

# Solid phase extraction of uranium(VI) on phosphorus-containing polymer grafted 4-aminoantipyrine

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Received: 1 August 2015 / Published online: 6 October 2015  
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**Abstract** Phosphorus-containing polymer grafted 4-aminoantipyrine has been synthesized and used for solid phase extraction of U(VI) prior to its UV–Visible spectrophotometric determination by using arsenazo(III). The adsorbent was characterized by using FT-IR and SEM analysis. The influence of parameters including pH, adsorbent dose, amount of complexing reagent, sample volume and matrix effect have been optimized. The detection limit was determined as  $1.4 \mu\text{g L}^{-1}$  with pre-concentration factor of 30 and RSD of 1.4 %. The accuracy was checked by the analysis of GBW07424 soil and TMDA-64.2 environmental water certified reference materials. The method was applied to natural water and soil samples.

**Keywords** Solid phase extraction · Spectrophotometry · Determination · Uranium · Arsenazo(III)

## Introduction

Uranium is used extensively in nuclear power plants for electric power generation [1]. Therefore the discharge of

uranium into the waste water and soil is increasing day by day. Uranium has toxicological effect, as it leads to renal failure and their compounds are occupational carcinogens [2]. Also due to radioactive nature of uranium it is responsible for environmental pollution. According to World Health Organization (WHO), the maximum permissible level of uranium in drinking water is  $30 \mu\text{g L}^{-1}$  [3, 4]. In Turkey, this limit of WHO is accepted as the maximum permissible level of uranium.

Different analytical methods have been employed for trace level assessment of uranium in environmental samples like neutron activation analysis [5], gamma spectrometer [6], electroanalytical technique [7], fluorescence [8] and inductively coupled plasma mass spectrometry [9]. But all these technique have certain limitations like there running cost is high, need perfect experimental condition to operate, expensive and difficult to operate [10]. Therefore, UV–Visible spectrophotometry is still a better choice for determination of uranium, as it is simple, sensitive, and easy to operate [11]. In order to determined uranium by UV–Visible spectrophotometry large number of chelating agent like 9-phenyl-3-fluorone [12], pyrocatechol violet [13], arsenazo III, *p*-carboxychlorophosphonazo (CPApK) [14], chromotrope 2R [15], 4-(2-pyridylazo) resorcinol [16], 2-(2-pyridylazo)-5-diethylaminophenol and benzoylacetone (BZAC) [17] are used by many research groups. Due to low concentration of uranium it is difficult to determined uranium directly by using analytical methods. The determination of uranium in the environmental samples needs a preconcentration step prior to its determination in order to achieve the detection limit of the analytical instrumental technique [18–20].

Liquid–liquid extractions have been extensively used for preconcentration of uranium by researcher. But due to some limitation like excessive discharge of organic waste,

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significant interfering effect from the matrix ion, the use of solid phase extraction based preconcentration methods become one of the promising preconcentration technique from the last few years. The SPE is cast effective, sensitive, high enrichment factor and environmental friendly [21, 22]. SPE have advantages over other preconcentration technique especially over liquid–liquid extractions which are given in the literature by various researchers [23].

Different researches have used different solid phase extractants for preconcentration of trace element like carbon nanotube (CNTs) [24], resins [25], activated carbon [26], clay [27], zeolite [28] and cross-linked chitosan [29]. The basic mechanism of SPE is the porous surfaces of the adsorbent having organic functional group that interact with metal ion [30]. In the recent past large number of polymeric substances are used for the SPE of trace metal which include Th(IV)-imprinted polymer [31], ionic imprinted polymer [22] and molecularly imprinted polymer [32]. Therefore the techniques based on solid phase extraction by using polymeric substances as adsorbent are highly selective in the presence of highly complex matrix nature of the samples [33].

The aim of the present work is to establish a new precise and accurate solid phase extraction method for uranium from water and soil samples on phosphorus-containing polymer grafted 4-aminoantipyrine (PhCP-AAP) as adsorbent. The analytical conditions like pH, adsorbent dose etc. were optimized.

