Electronic Supplementary Information (ESI†)

One step sample treatment and loading using deep eutectic solvent immobilized in porous substrate for thermal ionization mass spectrometry of Pu(IV) ions

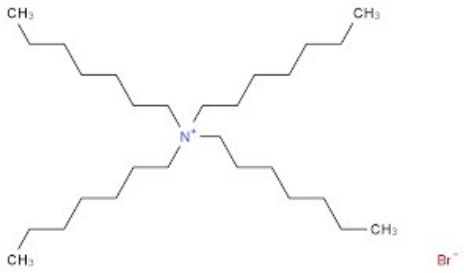
Raju V. Shah,[a,c*] Ashok K. Pandey,[b,c] S. Jagadish Kumar,[a]Sumana Paul,[a] Radhika M. Rao,[a*] P.G. Jaison[a]

[a.] *Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India. Email: rvshah_243@rediffmail.com (R.V. Shah); ashokk@barc.gov.in (A.K.Pandey); jkumars@barc.gov.in (S. Jagadish Kumar); sumana@barc.gov.in (Sumana Paul);rmrao@barc.gov.in (R.M. Rao); jaipg@barc.gov.in (P.G.Jaison)*

[b.] *Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085,India.*

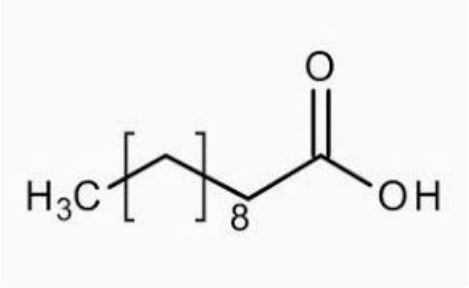
[c.] *Homi Bhabha National Institute, TSH, Anushaktinagar, Mumbai-400 094, India.*

Fig. S1. The machanochemical synthesis of DES.



