



# Synthesis and characterization of nano-pore thallium (III) ion-imprinted polymer as a new sorbent for separation and preconcentration of thallium

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## ABSTRACT

Thallium (III) ion-imprinted polymer (IIP) particles were synthesized by preparing the ternary complex of thallium (III) ions with 5,7-dichloroquinoline-8-ol (DCQ) and 4-vinylpyridine (VP). Thermal copolymerization with methyl methacrylate (functional monomer, MMA) and ethyleneglycoldimethacrylate (cross-linking monomer, EGDMA) was then performed in the presence of acetone (porogen) and 2,2-azobisisobutyronitrile (initiator, AIBN). The imprinted ion was removed from polymer by stirring of the above particles with 5 M HNO<sub>3</sub> to obtain the leached IIP particles. Moreover, control polymer (CP) particles were similarly prepared without the thallium (III) ions. The unleached and leached IIP particles were characterized by surface area analysis (BET), X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FT-IR), thermo gravimetric analysis (TGA) and scanning electron microscopy (SEM). The preconcentration of thallium (III) from aqueous solution was studied during rebinding with the leached IIP particles as a function of pH, the weight of the polymer material, the uptake and desorption times, the aqueous phase and the desorption volumes. Electrothermal atomic absorption spectrometry (ETAAS) was employed for determination of thallium in aqueous solution. The limit of detection for the method was 0.02 ng mL<sup>-1</sup>, while the relative standard deviation for five replicates was 2.6%.

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## 1. Introduction

Thallium is a heavy metallic element which exists in environment mainly combined with other elements (primarily oxygen, sulfur and the halogens) in inorganic compounds. Thallium can be found in nature as Tl (I) and Tl (III) ions but its monovalent state has higher stability, whereas its trivalent state forms complexes of greater stability. Each oxidation state of the element exhibits different bioavailability and toxicity property [1] and hence thallium speciation in environment is important. As the total concentration of thallium in aquatic environment is very low, an analytical technique featuring high sensitivity and low detection limit is required.

Great varieties of analytical procedures for thallium separation and preconcentration, based mainly on liquid–liquid extraction [2], single drop liquid-phase microextraction (SDME) [3], hydride generation [4] and solid phase extraction (SPE) [5–7] have been proposed.

The SPE procedure as a separation and preconcentration method exhibits numerous advantages such as flexibility, high preconcentration factors, speed and simplicity, possibilities for field sampling, and ease of automation [8]. However, it should be noted that the

extraction efficiency and selectivity of this technique is strongly dependent on the sorbent material used.

During the last years ion-imprinted polymers (IIPs), as selective sorbents for a particular chemical form of a given element, have received much attention. The high selectivity of IIPs can be explained by the polymer memory effects towards the metal ion interaction with a specific ligand, coordination geometry, metal ion coordination number, charge and size [9]. Numerous studies on ion-imprinted polymers and their use for selective separation and preconcentration of metal ions have been reported: UO<sub>2</sub>(II) [10–12], Cd(II) [13], Pd(II) [14–17], Cu(II) [18–21], Fe(III) [22,23], Hg(II) [24,25], Ni(II) [26,27], Cr(III) [28] and Zn(II) [29].

In this study, a thallium (III) ion-imprinted polymer as a new sorbent has been synthesized for the first time and characterized on the basis of surface area analysis, X-ray diffraction, Fourier transform infra-red spectroscopy, thermo gravimetric analysis and scanning electron microscopy. This sorbent was used for SPE and preconcentration of Tl (III) ions from aqueous solutions.

## 2. Experimental

### 2.1. Materials

A stock thallium (III) solution (1000 µg mL<sup>-1</sup>) was prepared by dissolving Tl(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (Fluka) and dilution to 100 mL with

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**Table 1**  
GFA heating program.