## Experimental

### Reagents and solutions

Analytical reagent grade standards for uranium ( $1000 \text{ mg L}^{-1}$ ) was provided by (High Purity Standards, Charleston, SC, USA) which was further diluted in ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}$ , Millipore) for preparation of standard solutions of U(VI).  $10 \text{ mg L}^{-1}$  of arsenazo III (3,6-bis[(2-arsenophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid) solution purchased from E. Merck (Darmstadt, Germany) was prepared in ultrapure water.

For pH adjustment Sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) and disodiumhydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ), hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ), carbontetrachloride and acetone were also provided by E. Merck (Darmstadt, Germany). TMDA- 64.2 Lake Ontario water and GBW07424 (GSS-10) soil certified reference materials were provided by National Water Research Institute, Ontario, Canada and by the Institute of Geophysical and Geochemical Exploration, Langfang, China, respectively.

### Instruments

All absorbance measurements of the complex in the preconcentration studies were carried out by using Hitachi 150-20 spectrophotometer with quartz micro-cell with a path length of 10 mm and a volume of  $700 \mu\text{L}$ . Desired pH solution adjustment was done by using pH meter with, Nel pH 900 (Ankara-Turkey) Model glass-electrode. Adsorbent was separated by using centrifuge with centrifugal vials (Shanghai surgical instrument factory, Shanghai, China). To increase the rate of adsorption, vortex mixer (Wiggen Hauser, Malaysia) was used for complete mixing of solutions.

The FT-IR spectrum of the phosphorus-containing polymeric sorbent (PhCP-AAP) was recorded by using Perkin-Elmer Spectrum 400 FT-IR spectrometer (Waltham, MA, USA). For the surface morphology of the adsorbent scanning electron microscope (SEM) images were obtained on a LEO 440 SEM with an accelerating voltage of 20 kV. For SEM measurements, the samples were covered with Au/Pd.

