



Selective solid-phase extraction of trace thorium(IV) using surface-grafted Th(IV)-imprinted polymers with pyrazole derivative

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ABSTRACT

A new pyrazole derivative 1-phenyl-3-methylthio-4-cyano-5-acrylicacidcarbamoyl-pyrazole (PMT-CAACP) was synthesized and chosen as a complexing monomer for the preparation of surface-grafted ion-imprinted polymers for selective solid-phase extraction of thorium(IV). The silica gel, modified with maleic anhydride, was prepared as a carrier material. In the ion-imprinting process, Th(IV) was complexed with PMTCAACP, and then imprinted in the polymers grafted to the surface of modified silica gel. Subsequently, the template Th(IV) ions were removed with 6 mol/L HCl solution. The obtained ion-imprinted particles for Th(IV) showed specific recognition, and rapid adsorption and desorption kinetics process. The maximum static and total dynamic adsorption capacity of the ion-imprinted polymers (IIPs) for Th(IV) was 64.8 and 37.4 mg/g, respectively. The relative selectivity coefficient values of the imprinted adsorbent for Th(IV)/U(VI), Th(IV)/Ce(III), Th(IV)/La(III), and Th(IV)/Zr(IV) were 72.9, 89.6, 93.8, and 137.2 times greater than non-imprinted matrix, respectively. The interference effect of common cations tested did not interfere with the recovery of Th(IV). The enhancement factor of 20.2, the detection limit of 0.43 $\mu\text{g/L}$, and the precision of 2.47% ($n=7$) of the method under the optimized conditions were obtained. Additionally, the calibration curve ($r=0.9993$) was linear in the range of 1.43–103 $\mu\text{g/L}$ of thorium(IV). The prepared IIPs were shown to be promising for solid-phase extraction coupled with UV-vis spectrophotometry for determination of trace Th(IV) in real samples.

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1. Introduction

Thorium, which is an important radioactive element widely distributed over the earth's crust, not only has extensive application in industry, e.g., optics, radio, gas mantle, aeronautics and aerospace, metallurgy and chemical industry, and material, but is also used for energy, for example, as nuclear energy for electricity production in power plants [1]. However, thorium is a toxic heavy metal, which is extremely mobile and once entered living bodies will provoke inner irradiation (especially due to the γ -active decay products), having as a final result the appearance of cancer [2]. Also, thorium and its compounds are hazardous causing environmental problems. In view of the extensive application, toxicity, and hazard, the development of reliable methods for the separation, monitoring, and recovery of thorium in environmental and geological samples is of a particular significance [3]. Direct determination of thorium is still difficult, owing to thorium's trace concentration in nature and presence of complex matrix [4]. As a result, a preconcentration or

sample cleanup step, to facilitate selective separation of analytes prior to its detection, is required [5].

Various separation techniques have been developed in the past for this purpose, including liquid-liquid extraction (LLE) [6,7], solid-phase extraction (SPE) [8,9], extraction chromatography [10], ion exchange [11], etc. Of these, although the use of LLE has remained as the preferred technique for several years due to its high selectivity behavior [12], it has several technical problems like the generation of amounts of organic wastes that are difficult to dispose of. In contrast, the use of SPE has turned out to be a more eminent and promising technique, owing to its many advantages, such as higher enrichment factors, lower consumption of reagents, flexibility, and more importantly environmental friendliness [13]. So far, many different types of adsorbents for SPE have been reported, for instance, XAD resins, ion-exchange resin, silica gel, cellulosic derivatives, and porous glass beads [14]. Unfortunately, these solid adsorbents have poor ion selectivity, which leads to high interference of other existing species with the target metal ions. By reason of this, the use of ion-imprinted polymers (IIPs) as adsorbents for SPE has increased substantially in recent years [15–18].

Ion imprinting is a versatile technique for preparing polymeric materials that are capable of high ionic recognition. In general, polymerization is carried out in the presence of a print ion or template, which forms a complex with the constituent monomers. The sub-

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sequent removal of the template leads to the formation of cavities within the polymeric structure that function as specific recognition sites [18]. Such an imprinted polymeric material shows an affinity for the template ion over other structurally related compounds. Surface imprinting is one of the important types of imprinting methods. Surface imprinting polymers not only can avoid grinding and sieving, but also possess high selectivity, good mass transfer, and fast binding kinetics. More importantly, the template ions can be removed completely from IIPs [19,20]. More recently, several studies have reported ion-imprinted polymers based on surface imprinting [21–23].

