



pH dependent separation of uranium by chelation chromatography using pyridine 2,6-dimethanol as a chelator: Single crystal X-ray structural confirmation of the chelated uranium complex

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ABSTRACT

A very effective sorbent material which exhibits exceptional capture of hexavalent uranium from other actinides and lanthanides at $\mu\text{g g}^{-1}$ level, features pyridine 2,6-dimethanol immobilized onto alumina. The maximum sorption capacity for dioxouranium(VI) was found as 1.96 mmol g^{-1} at pH 3.0. The adsorbed uranium complex was eluted completely by 0.05 mol L^{-1} $(\text{NH}_4)_2\text{CO}_3$ solution and the concentration of hexavalent dioxouranium ion was monitored spectrophotometrically using Arsenazo III. The structure of the chelated uranium complex has been confirmed by single crystal X-ray structure analysis and Fourier transform infrared red (FTIR) spectroscopy. Thermo gravimetric analysis/differential thermo gravimetric analysis (TGA/DTG) of the chelated uranium complex was performed. The method is reproducible with a relative standard deviation (RSD) of 1.2% ($N=10$) and the three sigma detection limits ($N=15$) $1.2 \mu\text{g mL}^{-1}$ respectively. A pre-concentration factor, almost 500, for uranium was achieved. Interferences from Th^{4+} , Mn^{2+} , Ni^{2+} and Cu^{2+} ions were masked with ethylene diamine tetra acetic acid (di-sodium salt) (Na_2EDTA) in the aqueous phase. The developed method has been tested for uranium recovery and estimation in some certified reference materials and environmental samples.

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1. Introduction

Uranium has a great importance in nuclear fuels. Extraction of uranium from its main source like, pitchblende or uraninite (U_3O_8) and carnotite ($\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$) is a multistep complicated process [1]. Depending on the nature of the source, some transition elements like nickel, copper, aluminium and manganese concentrated in the solution along with uranyl cation. Liquid–liquid and solid–liquid extractions are available for the selective recovery of the uranium ion [2]. Release of nuclear wastes from nuclear power plants, improper handling of their ores and minerals, testing of nuclear weapons in air/water, are the major sources of environmental contaminations with this radioactive substance, which is subsequently have a detrimental effect to human beings [3]. The conventional procedure for separation of uranium involves, pre-concentration of disulphatouranyl complex onto an anion exchanger followed by extraction with conc. nitric acid. The uranium nitrate is then extracted with tributylphosphate into an

organic layer like, hexane or methyl isobutyl ketone or diethyl ether. The uranium ion is then stripped out of the organic phase by sulphuric acid and precipitated as “yellow cake” or ammonium diuranate by adding ammonia. This is heated to form UO_3 , which subsequently converted to metallic uranium in several steps of reduction. The number of steps in these complicated extraction procedure has been significantly reduced by our chelation chromatographic technique using pyridine 2,6-dimethanol as a selective chelating ligand for uranium. The solid phase extraction (SPE) procedures have several advantages over liquid–liquid extraction [4,5]. Several authors have used a number of solid sorbents viz. octadecyl silica membrane disk [6], empore (TM) chelating resin disk [7], commercial resin [8,9], Dowex 1×8 and Dowex $50\text{W} \times 8$ [10,11], neutral polymer Amberlite XAD series [12], silica [13], activated silica gel [14], controlled pore glass [15], polyurethane foam [16] and cation or anion exchange resins [17] for the enrichment of uranium(VI) from dilute solutions prior to determination by a variety of analytical techniques. Selective binding of uranyl cation using different chelating ligands, either immobilized or chemically attached on the inert solid support like silica, alumina, naphthalene, benzophenone, polystyrene–DVB resin or activated charcoal matrix have also been reported [18–26].

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Few examples are: 2,2'-dihydroxyazobenzene [27], molecularly impregnated Chelex-100 polymer [17], chelating resin containing 4-(2-thiazolylazo) resorcinol [28,29], and polypyrrole resin [30]. To the best of our knowledge, none of the works as reported till date confirmed the structure of the extracted uranium complex by single crystal X-ray structure analysis, which nowadays provide a very strong evidence of metal complex formation. We are reporting here, not only a simplified procedure of selective extraction of uranium from highly acidic solution using pyridine 2,6-dimethanol as a chelating ligand, immobilized on alumina but also confirmed the structure of the extracted uranium complex by single crystal X-ray structure analysis. At pH 3.0, except Th(IV), Mn(II), Ni(II) and Cu(II) (masked by Na₂EDTA in aqueous solution) none other ions interfere to a significant extent. The newly developed methodology is verified by analysis of certified reference materials and applied to the analysis of environmental samples. Different analytical figures of merit are also reported.