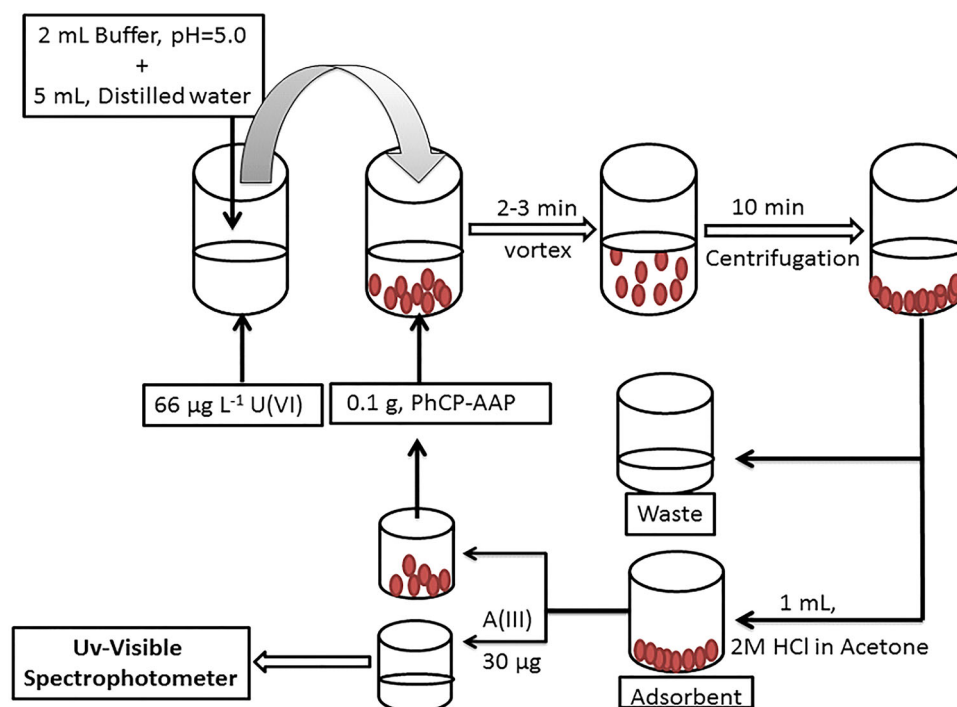
### Preparation of adsorbent

The phosphorus-containing polymer grafted 4-aminoantipyrine (PhCP-AAP) was synthesized on the base of polymer with P–Cl groups and 4-aminoantipyrine. Polymer with P–Cl groups was obtained as described in literature [34]. A 5 % solution of polybutadiene in  $\text{CCl}_4$  was subjected to oxidative chlorophosphorylation by  $\text{PCl}_3$  under the action of oxygen. The polymer with P–Cl bond was separated from liquid part by water-jet air pump. The reaction between polymer with P–Cl groups and 4-aminoantipyrine in mixture of solvent (p-xylene-chloroform–acetone) at  $45^\circ\text{C}$  for 4 h on the reaction flask was performed. The product was filtered, washed with distilled water up to pH neutral, then with acetone and dried in air. The ionization constants values of PhCP-AAP polymer is the following:  $pK_1 = 3.93$  and  $pK_2 = 8.62$ .

### Model studies

The schematic diagram of the procedure was given in Fig. 1. The solid phase extraction of uranium was carried out by taking  $3.3 \mu\text{g}$  U(VI) in 50 ml of centrifuge tube and added 5 ml of ultrapure water and pH 5 buffer solution. Then 0.1 g of PHCP-AAP was added in the centrifuge tube. The solution was allowed for 5 min in contact with adsorbent, under the influence of vortex having vortex speed of  $40 \times 100 \text{ rpm}$ , to increase the rate of adsorption of uranium. After the completion of adsorption reaction, the solution was put in the centrifuge for 10 min to separate the solid phase. Liquid phase was removed from surface of the adsorbent by using

**Fig. 1** Graphical representation of the proposed solid phase extraction of U(VI)



pipette. To adsorbent in centrifuge tube, 1 mL of 2 M HCl in acetone solution was added for elution of uranium from the adsorbent. After vortex and centrifugation the solution was separated and added to 30  $\mu\text{g}$  of arsenazo(III) at pH 1.5 to form a color complex with uranium [12]. After 5 min, the concentration of the solution was measured by using UV-Visible spectrometry at 650.5 nm. The minimum concentration of U(VI) required to have color complex with arsenazo III was 33  $\mu\text{g L}^{-1}$ .

### Application to real samples

The proposed method was applied to tap water from Analytical Chemistry Laboratory of Erciyes University, sea water from Marmara Sea, Turkey and soil sample from Kayseri, Turkey.

The accuracy of the method was validated by applying the method to certified reference materials (GBW07424 (GSS-10) soil and TMDA-64.2 Lake Ontario water. The water samples were passes through a membrane with 0.45  $\mu\text{m}$  size pore provided by (Millipore Corporation, Bedford, MA, USA) to eradicate the suspended particles. Then the procedure given above was applied.

Aqua-regia was used for wet digestion of soil sample and soil certified reference material, in which 24 mL of *aqua-regia* were added to each beaker having 1 g of soil sample (3 replicate) and 1 g of certified reference material (3 replicate). All the samples were kept at room temperature for 30 min, and then on hot plate at 95  $^{\circ}\text{C}$  till dry residue were obtained. The obtained residues were again

digested with of 24 mL of *aqua-regia* and follow the same procedure as discuss in above lines. Final residues were dissolved in 15 mL of distilled water and filtered. The clear solutions of the samples were subjected to the proposed solid phase extraction method given above.