Stage	Furnace temp (°C)	Mode	Time (s)	Ar flow rate (L min <sup>-1</sup> )
Drying	120	Ramp	10	1.5
Ashing	300	Step	15	1.5
Atomization	1900	Step	3	0 (gas stop)
Cleaning up	2500	Step	2	1.5

deionized water. 5,7-Dichloroquinoline-8-ol was obtained from Acros organics, New Jersey, USA and 4-vinyl pyridine, methyl methacrylate, ethylene glycol dimethacrylate, triethylamine and 2,2-azo bis isobutyronitrile (AIBN) were obtained from Merck. Moreover, stock solutions of KNO<sub>3</sub>, NaNO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> (1000 μg mL<sup>-1</sup> each) were prepared. Deionized water was used in all experiments.

## 2.2. Instrumental

A Shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer (GFA) with a D<sub>2</sub> lamp for background correction was used for determination of thallium.

A thallium hollow cathode lamp, adjusted at 5 mA, was used as the radiation source. Measurements were carried out in peak height mode at 276.8 nm, using a spectral bandwidth of 0.5 nm. The atomic absorption signal at 276.8 nm was recorded on a graphic printed PR-4, and the height of the peak was used for determination of thallium. The temperature program for the furnace is given in Table 1. A sampler (Ependorf, Germany) was applied to inject 20 μL of the solution into the graphite tube. An F20520162 Velp Scientifica magnetic stirrer (Italia) was employed to stir the sample solution.

The FT-IR spectra (4000–400 cm<sup>-1</sup>) using KBr were recorded with the aid of a MB-154 model Bomem spectrometer. Thermogravimetric analysis (TGA) was carried out using thermogravimetric analyzer TGA-50 (Shimadzu Japan) instruments. The XRD patterns were obtained with X-ray of 1.54056 Å wavelength by a Cu Kα X-ray source and a Philips PW 1710 diffractometer (The Netherlands). An Agilent model 8453 UV–visible spectrophotometer was employed to prepare the UV–vis spectrum of the reaction mixtures. pH values were measured with a Metrohm model 632 pH-Meter. The surface area analysis was carried out by using Quantachrome autosorbe-1 surface area analyzer (USA).

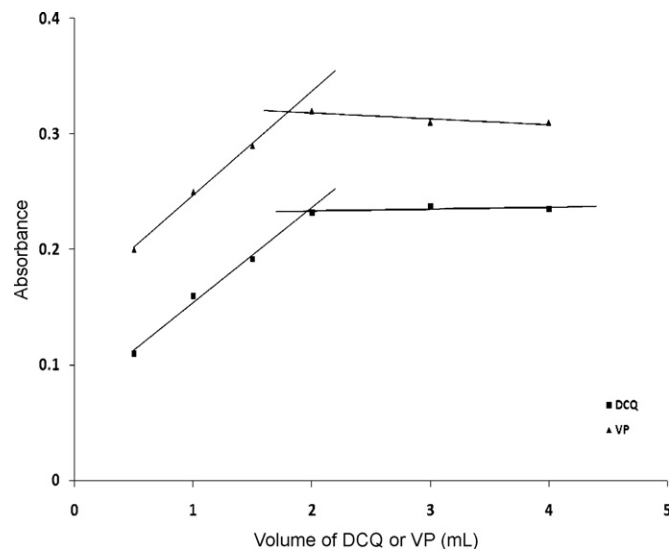
## 2.3. Synthesis of the thallium (III) IIP materials

The synthesis of thallium (III) IIP particles was performed in two steps: (i) ternary complex formation, (ii) ternary complex copolymerization of thallium with functional monomer (MMA) and cross-linking monomer (EGDMA).

## 2.4. Elucidation of stoichiometry of the ternary complex

The stoichiometry of ternary complex was established by the mole ratio method [36].