The pyrazole unit is one of the core structures in a number of natural products. It is very important in coordination chemistry because nitrogen-containing heterocycles have good coordination capability with metal ions [24,25]. Pyrazole derivatives also have strong chelation capability and large extraction capacity for Th(IV) ions [26–28]. But there is little information available in literature about applying pyrazole derivative to the Th(IV) ion-imprinted polymers as a monomer. Based on these aspects, in this study, 1-phenyl-3-methylthio-4-cyano-5-acrylicacidcarbamoyl-pyrazole (PMTCAAC P) was synthesized and chosen as a functional monomer, whose cyano and carbonyl groups were responsible for the thorium(IV) complexation. The silica gel was modified by amidation reaction between amino and maleic anhydride. The Th(IV)-imprinted polymers based on the modified silica gel were prepared via a surface-grafted approach in the presence of Th(IV) ion template. After removal of Th(IV) ions, the adsorption behavior of analytes on the imprinted polymers and the experimental conditions for the preconcentration process were investigated in detail. In addition, a method using Th(IV)-imprinted adsorbent for selective solid-phase extraction coupled with UV–vis spectrophotometry for determining Th(IV) was developed, and applied to the analysis of biological and water samples.

2. Experimental

2.1. Apparatus

A Perkin-Elmer Lambda 45 UV–vis spectrometer (USA) and 10-mm quartz cells were used for the determination of metal ions concentrations. IR Spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on IRPrestige-21 (Shimadzu, Japan) using KBr pellets. LC–MS was performed on Agilent 1100 Series LC/MSD (USA). ^1H NMR was taken on Varian INOVA-300 (USA) in $\text{DMSO-}d_6$ with TMS as the internal standard. A pHs-10C digital pH meter, Pengshun Scientific instruments research (Shanghai, China), was used for the pH adjustments. A peristaltic pump, Longfang instrument fitting factory (Wenzhou, China), was applied to the preconcentration process. A variable speed reciprocal shaker and lab-made glass column 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.

Propanedinitrile, phenyl hydrazine, carbon disulfide, dimethyl sulfate, silica gel (200–300 mesh), Arsenazo-III, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP), azobisisobutyronitrile (AIBN) (98%), L-ascorbic acid, N,N'-dimethyl formamide (DMF) (GP), and maleic anhydride were offered by Aladdin (Shanghai, China). 3-Aminopropyltrimethoxysilane (APS) and ethylene glycol dimethacrylate (EGDMA) were purchased from EHSY (Shanghai, China). Acetonitrile and propanoic acid were obtained from Ker-

mel (Tian Jin, China). $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (SP) and other chemicals were purchased from Hengrui New Materials Co. Ltd. (Chengdu, Sichuan).

Standard stock solutions of Th(IV), U(VI), Ce(III), La(III), and Zr(IV) (1 mg/mL) were carefully prepared by dissolving spectral pure grade chemicals and made up in 1 mol/L HNO_3 . The standard working solution was diluted daily prior to use. The buffer solution of pH 3.5 was prepared with sodium acetate-acetic acid. EGDMA was distilled under reduced pressure and stored at 4°C until use. AIBN was recrystallized from ethanol three times before use.

2.3. Preparation of samples

The reference materials: GBW 07424 (soil) and GBW 08513 (tea leaves) were purchased from the National Research Center for Certified Reference Materials (Beijing, China). Natural samples of poplar leaves, soil, and water samples were collected locally.

Immediately after sampling, the water samples analyzed were filtered through a cellulose membrane filter (Millipore) of $0.45\ \mu\text{m}$ pore size, acidified to pH 1 with hydrochloric acid and stored in precleaned polyethylene bottles, while tap water samples were analyzed without pretreatment. The pH value was adjusted to 3.5 with 0.1 mol/L HCl or 0.1 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ prior to use.

The solid samples were dried in an oven at 80°C to constant weight. The preparation of samples was carried out as reported in references [8,17]: 0.5000–1.0000 g of the samples were digested with aqua regia (concentrated hydrochloric acid (12 mL): concentrated nitric acid (4 mL)). The samples were left at room temperature for one night then heated to 95°C . After the evolution of NO_2 fumes had ceased, the mixture was evaporated almost to dryness on a sand-bath. Upon cooling they were redissolved in aqua regia (8 mL). Then the mixture was again evaporated to dryness. After that, fresh HF (8 mL) 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 6 mol/L HCl (5 mL) and heated strongly ($>140^\circ\text{C}$) to dryness. A second high temperature evaporation step was carried out after addition 6 mol/L HCl (2 mL). Next, 1 mol/L HCl (5 mL) was added, and the sample was mixed. The resulting mixture was filtered through a blue band filter paper, and the filter cake was washed with 10 mL of DDW. The filtrate was adjusted to pH 3.5 with 1 mol/L NH_3 , and diluted to 100 mL with the buffer solution of pH 3.5 in a calibrated flask.