2. Experimental

2.1. Instrumentation

A JASCO (model V-570) UV-vis spectrophotometer was used for measuring the concentration of uranyl cation. FTIR spectra were recorded on a JASCO FTIR spectrophotometer (model: FTIR-H20). Thermogravimetric analysis was done on a Perkin Elmer TG/DTA lab system I (Technology by SII). pH measurements were performed with Systronics digital pH meter (model 335). Their X-ray crystal data were collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system. Intensities were corrected for Lorentz polarization and for absorption. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealized. Structural refinements were obtained with full-matrix least-squares based on F^2 by using the program SHELXTL [31].

2.2. Chemicals and reagents

A stock solution of uranium(VI) at a concentration of 1000 $\mu\text{g mL}^{-1}$ was prepared by dissolving appropriate quantity of uranyl acetate trihydrate (British Drug House Ltd.) in distilled water containing 1% HCl and standardized gravimetrically [32]. A working solution containing 100 $\mu\text{g mL}^{-1}$ uranium(VI) was prepared by appropriate dilution. Arsenazo III (S.D. Fine Chemicals) was prepared as a 0.100% (w/v) aqueous solution. Hydrogen peroxide (SRL, India) was used as received. Spectroscopic grade KBr was purchased from SRL, India and used for making pellets for FTIR studies. The monazite sand was collected from Quilon, Kerala (India). The sample was stored in a clean plastic bottle after being dried at 110 °C and grinded to very fine powder and screened with a 200 mesh sieve. The certified monazite sample was obtained from the Geological Survey of India (GSI), Kolkata and Uranium was recovered from monazite sand sample. Alumina (60–80 mesh) obtained from SRL, India was used without purification. All other chemicals and reagents used were of Analytical Reagent (A.R.) grade.

2.3. Preparation of column

The impregnation of the chelating ligand, pyridine 2,6-dimethanol was done using equal quantities (0.200 g) of the chelator in methanol and silica beads. The mixture was then stirred till the solvent was almost evaporated. The resin beads thus obtained were kept overnight at ambient temperature. The impregnated silica beads were uniformly packed in a glass column plugged

with glass wool having 150 mm length and 10 mm internal diameter.

2.4. General procedure

The column was pre-conditioned with $1 \times 10^{-3} \text{ mol L}^{-1}$ HCl prior to use. A sample solution containing 100 $\mu\text{g mL}^{-1}$ uranium(VI) was passed through the column and desorbed with dimethyl formamide. The organic solvent was removed using a hot plate and the aqueous extract containing uranium(VI) was determined spectrophotometrically as its Arsenazo III complex at 650 nm [33]. Different experimental parameters such as sample volume, flow rate, pH, equilibration time, effect of foreign ions and varying nature and concentration of eluents were studied to optimize the sorption and desorption conditions for uranium(VI). Effect of temperature on the sorption of uranium by PDM loaded alumina was also monitored. To prove that no decomposition of the uranium complex occurs at this elevated temperature, thermal study of the metal complex was performed. LOD (defined as that analyte concentration giving a signal equal to three times standard deviation of blank signal [10]) was estimated. Separation of uranium(VI) from other rare earth elements (binary mixtures) was performed. The developed methodology was verified by analyzing certified reference material (Monazite sand sample, gifted by GSI, Kolkata) which was brought into solution following the literature procedure [34].

3. Results and discussion

3.1. Sorption studies with impregnated resins

A sample solution containing 25 μg of uranium(VI) in HCl acid media (pH 3.0) at different concentrations (1×10^{-4} – 2.0 mol L^{-1}) was passed through the column packed with pyridine 2,6-dimethanol (PDM) impregnated alumina (1:1, 1 g). The sorption of uranium(VI) on the impregnated resins was evaluated in terms of the distribution ratio (D), defined as the ratio of the amount of metal ion sorbed on the resin to its amount in the aqueous phase at equilibrium. The effect of sample flow rate on the sorption of uranium(VI) onto PDM impregnated sorbent was studied and it was found that an optimum flow rate of 1.0 mL min^{-1} resulted in its quantitative sorption ($99.2 \pm 0.4\%$). Eluent flow rate greater than 1.0 mL min^{-1} decreased the recovery of uranium(VI) due to lesser contact time between the eluent and uranium(VI) sorbed on the impregnated resin. Hence 1.0 mL min^{-1} flow rate was maintained throughout the studies.