## Results and discussion

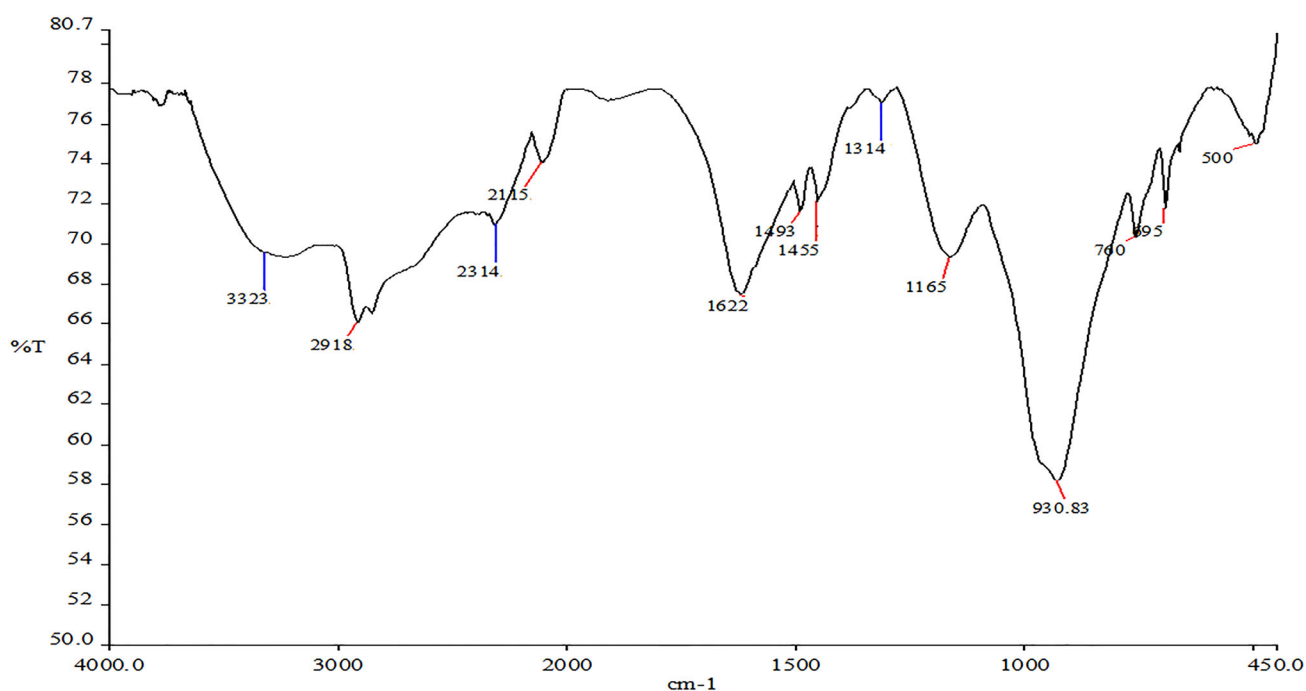
### Characterization of adsorbent

The FT-IR spectrum of phosphorus-containing polymer grafted 4-aminoantipyrene (PhCP-AAP) is shown in Fig. 2. The typical bands can be assigned as follows: O-H: 3323  $\text{cm}^{-1}$ , C-H: 2918  $\text{cm}^{-1}$ , O-H (P-O-H): 2314  $\text{cm}^{-1}$ , P=O (Resonance state): 1622  $\text{cm}^{-1}$ , C=C: 1493, 1455, 1314  $\text{cm}^{-1}$ , P=O: 1165  $\text{cm}^{-1}$ , C-O (P-C-O): 930  $\text{cm}^{-1}$ , C-O: 760  $\text{cm}^{-1}$  and C-H: 695  $\text{cm}^{-1}$  respectively.