2.4. Synthesis of SPE polymers

2.4.1. Synthesis of 1-phenyl-3-methylthio-4-cyano-5-acrylicacidcarbamoyl-pyrazole

The synthesis of 1-phenyl-3-methylthio-4-cyano-5-amino-pyrazole (PMTCAP) was carried out as reported in literature [29].

1-Phenyl-3-methylthio-4-cyano-5-acrylicacidcarbamoyl-pyrazole (PMTCAACP) was prepared as follows: Maleic anhydride (1.2 g) in propanoic acid (8 mL) was added to the round bottom flask containing PMTCAP (2.3 g, 10 mmol). After the mixture was refluxed for 5 h, it was poured into the beaker containing water (20 mL), and yellow precipitate was obtained. The resulting products were filtered off, and purified by column chromatography over silica gel.

The IR spectra bands of the PMTCAACP at 3464, 1664 and 1693, 3169, and 2208 cm^{-1} correspond to N–H, C=O, O–H, and C≡N stretching vibrations, respectively. The peaks at 3074 and 2926 cm^{-1} were assigned to vinyl C–H band and methyl C–H band, respectively. ^1H NMR ($\text{DMSO-}d_6$) δ : 2.63 (s, 3H, SCH_3), 7.02–7.62 (m, Ph, 5H), 8.06 (s, 2H, CH=CH), 12.70 (s, NH, 1H). LC–MS (m/z , rel. int.) 328 (M^+ , 13).

2.4.2. Preparation of carboxylic acid-functionalized silica gel

The silica gel silylation (Silica-NH₂) with APS was synthesized according to the method reported in literature [30].

Carboxylic acid-functionalized silica gel (Silica-COOH) was prepared using the following procedure [31]: a solution of maleic anhydride (2.5 g) in DMF (25 mL) was added to the flat bottom flask containing Silica-NH₂ (5 g) and DMF (25 mL). After the mixture was stirred for 24 h at room temperature, the resulting products were filtered off, washed with DMF, anhydrous ethanol and anhydrous ether, and dried under vacuum at room temperature.

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

A solution of Th(NO₃)₄·4H₂O (1.2 g) in methanol (25 mL) was slowly added to a glass reactor containing PMTCAACP (4 mmol) in DMF (25 mL) with continuous stirring. After the mixture was stirred for 3 h at room temperature, Silica-COOH (2.0 g), AIBN (0.12 g) and EGDMA (4 mL) were added. Then, the reactor was removed oxygen for 15 min and flushed by bubbling nitrogen for 25 min. The mixture was stirred and heated at 60 °C for 24 h under nitrogen atmosphere. The synthesis scheme for Th(IV)-imprinted polymers is represented in Scheme 1. After the mixture was allowed to cool to room temperature, the products were filtered off, washed with methanol/water/DMF (1:1:1) and treated with 6 mol/L HCl for 12 h to remove Th(IV) from the polymers. The final products were cleaned with DDW several times until acid-free, and the exiguous granules were removed by rinsing with acetone, then dried under vacuum at 70 °C for 48 h. Non-imprinted polymers were also prepared with the same method omitting Th(NO₃)₄·4H₂O.

2.5. Procedure

2.5.1. Static adsorption procedure

A series of thorium(IV) standard solutions were transferred into a 25 mL color comparison tube, and the pH values were adjusted to the desired value with 0.1 mol/L HNO₃ or 0.1 mol/L NH₃·H₂O. After the volume was adjusted to 25 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 HNO₃ medium at a wavelength of 658 nm. The amount of the Th(IV) adsorbed on the polymer was calculated by using the following equation:

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

where Q represents the amount of the Th(IV) adsorbed on the polymer (mg/g), C_0 and C_e represent the initial and equilibrium concentration of Th(IV) (μg/mL), respectively, W is the amount of polymer (g), and V is the volume of metal ions solution (L).