The effect of pH on the sorption process (Fig. 1) indicates that with increasing pH, sorption of uranium gradually increases to level off at pH 4.5. The observed trend of the decrease of adsorption capacity at higher acidity may be due to the protonation of donor sites. Hence pH 4.5 was preferred throughout the studies. Pyridine 2,6-dimethanol is a hard base due to the presence of 'O' and N donor sites, which preferentially binds hard metal ion U(VI). It is evident from Fig. 2 that with increase in temperature, adsorption of uranium gradually increases and becomes maximum at 45 °C and after that it starts decreasing. Fig. 3 shows that no decomposition of the uranium complex occurs at this elevated temperature.

3.2. Elution studies

Quantitative recovery of the uranium(VI) ion from the sorbed material is necessary for repeated use of the same solid phase. Table 1 presents the efficiency of different eluents for recovery of uranium(VI) from packed column. Recovery of uranium(VI) was quantitative ($99.2 \pm 0.4\%$) with all the three reagents viz. 1 mol L^{-1} HCl, dimethyl formamide (DMF) and 0.05 mol L^{-1} $(\text{NH}_4)_2\text{CO}_3$ solution. But it was observed that DMF results in desorption of the

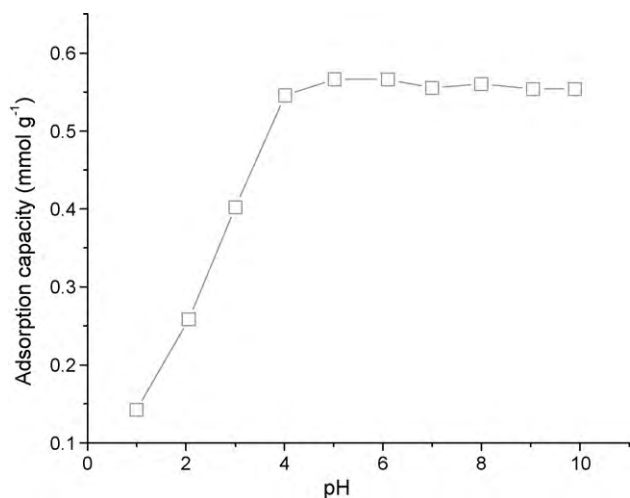


Fig. 1. Adsorption capacity of the SPE system towards uranyl cation as a function of pH.

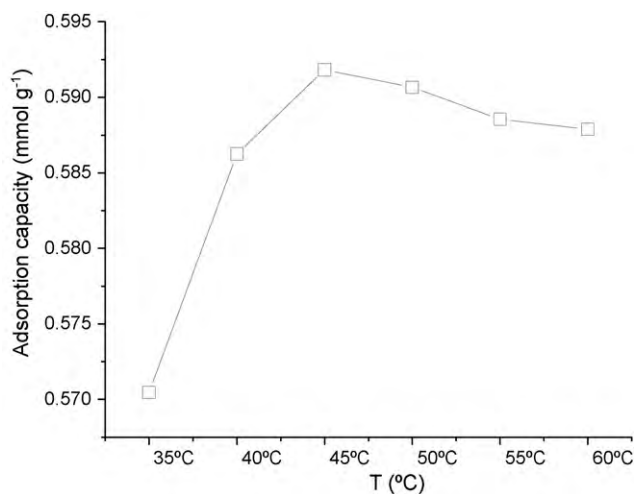


Fig. 2. Adsorption capacity of the SPE system towards uranyl cation as a function of temperature.

whole uranium–PDM complex (proved by the single crystal X-ray structure of the eluted complex grown from that eluted solution) leaving only alumina in the column. So the column cannot be reused as the chelating ligand is lost. We have to load the column

Table 1

Effect of different eluents on the % recovery of uranyl ion adsorbed on the PDM loaded alumina bed.

