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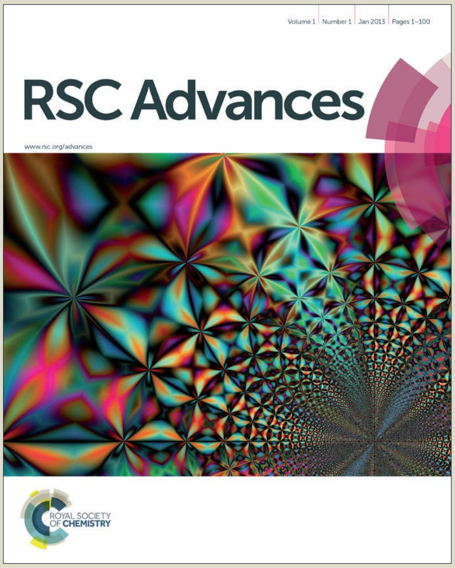

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Manuscript title: Simultaneous preconcentration of uranium and thorium in aqueous samples using cloud point extraction

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Abstract

Uranium (U) and thorium (Th) are both chemically and radiologically toxic even at ultratrace concentrations. Hence development of new preconcentration procedures for their precise determination by simple, versatile and cost effective analytical technique is desirable. A novel, simple and simultaneous cloud point extraction (CPE) procedure has been developed for preconcentrating trace amounts of U and Th in aqueous samples. The preconcentration of the metal ions in the surfactant rich phase of Triton X-114 was carried out by complexing them with trioctylphosphine oxide (TOPO) and N,N,N',N'-tetraoctyldiglycolamide (TODGA). The preconcentrated solution was subjected to UV-Visible spectrophotometry employing arsenazo-III. Partial least square regression analysis was then utilized to resolve their overlapping absorbance spectra and thereby allowing their determination in presence of one another. The CPE procedure was optimized with respect to: pH of the solution, ionic strength, extraction temperature, phase separation temperature and concentration of extractants, surfactant and co-surfactant. The developed CPE procedure resulted in percentage extraction efficiencies (EEs) of 98.0±0.5 for U and 99.5±0.5 for Th. Interference studies were also carried out and it was found that the recoveries of U and Th were 98% and 99% respectively in absence and ≥ 95% in presence of interfering ions. The linear dynamic concentration range of the procedure was found to be 15-1000 ng mL^{-1} and 10-1000 ng mL^{-1} for U and Th respectively. The developed methodology was successfully employed for the determination of U and Th in the unspiked and spiked samples of ground water, lake water and sea water samples with ≤ 4% relative standard deviations. These samples were also directly analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and the agreement between these two results at 95% confidence level validates the developed methodology. The proposed CPE procedure can be used effectively for

the simultaneous extraction of U and Th quantitatively with PFs of 94 for U and 100 for Th and can tolerate much higher level of interfering ions.

1. Introduction

Uranium (U) and thorium (Th) are the two most naturally abundant actinides found in the environment. In addition their anthropogenic isotopes ($^{232, 233, 236}$U and ^{229}Th) which are being generated in nuclear power plants, nuclear explosions and nuclear accidents too contribute to the environmental toxicity. Their soluble compounds are known to have both chemical and radiological toxicity.[1-3] As per the World Health Organization (WHO) and Atomic Energy Regulatory Board (AERB), India guidelines, the permissible limit of U in drinking water should be less than 30 and 60 ng mL^{-1} respectively.[4,5] The Environmental Protection Agency (EPA), USA had specified the maximum contaminant level (MCL) of 15 nCi mL^{-1} for alpha activity, excluding radon and uranium in drinking water.[6] Th being an alpha emitting nuclide, its approximate maximum permissible concentration limit in drinking water should to be less than 68 ng mL^{-1} and this value has been arrived at by considering only the specific activity of natural Th. In view of their toxicity even at trace and ultratrace level precise determination of these actinides in environmental and biological samples is a challenging task.

Direct determination of U and Th in environmental samples by simple and versatile spectroscopic techniques viz. UV-Visible spectrophotometry, inductively coupled plasma atomic emission spectroscopy (ICP-AES) and liquid scintillation counting (LSC) etc. is quite difficult because of their low concentrations and the presence of complex matrices in such samples. Hence development of simple and novel analytical strategies for improving the detection of these elements are always desirable. A number of preconcentration and separation techniques like liquid-liquid extraction (LLE), solid phase extraction (SPE), ion-exchange chromatography (IEC) etc. have been developed in the past.[7-12] However, generation of significant to large volumes of organic waste in LLE can increase the environmental hazard and hence it is not considered to be eco-friendly. The lower retention capacity of commercially available resins (TEVA/UTEVA/DGA), its limited reusability, chances of cross contamination and also generation of significant amount of contaminated waste in SPE makes this technique disadvantageous.[8,9] The poor selectivity of the metal ions in IEC due to the mass-to-charge ratio driven interaction with the functional groups makes this technique least attractive.[7]

Over the last decade, cloud point extraction (CPE) has emerged as a simple and powerful method for separation and preconcentration of metal ions.[3, 13-18] CPE is essentially based on the extraction of metal ion into the dispersed micelle phase of non-ionic polyoxyethylene surfactants followed by temperature driven phase separation and aggregation of micelles, referred as coacervation. The temperature at which the surfactant solution separates into two immiscible phases i.e., (i) bulk aqueous phase containing surfactants at a concentration less than or equal to critical micelle concentration (CMC) and (ii) the surfactant rich phase (SRP), is called its cloud point temperature (CPT). The extraction of metal ions from bulk aqueous phase to the SRP is achieved by dispersing the selected organic extractant into the aqueous phase with the help of surfactants. This in turn enhances the interaction between the metal and ligand and hence no external forces are required as in LLE. [19] The improvement in the extraction efficiency (EE) of a particular metal ion depends on a number of modifications of the CPE system, the most common being: choice of a suitable extractant, maintenance of the required pH, addition of a co-surfactant if required, extraction temperature and phase separation temperature etc. Because this technique uses millimolar amounts of surfactants and micro- to milli-molar amounts of extractants, it is seen as a greener alternative to LLE. [20] Furthermore, the CPE was recently demonstrated by Favre-Réguillon et al. to have a higher EE than LLE. [21]

A significant number of literatures are available on the CPE of U [18,21-27] and a few for Th [28-30] but only one report is available on the simultaneous preconcentration of U and Th along with zirconium and halfnium[3]. In the work of S. Shariati et al.[3] the enrichment factors (EFs) obtained for U and Th upon preconcentration are 37.0 and 43.6 respectively. However precise determination of U and Th around their guideline values by a cost effective and versatile spectroscopic technique like UV-Visible spectrophotometry requires higher EEs and preconcentration factors (PFs) because it provides acceptable sensitivities and enables detection of U and Th at µg mL^{-1} level. [31-35] Hence there is a need for the development of CPE procedure for simultaneous preconcentration of U and Th with higher EEs and PFs.

In this paper, we have developed a new CPE method using trioctylphosphine oxide (TOPO) as neutral extractant and N,N,N',N'-tetraoctyldiglycolamide (TODGA) as co-extractant for simultaneous preconcentration of U and Th. The cloud point conditions were optimized with respect to pH, extractant concentration~~s~~, surfactant concentration~~s~~, temperature and tolerance level of interfering ions. The preconcentrated fraction was analysed by UV-Visible spectrophotometry using arsenazo-III as the complexing agent. A multivariate calibration method i.e., partial least square regression (PLSR) was employed to resolve the overlapping absorption spectra of the constituent analytes. Strong acidic media was chosen for their spectrophotometric determination to eliminate the interferences from other elements which form arsenazo-III complex at high pH and thereby making the method simple and convenient. The stability of the U- and Th-arsenazo-III complexes was studied in different mineral acids to find the perfect medium with optimum concentration. The proposed method was applied for the analysis of three natural water samples and these were also directly analyzed by ICP-mass spectrometry (ICP-MS) to validate the developed methodology.

2. Experimental

2.1. Instrumentation

A UV-Visible-NIR double beam spectrophotometer (JASCO, Japan make, model V-670) was used for the measurement of absorbance of U- and Th-arsenazo-III complex. The pH of the solutions were measured with a pH meter (LABINDIA, India make PICO$^+$). The PLSR calculations were carried out in The Unscrambler® X (M/s Camo Software, India) software. Direct analysis of the samples were carried out by ICP-quadrupole MS (PQ2 plus, V.G., UK). An ultracentrifuge (Sigma make, model no. 3K30) was used for centrifugation.

2.2. Reagents and materials

MilliQ water (18MΩ.cm, Millipore Corporation, Bedford) was used throughout the experiment. High purity $UO_2(NO_3)_2.6H_2O$ (99.9%) and $Th(NO_3)_4.5H_2O$ (99.9%) were obtained from Indian Rare Earth (IRE), India to prepare 1000 μg mL^{-1} stock solution of each analyte in 1% (v/v) HNO_3 medium. These individual standard solutions were mixed in appropriate amount and diluted with MIlliQ water to obtain a mixed stock solution of concentration 10 μg mL^{-1} with respect to each analyte. Other reagents used in the development of CPE system are: HNO_3 and NaOH (Merck), sulfamic acid (Sigma-Aldrich), KNO_3 (Alfa Aesar), Triton X-114 (TTX-114; Sigma-Aldrich) and sodiumdodecyl sulphate (SDS; Sigma-Aldrich), and TOPO (Sigma-Aldrich). TODGA was synthesized using the procedure proposed by D.D. Dicholkar et al.[36] TOPO and TODGA were dissolved separately in solutions of Triton X-114 to enhance their solubility. 50 mL conical glass centrifuge tubes with stopper from Borosil (India) were used.