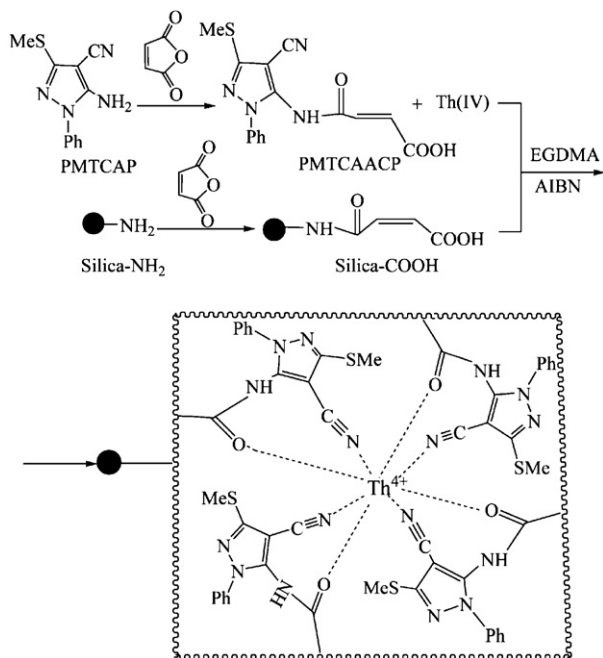
2.5.2. Dynamic adsorption procedure

Th(IV)-imprinted or non-imprinted polymers (50 mg) were packed into a glass column (120 mm × 5.5 mm i.d.). Upon activation with methanol, the column was treated with 0.5 mol/L HCl, washed with DDW once and then it was conditioned to the desired pH with sodium acetate-acetic acid buffer. Then each solution was passed through the column after adjusting the appropriate pH at a flow rate of 4 mL/min. Afterwards, the bound metal ions were stripped off from the column with 0.5 mol/L HCl (5 mL) at a flow rate of 2 mL/min. 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 HCl medium at a wavelength of 660 nm. In addition, Th(IV) ions were purified from other ions after preconcentration in the couple mixture by extraction with 0.03 mol/L solution of PMBP in benzene (10 mL) and L-ascorbic acid solution (1 mL, 100 g/L) at 0.5 mol/L HCl (10 mL) followed by stripping with 5 mol/L HCl (15 mL) [32]. 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 HCl medium at a wavelength of 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.

3. Results and discussion

3.1. Characteristic of the FT-IR spectra

IR spectra were obtained from Silica-COOH, imprinted and non-imprinted polymers. The IR spectra of the Silica-COOH showed vinyl C-H band at 3079 and methyl C-H band at 2955 cm⁻¹, respectively. Bands around 1707 cm⁻¹ was assigned to C=O of COOH stretching vibrations. Around 1101, 798 and 471 cm⁻¹ resulted from stretching and bending vibrations of Si-O-Si, respectively [14]. Compared with the Silica-COOH, the IR spectra of the ion-imprinted polymers showed some new peaks as follows: at 1387 cm⁻¹ (-CH₃ bending vibrations), 1452 cm⁻¹ (-CH₂ bending vibrations), 1570 cm⁻¹ (C=C stretching vibrations of pyrazole ring) [26], 758 cm⁻¹ (C-H bending vibrations of aromatic ring) [17], 420 cm⁻¹ (Th-O stretching vibrations) [33], and 536 cm⁻¹ (Th-N stretching vibrations) [34]. In addition, the peaks for C=O stretching vibrations around 1728 cm⁻¹ and for C-H stretching vibrations around 2955 cm⁻¹ were significantly stronger. After Th(IV) leached from the imprinted polymers, Th-O and Th-N bands were not seen at 420 and 536 cm⁻¹, respectively. The leached imprinted and non-imprinted polymers showed very similar location and appearance of the major bands. These indicate that the polymers are grafted successfully onto the surface of the modified silica gel, and also, the imprinted cavities for Th(IV) on the imprinted polymers are formed.



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

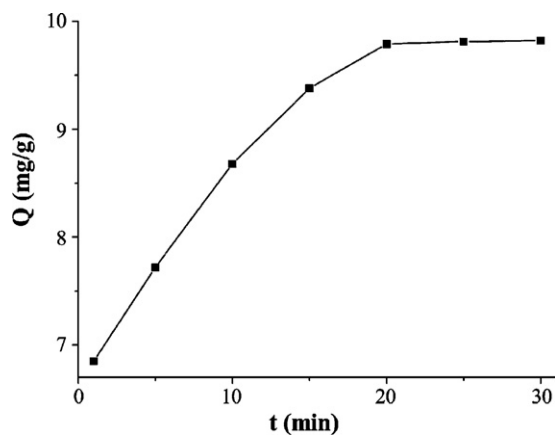


Fig. 1. Effect of time on the adsorption of Th(IV) on the Th(IV)-imprinted polymers; Th(IV) 10 $\mu\text{g/mL}$; pH 3.5; temperature: 25 $^{\circ}\text{C}$.

3.2. Effect of pH

The effect of pH on the adsorption of thorium ions was tested in the pH range of 1.0–5.0. The results showed that the adsorption percentage of the Th(IV) increased as the pH of the aqueous solution was increased from 1 to 3.5, then remained constant with further increase in pH from 3.5 to 5. The amount of Th(IV) adsorbed was under 5% below pH 1.5, because the protonation of main O and N in adsorbent made the bonding capability decrease at higher acidities. In order to ensure quantitative adsorption and avoid hydrolysis and precipitation of Th(IV) at higher pH values, pH 3.5 was selected as the enrichment acidity for subsequent experiments.