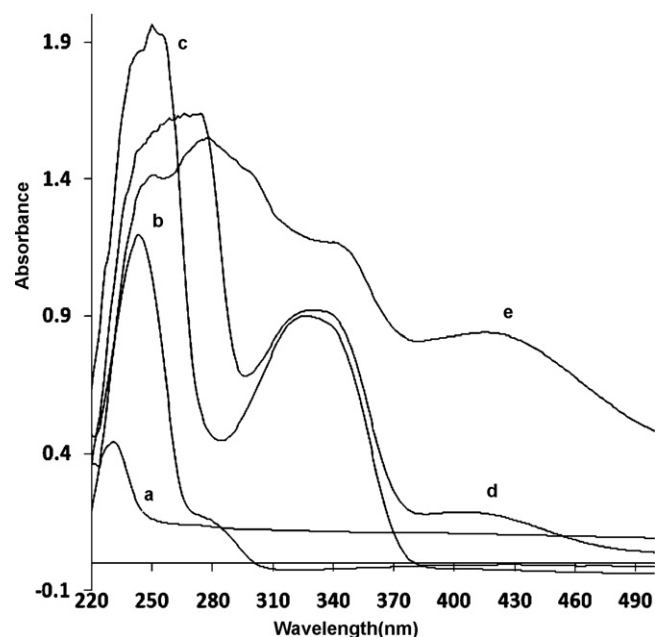
For a stable binary complex ML<sub>n</sub>, a plot of the absorbance against the mole ratio of the component L to component M, with constant concentration of M, rises from origin as a straight line and breaks sharply at absorbance corresponding to the mole ratio of components. This procedure was used to investigate the ratio of thallium (III) to DCQ and thallium (III) to VP in the ternary complex by converting it into a pseudobinary one. This was accomplished by adding a large excess of VP or DCQ for a fixed concentration of thallium (III) and then varying concentrations of DCQ or VP. A series of solutions were prepared by adding varying volumes of 1 mM DCQ

**Fig. 1.** Mole ratio plot.

or VP to 1 mL of 1 mM thallium (III), after the addition of 4 mL of 1 mM VP or DCQ and then diluting to 10 mL. The absorbances of these solutions were measured at λ<sub>max</sub> of 412 nm and are plotted in Fig. 1 with respect to volume of 1 mM DCQ or VP. From this plot, it is clear that the mole ratio of thallium to DCQ and thallium to VP is both 1:2.

## 2.5. Ternary complex formation

The Tl (III) ternary complex was prepared by dissolving 1 mmol Tl (III) nitrate trihydrate (0.444 g) in 5 mL of acetonitrile. This mixture was then added dropwise while stirring to a solution of 2.0 mmol 5,7-dichloroquinoline-8-ol (0.44 g) and 2.0 mmol vinyl pyridine (0.21 g) in 5 mL of acetonitrile. The resulting orange solution was stirred for 1 h in order to complete the reaction. Fig. 2 depicts the absorption spectra of the acetonitrile solutions of DCQ, VP, Tl<sup>3+</sup> ion, Tl<sup>3+</sup>-DCQ and Tl<sup>3+</sup>-DCQ-VP against the solvent.

**Fig. 2.** UV–vis absorption spectra of Tl<sup>3+</sup> + DCQ and Tl<sup>3+</sup> + DCQ + VP.

These spectra clearly indicated the formation of a ternary complex with  $Tl^{3+}$  in the presence of DCQ and VP. The absorbance maximum was evident at 412 nm for the ternary complex.

## 2.6. Copolymerization of the prepolymerization mixtures

The prepolymerization mixture was proposed by blending of 5 mmol of MMA (0.500 g), 20 mmol of EGDMA (4.20 g) and 100 mg of AIBN to the thallium (III) ternary complex solution, as described (in Section 2.4). This solution was stirred for about 30 min until a homogeneous solution was attained. The prepared solution was cooled to 0 °C, purged with Argon (99.999%) for 10 min, sealed and heated at 60 °C during stirring for 24 h. The obtained particles were grounded in a mortar and dried in a hot air oven at 60 °C for 2 h and sieved to acquire the powdered particles. About 3 g of these powdered particles were subjected to leaching with 200 mL of 5 M  $HNO_3$  for 5 h to obtain thallium IIP particles. The control polymer particles were prepared in a similar way to that of the IIP preparation, but without the thallium (III) ions. The resultant CP particles were compared with the IIP particles in terms of extraction ability.