Ground water from Punjab (India), lake water from West Bengal (India) and sea water from Mumbai coast (India) were collected for analysis.

2.3. Sample pretreatment

The water samples were first filtered through Whatman^{TM} filter paper 541 and then through a 0.2 µm syringe filter to get clear solutions.

2.4. CPE system

40 mL aliquot of the sample containing the analytes was adjusted to pH 6 by adding dilute HNO_3 and NaOH in a volumetric flask. Afterwards, 100 µL of 0.25 mol L^{-1} SDS, 2.5 mL of both 1x 10^{-2} mol L^{-1} TOPO and 2 x 10^{-3} mol L^{-1} TODGA in 4 x 10^{-2} mol L^{-1} TTX-114 were added to it. 1mL of 5mol L^{-1} KNO_3 was added to maintain the proper ionic strength and the solution was diluted to 50 mL using water. The solution was then continuously stirred for 1 h in an ice bath to attain equilibrium. Subsequently the solution was transferred to a 50 mL conical centrifuge tube and kept in a thermostat water bath at 50^{o}C for 1 h. In this step the solution becomes cloudy and the SRP get separated by the gravitational force. The complete phase separation was achieved by centrifugation at 4000 rpm for 10 min at room temperature. The tube was then placed in an ice bath for 5 min to make the SRP phase more viscous and hence facilitate separation of the aqueous phase by decantation. A schematic representation of the above demonstrated CPE procedure is given in Figure 1.

2.5. Spectrophotometric procedure

After separating the bulk aqueous phase the SRP was made less viscous by adding 2 mL of a solution containing 10:90 (v/v) methanol/conc. HNO_3 and transferred into a 5 mL beaker. The solution was then evaporated near to dryness and allowed to cool down at room temperature. Then the solution was made upto 1 mL volume by adding oxalic acid (0.1 mol L^{-1}), HNO_3 (6 mol L^{-1}), sulfamic acid (0.1 mol L^{-1}), arsenazo-III (0.07% w/v) and MilliQ water. Higher dilution factors were sometimes required depending upon the maximum peak absorbance. The solution was mixed well for 1 min for complete complexation of all the metal ions by the organic dye. The solution was consequently transferred into a 0.5 cm quartz cell and the absorbance was measured in the 600-750 nm range.

2.6. Partial Least Square Regression analysis

The complete absorption spectra (600-750 nm) of the samples were used for PLSR analysis, which is a purely empirical approach. Two sets of standard samples were prepared for PLSR i.e., calibration set (CS) consisting of 15 standards which was used for constructing the calibration curves and the validation set (VS) consisting 5 samples to validate the calibration models generated by PLSR algorithm. The concentrations of U and Th in these standard sample sets are tabulated in Table 1. The PLSR algorithm used in this work is similar to the one previously described. [37,38] The predictive capability of the PLSR method was validated by determining the root mean square error of prediction (RMSEP) and percentage relative error of prediction (REP) of VS sample analysis.

3. Results and discussion

3.1. Optimization of CPE procedure

The optimized CPE conditions represented in Table 2 were obtained through cross-optimization process of all parameters. The method was assessed by calculating extraction efficiency (EE,%), recovery (%) and preconcentration factor (PF) for each individual analyte by using the following equations:

$$\mathrm{EE}(\%) = \frac{C_{\text{initial}}V_{\text{initial}} - C_{\text{supernatant}}V_{\text{supernatant}}}{C_{\text{initial}}\,V_{\text{initial}}}\ \mathrm{X}\ 100 \qquad (1)$$

$$\mathrm{Recovery}(\%) = \frac{C_{\text{SRP}}V_{\text{SRP}}}{C_{\text{initial}}V_{\text{initial}}}\ \mathrm{X}\ 100 \qquad (2)$$

$$\mathrm{PF} = \frac{C_{\text{initial}}V_{\text{initial}} - C_{\text{supernatant}}V_{\text{supernatant}}}{C_{\text{supernatant}}V_{\text{supernatant}}} \qquad (3)$$

where C_{initial}, C_{SRP} and $C_{\text{supernatant}}$ are the concentrations of respective analyte initially taken, in the SRP and in the supernatant after phase separation respectively. Similarly V_{initial}, $V_{\text{supernatant}}$ and V_{SRP} are the initial volume of the solution (50 mL), volume of the supernatant phase after phase separation and volume of the redispersed SRP respectively. The concentration of analytes in the supernatant, after phase separation, being very low were determined by ICP-MS.

3.1.1. Effect of ligand(s) concentration

TOPO is known to have high selectivity for tri, tetra and hexa-valent actinides and hence is widely used for the extraction of U and Th from various matrices.[39] The effect of TOPO concentration from 0 to 0.5 x 10^{-3} mol L^{-1}, on the recoveries of U and Th are shown in Figure-2. The recoveries were in the range 10-85% for U and 15-99% for Th. The EEs for both U and Th were almost maximum when the concentration of TOPO was in the range of (0.1-0.5) x 10^{-3} mol L^{-1}. However TOPO can extract tri-valent lanthanides when acid concentration is less than 2 mol L^{-1}.[39] Consequently studies were also carried out by taking equal quantities of lanthanum (as a representative of lanthanides) along with U and Th, for the same TOPO concentration range, and the results are represented in Figure2. As reported earlier, the efficiency of CPE of U by TOPO decreases in presence of equal amount of lanthanum[40] and a similar decreasing trend was observed both for U and Th for the entire TOPO concentration range of (0.025 - 0.5) x 10^{-3} mol L^{-1}. Recoveries were found to increase from 0.025 x 10^{-3} to 0.2 x 10^{-3} mol L^{-1} and later remain the same. Hence 0.5 x 10^{-3} mol L^{-1} of TOPO concentration was fixed to prevent the large reduction in the recoveries of analytes in presence of lanthanides. According to S. Gao et al.[40] the improvement in the recovery of U, by TOPO, in presence La was obtained by the addition of bis[(trifluromethyl)sulphonyl]imide (NTf^{2-}) based ionic liquid. The improvement was due to the formation of smaller uranyl complex than lanthanum and it was the steric factor which was attributed to be the reason for less extraction of La^{3+}. However this method cannot be applied to the simultaneous extraction of U and Th as by the same analogy thorium would not be extracted into the SRP. Hence we thought of introducing a co-extraxtant along with TOPO which would prefentially complex trivalent lanthnides therby minimizing the competition of complexation of lanthanides with TOPO and making it available for complexation with U and Th. TODGA was explored as co-extraxtant as it is known to have very high selectivity towards lanthanides and tri-valent actinides and also have good selectivity for tetra- and hexa-valent ions.[41] The concentration of TODGA was varied in the range of (0.02 - 0.2) x 10^{-3} mol L^{-1}, in presence of 0.5 x 10^{-3} mol L^{-1} of TOPO, to observe the recoveries of both U and Th in presence of equal amount of lanthanide. The findings are shown in Figure3. It may be inferred from Figure3 that 0.1 mmol L^{-1} of TODGA is optimum for quantitative extraction of both U and Th in absence and presence of equal amount of lanthanide.

3.1.2. Effect of non-ionic surfactant

Triton X-114 (TTX-114) was chosen as the surfactant because its theoretical CPT (28°C) is near the room temperature and it's CMC of 0.2 x 10^{-3} mol would not have significant toxicological impact on the environment. [42] The higher density of the TTX-114 SRP compared to water facilitates the phase separation process which was further improved by centrifugation. The goal of a successful CPE is to achieve highest EE and minimum phase volume ratio of the surfactant to improve PF. The effect of TTX-114 concentration on the recovery of U and Th was studied in range of (1-10) x 10^{-3} mol L^{-1}. The analyte recoveries were found to increase with surfactant concentration upto 4x 10^{-3} mol L^{-1} and later it remains constant. Hence 4x 10^{-3} mol L^{-1} of TTX-114 concentration was selected for further experiments.