3.3. Uptake kinetics

Uptake kinetics of Th(IV) on the imprinted polymers were also examined by static procedure. The adsorption equilibrium of Th(IV) was achieved within 20 min (see Fig. 1). 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 [35]:

$$-\ln(1 - F) = K_{\text{ad}}t \quad (2)$$

where F is equal to Q_t/Q_e , Q_e and Q_t are the amount of metal ions adsorbed per gram of the imprinted polymers at equilibrium and at time t , respectively, and K_{ad} is the rate constant of adsorption. The linear plot of $-\ln(1 - F)$ versus t (Fig. 2) suggests the applicability of the above equation for adsorption of Th(IV) on the imprinted

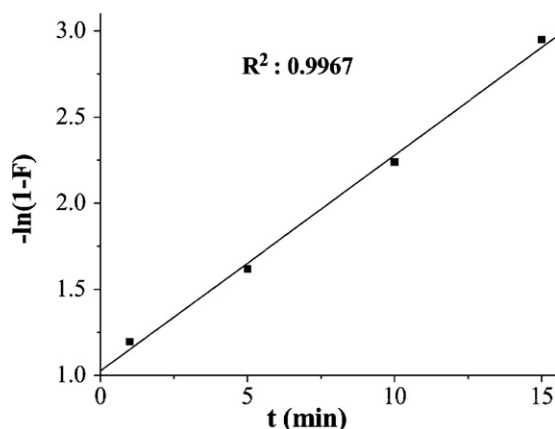


Fig. 2. Lagergren plot for the adsorption of Th(IV) on the Th(IV)-imprinted polymers; pH 3.5; temperature: 25 $^{\circ}\text{C}$.

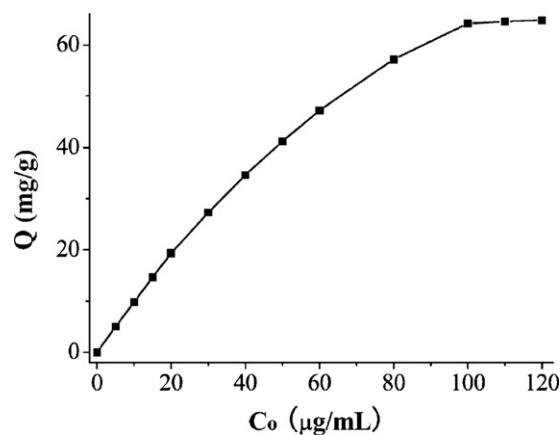


Fig. 3. Adsorption capacity of Th(IV) ions on the Th(IV)-imprinted polymers; pH 3.5; temperature: 25 $^{\circ}\text{C}$.

polymers. The K_{ad} value calculated from the slope of the plot was 0.147 min^{-1} .

3.4. The static adsorption capacity

The adsorption capacity is an important factor to evaluate the IIPs. The amount of the Th(IV) adsorbed per unit mass of the imprinted polymer increased with the increase of concentration of Th(IV), and a saturation value was achieved (Fig. 3). The max adsorption capacity of the imprinted and non-imprinted particles was calculated to be 64.8 and 22.3 mg/g , 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 behavior. 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 the non-imprinted adsorbent [17].

Langmuir isotherm is the simplest for the adsorption of adsorbate on the adsorbent, which is based on the following assumptions [36]: (i) the molecules are adsorbed at a fixed number of well-defined sites; (ii) only one monolayer of an adsorbing molecule can be sorbed onto the surface of the adsorbent; (iii) the enthalpy of adsorption is constant. The Langmuir adsorption isotherm in the liquid phase is given by the following expression [35]:

$$\frac{1}{q_e} = \frac{1}{q_{\text{max}}bC_e} + \frac{1}{q_{\text{max}}} \quad (3)$$

where q_e is the amount of Th(IV) adsorbed on the adsorbent at equilibrium ($\mu\text{mol/g}$), q_{max} is the adsorption capacity ($\mu\text{mol/g}$), C_e is the equilibrium concentration of Th(IV) ions in the solution ($\mu\text{mol/L}$), and b is the Langmuir constant ($\text{L}/\mu\text{mol}$).

The linear plot of $1/q_e$ versus $1/C_e$ (Fig. 4) suggests that the adsorption of Th(IV) on the imprinted polymers obeys the Langmuir adsorption model, which represents the presence of monolayer adsorption. It should also be noted that maximum adsorption capacity (q_{max}) and the Langmuir constant (b) were calculated to be 316.8 $\mu\text{mol/g}$ and 0.186 $\text{L}/\mu\text{mol}$, respectively. Furthermore, it is found that the theoretical q_{max} (316.8 $\mu\text{mol/g}$) and calculated Q_{max} (279.3 $\mu\text{mol/g}$) are near. This indicates that the surface imprinted polymers possess good mass transfer, facilitating diffusion of Th(IV) to the bulk of binding sites. On the other hand, a fraction of binding sites, which formed during the imprinting process, stay inside the polymer matrix, blocking Th(IV) ions from reaching these binding sites, resulting in a lower calculated Q_{max} is compared to the theoretical q_{max} .