## 2.7. Extraction procedure

Thallium (III)-imprinted or non-imprinted polymers were added to 50 mL metal ions solution and the pH value was adjusted to  $6.8 \pm 0.2$  after the addition of the triethylamine (0.1 M).

0.01 g of the IIP particles were added to this solution and stirred for 30 min with the use of a magnetic stirrer. The thallium ions were desorbed from the IIP particles using 5 mL of 1.0 M  $HNO_3$ , through a filter paper and were subsequently determined with ETAAS at 276.8 nm.

## 3. Result and discussion

### 3.1. Characterization studies

The thallium IIP particles were characterized by different characterization techniques.

The specific surface area of the polymers was determined in BET method. The surface area ( $m^2 g^{-1}$ ) is: 254 for IIP and 230 for CP. Pore size analysis shows an average pore diameter of 19 Å. These data indicate the formation of polymer particle with nano-pore and excessive surface area. The surface morphology of the leached and unleached polymers was observed by SEM. The SEM image was obtained in order to account for the effect of Tl (III) removal from the polymer as depicted in Fig. 3. Moreover, an enhanced surface area was also observed from the SEM image of the leached rather than unleached polymer. Thus, the ordered nano-pattern observed in SEM image of leached polymer is probably due to the metal ion imprinting of thallium (III) on the polymer.

The XRD patterns of thallium nitrate (a), the unleached (b) and leached (c) IIP particles are given in Fig. 4. The XRD patterns of the leached and unleached IIP particles exhibited similar patterns, except for the peaks corresponding to thallium nitrate. These peaks were absent in the c curve (leached), indicating the complete removal of thallium ions after leaching.

The TGA analyses of the leached and unleached polymers are shown in Fig. 5. TGA plots with identical characteristics were obtained for the unleached and leached blank polymer particles, respectively. These observations revealed the rigidity of the leached blank and the IIP particles, compared with that of the unleached materials. The former demonstrated decomposition above 300 °C. All the materials were completely decomposed prior to 570 °C. The FT-IR spectra of the unleached and leached IIP particles were

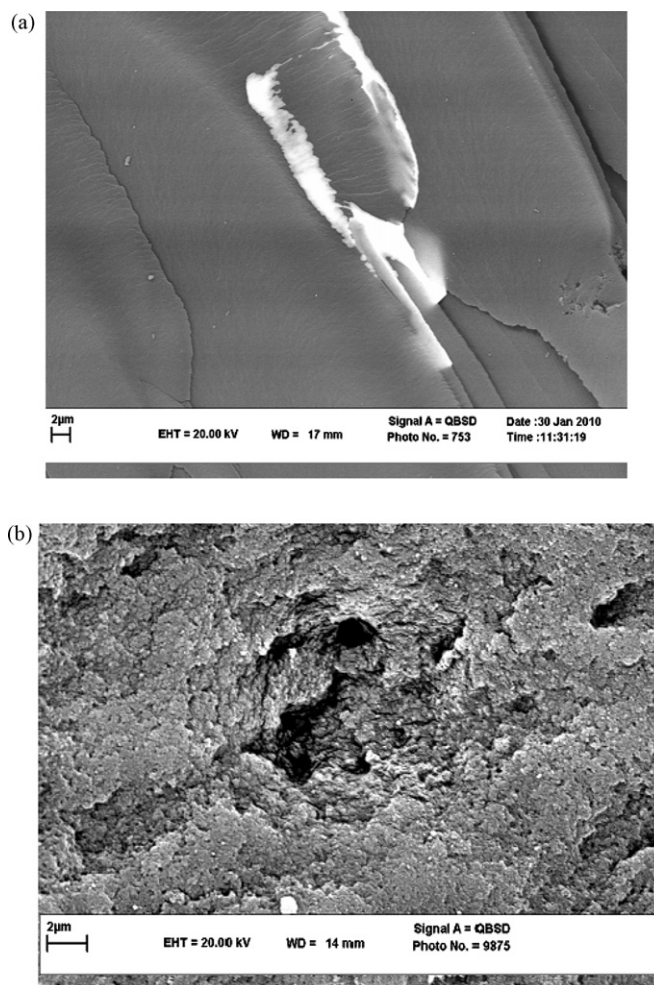


Fig. 3. SEM photographs of IIP (a) unleached and (b) leached.

recorded by the KBr pellet method using a Bomem spectrometer. The strong peak near  $756 cm^{-1}$  corresponded to  $\nu_{C-Cl}$  in the spectra of both the leached and unleached polymers, illustrating that DCQ was kept intact in the polymer even after leaching (Fig. 6).