Eluents (mol L ⁻¹)	% Recovery ^a
HNO ₃ (0.5)	94.2 ± 0.4
HNO ₃ (1.0)	96.8 ± 0.8
HNO ₃ (2.0)	97.5 ± 0.3
HCl (0.5)	97.2 ± 0.2
HCl (1.0)	98.5 ± 0.6
HCl (2.0)	99.2 ± 0.4
HClO ₄ (2.0)	90.8 ± 0.2
CH ₃ COOH (2.0)	49.1 ± 2.0
H ₂ C ₂ O ₄ (2.0)	73.1 ± 0.4
Dimethylformamide	99.2 ± 0.4
(NH ₄) ₂ CO ₃ (0.05)	99.2 ± 0.8

^a Average of three replicate measurements ± % RSD.

again with PDM impregnated sorbent. So either 1.0 mol L⁻¹ HCl or 0.05 mol L⁻¹ (NH₄)₂CO₃ solution was chosen as eluent.

3.3. FTIR and single crystal X-ray structural confirmation of the extracted chelating complex

To establish the fact that the ligand really binds to uranium ion, we compared FTIR spectra of the PDM loaded alumina (Fig. 4) with the uranium bonded PDM on alumina (Fig. 5). For this purpose, spectroscopic grade KBr (after removal of moisture at 100 °C in hot air oven followed by cooling at room temperature in a desiccator) was mixed with the sample and the mixture was ground with mortar and pestle to make very fine powder and the powder was used to make a transparent pellet using a hydraulic system. The pellet was placed in the FTIR instrument to record the FTIR spectra. By comparing Fig. 4 and Fig. 5, one can easily justify the complex formation between the PDM and uranyl cation. The O–H band of the free PDM ligand at 3360.81 cm⁻¹ has been blue shifted by 27 cm⁻¹ in the chelated uranium–PDM complex, indicating the “O” donor site of PDM is involved in uranium binding. Similarly, other characteristics stretching frequencies of the free PDM ligand have also been shifted and some new bands appeared in the chelated uranium–PDM complex, which altogether indicate a strong binding of the PDM ligand with uranyl cation. The more powerful proof of the uranium binding ability of PDM has been established by the single crystal X-ray structure of the chelated uranium–PDM complex (Fig. 6). The single crystals of the chelated uranium–PDM complex, suitable for X-ray diffraction studies were grown from the dimethyl formamide solution of the uranium–PDM complex eluted from the column by slow evaporation technique. After two weeks, bright yellow crystals were

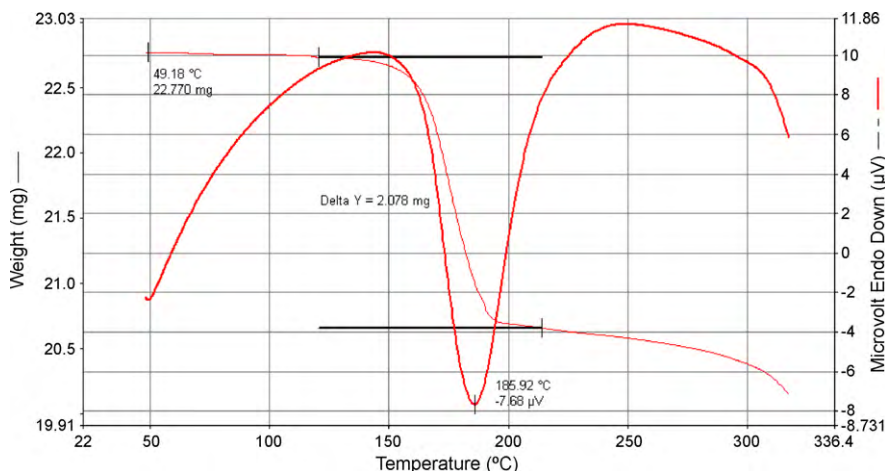


Fig. 3. TGA/DTG graph uranium complex of PDM.