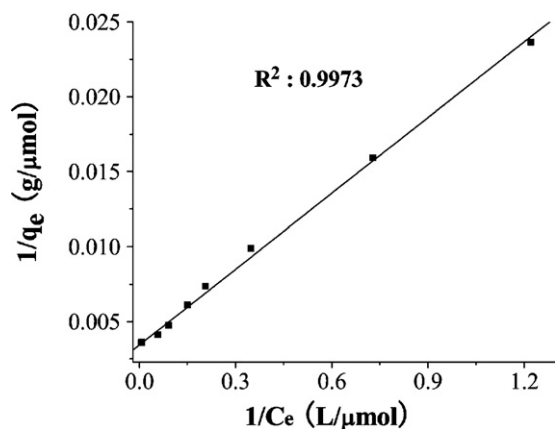


Fig. 4. Langmuir isotherm for the adsorption of Th(IV) on the Th(IV)-imprinted polymers; pH 3.5; temperature: 25 °C.

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 25–45 °C. Thermodynamic parameters such as free energy change ΔG° (kJ/mol), enthalpy change ΔH° (kJ/mol), and entropy change ΔS° (kJ/(molK)) were determined using the following equations:

$$\Delta G^\circ = -RT \ln K \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where K is equilibrium constant ($K = C_a/C_s$, where C_a and C_s are the equilibrium concentration of Th(IV) on adsorbent and in the solution, respectively), T is the absolute temperature (K), and R is the gas constant ($R = 8.314 \text{ J/(K mol)}$).

When $\ln K$ was plotted against $1/T$ (see Fig. 5), a straight line is obtained with the slope $-\Delta H^\circ/R$ and the values of ΔH° and ΔS° were obtained from the slope and intercept of the van't Hoff plot. ΔH° and ΔS° were calculated to be 64.37 kJ/mol and 0.249 kJ/(molK), respectively, while ΔG° calculated by Eq. (4) from 298.15 to 318.15 K was -9.83 kJ/mol (298.15 K), -11.08 kJ/mol (303.15 K), -12.32 kJ/mol (308.15 K), -13.57 kJ/mol (313.15 K), and -14.81 kJ/mol (318.15 K), respectively. The positive ΔH° indicates the endothermic character of the adsorption process, however, the negative ΔG° reveals the spontaneous and quick nature of

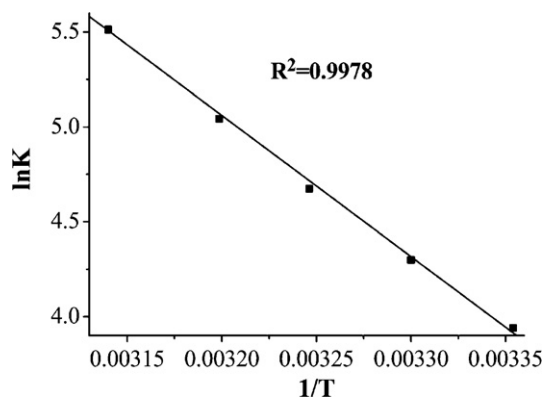


Fig. 5. Effect of temperature on the adsorption of Th(IV) on the Th(IV)-imprinted polymers; Th(IV) 10 μg/mL; pH 3.5.

Th(IV) adsorption. The positive ΔS° represents an increase in the randomness of the adsorption process in the investigated system.

3.6. Effect of the flow rate on adsorption

The effect of the flow rates on the retention of Th(IV) was investigated by 25 mL of sample solution at pH 3.5 through the column with a peristaltic pump by changing the flow rates between 1 and 10 mL/min. The initial concentration of Th(IV) ions was kept at 10 μg/mL. It was found that quantitative recovery of Th(IV) ions was obtained with flow rates of up to 6 mL/min. There was a decrease in the percentage of adsorption when the flow rates were over 6 mL/min. The reason is the insufficient contact time of the sample solution with the adsorbent. The solid-phase extraction process of the present adsorbent is faster than most of the traditional ion-imprinted adsorbents [16,18]. This indicates that the imprinted polymers have high retainability for Th(IV) ions, which are adsorbed easily and diffuse quickly to the binding sites. 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 4 mL/min was chosen for subsequent experiments.