3.1.3. Effect of ionic surfactant concentration

The highest LLE extraction of both U and Th, by TOPO, from 3 mol L^{-1} HNO_3 medium are known to occur via the $UO_2(NO_3)_2$.2TOPO and $Th(NO_3)_4$.3TOPO neutral complex formation. [39] TODGA is also known to extract these metal ions as their neutral nitrate complexes in strong acidic conditions. [41] However in the typical pH range for CPE analysis the extraction is dominated by the positively charged complexes of U and Th and this is due to the lack of nitrate concentration. SDS was chosen as the ionic co-surfactant to increase the EEs of U and Th because of its negatively charged hydrophilic head group. In order to ensure that the surface-active ions remains either as monomers or as mixed micelles with TTX-114, the concentration range of the co-surfactant (0.1 x 10^{-3} -1x 10^{-3}mol L^{-1}) was set far below its critical micelle concentration (CMC: 8.5 x 10^{-3} mol L^{-1} at 25°C). The observations are shown in Figure4. A sharp increase in analyte recoveries was observed with increase in SDS concentration from 0 to 0.2 x 10^{-3}mol L^{-1} followed by a slow increase at higher concentrations. The highest reproducible recoveries were obtained at 0.5 x 10^{-3} mol L^{-1} of SDS concentration. The recoveries of U and Th were found to drop sharply above SDS concentration of 0.6 x 10^{-3} mol L^{-1} and resulted in less than 40% of recoveries. At high SDS concentrations the CPT of the CPE system becomes high which results in lower EEs as demonstrated by Gu et al.[43] Hence the concentration of SDS was kept at 0.5 x 10^{-3} mol L^{-1}.

3.1.4. Effect of salt concentration

As discussed above it is essential to maintain a particular nitrate concentration to facilitate quantitative complexation of U and Th with TOPO. Hence KNO_3 was added to the system to maintain the ionic strength of the solution. KNO_3 also acts as a salting-out agent and thereby forcing the metal-ligand complexes to be formed inside the micelles. A 0.1 mol L^{-1} concentration of KNO_3 was found to be optimal and there was no appreciable effect on the recovery of analyte with increase in ionic strength.

3.1.5. Effect of pH

TOPO is known to have the highest distribution ratio for both U and Th at 3 mol L^{-1} HNO_3 medium. But such high acid concentration hampers the coacervation of micelles and is not recommended for CPE. Hence the recoveries for both U and Th were determined for the pH range from 1 to 10, typical for CPE procedure. [18] The effect of pH on the recoveries is shown in Figure5. The low recoveries in lower pH region can be attributed to the protonation of the sulphate group of SDS. The optimal recoveries were obtained for pH values ranging from 5.5 to 7 for U and 5 to 8 for Th. The decrease in recoveries at higher pH is due to the formation of carbonate and/or bicarbonate complexes of U and Th in environmental samples. Therefore a pH value of 6 was selected as the optimum one.

3.1.6. Effect of temperature

The CPE is mainly dominated by two temperature dependent steps, namely the analyte extraction temperature and the phase separation temperature. The addition of additives to a system of non-ionic surfactant is known to change the CPT drastically. The addition of SDS will increase the CPT whereas the addition of an electrolyte (KNO_3) will decrease the same. [43] The developed system was found to coacervate near its theoretical CPT of ~30^{o}C. The analyte recoveries were examined at different extraction temperatures in conjugation with different phase separation temperatures. In the first case the solutions were allowed to stand for 1 h in an ice bath (5-6^{o}C) with constant stirring and then phase separation was carried out at different temperatures ranging from 30-70^{o}C with constant incubation time of 1 h. In the second case the extraction was carried out at room temperature (25^{o}C) and rest of the conditions were maintained same as in the previous case. In the third case the extraction and phase separation was carried out at temperatures ranging from 30-70^{o}C for 2 h. After the incubation period the complete phase separation was done by centrifugation at 4000 rpm for 10 min at room temperature. The analyte recoveries found in all three cases are represented in Figure6. The highest recoveries were obtained with the extraction temperature 5-6^{o}C and phase separation temperature 50-70^{o}C respectively. At higher extraction temperature the micelles tend to coacervate and hence the viscosity of the surfactant phase increases thereby causing lesser interaction of the ligand with the metal ion. On the other hand at low extraction temperature there is greater interaction of the metal ion with ligand present in miceller medium resulting in quantitative recoveries of analytes. Similar type of observations was previously made by Labrecque et al.[16] It was reported by Safavi et al. [42] that the highest PFs were obtained when phase separation temperature is above the CPT of the system. Hence 5-6^{o}C was chosen as the extraction temperature with 1 h incubation time and 50^{o}C as the phase separation temperature with 1 h followed by centrifugation at 4000 rpm for 10 min.

3.2. Optimization of spectrophotometric procedure

The use of organic dyes for the spectrophotometric determination of actinides had been reported. [31] Among them arsenazo-III has the advantage of forming stable complexes with U and Th even at strong mineral acid medium.[31] The strongly acidic media also excludes the possibilities of hydrolysis, formation of polynuclear species and formation of complexes of arsenazo-III with other elements which may interfere with the spectrophotometric determination of the analytes. [31] The type of the mineral acid medium i.e. HCl, mixture of HNO_3 and sulfamic acid, $HClO_4$ and their molarities plays an important role in the determination of U and Th as reported in the literature.[31-35,44,45] The stability of arsenazo-III was found to be comparable in all the acids in the range of 5-6 mol L^{-1} for a long period. Both U and Th form complexes with arsenazo-III instantaneously. The U-arsenazo-III complex was found to be stable upto 3 to 4 weeks in all three mineral acids whereas the stability of Th-arsenazo-III complex was found to be dependent on Th concentration as well as the acid medium.[32] The observations for Th-arsenazo-III complex are depicted in Figures7 and 8. The decrease in absorbance is due to the degradation of Th-arsenazo-III complex. In HCl medium the decrease in absorbance was observed for Th concentration above 1.5 μg mL^{-1} and below that the absorbance was found to be quite stable for 1 h period. Whereas in $HClO_4$ medium the decrease was observed at 1.0 μg mL^{-1} of Th and the rate of decrease in absorbance was much faster than that in HCl medium. Only in HNO_3 medium containing sulfamic acid no appreciable decrease in absorbance of Th complex was observed for a period of 1 h and Beer's Law was found to be followed in the concentration range of 0.25-6.0 μg mL^{-1}. In case of U the Beer's law was found to be followed in the concentration range of 0.5-

15.0 μg mL^{-1}. The molar absorptivities for U and Th at 656 nm and 662 nm were found to be 2.2 x 10^4 and 6.4 x 10^4 mol^{-1} L cm^{-1} respectively at room temperature. Sulfamic acid was added during the spectrometric determination of U and Th by arsenazo-III in HNO_3 medium to destroy any nitrous acid and oxides of nitrogen which are invariably present in equilibrium with nitric acid. [45] The simultaneous determination of U and Th is difficult due to the closeness of their absorbance maxima resulting in high degree of spectral overlapping. In order to overcome this difficulty it is necessary to resolve their spectra by the application of PLSR algorithm. In order to maintain the peak absorbance below 2 the concentration of U and Th in CS and VS solutions were maintained accordingly and preconcentrated samples were diluted suitably.

3.3. Partial Least Square Regression analysis

The simultaneous spectrophotometric determination of U and Th by arsenazo-III was carried out applying PLSR algorithm to deconvolute their overlapping complex spectra.

3.3.1. Factor optimization

In PLSR calibration approach, the number of factors (which is equivalent to principle component in principle component analysis) to be included in the algorithm was determined by comparing root mean square error of cross validation (RMSEcv). The optimization of the number of factors has great impact on the accuracy and precision of the model. Since these factors are the re-distributed version of the total variance, hence introduction of more than necessary factors will increase the noise portion in the regression. In this work the number of factors was optimized by determining the RMSEcv of VS samples for U and Th. The change in RMSEcv values for both U and Th with the change in number of factors in the PLSR model is shown in Figure9. It can be seen that minimum 6 factors are required for both U and Th to obtain the minimum RMSEcv values of the elements. Further increase in the number of factors did not show any appreciable improvement in RMSEcv values.

3.3.2. PLSR coefficient

In PLSR, the acquired spectra for corresponding concentrations were correlated with each other mathematically and a column matrix or vector, also known as PLSR coefficient (PLSRC) for individual element was constructed. A graphical representation of the PLSRC, obtained by using 6 factors, is represented in Figure10. The positive PLSRC values indicate a positive correlation between the intensity at the pixels and the elemental concentration used in unknown sample and a negative PLSRC indicate the reverse. It can be seen from the Figure10 that both U and Th have two positive correlation peaks at different places indicating high sensitivity of those area to the corresponding element.

3.3.3. Accuracy and precision

The accuracy and precision of the PLSR model was obtained by analyzing the VS samples. Five replicate spectra of each sample were treated to calculate those parameters. The accuracy was examined by checking the elemental percentage recovery and the precision was expressed in terms of RMSEP and REP(%). All the calculated values are tabulated in Table 3.

3.4. Effect of common interfering ions

Studies were carried out to demonstrate the applicability of the proposed method in presence of common interfering ions, which are likely to be present along with U and Th in environmental samples. For this purpose 50 ng mL^{-1} solutions of the analyte ions were analyzed in presence of different concentration of the interfering ions. Even though the alkali metals may not get extracted but could affect the clouding behavior due to their large abundance in nature, it was necessary to carry out the recovery studies of the analytes in their presence. However the alkaline earth metal ions, the transition metal ions and the lanthanides are expected to be extracted along with the analytes due to their higher oxidation states. The effects of commonly occurring anions were also studied. The maximum tolerable limit of the interfering ions on the CPE procedure was considered as acceptable only when the recoveries of U and Th were ≥ 95%. The results of the interference studies are tabulated in Table 4. A pictorial representation depicting the mean recoveries and relative standard deviations (RSDs) of U and Th in absence and presence of interfering ions at the maximum tolerance limit is shown in Figure11.