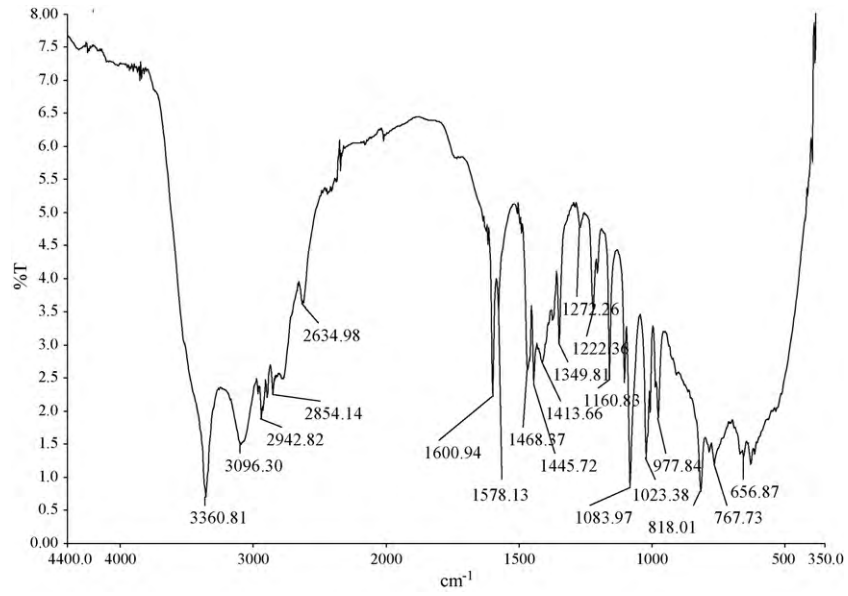


Fig. 4. IR spectra of PDM immobilized alumina.

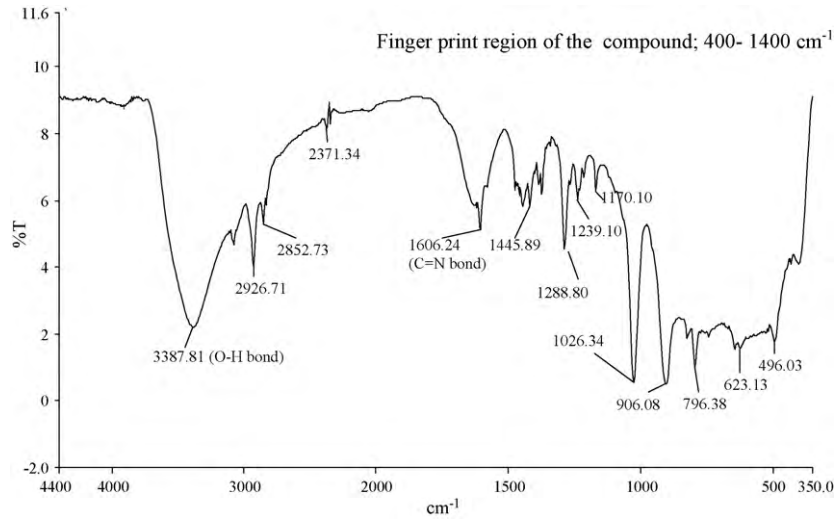


Fig. 5. IR spectra of U complex of PDM supported on alumina.

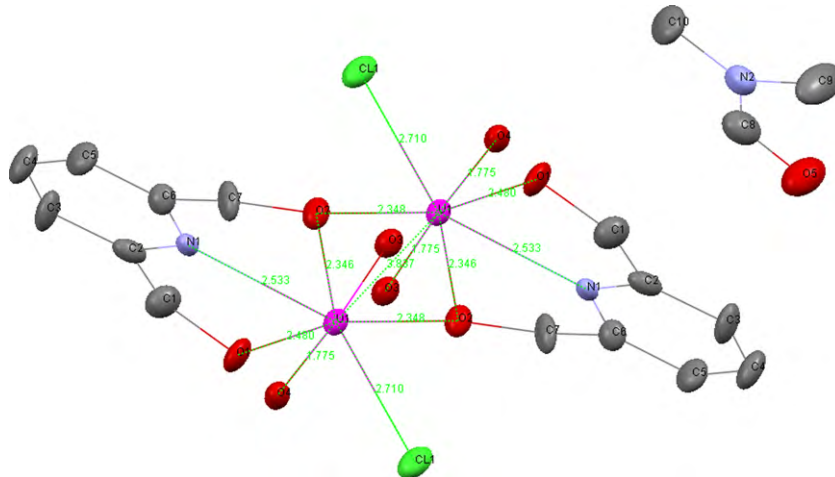


Fig. 6. Ellipsoid (50% probability) view of an isolated molecule with some important bond distances in Å (H atoms are removed for clarity).