### 3.2. Preconcentration and rebinding studies

Various experimental parameters (e.g. pH, uptake time, desorption time, IIP weight, aqueous phase volume and  $HNO_3$  desorption volume) were examined. The percentage recovery of thallium was calculated from the ETAAS results. A set of solutions (50 mL volume each) were prepared each containing  $100 ng mL^{-1}$  solution of thallium (III). The effect of pH on Tl (III) uptake was investigated using the batch procedure. The experiments were triplicates. It is evident from Fig. 7 that the adsorption capacity of IIP particles increases with the increase in pH. The increase in extraction percentage in the pH range of 7.0–4.0 for IIP particles is attributed to the competition of Tl (III) ions with  $H^+$  ions which forms a complex with 5,7-dichloroquinoline-8-ol. By increasing the pH, the ratio of free DCQ to the protonated DCQ increases resulting in higher extraction efficiency. On the other hand, the extraction percentage is decreased at pHs greater than 7 in which thallium (III) ions could be precipitated as thallium hydroxide ( $K_{sp} = 1.68 \times 10^{-44}$ ) [30]. Triethylamine was added to the solutions for both adjustment of pHs and to avoid the formation of thallium (III) hydroxide at pHs below 7. For subsequent works; the pH value was adjusted to  $6.8 \pm 0.2$ , after the addition of the triethylamine.

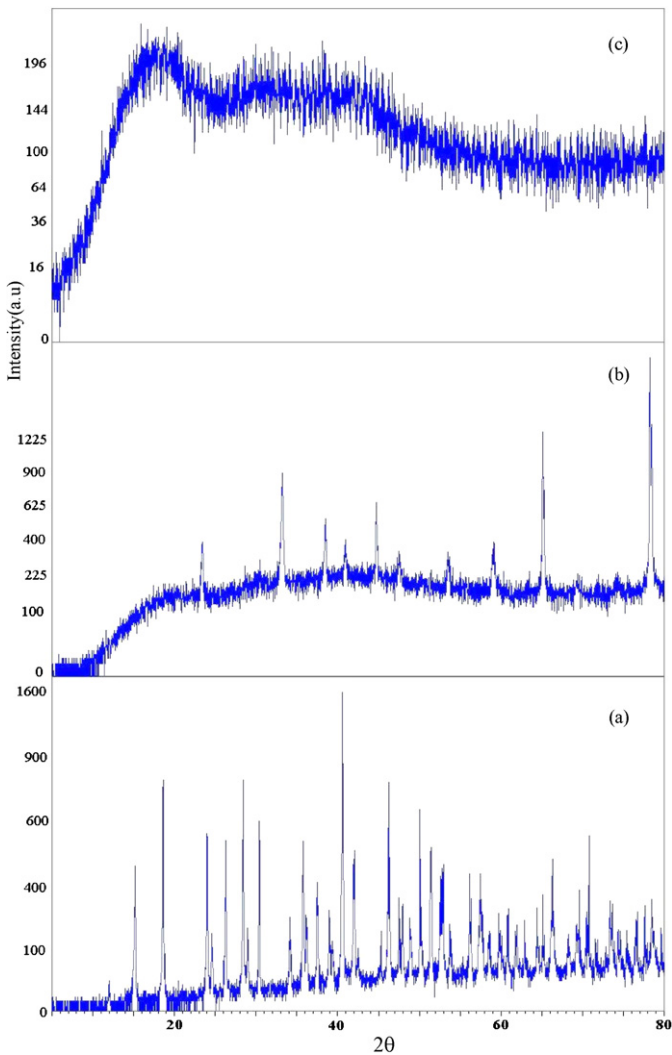


Fig. 4. XRD patterns of pure thallium (III) nitrate(a), unleached(b) and leached (c) thallium IIP particles.