3.5. Analytical figures of merit

The proposed CPE method was found to provide quantitative EEs of (98.0±0.5)% for U and (99.5±0.5)% for Th and recoveries of 98% for U and 99% for Th. The proposed method will find applicability in decontamination, extraction and quantification of trace amounts of U and Th as the preconcentration step leaves nearly negligible amount of the analytes in the supernatant. The PFs were found to be 94 for U and 100 for Th. The linear dynamic concentration range of the procedure was found to be 15-1000 ng mL^{-1} and 10-1000 ng mL^{-1} for U and Th respectively. The RSDs (1σ) were found to be between 1-3% and 2-5% respectively in absence and presence of interfering ions.

The analytical performance of the developed methodology has been compared with the previously reported CPE procedures for U and Th as shown in Table 5. It can be seen from the table that only a single work had been reported for simultaneous preconcentration of U and Th,[3] but no data on EEs had been provided and the determined PFs were quite low. In the present work, we have evaluated all the parameters and these are relatively higher than those reported by S. Shariati et al.[3] These values are also found to be comparable and in some cases even better than the earlier reported CPE procedures for either U or Th.[18, 21-30] The minimum concentration level of U and Th which had been reported by S. Shariati et al.[3] is lower than the present work and this is obvious as they have used ICP-OES which is more sensitive than UV-Visible Spectrophotometer. The proposed method however can be effectively used for quantification of U and Th in drinking water. The percentage RSD of the proposed method is much better than many of the previously published works. [3,18,22,26,27,28,30] According to S. Shariati et al. [3] the interference of Cr^{3+} (5 µg mL^{-1}) and Hg^{2+} (5 µg mL^{-1}) was observed on the recovery of U, Th, Zr and Hf by CPE and it was taken care of by increasing the concentration of ligand from 2 x 10^{-4} mol L^{-1} to 5 x 10^{-4} mol L^{-1}. However in the present work it was observed that 10 µg mL^{-1} of $Cr^{3+}$and 5 µg mL^{-1} of and Hg^{2+} can be tolerated without increasing the concentration of the extractant. The tolerance of other elements on the extraction of U and Th were experimentally examined and this was done with a much higher level concentration of the former. The effect of lanthanides on the recoveries of U and Th has been studied for the first time.

The main advantages of the developed methodology are: (i) simultaneous preconcentration of U and Th with high degree of EEs, (ii) simultaneous spectophotometric determination of U and Th by employing PLSR, (iii) PFs comparable or better than earlier reported methods, (iv) wide dynamic linear concentration range, (v) better precision than that obtained by earlier reported methods (vi) better tolerance towards common interfering ions and lanthanides, (vii) cost effectiveness and (viii) simplicity of the operation. However the proposed analytical procedure cannot be used for quantification of U and Th in environmental samples if the concentration of zirconium, halfnium and lanthanides is more than double the total concentration of the analytes.

3.6. Analysis of natural water samples

The applicability of the developed method was demonstrated by analyzing different kinds of natural water samples. These samples were spiked with U and Th because of their very low analyte content. Different sources of water i.e., ground, sea and lake water were analyzed by the proposed method. Ground water sample from Punjab, India was considered because of high uranium content. [46] Sea water from Mumbai coast, India was chosen to observe how the developed method is affected in presence of high salt content. A fresh water lake sample from West Bengal, India was also analyzed. All the three samples were also analyzed directly by ICP-MS. The results are listed in Table 6. The results obtained by the proposed method are found to be in agreement with the values by ICP-MS within 95% confidence interval.

4. Conclusion

The developed analytical methodology provides a simple, sensitive and low cost procedure for simultaneous preconcentration and determination of U and Th in aqueous samples. The use of surfactants in place of organic diluents, such as dodecane, carbon tetrachloride etc., for extraction purpose reduces the environmental toxicity. The use of TOPO and TODGA was found to provide maximum recoveries of both U and Th in environmental samples. A temperature of 5-6^{o}C was found to be optimum for quantitative extraction of the analyte ions while a temperature of 50^{o}C was ideal for phase separation. The simultaneous spectrophotometric determination of U and Th using arsenazo-III was made possible by the application of PLSR algorithm. The preconcentration factors obtained for U and Th are 94 and 100 respectively. The CPE procedure was found to extract U and Th quantitatively, from aqueous solutions, even in presence of large amount of interfering ions. The analysis of real environmental water samples were found to provide satisfactory results with ≤ 4% relative standard deviations.

Acknowledgement

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Table 1

Concentration of the analytes in the calibration set (CS) and validation set (VS) used for the PLSR analysis of U and Th

Sample code	Uranium (μg mL^{-1})	Thorium (μg mL^{-1})	Sample code	Uranium (μg mL^{-1})	Thorium (μg mL^{-1})
CS1	0.5	0.25	CS11	3	1
CS2	0.75	0.5	CS12	5	2
CS3	1	1	CS13	7.5	2.5
CS4	1	2.75	CS14	10	1
CS5	1	6	CS15	15	1
CS6	1.5	4	VS1	1	4
CS7	1.5	5	VS2	1.5	2.5
CS8	2	1.5	VS3	3	3
CS9	2	3.5	VS4	6.5	1.5
CS10	2.5	2.5	VS5	8	2

Table 2

Optimized conditions for CPE system

Parameters	Optimized conditions of total aqueous phase before coacervation	Units
Sample volume	40	mL
pH	6	---
[TTX-114]	$4x\ 10^{-3}$	mol L^{-1}
[SDS]	0.5×10^{-3}	mol L^{-1}
[TOPO]	0.5×10^{-3}	mol L^{-1}
[TODGA]	0.1×10^{-3}	mol L^{-1}
[KNO_3]	0.1	mol L^{-1}
$T_{extraction}$	5-6	(^oC)
$t_{extraction}$	1	(h)
$T_{phase\ separation}$	50	(^oC)
$t_{phase\ separation}$	1	(h)

Table 3

Concentrations of U and Th in VS solutions as predicted by PLSR and statistical parameters of the PLSR algorithm

Sample code	Spiked amount (μg mL^{-1})		PLSR predicted amount (μg mL^{-1})		Recovery (%)	
	U	Th	U	Th	U	Th
VS1	1	4	1.01±0.01	3.96±0.02	101	99
VS2	1.5	2.5	1.53±0.03	2.47±0.01	102	99
VS3	3	3	2.98±0.01	3.03±0.02	99	101
VS4	6.5	1.5	6.52±0.06	1.46±0.01	100	97
VS5	8	2	8.0±0.1	2.00±0.01	99	100
Mean recovery (%)					100	99
RMSEP					0.029	0.032
REP (%)					0.734	1.224

Table 4

Tolerance limit of the developed method in the presence of selected cations and anions; Concentration of U and Th: 50 ng mL^{-1} each

Serial number	Ion	Tolerance limit (µg mL^{-1})
A1	Li^+, Na^+, K^+	2000
A2	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	500
A3	Zr^{4+}	Double the total target ions concentration
A4	Hf^{4+}	
A5	La^{3+}, Ce^{4+}, Eu^{3+}	
A6	Cd^{2+}	250
A7	Fe^{3+}	10
A8	Pb^{2+}	200
A9	Co^{2+}	250
A10	Cu^{2+}	200
A11	Ni^{2+}	200
A12	Zn^{2+}	250
A13	Mn^{2+}	200
A14	Hg^{2+}	5
A15	Cr^{3+}	10
A16	CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, Cl^-, Br^-	1500

Table 5

Comparison of analytical performance of the developed method with the earlier published works

Ion(s)	Instruments	DLR (ng mL^{-})	EE (%)	Recovery (%)	PF	RSD (%)	Reference
U(VI)-Th(IV)	UV-Visible	U:15-1000; Th:10-1000	U: 98.0±0.5; Th: 99.5±0.5	U:98; Th:99	U:94; Th:100	1-3	Proposed method
U(VI)-Th(IV)-Zr(IV)-Hf(IV)	ICP-OES	U:2.5-1240; Th0.5-1500	N.P.	N.P.	U:37; Th:43.6	<6.1	[3]
U(VI)	ICP-MS	U: 0.01-1000	99.5±0.5	99	92	4	[18]
U(VI)	UV-Visible	N.P.	N.P.	98	100	5.1	[22]
U(VI)	UV-Visible	15-300	N.P.	98	62	<3.7	[23]
U(VI)	UV-Visible	N.P.	98	N.P.	122	N.P.	[24]
U(VI)	UV-Visible	0.18-10	N.P.	N.P.	14.3	3	[25]
U(VI)	UV-Visible	6-10	N.P.	105	N.P.	9	[26]
U(VI)	LSC	N.P.	N.P.	50	N.P.	10	[27]
U(VI)	ICP-OES	N.P.	95	98	122	N.P.	[21]
Th(IV)	LSC	N.P.	N.P.	60	N.P.	5	[28]
Th(IV)	UV-Visible	0.5-15	N.P.	N.P.	33.33	1.6	[29]

