol) in methanol (25 mL) was added dropwise into a glass reactor containing MAA (4 mmol) in methanol (25 mL) with continuous stirring for 3 h at room temperature. And then SIL-COOH (2 g), AIBN (0.12 g) and EGDMA (4 mL)



Scheme 1. Preparation of the Th(IV)-imprinted polymers.

was added. Afterwards, the reactor was degassed by an ultrasonic steric-cleaner and flushed by bubbling nitrogen for 15 min then sealed. The mixture was stirred and heated at 60°C for 24 h. The synthesis scheme for Th(IV)-imprinted polymers is described in Scheme 1. The resulting products were filtered off, washed with methanol/water (1 : 1), and treated with adequate 3 mol L^{-1} HCl solution for 12 h to remove Th(IV) from the polymers. The final polymers were cleaned with DDW several times until acid-free and dried under vacuum at 70°C for 24 h. Non-imprinted polymers were also prepared using an identical procedure without adding $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$.

2.4 Procedure

2.4.1 Static adsorption test

A series of thorium(IV) standard solutions were transferred into the 10 mL colour comparison tubes, and the pH values were adjusted to the desired values with 0.1 mol L^{-1} HNO_3 or 0.1 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$. After the volume was adjusted to 10 mL with DDW, Th(IV)-imprinted or non-imprinted polymers (25 mg) were added, and the mixture was shaken vigorously for 30 min. After the mixture was centrifuged (3000 rpm, 5 min), the concentrations of thorium ions in the solutions were determined by spectrophotometry using Arsenazo-III (0.05% w/v) as a chromogenic agent in 3 mol L^{-1} HNO_3 medium at 658 nm. The amount of the Th(IV) adsorbed on the polymer was calculated by using the following equation:

$$Q = (C_0 - C_e) \frac{V}{W} \quad (1)$$

Table 1. Elemental analysis of each step product and after saturation adsorption of Th(IV) on IIPs.

	C (%)	H (%)
SIL-OH	4.52	2.17
SIL-COOH	5.81	1.94
NIIPs	19.83	3.32
IIPs	19.83	3.32
IIPs (After saturation adsorption of Th(IV))	16.74	3.19

Here, Q represents the amount of the Th(IV) adsorbed on the polymer (mg g^{-1}), C_0 and C_e represent the initial and equilibrium concentration of Th(IV) ($\mu\text{g mL}^{-1}$), respectively, W is the amount of polymer (g), and V is the volume of metal ions solution (L).

2.4.2 Dynamic adsorption test

Th(IV)-imprinted or non-imprinted polymers (100 mg) were packed into a glass column (120 mm \times 5.5 mm i.d). Upon activation with methanol, it was treated with 0.5 mol L^{-1} HCl, washed with DDW once then the column was conditioned to the desired pH with buffer solution of pH 3. Then each solution was passed through the column after adjusting the appropriate pH at a flow rate of 3 mL min^{-1} . Afterwards, the bound metal ions were stripped off from the column with 1 mol L^{-1} HCl solution (5 mL) at a flow rate of 0.8 mL min^{-1} . The concentration of the Th(IV) ions in the eluent was determined by spectrophotometry using Arsenazo-III (0.1% w/v) as a chromogenic agent in 5 mol L^{-1} HCl medium at 660 nm. U(IV) (at 658 nm) and Ce(III)-La(III) (at 652 nm) were determined in buffer solutions of chloroacetic acid-sodium chloroacetate of pH 2.5 and 2.8, respectively, while Zr(IV) was determined in 6 mol L^{-1} HCl medium at 662 nm using Arsenazo-III as a chromogenic agent and against a reagent blank as the reference for all. All the experiments were carried out in triplicates and the error limit was within the relative standard deviation of 5%.

3. Results and discussion

3.1 The IR spectra and elemental analysis of synthesised compounds

The specific surface areas were found to be $197.3 \text{ m}^2 \text{ g}^{-1}$ for non-imprinted and $213.6 \text{ m}^2 \text{ g}^{-1}$ for Th(IV)-imprinted polymers. The pore diameter of non-imprinted and imprinted polymers was 4.09 nm and 4.42 nm, respectively. The IR spectra of the SIL-COOH showed vinyl C-H band at 3071.98 cm^{-1} and methyl C-H band at 2940.75 cm^{-1} , respectively. Around 1098.15 and 798.45, and 468.63 cm^{-1} resulted from Si-O-Si and Si-O vibrations, respectively. And around 1713.21 cm^{-1} was assigned to C=O of ester stretching vibrations [22]. Compared with the SIL-COOH, the IR spectra of the IIPs showed some new peaks at 1384.82 cm^{-1} ($-\text{CH}_3$ bending vibration), 1452.40 cm^{-1} ($-\text{CH}_2$ bending vibration), and 1148.99 cm^{-1} (C-O-C stretching vibration), respectively. In addition, the peaks for C=O vibrations around 1732.33 cm^{-1} and for C-H vibrations around 2940.95 cm^{-1} were significantly stronger. Imprinted and non-imprinted polymers showed very similar location and appearance of the major bands. Table 1 summarises