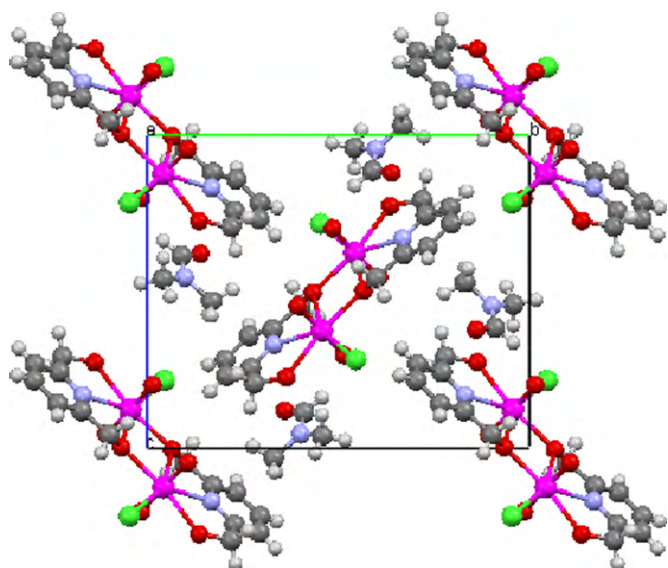


Fig. 7. Packing diagram of the molecular complex along crystallographic *a* axis.

Table 2
Crystal data and structure refinement for UO₂–PDM comple.

Empirical formula	C ₂₀ H ₃₂ Cl ₂ N ₄ O ₁₀ U ₂
FW	1035.46
Temp. (K)	93(2)K
Crystal color	Yellow
Crystal dimension (mm)	0.15, 0.10, 0.10
Crystal system	monoclinic
Space group	P 2 ₁ /n
Z	2
<i>a</i> (Å)	7.293 (10)
<i>b</i> (Å)	15.533 (3)
<i>c</i> (Å)	12.892 (18)
α (°)	90.00
β (°)	99.025 (3)
γ (°)	90.00
<i>V</i> (Å ³)	1442.3 (4)
ρ (calcd.) (g/cm ³)	2.384
μ (Mo K α) (cm ⁻¹)	11.46
<i>F</i> (000)	956
Goodness-of-fit	1.026
<i>R</i> 1, <i>wR</i> 2 ^a <i>I</i> > 2 σ (<i>I</i>)	0.0451, 0.0782
All data	0.0625

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

Table 3
Selected bond distances (Å) and angles (°) for UO₂–PDM complex.

Distances (Å)		Angles (°)	
U1–O1 (pyridine part)	2.480	U1–O2–U1	109.6
U1–O2 (pyridine part, bridging)	2.346	O3–U1–O4	176.3
U1–O3/O4 (oxo–uranium bond)	1.775	O3–U1–O2	90.0
U1–N1 (pyridine)	2.533	O3–U1–O1	87.2
U1–Cl1	2.711	O3–U1–N1	94.1
		O3–U1–Cl1	94.1
		O4–U1–O2	87.5/91.7
		O4–U1–O1	92.0
		O4–U1–N1	82.3
		O4–U1–Cl1	89.2
		O2–U1–O2	70.3
		O2–U1–N1 (same pyridine part)	65.6
		O2–U1–Cl1	155.6
		O2–U1–O1	161.8
		O2–U1–N1 (other pyridine part)	135.8
		O2–U1–Cl1	85.6
		O1–U1–N1	62.3
		O1–U1–Cl1	76.7
		N1–U1–Cl1	137.6

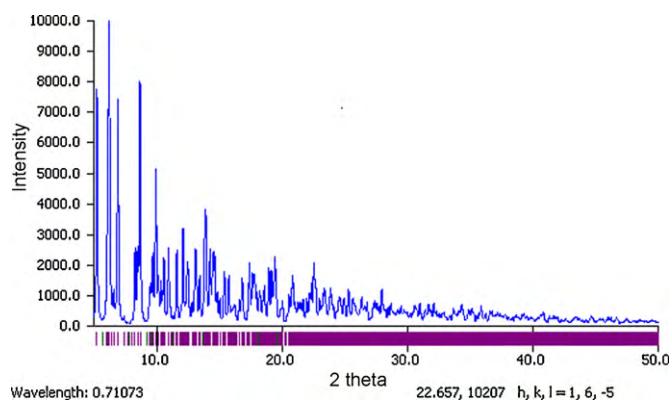


Fig. 8. Powder diffraction pattern of the extracted chelating uranium complex.