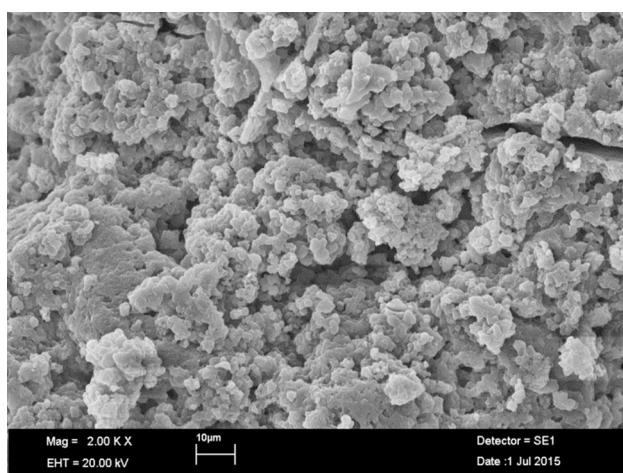
Information about the surface morphology of PhCP-AAP can be obtained by studying the Scanning electron microscopy (SEM) micrographs that are presented in Fig. 3 confirmed porous and rough surface morphology of PhCP-AAP that providing a large exposed surface area for adsorption of uranium.

### Influence of pH

In the solid phase extraction studies, pH is one of the most important factors that influence the recovery of trace metal ion on the adsorbent [35–38]. The effect of pH on percent

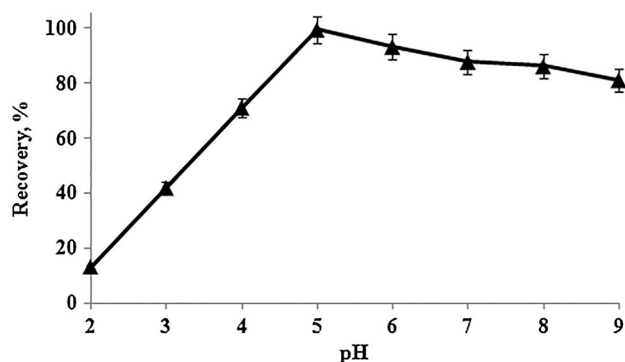


**Fig. 2** FT-IR spectra of adsorbent PhCP-AAP



**Fig. 3** SEM images of adsorbent PhCP-AAP

recovery of uranium on PHCP-AAP was studied at different pH, ranging from 2 to 9 while keeping other parameter constant. The results are depicted in Fig. 4. The recovery of uranium increases rapidly in the pH range of (2–5) and quantitative recoveries of uranium was obtained at pH 5 ( $99 \pm 1$ ). The decline in recovery ( $99 \pm 1$ – $81 \pm 1$ ) at pH range of (5–9) can be explained as: hydrolysis of uranyl ion takes place as the pH increases from 2 to 5 and the following ionic species of uranium has been established that exchange at surface functional group of the adsorbent:  $\text{UO}_2^{2+}$ ,  $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$  dimer,  $[(\text{UO}_2)_3(\text{OH})_5]^+$  trimer.



**Fig. 4** Effect of pH on the recovery of U(VI). (Experimental conditions; amount of PhCP-AAP: 100 mg, amount of arsenazo(III): 30  $\mu\text{g}$ , volume of sample: 10 mL  $N = 3$ )

Above pH 5, complexation of uranium in aqueous solution takes place which decreases the recovery of uranium [39].

#### Effect of amount of PhCP-AAP

The amount of adsorbent is an important parameter for the quantitative recoveries of analytes on the solid phase extraction studies. In order to investigate the amount of adsorbent, the solid phase extraction of uranium(VI) on PhCP-AAP was carried out at different adsorbent doses ranging from 20 to 140 mg. The amount of uranium in was constant and 3.2  $\mu\text{g}$  at 30 mL of sample solution. The results are depicted in Fig. 5. The quantitative recoveries of uranium(VI) were obtained in the range of 100–140 mg of

PhCP-AAP. Therefore 100 mg of PhCP-AAP was used in further studies.