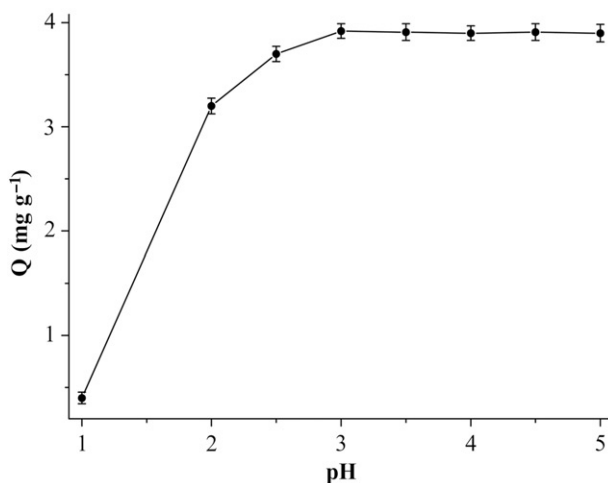


Figure 1. Effect of pH on Th(IV) adsorption on the Th(IV)-imprinted polymers; Th(IV) $10 \mu\text{g mL}^{-1}$; temperature: 25°C .

elemental analysis of product in each step and after saturation adsorption of Th(IV) on IIPs. The contents of C obvious increase in each step intuitively indicate success of bonding reaction. It should also be noted that the percentage of C and H in imprinted and non-imprinted polymers are the same, which can indicate the Th(IV) ions are completely leached from the imprinted polymers. Moreover, after saturation adsorption of Th(IV) on IIPs, the amounts of C and H are low, as expected. The results of the IR spectra and elemental analysis of the IIPs showed that polymers were grafted successfully onto the surface of silica gel.

3.2 Effect of pH

The acidity of a solution has two effects on metal adsorption. First, ionisation of the metal-complexing ligand change with the pH. Second, the hydroxide in a basic solution may complex and precipitate many metals ions. Therefore, the pH of a solution is the first parameter to be optimised. The effect of pH on the adsorption of thorium ions ($10 \mu\text{g mL}^{-1}$) was tested in the pH range of 1.0–5.0. The results in Figure 1 showed that the amount of the Th(IV) adsorbed increased as the pH of the aqueous solution was increased from 1 to 3, then remained relatively constant with further increase in pH from 3 to 5. But in order to ensure quantitative adsorption and avoid hydrolysis and precipitation of Th(IV) at higher pH values, pH 3 was selected as the enrichment acidity for subsequent experiments.

3.3 Uptake kinetics

Uptake kinetics of Th(IV) by the polymers were also examined by a static procedure. The equilibrium of Th(IV) was achieved within 25 min (Figure 2).

The kinetics for adsorption of Th(IV) on the imprinted polymers was found to follow the first order rate expression given by Lagergren as follows [23]:

$$-\ln(1 - F) = Kt, \quad (2)$$

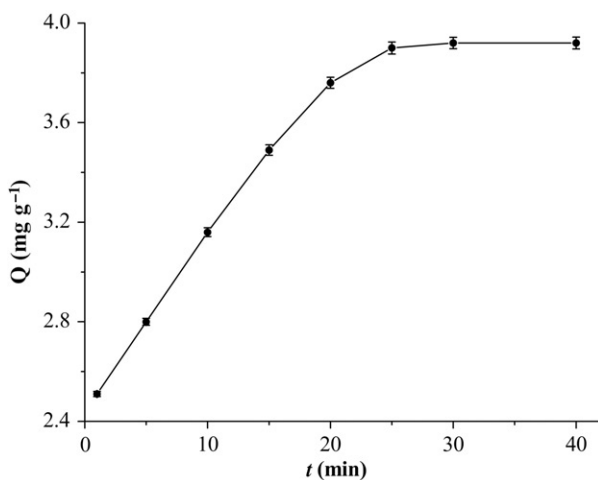


Figure 2. Uptake kinetics of Th(IV) ($10 \mu\text{g mL}^{-1}$) on the Th(IV)-imprinted polymers at different time; pH 3; temperature: 25°C .