The effects of the polymer particles weight on the thallium enrichment percentage were studied with the CP and IIP particles. Moreover, the minimum quantity of 0.10 g IIP particles was necessary for quantitative enrichment of the thallium (III) ions in 50 mL solution containing  $100 \text{ ng mL}^{-1}$  of thallium.

Other parameters which affected the preconcentration of the thallium (III) ions by the CP and IIP particles were systematically evaluated. In order to evaluate these effects, 50 mL solution of  $100 \text{ ng mL}^{-1}$  thallium plus 100 mg IIP particles was stirred for 30 min. Five millilitre of  $1.0 \text{ M HNO}_3$  were required for the recovery of the preconcentration thallium from polymer material with

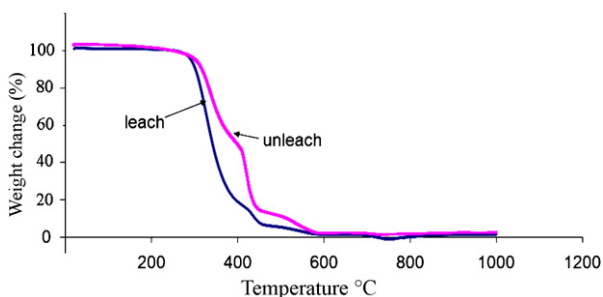


Fig. 5. TGA plots of unleached and leached thallium IIP particles

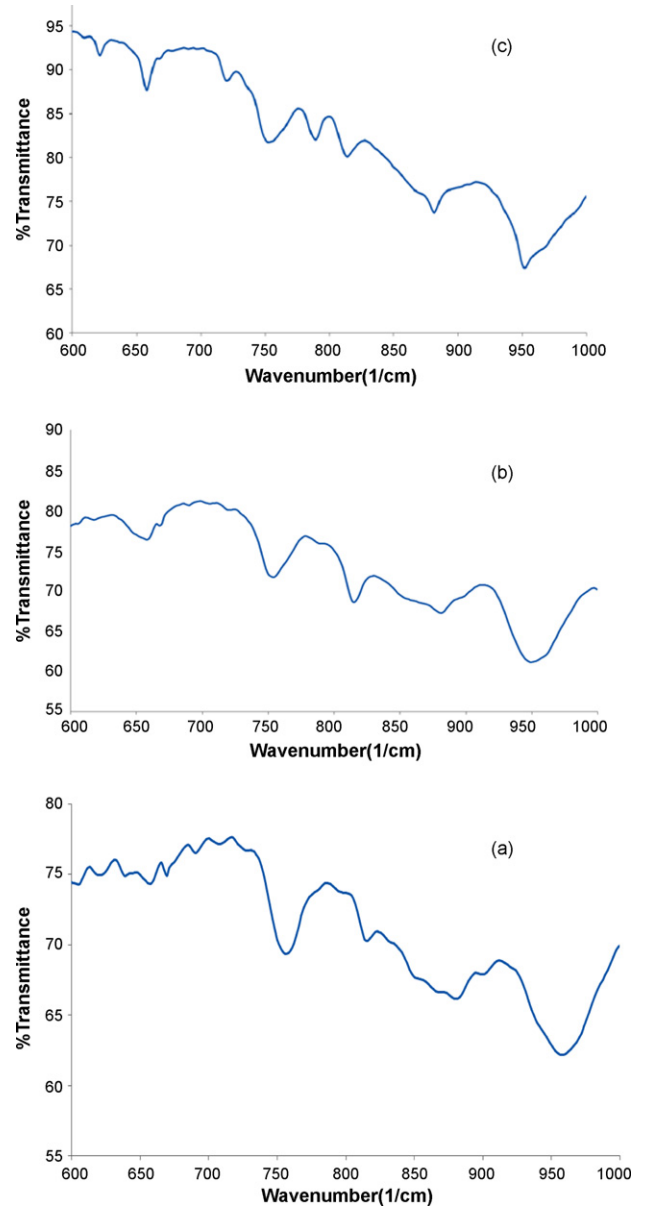


Fig. 6. FT-IR spectra of the leached (a), unleached (b) IIP particles and control polymer (c).