### Effect of amount of arsenazo(III)

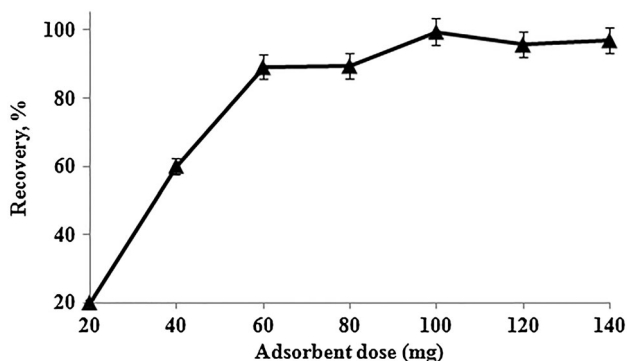
Arsenazo(III) forms (1:1) stable chelate with uranium in wide range of pH [13, 14]. The amount of chelating agent was then investigated by carried out the solid phase extraction of uranium on PhCP-AAP at different amount of A(III) ranging from (10–70 µg) as shown in the Fig. 6. It can be concluded that 30 µg is the most suitable amount of arsenazo(III) in the proposed extraction method of uranium, because below 30 µg, the amount of A(III) is insufficient, while amount of A(III) greater than 30 µg has no effect on recovery of uranium. Therefore 30 µg was used in further solid phase extraction experiments of uranium using PhCP-AAP.

### Effect of sample volume

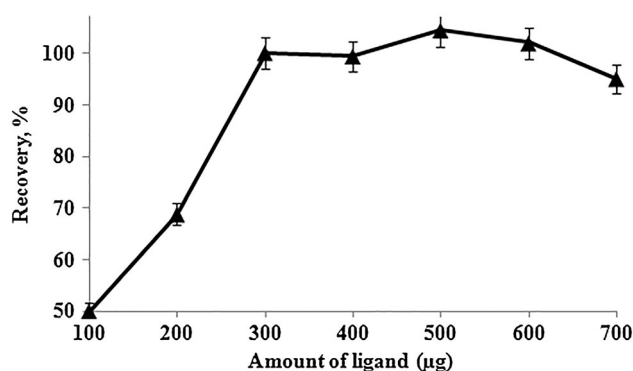
To obtain high preconcentration factor in separation-preconcentration studies, the sample volume is a key factor [40–45]. The required highest preconcentration factor can be determined by applying the proposed solid phase extraction of uranium to different sample volume ranging from (5 to 50 mL) while keeping all the parameter constant. Each sample has 3.3 µg of uranium(VI). Uranium was quantitatively (99 ± 3) extracted till 30 mL of the sample volume. Highest preconcentration of 30 was obtained using 30 mL of sample volume and 1 mL of final volume.

### Desorption studies

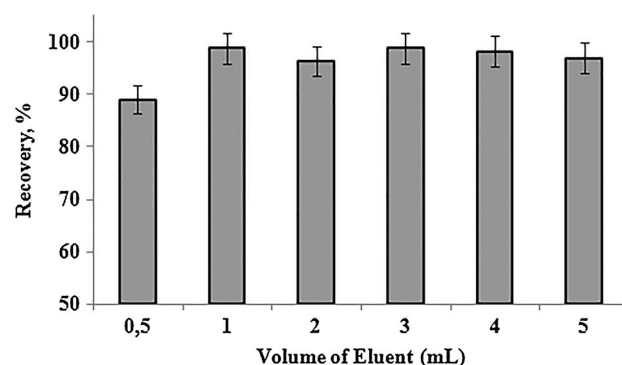
Desorption studies of uranium were carried out by using different type, volume and concentration of eluting agents shown in the Table 2. It can be concluded from the Table 2



**Fig. 5** Effect of adsorbent dose on the recovery of U(VI). (Experimental conditions; pH 5, amount of arsenazo(III): 30 µg, sample volume: 10 mL, *N* = 3)



**Fig. 6** Effect of amount of arsenazo(III) on recovery of U(VI). (Experimental conditions; pH 5, amount of adsorbent: 100 mg, sample volume: 10 mL, *N* = 3)



**Fig. 7** Effect of volume of eluent on the recovery of U(VI). (Experimental conditions; pH 5, amount of adsorbent: 100 mg, amount of arsenazo(III): 30 µg, sample volume: 10 mL, *N* = 3)