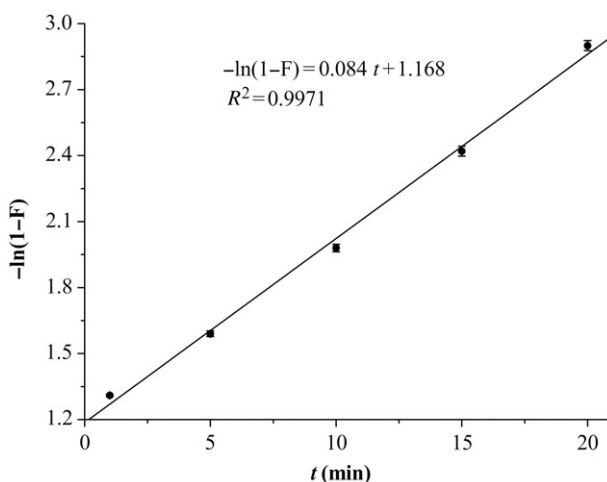


Figure 3. Lagergren plot for the Th(IV) ions adsorbed on the Th(IV)-imprinted polymers; temperature: 25°C .

where F is equal to q_t/q_∞ , q_∞ and q_t are the amount of metal ions adsorbed per gram of the imprinted polymer at equilibrium and at time ' t ', respectively, and K is the adsorption rate constant. The linear plot of $-\ln(1-F)$ versus ' t ' (Figure 3) suggests the applicability of the above equation for adsorption of Th(IV) on the imprinted polymers. The K value from the slope of the plot was 0.084 min^{-1} .

3.4 The static adsorption capacity

To measure the static adsorption capacity, imprinted or non-imprinted polymers (25 mg) were equilibrated with Th(IV) solutions (25 mL) within the concentration range of

5.0–50 $\mu\text{g mL}^{-1}$ at pH 3. The adsorption value increasing with the increase of concentration of Th(IV) (5.0–40 $\mu\text{g mL}^{-1}$), and a saturation value was achieved in the concentration range of 40–50 $\mu\text{g mL}^{-1}$. The adsorption capacity of the imprinted and non-imprinted polymers was calculated to be 33.2 and 14.7 mg g^{-1} , respectively. The capacity of imprinted particles is larger than that of non-imprinted ones. This difference indicates that the imprinting plays an important role in the adsorbent behaviour. During the preparation of the imprinted adsorbent, the presence of Th(IV) encouraged an orderly ligand arrangement. After removal of Th(IV), the imprinted cavities and specific binding sites of functional groups in a predetermined orientation are formed; however, no such specificity is found in non-imprinted polymers [18].

3.5 Uptake thermodynamics

Uptake thermodynamics of Th(IV) on the imprinted polymers were also examined by static procedure. The effect of temperature for the adsorption of Th(IV) on the imprinted polymers was studied in the temperature range of 25–50°C. The change in the distribution ratios (K_d) with temperature is expressed by Van't Hoff equation [24]:

$$\left[\frac{\partial \lg K_d}{\partial \left(\frac{1}{T}\right)} \right]_p = -\frac{\Delta H}{2.303R}, \quad (3)$$

where K_d is the distribution coefficient (mL g^{-1}) ($K_d = Q/C_e$, where Q is the amount of the Th(IV) adsorbed on the polymer, C_e is the equilibrium concentration of Th(IV) ($\mu\text{g mL}^{-1}$) in solution), T is the absolute temperature (K), ΔH is the reaction enthalpy (kJ mol^{-1}), R is the gas constant ($R = 8.314 \text{ J (K} \cdot \text{mol}^{-1})$).

The free energy, ΔG is also calculated based on the logarithmic value of the distribution ratio ($\lg K_d$) at 25°C:

$$\Delta G = -2.303RT \lg K_d. \quad (4)$$

The entropy variation, ΔS is obtained from ΔG and ΔH as:

$$\Delta S = \frac{\Delta H - \Delta G}{T}. \quad (5)$$

The plot of $\lg K_d$ versus $1000/T$ (see Figure 4) was employed to generate the slope of $-\Delta H/2.303R$. ΔH , ΔG , and ΔS were calculated to be 62.59 kJ mol^{-1} , -24.54 kJ mol^{-1} , and 0.292 kJ (mol K)^{-1} , respectively. The positive ΔH indicates the endothermic character of the adsorption process; however, the negative ΔG reveals the spontaneous and quick nature of Th(IV) adsorption. The positive ΔS represents an increase in the randomness of the adsorption process in the investigated system.