N.P. = Not provided

Table 6

Analysis of real samples (n=5)

Sample	Added (ng mL^{-1})		Found by CPE-UV-Visible (ng mL^{-1})		Found by ICP-MS (ng mL^{-1})	
	U	Th	U	Th	U	Th
Ground water	0	0	110±3	ND	110±5	ND
	15	15	124±4	14.3±0.5	124±4	15±1
	25	25	135±5	24.2±0.7	136±4	25±1
Lake water	0	0	ND	ND	ND	ND
	15	15	14.5±0.4	14.8±0.4	15±1	15±1
	25	25	24.0±0.6	25.1±0.7	25±2	24±2
Sea water	0	0	ND	ND	2.8±0.3	ND
	15	15	17.6±0.5	14.6±0.5	18±2	15±1
	25	25	28±1	25.0±0.9	28±2	25±2

ND = Not detected

Figure 1

Schematic representation of the developed CPE procedure

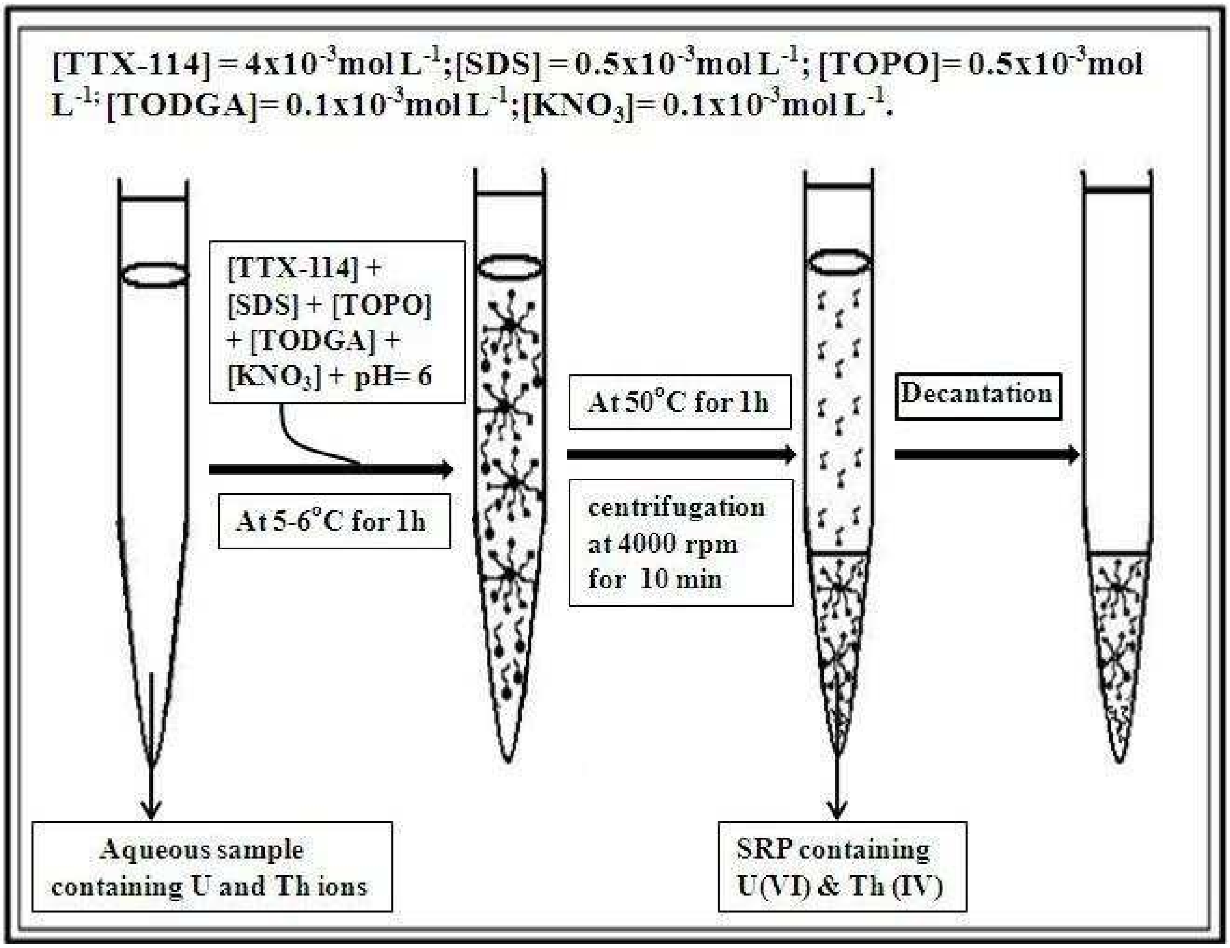


Figure 2

Effect of TOPO concentration on the recoveries of 50 ng mL^{-1}of U and Th each in absence and presence of 50 ng mL^{-1} La. TODGA had not been added during this exercise and the other parameters were kept constant as presented in Table2.

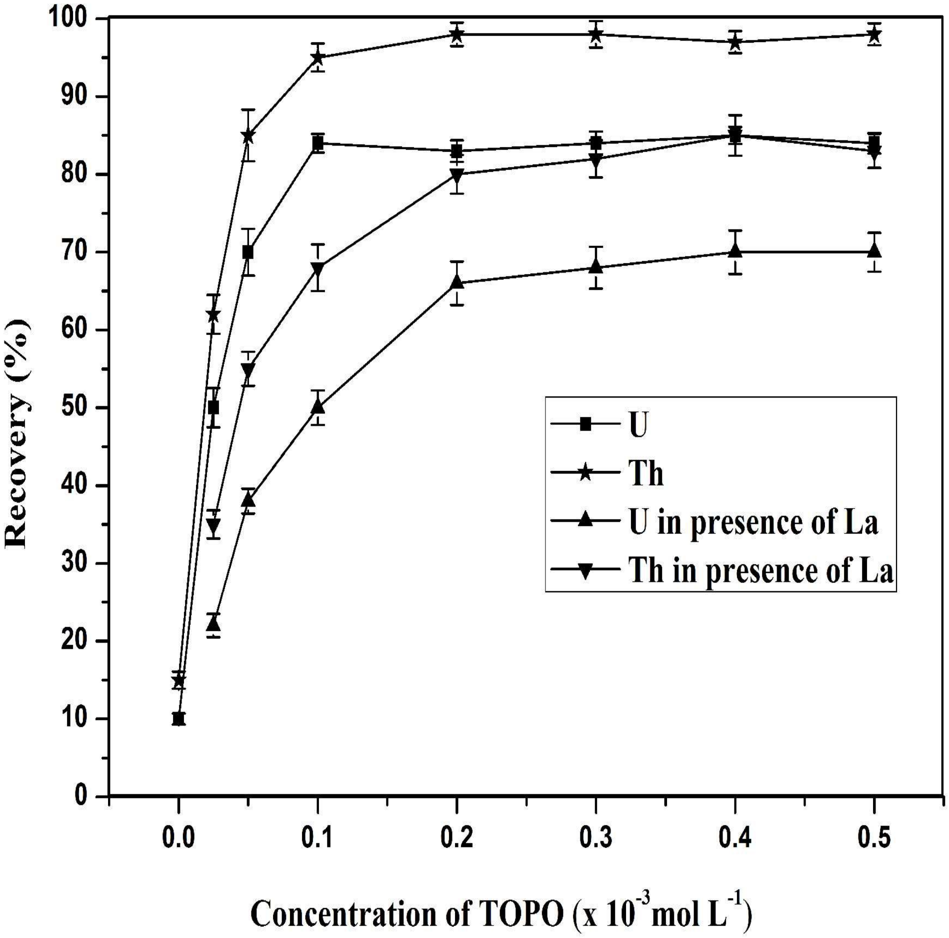


Figure 3

Effect of TODGA concentration on the recoveries of 50 ng mL^{-1} of U and Th each in presence of 50 ng mL^{-1} La. Other parameters were kept constant as presented in Table 2.