Table 4
Tolerance limit of diverse ions on the determination of 5.00 $\mu\text{g L}^{-1}$ uranium ion (binary mixture).

Foreign ions	Tolerance limit ^a
Na ⁺ , K ⁺ , Li ⁺	5000
Cr ³⁺ , Ce ³⁺ , Hg ²⁺ , Ag ⁺	3000
Ni ²⁺ , Pb ²⁺ , Cd ²⁺ , Ca ²⁺ , Mg ²⁺ , Co ²⁺	2000
Cu ²⁺ , Mn ²⁺ , Ce ⁴⁺ , Dy ³⁺ , Gd ³⁺ , La ³⁺ , Nd ³⁺ , Pr ³⁺ , Yb ³⁺ , V ³⁺ , Bi ³⁺ , Al ³⁺ , Fe ³⁺	500 ^b
Zr ⁴⁺ , Th ⁴⁺	75 ^b
Ti ⁴⁺ , V ⁵⁺	1000 ^c
SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , PO ₄ ³⁻	50,000

^a Average of triplicate analysis.

^b After addition of 0.5 mL EDTA (0.1%).

^c After addition of 2.0 mL 30% hydrogen peroxide.

formed. The crystal structure of the chelated uranium–PDM complex was obtained as described earlier (Section 2.1). The packing diagram of the extracted chelated uranium complex of pyridine 2,6-dimethanol ligand is presented in Fig. 7. Fig. 8 shows the powder diffraction pattern of the complex, which really proves the crystallinity and purity of the isolated uranium–PDM complex. Table 2 shows the crystal data and structure refinement for UO₂–PDM complex. The selected bond length, bond angles of the complex have been presented in Table 3. From Fig. 6, Tables 2 and 3, it can be said that the chelated uranium–PDM complex is a di-oxo-bridged dinuclear one and each uranyl cation is hepta coordinated (UNO₅Cl chromophore). The two chlorine atoms present in the chelated

Table 5

Comparison of sorption characteristics of the present method with other uranium sorbents loaded on silica or alumina.

Matrix	Capacity (mmol g ⁻¹)	LOD (ng mL ⁻¹)	Eluent	Preconcentration factor	Samples analyzed
Quinoline 8-ol [12]	–	0.001	0.7 mol L ⁻¹ HCl	–	Sea water
Murexide [33]	1.13	1.0	0.1 mol L ⁻¹ HCl	400	Synthetic sea water and ground water
Benzoylthiourea [34]	0.85	2.0	0.1 mol L ⁻¹ HCl	250	Synthetic sample and soil sample
Calix[4]arene semicarbazone [35]	0.0127	–	0.25 mol L ⁻¹ HCl	108	Geological samples
N-triisopropionate substituted tetraazamacrocyclic [36]	0.032	0.0985	2 mol L ⁻¹ HNO ₃	50	Nuclear center effluents
Pyridine 2,6-dimethanol (PDM) [present study]	1.96	1.2	2.0 mol L ⁻¹ HCl	500	Monazite sand sample

uranium–PDM complex comes from the HCl solution wherefrom the extraction of uranium performed using PDM loaded alumina. As DMF was used for the elution of the chelated uranium complex from the column and the crystallization took place in DMF medium, it took part in the crystal packing and played an important role by placing itself in the unit cell of the crystal. Thus all the experimental results can be best explained by examining the single crystal X-ray structure of the chelated uranium–PDM complex. As the chelated uranium–PDM complex is an inner-metallic complex of the first order (both charge and coordination number are satisfied by the PDM ligand), it is insoluble in aqueous solution and remains stacking on the alumina column.

4. Effect of foreign ions on the sorption process

Uranium(VI) was selectively extracted from binary mixtures, including some rare earth elements (Table 4). The separation factor (k) was calculated as the ratio of the distribution ratio ($D = [M]_{org.} : [M]_{aq.}$) of uranium(VI) to that of the foreign metal ions ($k = D_U : D_M$). In all these separations uranium(VI) was preferentially sorbed leaving the rare earth elements in the aqueous phase and thus very high separation factors were achieved. As thorium(IV), Mn(II) and Cu(II) interferes to some extent during the extraction of uranium(VI), the separation was achieved by masking these ions in aqueous phase using EDTA [25]. The probable reason that the above-mentioned metal ions interfere in the extraction of uranium from the synthetic mixture may be attributed to the formation of metal complex with the chelator.