3.6 Effect of flow rate

The effect of flow rate on the retention of Th(IV) was investigated by sample solution (50 mL) at pH 3 through the column with a peristaltic pump by changing the flow rates between 1 mL min^{-1} and 8 mL min^{-1} . The initial concentration of Th(IV) ions was kept at 10 $\mu\text{g mL}^{-1}$. It was found that quantitative recovery of Th(IV) ions was obtained with flow rates of up to 5 mL min^{-1} . There was a decrease in the percentage of adsorption when the

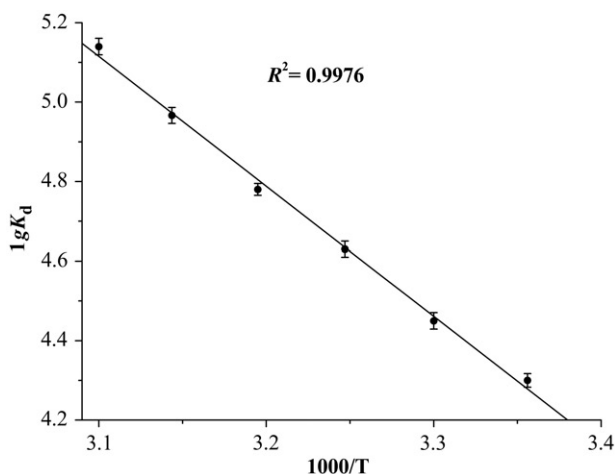


Figure 4. Uptake thermodynamics of Th(IV) on the Th(IV)-imprinted polymers ($10 \mu\text{g mL}^{-1}$); pH 3.

flow rates were over 5 mL min^{-1} . Optimum flow rate may be defined as the rate of flow of the effluent through the column at which more than 98% adsorption takes place. Thus, the flow rate of 3 mL min^{-1} was chosen for subsequent experiments.

3.7 The dynamic adsorption capacity

The dynamic capacity is an important parameter for the imprinted adsorbent in application. It was obtained by pumping $10 \mu\text{g mL}^{-1}$ of Th(IV) solution at pH 3 through the column at the flow rate of 3.0 mL min^{-1} , then collecting continuously per 10 mL of the column effluent to determine the concentration until a saturation value was achieved. The total dynamic capacity of the imprinted adsorbent was calculated to be 17.3 mg g^{-1} .

3.8 Effect of desorption condition and repeated use

Under strong acid conditions, the coordination interaction of uploaded Th(IV) ions could be easily disrupted and subsequently Th(IV) ions are released from the adsorbent into the desorption medium. The effect of HCl concentration on the elution of the retained Th(IV) was examined. The results revealed the quantitative recovery of Th(IV) can be obtained using 1 mol L^{-1} HCl solution (5 mL). When the flow rate for desorption of Th(IV) was varied from 0.5 to 4.0 mL min^{-1} , the results showed that Th(IV) ions can be quantitatively below 1 mL min^{-1} . Therefore, the flow rate of 0.8 mL min^{-1} was selected for further studies.

In order to show the reusability of the Th(IV)-imprinted polymers, the adsorption-desorption cycles were repeated five and ten times by using the same imprinted polymer and it was observed that the adsorption capacity was decreased by only 3.1% and 7.7%, respectively. The results showed that the Th(IV)-imprinted polymers can be used many times without decreasing their adsorption capacity significantly.

Table 2. K_d , k , and k' values of U(VI), Ce(III), La(III), and Zr(IV) with respect to Th(IV).

Metal ions ^a	K_d (imprinted) (mL g ⁻¹)	K_d (non-imprinted) (mL g ⁻¹)	$k_{\text{imprinted}}$	$k_{\text{non-imprinted}}$	k'
Th(IV)	70928.6	1401.8	–	–	–
U(VI)	2876.4	3345.1	24.7	0.42	58.8
Ce(III)	552.7	1162.6	128.3	1.20	107
La(III)	493.9	1037.8	143.6	1.35	106.4
Zr(IV)	3896.4	11972.5	18.2	0.12	151.7

Note: ^aInitial concentration: 10 $\mu\text{g mL}^{-1}$; Volume: 50 mL.

Table 3. Effect of foreign ions on percentage recovery of 1.0 $\mu\text{g mL}^{-1}$ Th(IV) on the adsorbent followed by elution with 5 mL of 1 mol L⁻¹ HCl.