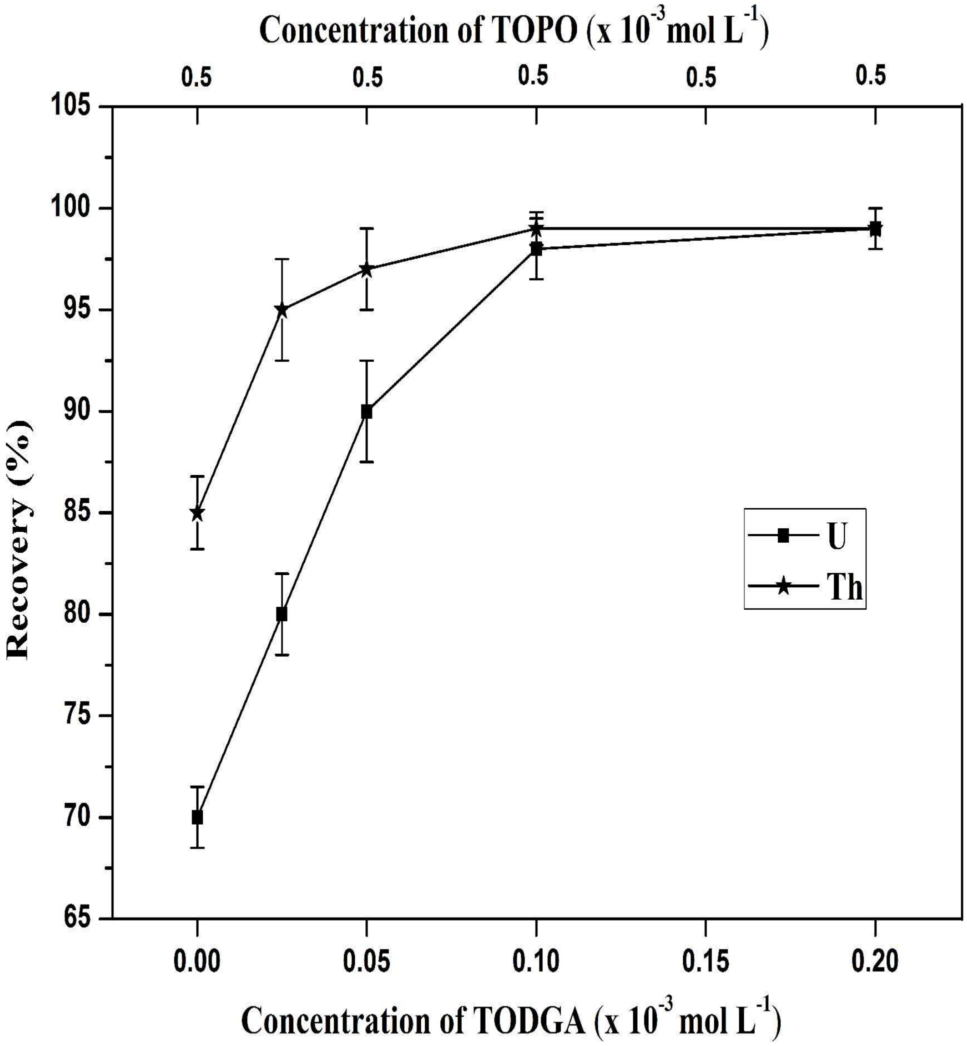


Figure 4

Effect of SDS concentration on the recoveries of 50 ng mL^{-1} of U and Th each. Other parameters were kept constant as presented in Table 2.

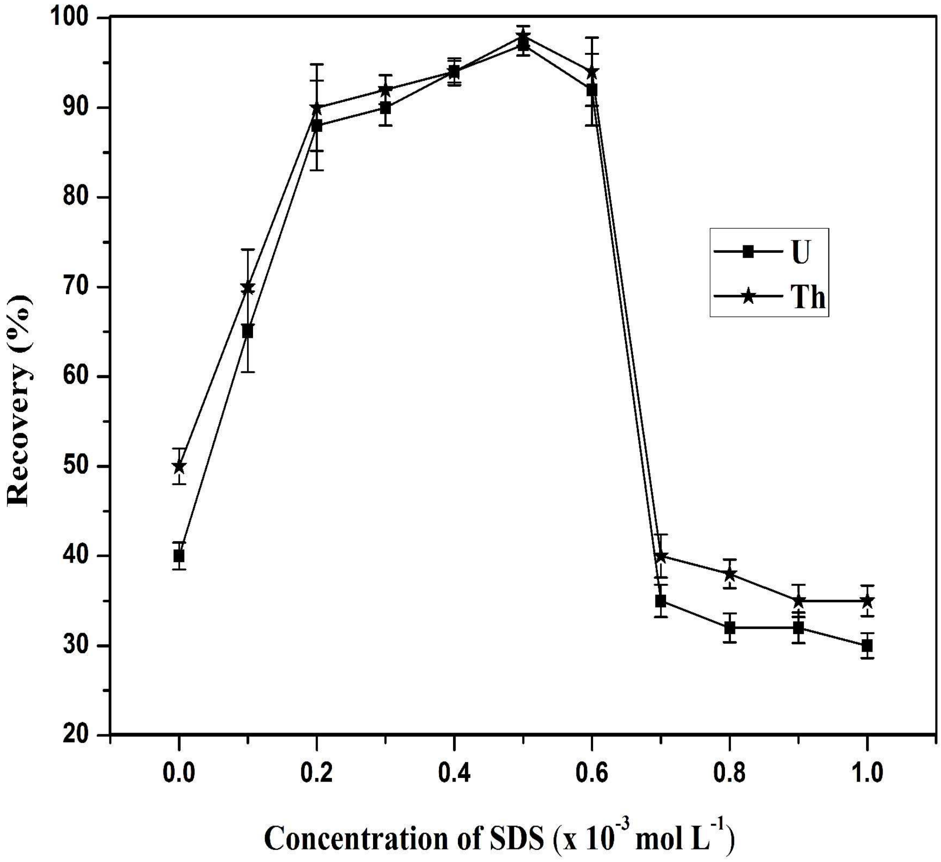


Figure 5

Effect of pH on the recovery of 50 ng mL^{-1} of U and Th each. Other parameters were kept constant as presented in Table 2.

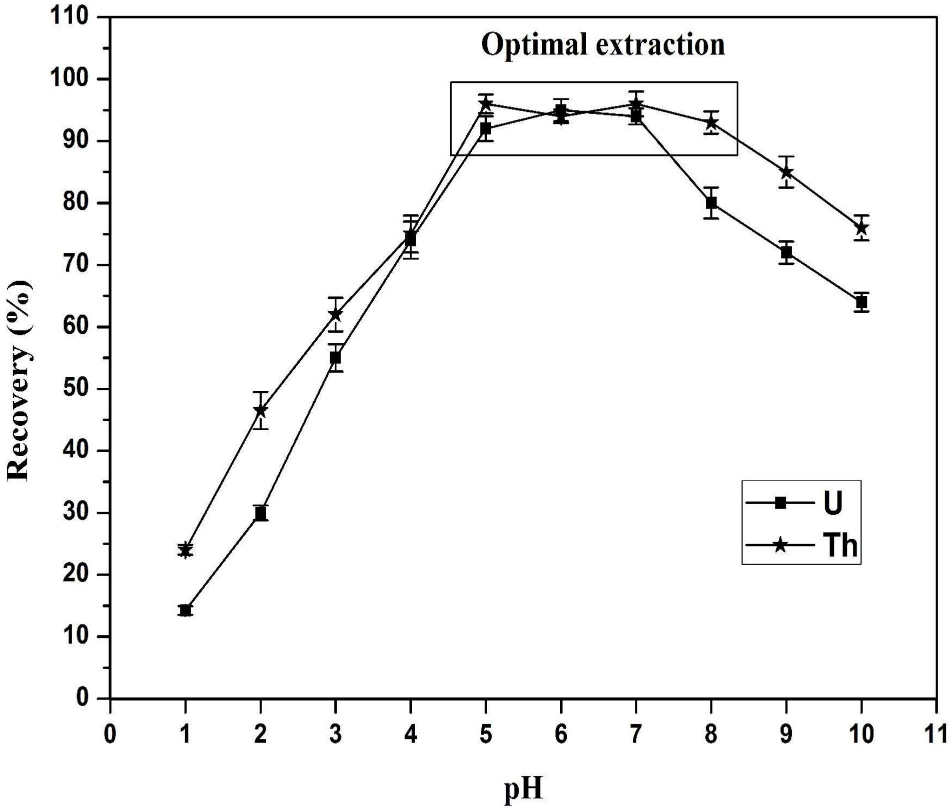


Figure 6

Effect of extraction and phase separation temperatures on the recovery of 50 ng mL^{-1} of U and Th each. Other parameters were kept constant as presented in Table 2.