3.7. The dynamic and breakthrough capacity

Dynamic capacity was obtained by pumping 10 μg/mL of Th(IV) solution at pH 3.5 through the column at the flow rate of 4.0 mL/min, 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 37.4 mg/g. For column operation, breakthrough capacity is more significant and useful than the dynamic capacity in application of SPE as it gives actual working capacity of the adsorbent in the column [37]. The breakthrough capacity represents the exhaustion point in terms of feed volume, after which the adsorbate leaks through into the effluent in gradually increasing amounts that can exceed the preset or desired value [38]. The thorium breakthrough column started after 20 mL (Fig. 6), and the breakthrough capacity was 5.92 mg/g.

3.8. Effect of desorption condition and repeated use

Since, the adsorption amount of Th(IV) on the imprinted adsorbent is very low below pH 1.5, one can expect that elution will be favoured in acidic solution. Thereby, elution of Th(IV) was

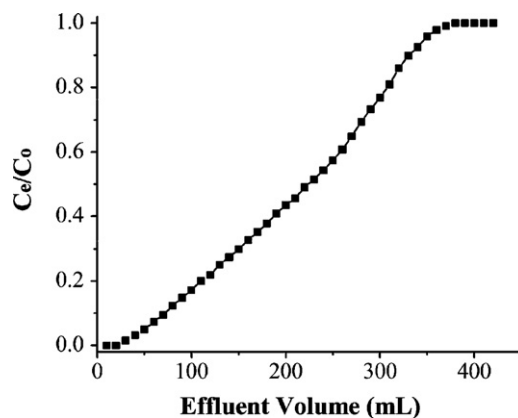


Fig. 6. Breakthrough curve of the Th(IV)-imprinted adsorbent for Th(IV) ions at various sample volumes; pH 3.5; temperature: 25 °C.

Table 1
The selectivity parameters of adsorbents for Th(IV).

Adsorbent	K_d		k	k'	K_d		k	k'
	Th(IV)	Ce(III)			Th(IV)	La(III)		
Non-imprinted	1380.0	992.6	1.39	–	1678.4	1001.7	1.67	–
Th(IV)-imprinted	35214.3	282.7	124.6	89.6	37961.5	242.4	156.6	93.8

Adsorbent	K_d		k	k'	K_d		k	k'
	Th(IV)	U(VI)			Th(IV)	Zr(IV)		
Non-imprinted	894.7	3768.2	0.24	–	637.3	6784.3	0.094	–
Th(IV)-imprinted	27277.8	1385.2	19.7	72.9	24500	1892.4	12.9	137.2

studied following the dynamic procedure where various concentrations (0.1–1 mol/L) and volumes (2–8 mL) of HCl solutions were used for the desorption of retained Th(IV). These results indicate that 0.5 mol/L HCl (5 mL) is sufficient for quantitative recovery for Th(IV). Moreover, when the flow rate for desorption of Th(IV) was varied from 1.0 to 4.0 mL/min, the Th(IV) ions can be eluted quantitatively at flow rate below 2.5 mL/min. Therefore, the flow rate of 2 mL/min was selected for subsequent experiments.

To investigate the reusability of the Th(IV)-imprinted adsorbent, the adsorption and desorption cycles were repeated 5 and 10 times by using the same imprinted adsorbent and the breakthrough capacity was decreased by only 2.2% and 4.9%, respectively. The results indicate that the Th(IV)-imprinted adsorbent can be used many times without decreasing its breakthrough capacity significantly.

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) from their couple mixture (25 mL) was also investigated by dynamic procedure because these ions have similar properties, often coexist in their minerals and products, or hold 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 summarized in Table 1. The K_d , k and k' were calculated according to the study by Say et al. [39].

The relative selectivity coefficient values of the imprinted adsorbent for Th(IV)/U(VI), Th(IV)/Ce(III), Th(IV)/La(III), and Th(IV)/Zr(IV) were 72.9, 89.6, 93.8, and 137.2 times greater than non-imprinted adsorbent. The results indicate the Th(IV)-imprinted adsorbent has high selectivity for Th(IV). That is, Th(IV) can be determined even in the presence of U(VI), Ce(III), La(III), and Zr(IV). There are two possible factors for the selectivity environment, one of which is the hole-size selectivity. In other words, the size of Th(IV) exactly fits the cavity of the Th(IV)-imprinted adsorbent. 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 interference effect of commonly associated cations such as Fe(II), Fe(III), Al, Co(II), Ni(II), Mn(II), Zn(II), Cu(II), alkali [Li, Na, and K], and alkaline earth [Mg, Ca, and Ba], and heavy metal ions [Cd(II) and Pb(II)] had also been studied. To investigate the interference effect of these ions, 10 mL of a solution containing 200 $\mu\text{g/L}$ of the Th(IV) ions and these cations in different interference-to-analyte ratios were subjected to the dynamic procedure. The results show that up to 2000 $\mu\text{g/mL}$ of K, Li and Na, 1500 $\mu\text{g/mL}$ of Ca, Mg and Ba, 240 $\mu\text{g/mL}$ of Co(II), Ni(II), Fe(II) and Mn(II), 210 $\mu\text{g/mL}$ of Cu(II) and Zn(II), 200 $\mu\text{g/mL}$ of Fe(III) and Al, and 350 $\mu\text{g/mL}$ of Cd(II) and Pb(II) have no significant interference with the solid-phase extraction of 200 $\mu\text{g/L}$ of Th(IV).