Coexisting ions concentration ($\mu\text{g mL}^{-1}$)	Recovery of analytes (%)	
	Th ⁴⁺	
K ⁺ , Na ⁺	1500	99
Ca ²⁺ , Mg ²⁺	1000	100
Co ²⁺ , Ni ²⁺ , Mn ²⁺ , Cu ²⁺ , Zn ²⁺	210	99
Fe ³⁺	150	98
Hg ²⁺ , Pb ²⁺ , Cd ²⁺	280	99

3.9 Selectivity of the imprinted adsorbent

The competitive adsorption of Th(IV)/U(VI), Th(IV)/Ce(III), Th(IV)/La(III), and Th(IV)/Zr(IV) was also investigated by dynamic procedure because these ions have similar properties, often coexist in their minerals and products, or hold the similar ionic radius or the same ionic charge. The distribution coefficient (K_d), the selectivity coefficient (k), and the relative selectivity coefficient (k') values of U(VI), Ce(III), La(III), and Zr(IV) with respect to Th(IV) are summarised in Table 2. The K_d , k , and k' were calculated according to the study by Say *et al.* [25].

According to the relative selectivity coefficient values, the imprinted adsorbent shows excellent selectivity for the target Th(IV) ions. There are three possible factors for the selectivity environment. One is the recognition sites number on the ligand which has an important role in ionic recognition. MAA shows higher affinity to Th(IV) than La(III), Ce(III), U(VI) and Zr(IV), which may be due to the difference in coordination numbers for La(III), Ce(III), U(VI), Zr(IV), and Th(IV). The second is the coordination-geometry selectivity due to the Th(IV)-imprinted adsorbent providing the ligand groups in preferred orientation for the coordination of Th(IV) ions. The third is hole-size selectivity. In other words, the size of Th(IV) exactly fits the cavity of the Th(IV)-imprinted adsorbent. Thus, competitive adsorption studies show that Th(IV)-imprinted adsorbent are only selective to Th(IV) even in the presence of U(VI), Ce(III), La(III), and Zr(IV).

To investigate the interference effect of different species, 10 mL of a solution containing 1 $\mu\text{g mL}^{-1}$ of the Th(IV) ions and foreign ions in different interference-to-analyte ratios were subjected to the column procedure. The obtained results (Table 3)

Table 4. Analysis of water samples.

Sample	Concentration of Th(IV) ($\mu\text{g L}^{-1}$)		
	Added	Found ^a	Recovery (%)
Tap water	0	N.D. ^b	–
	10	9.84 ± 0.11	98.4
	20	19.87 ± 0.14	99.3
Wastewater	0	N.D.	–
	10	9.61 ± 0.31	96.1
	20	20.20 ± 0.33	101.0

Notes: ^aMean of five replicates \pm S.D.

^bNot detected.

showed that the major cations in the water samples did not effect the recovery of Th(IV). This is due to the low adsorption capacity or rates for interfering ions. The reported tolerance limit was defined as the ion concentration causing a relative error $\leq \pm 5\%$.

3.10 Analytical performance

The analytical figures of merit of the SPE using the imprinted polymers coupled with spectrophotometry for the determination of trace thorium were evaluated under optimal experimental conditions. Calibration curve was obtained using the standard solutions of Th(IV) (100 mL) in the concentration range of 2.03–140 $\mu\text{g L}^{-1}$. The calibration curve exhibited good linearity with correlation coefficient 0.9991 with a calibration function of A (absorbance) = $0.00373 C$ ($\mu\text{g L}^{-1}$) – 0.00441. The enrichment factor (EF), defined as the ratio of slope of the preconcentrated samples to that obtained without preconcentration, was 14.6. The limit of detection (LOD), calculated as the concentration equivalent to three times of the blank standard deviation divided into the slope of the calibration curve, was 0.59 $\mu\text{g L}^{-1}$. The relative standard deviation (R.S.D.) for 7 replicates SPE of 20 $\mu\text{g L}^{-1}$ Th(IV) was 2.1%, which indicates that the method has good precision for the analysis of trace Th(IV) in samples solution.

3.11 Application of the proposed method

To evaluate the accuracy and applicability of the developed solid-phase extraction coupled with spectrophotometry for the determination of trace thorium two real samples were analysed. During the analysis of water samples, the standard addition method was adopted. The analytical results showed that the recoveries of analytes were in the range of 96.1–101% (Table 4). These results clearly indicate that the proposed method was accurate, reliable and satisfactory.

4. Conclusions

In this study, a novel Th(IV)-imprinted material with MAA as a monomer and the surface-modified silica gel as a carrier material was prepared successfully by a surface-grafted technique. The imprinted polymers for Th(IV) exhibited good characteristics, such as high

affinity, selectivity and adsorption capacity, good reusability, and relatively fast kinetics process. At the same time, the results obtained from the analysis of natural water samples prove the reliability of the proposed method, which may be applied to the analysis of monazite sand and standard geological samples.

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