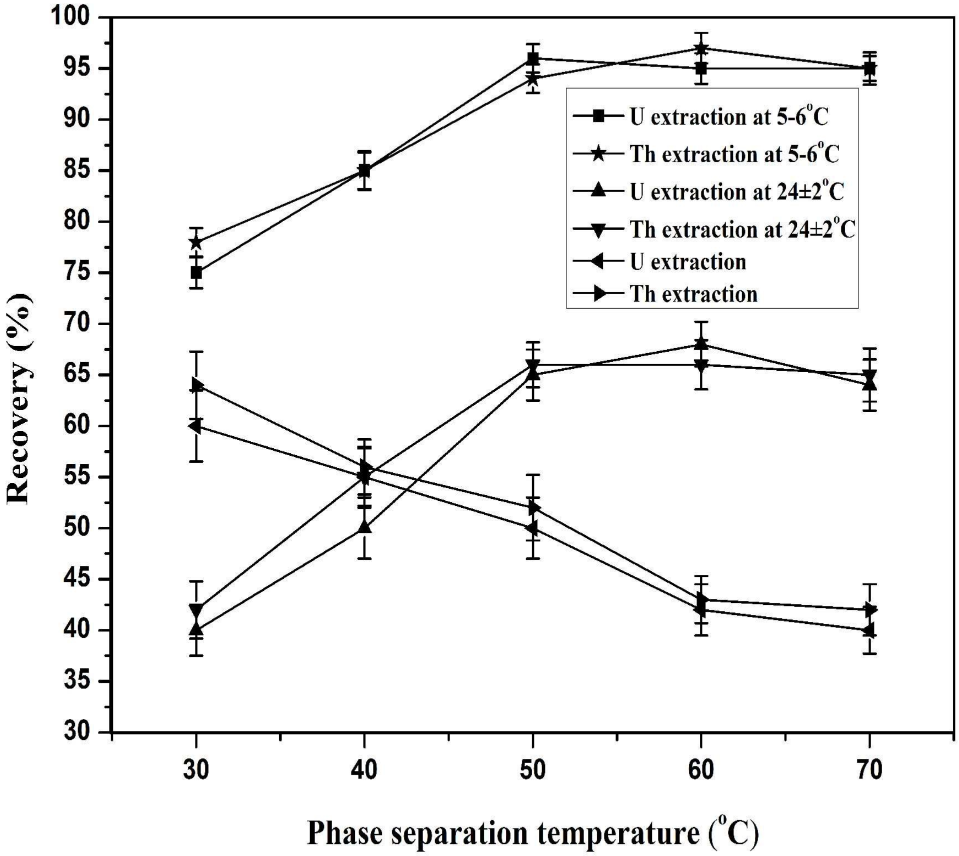


Figure 7

Effect of minaral acids, 6 mol L^{-1} of HCl (a and d), HNO_3 + 0.1 mol L^{-1} sulfamic acid (b and e) and $HClO_4$ (c and f), and metal ion concentration, 1 µg mL^{-1} (a, b and c) and 5 µg mL^{-1} (d, e and f), on the absorption maximum of Th using arsenazo-III with time. Spectra were recorded after (1) 5 min, (2) 15 min, (3) 25 min, (4) 35 min and (5) 45 min of the addition of arsenazo-III.

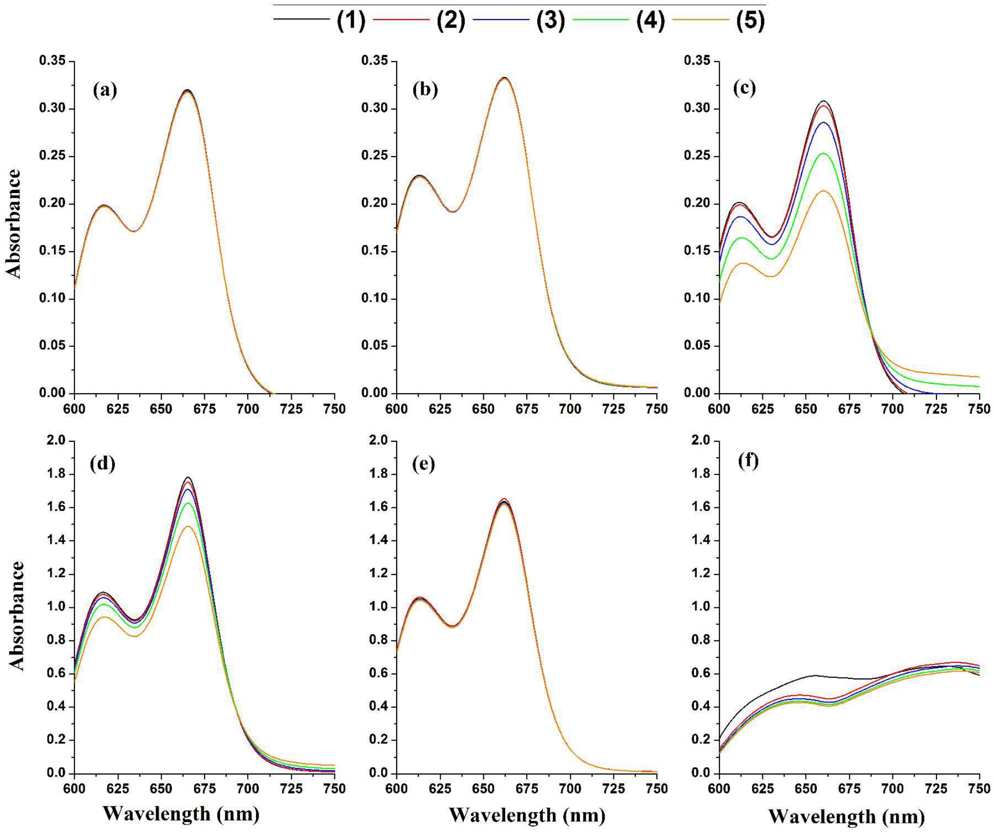


Figure 8

Visual colour change of Th-arsenazo-III complex with time in different mineral acid mediums, where the Th concentration is 2.5 μg mL^{-1}.

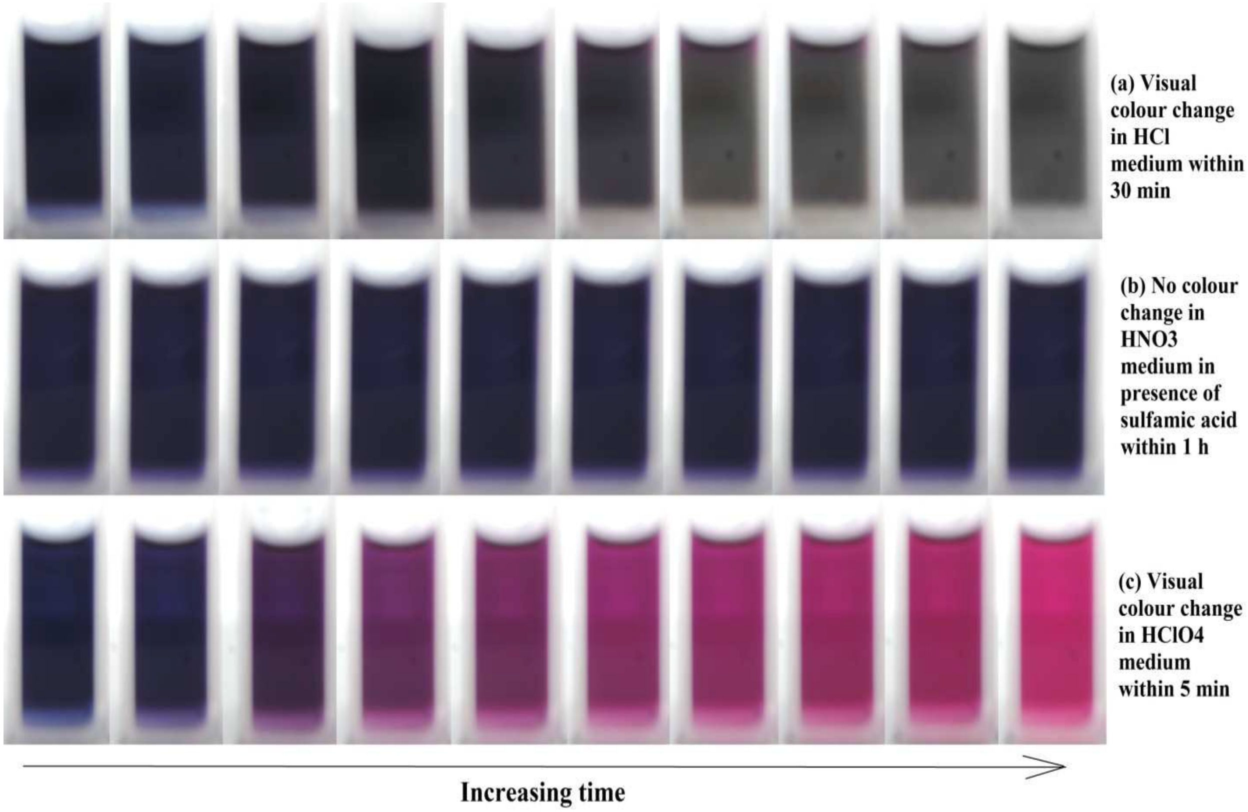


Figure 9

Optimization of PLSR algorithm factor

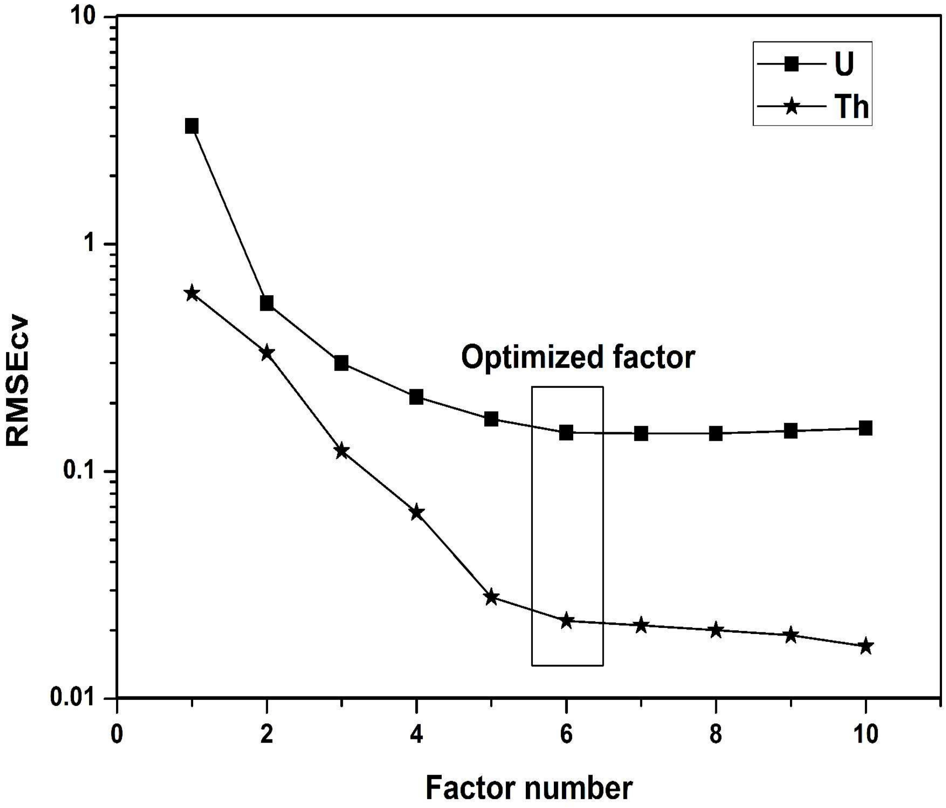


Figure 10

Absorption spectra of U and Th mixtures and the individual PLSRC's for U and Th.