Table 2
Analytical results for the determination of thorium in certified reference materials.

Samples	Concentration of Th(IV) ($\mu\text{g/g}$)	
	Certified	Measured ^a
GBW 07424	11.3 \pm 0.4	10.8 \pm 0.3
GBW 08513	0.104 \pm 0.014	0.107 \pm 0.021

^a Mean of three replicates \pm S.D.

3.10. Figures of merit

The analytical figures of merit of the SPE using the imprinted polymers coupled with UV–vis spectrophotometry for the determination of trace thorium were evaluated by dynamic procedure under the optimal experimental conditions (e.g., pH, flow rate, and eluent). Calibration curve was obtained using the standard solutions of Th(IV) (100 mL) in the concentration range of 1.43–103 $\mu\text{g/L}$. The calibration curve obeyed the equation, A (absorbance) = 0.00513C ($\mu\text{g/L}$) – 0.00361 ($r = 0.9993$). The enrichment factor (EF), defined as the ratio of slope of the preconcentrated samples to that obtained without preconcentration, was 20.2. 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 0.43 $\mu\text{g/L}$. The obtained LOD is better than those obtained by some previously published methods [17,37]. The relative standard deviation (R.S.D.) for 7 replicate solid-phase extractions of 20 $\mu\text{g/L}$ Th(IV) was 2.47%, which shows 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 of the developed solid-phase extraction coupled with UV–vis spectrophotometry for the determination of trace thorium, two certified reference materials (CRMs) (GBW 07424, soil and GBW 08513, tea leaves) were analyzed. The analytical results for CRMs were in good agreement with the certified values (Table 2). The results also indicated that the developed preconcentration method for Th(IV) was not affected by poten-

Table 3
Analytical results for the determination of thorium in biological samples.

Samples	Concentration of Th(IV) ($\mu\text{g/g}$)		Recovery (%)
	Added	Measured ^a	
Poplar leaves	0	0.09 \pm 0.01	–
	1.0	1.08 \pm 0.10	98
	2.0	2.15 \pm 0.13	100.5
Soil	0	3.52 \pm 0.23	–
	1.0	4.49 \pm 0.09	97
	2.0	5.55 \pm 0.11	101.5

^a Mean of three replicates \pm S.D.

Table 4
Analytical results for the determination of thorium in water samples.

Th(IV) added ($\mu\text{g/L}$)	Measured ^a ($\mu\text{g/L}$)	Recovery (%)
Well water		
0	N.D. ^b	–
10	9.81 \pm 0.34	98.1
20	19.76 \pm 0.41	98.8
Pool water		
0	N.D.	–
10	9.67 \pm 0.34	96.7
20	19.50 \pm 0.32	97.5
Tap water		
0	N.D.	–
10	9.89 \pm 0.17	98.9
20	19.87 \pm 0.23	99.3
Wastewater		
0	N.D.	–
10	10.13 \pm 0.37	101.3
20	19.84 \pm 0.42	99.2

^a Mean of three replicates \pm S.D.

^b Not detected.

tial interferences from the major matrix elements of the analyzed standard materials. The proposed method was also applied to analysis of soil, poplar leaves and four water samples. For the analysis of water samples, the standard addition method was adopted. The results were given in Tables 3 and 4. The recoveries of Th(IV) ions were in the range of 96.7–101.5%. These results clearly indicate that the proposed method is accurate, reliable and satisfactory.

4. Conclusion

A new surface-grafted Th(IV)-imprinted material with PMT-CAACP as the functional monomer and the surface-modified silica gel as the support was prepared successfully for selective solid-phase extraction of thorium(IV). The imprinted polymers showed good characteristics, such as high affinity, selectivity and adsorption capacity, good reusability, and fast kinetics process for Th(IV). The kinetics and mechanism for the adsorption of Th(IV) on the imprinted polymers followed the Lagergren first order rate kinetics and the Langmuir adsorption isotherm, respectively. In addition, the thermodynamics studies indicated the adsorption of Th(IV) was an endothermic and spontaneous process. At the same time, an accurate and sensitive method was developed and successfully applied to the determination of trace Th(IV) in certified and natural samples with satisfactory results.

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