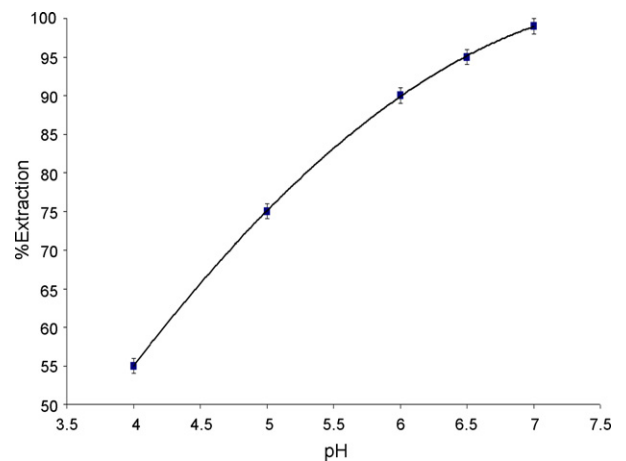


Fig. 7. pH effect on the uptake of the thallium ions using leached IIP particles.



**Table 2**  
Optimum condition for various parameters on uptake of thallium with IIP.

Parameter	Range	Optimum conditions
Weight of IIP (g)	0.02–0.15	0.1
pH	4–7	6.8
Uptake time (min)	10–30	30
Desorption time (min)	5–15	15
HNO <sub>3</sub> desorption volume (mL)	2–5	5
Aqueous phase volume (mL)	50–500	50

**Table 3**  
Percent extraction, distribution ratio and selectivity coefficients of leached IIP particles.

Element	% Extraction	Distribution ratio(D)	Selectivity coefficient ( $S_{Tl^{3+}/M^{n+}}$ )
Tl (III)	98 ± 1	49	–
Na	15 ± 1	0.18	272.2
K	12 ± 2	0.14	350.0
Mg	31 ± 1	0.45	108.8
Ca	23 ± 1	0.30	163.3
Cu	35 ± 1	0.54	90.7
Tl (I)	21 ± 2	0.26	188.5

the minimum desorption time of 15 min. The change of the aqueous phase volume from 50 to 500 mL did not affect the adsorption efficiency of thallium (III). Higher volumes resulted in decrease of absorption efficiency. The relevant results are shown in Table 2.

### 3.3. Adsorption capacity

The adsorption capacity is an important factor to evaluate the IIPs. In order to investigate the adsorption capacity of thallium on imprinted and non-imprinted polymer particles, 100 mg of polymer particles was introduced into a saturated solution of thallium under the optimum conditions. The adsorption capacity of the imprinted and non-imprinted sorbent was calculated to be 9.6 and 5.1 mg g<sup>-1</sup>, respectively.

### 3.4. Selectivity studies

In order to evaluate the selectivity of the imprinted adsorbent, competitive enrichment of Tl<sup>3+</sup>/Na<sup>+</sup>, Tl<sup>3+</sup>/K<sup>+</sup>, Tl<sup>3+</sup>/Ca<sup>2+</sup>, Tl<sup>3+</sup>/Mg<sup>2+</sup>, Tl<sup>3+</sup>/Ti<sup>4+</sup> and Tl<sup>3+</sup>/Cu<sup>2+</sup> from their mixtures was conducted. These ions were chosen because they coexist with thallium ions in natural sources. Under the optimum conditions, Tl (III) at a concentration of 100 ng mL<sup>-1</sup> with each of the inorganic species at a concentration 10 times of Tl (III) was equilibrated with 100 mg of IIP particles. The concentration of these ions was monitored by ETAAS and flame AAS. The percent uptake of thallium ions and other metals ions is given by:

Percent adsorption =  $A_2/A_T \times 100$  where  $A_2$  is the amount of ion enriched by IIP at equilibrium and  $A_T$  is the total amount of ion used in aqueous solution. The distribution ratio ( $D$ ) was determined using  $A_2$  and  $A_1$ .