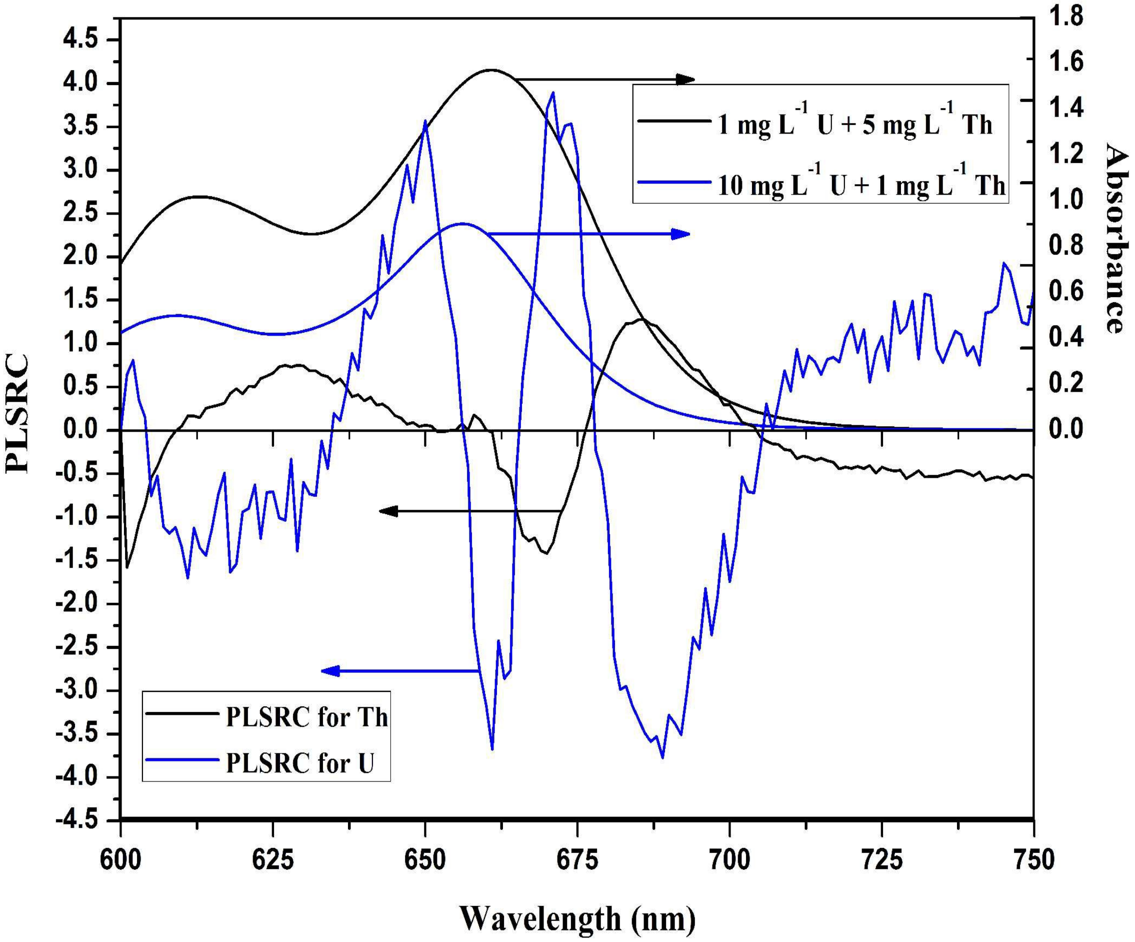
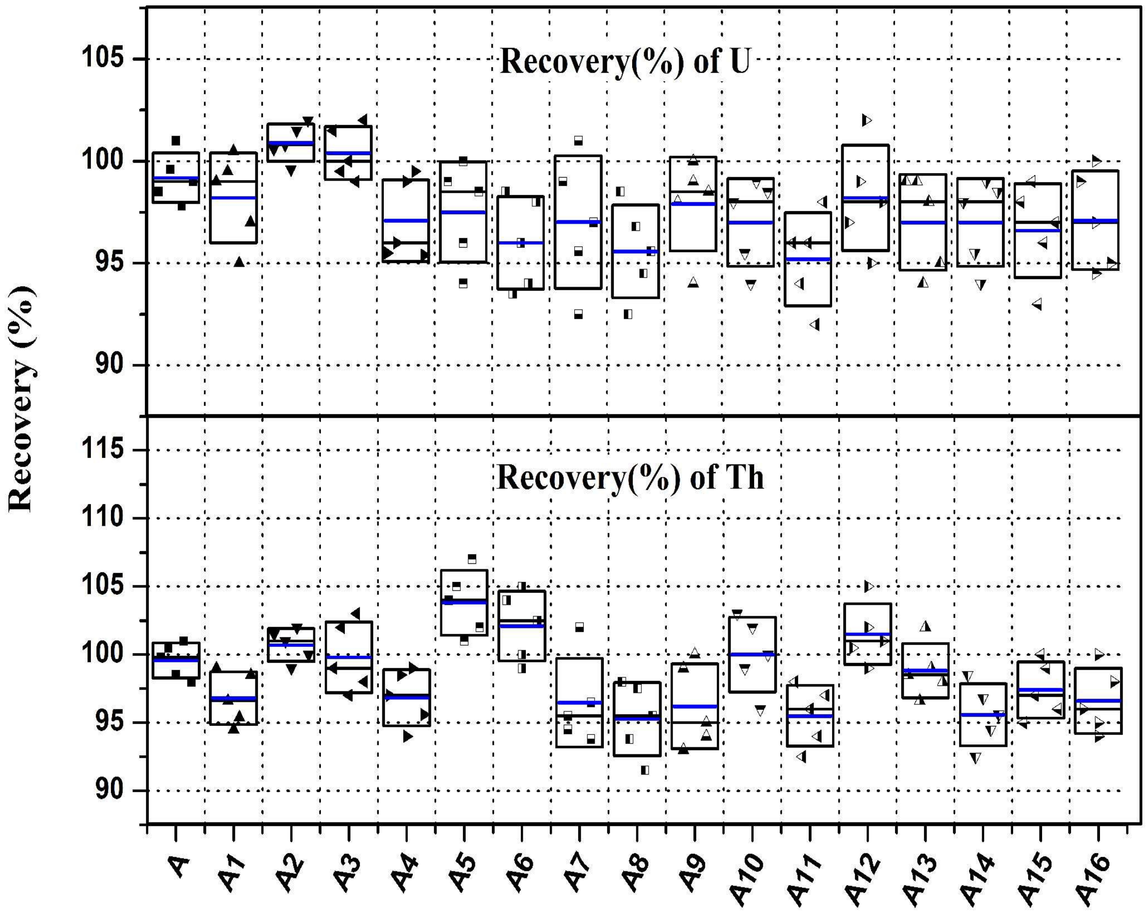


Figure 11

A box chart comparison of recovery studies of 5 replicate determinations of U and Th. The box represents the experimental standard deviation (Mean ± 1σ). The black line inside the box represents the median and the blue line represents the mean of the 5 replicates. A = recoveries in absence of interfering ions and A1 to A16 = recoveries in presence of interfering ions (concentration as per Table 4).



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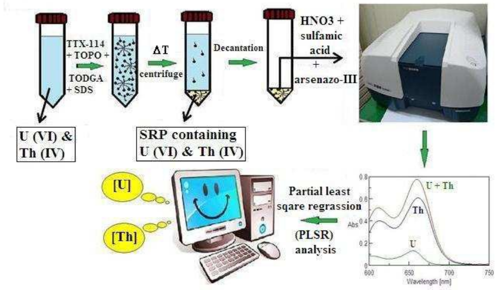
Entry	Content
Graphic	
Novelty of the work	Simultaneous cloud point extraction of uranium and thorium in aqueous samples with highest reported extraction efficiencies and preconcentration factors.