5. Analytical performance

The pre-concentration factor is one of the most important parameters to evaluate the performance of solid phase extraction methodologies. It was calculated as the ratio of sample volume to the volume of eluent used for quantitative recovery ($99.2 \pm 0.4\%$) of uranium(VI). A pre-concentration factor, 500 has been achieved. Precision of the method developed was investigated using optimum conditions for sorption and desorption of uranium(VI) on column and expressed in terms of the relative standard deviation (RSD). In six replicate experiments using the general procedure, RSD of 0.8% was achieved for uranium(VI). The limit of detection (LOD) of the proposed method for the determination of uranium(VI) was studied under its optimal sorption conditions. The LOD of the method was $1.2 \mu\text{g L}^{-1}$ for uranium(VI). The stability and potential reusability of the column packed with impregnated sorbent were assessed by monitoring the maximum sorption capacity of uranium(VI) through several sorption–desorption cycles. No significant change was observed up to 25 cycles, indicating repeated use of the same sorbent may provide an economical route for isolation of uranium(VI). The sorption characteristics of the present method are compared with

other uranium sorbents loaded on silica or alumina in Table 5 [13,34–37].

6. Application

The monazite sand sample (1 g, supplied by the GSI, Kolkata, India) was brought into solution by the reference method [38]. 50 mL stock solution was added to 200 mL water in a beaker and pH was maintained to 3.0 using 0.1 mol L^{-1} sodium hydroxide solution. Then 2 mL 30% hydrogen peroxide were added to it to form complex with any titanium or vanadium present in it. Uranium does not combine with hydrogen peroxide at $\text{pH} < 7$. The solution was allowed to pass through the pre-conditioned PDM loaded alumina bed. Then the bed was washed with distilled water. Finally, the adsorbed uranyl cation was eluted with 150 mL 0.05 mol L^{-1} $(\text{NH}_4)_2\text{CO}_3$ solution. Uranium concentration in the eluent was measured spectrophotometrically using Arsenazo III as described earlier. It is found that the observed concentration of uranium ($0.115 \pm 0.007\%$) is very close to the supplied value (0.130%) by GSI, Kolkata, India.

7. Conclusion

The proposed method is based upon the preferential sorption of the cationic species of uranium(VI) prevailing in $1 \times 10^{-3} \text{ mol L}^{-1}$ HCl media using pyridine 2,6-dimethanol (PDM) impregnated on alumina. The method is simple, easy to operate and selective for separation and pre-concentration of uranium(VI). As PDM contains hard donor sites 'O' for binding hard metal ion like uranium(VI), it was utilized for achieving high enrichment factor for uranium(VI). The characterization of the chelating extracted uranium complex has been confirmed by single crystal X-ray analysis as well as by FTIR techniques. Finally, the proposed method has been verified by analyzing standard reference material. Using the PDM impregnated resin, high pre-concentration factor (>500), a very high reusability for continuous usage (25 cycles) and good LOD ($1.2 \mu\text{g L}^{-1}$) were achieved.

List of symbols

RSD	relative standard deviation
SPE	solid phase extraction
PDM	pyridine 2,6-dimethanol
Na ₂ EDTA	ethylene diamine tetra acetic acid (di-sodium salt)
A.R.	analytical reagent
FW	formulae weight
Z	no. of molecules present per unit cell
a	crystallographic distance along 'x' axis, in a unit cell (Å)
b	crystallographic distance along 'y' axis, in a unit cell (Å)
c	crystallographic distance along 'z' axis, in a unit cell (Å)
α	crystallographic angle in a unit cell between b and c (°)
β	crystallographic angle in a unit cell between c and a (°)

γ crystallographic angle in a unit cell between a and b ($^\circ$)
 V volume (\AA^3)
 ρ density (g cm^{-3})
 $\text{Mo K}\alpha$ molybdenum $\text{K}\alpha$ radiation in wave number used in X-ray diffraction (cm^{-1})
 $F(000)$ it is crystallographic (000) plane
 $R1, wR2^d$ $I > 2\sigma(I)$ represents goodness-of-fit; σ = standard deviation

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