**Table 1** Effect of coexisting ions on recoveries of U using phosphorus-containing polymer grafted 4-aminoantipyrine (PhCP-AAP) as an adsorbent pH: 5, concentration of uranium: 66 µg L<sup>-1</sup>, volume of sample solution: 5 mL, amount of adsorbent: 0.1 g (*N* = 3)

Matrix ion	Amount added (µg)	Added as	Recovery (%)
Na <sup>+</sup>	5000	NaNO <sub>3</sub>	96 ± 3
K <sup>+</sup>	5000	KCl	98 ± 2
Ca <sup>2+</sup>	1000	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	94 ± 1
Mg <sup>2+</sup>	1000	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	98 ± 8
Al <sup>3+</sup>	100	Al(NO <sub>3</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	94 ± 4
Cd <sup>2+</sup>	100	Cd(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	97 ± 0
Pb <sup>2+</sup>	100	Pb(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	99 ± 3
Cu <sup>2+</sup>	100	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	97 ± 5
Ni <sup>2+</sup>	100	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	97 ± 4
Co <sup>2+</sup>	100	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	100 ± 3
SO <sub>4</sub> <sup>2-</sup>	500	Na <sub>2</sub> SO <sub>4</sub>	100 ± 7
CO <sub>3</sub> <sup>2-</sup>	500	Na <sub>2</sub> CO <sub>3</sub>	98 ± 8
F <sup>-</sup>	1000	NaF	95 ± 6

<sup>a</sup> Mean ± standard deviation



**Table 2** Effect type and concentration of eluent on recovery of U(VI) on PhCP-AAP, pH: 5, concentration of uranium:  $66 \mu\text{g L}^{-1}$ , volume of sample solution: 10 mL, amount of adsorbent: 0.1 g ( $N = 3$ )

Eluent type	Recovery (%)
Methanol	$7 \pm 3^a$
1 M HCl in methanol	$16 \pm 0$
2 M HCl in methanol	$38 \pm 4$
3 M HCl in methanol	$81 \pm 1$
1 M HNO <sub>3</sub> in methanol	$50 \pm 7$
2 M HNO <sub>3</sub> in methanol	$79 \pm 3$
3 M HNO <sub>3</sub> in methanol	$94 \pm 1$
1 M HCl in acetone	$88 \pm 3$
2 M HCl in acetone	$99 \pm 2$
3 M HCl in acetone	$96 \pm 1$

<sup>a</sup> Mean  $\pm$  standard deviation

**Table 3** Analytical parameter for the proposed method of solid phase micro-extraction of Uranium on PhCP-AAP

Analytical parameter	
Limit of detection, ( $\mu\text{g L}^{-1}$ )	1.4
Limit of quantification, ( $\mu\text{g L}^{-1}$ )	4.8
Preconcentration factor	30
Enhancement factor	28
Relative standard deviation, %	1.4
Correlation coefficient ( $r^2$ )	0.997

that the best eluent that gives quantitative recovery of uranium(VI) was 2 M HCl in acetone. Therefore, 2 M HCl in acetone was selected as eluting agent.

After selecting elution type, the solid phase extraction was carried out at different volume of 2 M HCl in acetone in the range of 0.5–5 mL (Fig. 7). 1 mL of the eluent was the smallest volume which was enough for quantitative recovery of uranium. Hence, 1 mL of 2 M HCl in acetone was used in the further solid extraction experiment of uranium.

**Table 4** Application of proposed the method on certified reference material, pH: 5, Amount of adsorbent: 0.1 g ( $N = 3$ )

Certified reference material	Certified value ( $\mu\text{g g}^{-1}$ )	Found value ( $\mu\text{g g}^{-1}$ )	Recovery (%)
GBW07424 (GSS-10) soil	2.24	$2.21 \pm 0.3^a$	98
Certified reference material	Certified value ( $\mu\text{g L}^{-1}$ )	Found value ( $\mu\text{g L}^{-1}$ )	Recovery (%)
TMDA-64.2 Lake Ontario water	142	$149 \pm 3$	105