$D = A_2/A_1$  where  $A_1$  is the amount of ion in aqueous solution at equilibrium.

Selectivity coefficient is defined as  $S_{Tl^{3+}/M^{n+}} = D_{Tl^{3+}}/D_{M^{n+}}$

The obtained results are summarized in Table 3. As evident from these results, the quantitative separation of thallium ions from the Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ti<sup>4+</sup> and Cu<sup>2+</sup> metal ions was possible and reasonably good selectivity coefficients could be obtained.

### 3.5. Statistical and calibration parameters

Under the optimum conditions (Table 2), the calibration curve was linear over the concentration range of 1–600 μg L<sup>-1</sup> thal-

**Table 4**  
Comparison of different methods for preconcentration of thallium (III) with proposed method.

Method	DL (ng mL <sup>-1</sup> ) <sup>a</sup>	LDR (ng mL <sup>-1</sup> ) <sup>b</sup>	Reference
Solid–liquid extraction	1	3.75–17.5	[31]
Liquid–liquid extraction	4	5–20	[32]
Microcrystalline naphthalene	0.3	0.73–4000	[33]
Solid phase extraction	0.003	0.88–0.91	[34]
On-line solid phase extraction	0.009	0.5–2	[35]
Proposed method	0.02	1–600	–

<sup>a</sup> Detection limit.

<sup>b</sup> Linear dynamic range.

lium (III) ion. The linear regression equation for thallium was  $A = 0.7987C_{Tl} + 0.169$  ( $R^2 = 0.999$ ).

Five replicate determinations of 100 μg L<sup>-1</sup> thallium solutions resulted a relative standard deviation of 2.6%. The limit of detection corresponding to three times of the standard deviation of blank was found to be 0.02 μg L<sup>-1</sup>. All the statistical calculations are based on the average of triplicate experiments for each standard solution in the given range. The results suggest that these IIP can be used six times without any considerable loss of adsorption capacity.

The reported method is simple and selective. The comparison of this method with other similar methods is given in Table 4.

### 3.6. Analysis of real sample

In order to evaluate the accuracy of the proposed method, a standard rock reference material, NCSDC 73301, obtained from the geological survey of Japan was analyzed for its thallium content. The rock sample (1 g) was dissolved in a mixture of HF (500 mL), HNO<sub>3</sub> (45 mL) and H<sub>2</sub>SO<sub>4</sub> (165 mL) in a Teflon beaker, and heated until 2 mL of solution was remained. To this solution concentrated HNO<sub>3</sub> (8 mL) and 1.0 mL H<sub>2</sub>O<sub>2</sub> (30%) were added. After heating, it was treated with distilled water to give a clear solution and was finally made to 100 mL by further addition of distilled water. This solution was analyzed for its Tl (III) content according to the proposed procedure and was determined to be  $1.72 \pm 0.30 \mu\text{g g}^{-1}$  which is in good agreement with its certified value ( $1.93 \pm 0.55 \mu\text{g g}^{-1}$ ).

## 4. Conclusion

Ion-imprinted polymers find broad applications as preconcentration and separation purposes for metal ions. In the present work, a DCQ–Ti–VP complex was used for preparation of the ion-imprinted sorbent. The imprinted polymers exhibited good characteristics for the adsorption and preconcentration of the target Tl (III) ions in the aqueous solution.

The maximum adsorption capacity of Tl (III) on IIP particles was 9.6 mg g<sup>-1</sup>, and the optimal pH for quantitative enrichment was 6.8 ± 0.2. Competitive adsorption studies showed that Tl (III) ion-imprinted particles offer the advantage of selectivity towards Tl (III) ion even in the presence of Cu (II) and Mg (II) ions with similar ionic radii. The adsorption capacity of non-imprinted particle for Tl (III) ions was evidently lower than Tl (III)-imprinted particle.

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