<sup>a</sup> Mean  $\pm$  standard deviation

**Table 5** Application of the proposed method to water and soil samples (pH 5.0, amount of PhCP-AAP: 0.1 g ( $N = 3$ ))

Sample	Added ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery (%)
Soil sample	0.0	$0.2 \pm 0.02^a$	–
	4.0	$4.1 \pm 0.01$	98
	5.0	$4.8 \pm 0.10$	94
Tap water	0.0	BDL <sup>b</sup>	–
	2.0	$1.9 \pm 0.03$	95
	3.0	$3.1 \pm 0.05$	104
Sea water	0.0	$0.7 \pm 0.06$	–
	3.0	$3.4 \pm 0.07$	92
	6.0	$9.4 \pm 0.03$	96

<sup>a</sup> Mean  $\pm$  standard deviation

<sup>b</sup> BDL below of the detection limit

### Matrix effects

The major problem related with spectrophotometric determination is the lack of selectivity, because large number of coexisting ions are present in the matrix of samples that lead to either positive or negative interferences [46–51]. To investigate the effect of various coexisting ions the solid phase extraction of uranium was carried out (Table 1). Results found designate that, there are no substantial interfering effects even at the presence of high concentration of these ions. Thus it is confirmed that the proposed method has an excellent selectivity for separation and preconcentration of uranium (Table 2).

### Analytical merits of the proposed method

Various analytical parameter like limit of detection (LOD), relative standard deviation (RSD), enhancement factor (EF) and preconcentration factor (PF) were explored under the optimized experimental conditions using the same method of calculation as given by [35]. The values are given in the Table 3. The method obeys Beer's law in the concentration range of ( $33\text{--}233 \mu\text{g L}^{-1}$ ). The molar absorptivity of the complex was calculated as  $1.07 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 650.3 nm.

**Table 6** Comparison of the developed method with other pre-concentration methods for uranium

Method	Analysis	LOD ( $\mu\text{g L}^{-1}$ )	REF
Solid phase extraction	UV-Vis	1.9	[10]
Dispersive liquid-liquid extraction	UV-Vis	2.4	[11]
Solid phase extraction	ICP-MS	4.5	[12]
Solid phase extraction	UV-Vis	2	[52]
Solid phase extraction	UV-Vis	2	[53]
Solid phase extraction	UV-Vis	2	[54]
Solid phase extraction	UV-Vis	1.4	This work

### Application of the proposed method

The method was validated by applying the proposed method to GBW07424 (GSS-10) soil and TMDA-64.2 Lake Ontario water certified reference materials. The results are given in the Table 4 and shows that the method can be successfully applied for the determination and preconcentration of uranium at trace level.

The method was also applied to tap water, sea water and soil samples for addition recoveries in order to evaluate the accuracy of the method. The recoveries results are given the Table 5 show that the method is highly accurate and can be successfully applied to real samples irrespective to their complex matrix nature.

The proposed solid phase extraction method was also compared to other extraction method regarding limit of detection. Table 6 shows that the proposed method is superior to other extraction method present in the literature [52–56].

### Conclusions

Phosphorus-containing polymer grafted 4-aminoantipyrine (PhCP-AAP) has been synthesized, characterized and was used for the extraction of uranium. This adsorbent was characterized by using FT-IR and SEM. The method is highly sensitive with low detection limit of  $1.4 \mu\text{g L}^{-1}$  with preconcentration value of 30, highly reproducible with RSD value of 1.4 %. The method is highly selective as there is no interferences from the coexisting cation and anion present in the matrix samples of highly complex samples. Therefore the method was successfully applied to water and soil sample without effecting by their complex matrix nature. The application of the method to certified reference materials like GBW07424 (GSS-10) soil, TMDA 64.2 Lake Ontario water confirm that the method can be successfully applied for the determination of uranium at trace level.

**Acknowledgments** Mansoor Khan is thankful to the Scientific and Technological Research Council of Turkey (TUBITAK) under “2216 Research Fellowship Programme for Foreign Citizens” for financial support. Authors are also thanks to Erkan Yilmaz for his helps.

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