M.W. : 490.7 g/mol
Mp :87-89 °C

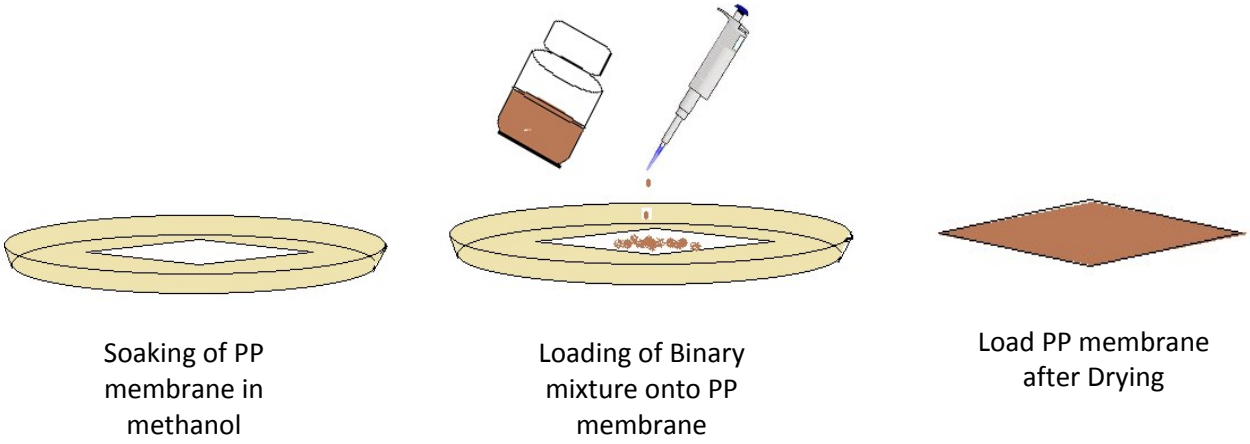
1:2



M.W.: 186.3
mp :28-31 °C

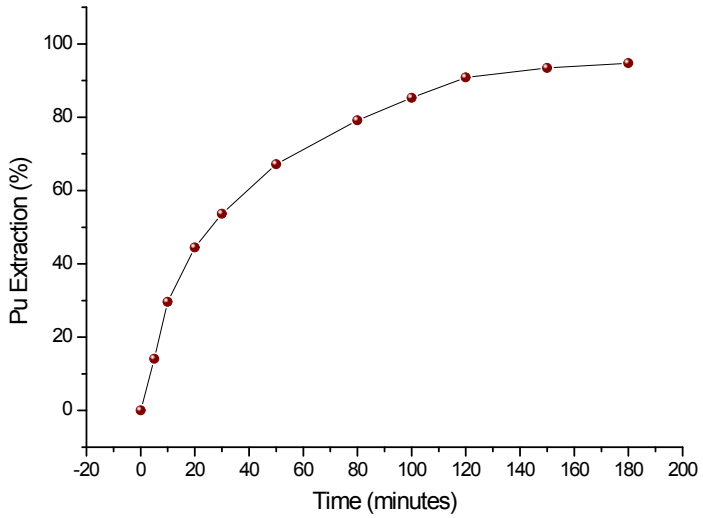
Tetraheptylammoniumbromide(≥99.0%) and undecanoic acid (98%)were obtained from Sigma-Aldrich.

Fig.S2. Preparation of DES-PPM by physical immobilization of UDA-THAB DES in the microporous poly(propylene) membrane.



Membrane**:**Poly (propylene) membrane (Sterlitech make) having 0.2 µm pore-size and 150±15 µm thickness.Methanol-AR was obtained from S.D.Fine Chemical Ltd., Mumbai.

Fig. S3. The sorption profile of Pu (IV) from aqueous solution to the DES-PPM as function of equilibration time.



Conditions for extraction: Aqueous phase-3 M HNO_3, Volume: 10 ml, Membrane size: 1 cm * 2 cm,stirring @ 600 rpm.

Fig. S4. TGA/DTA analyses of UDA-THAB DES.

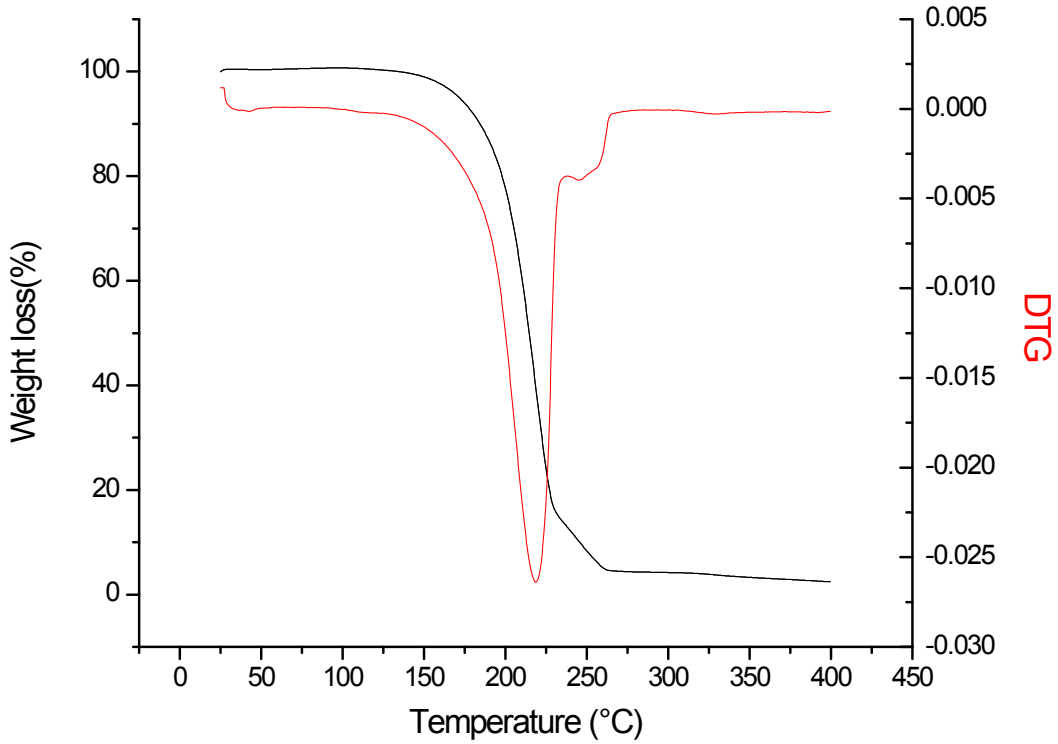
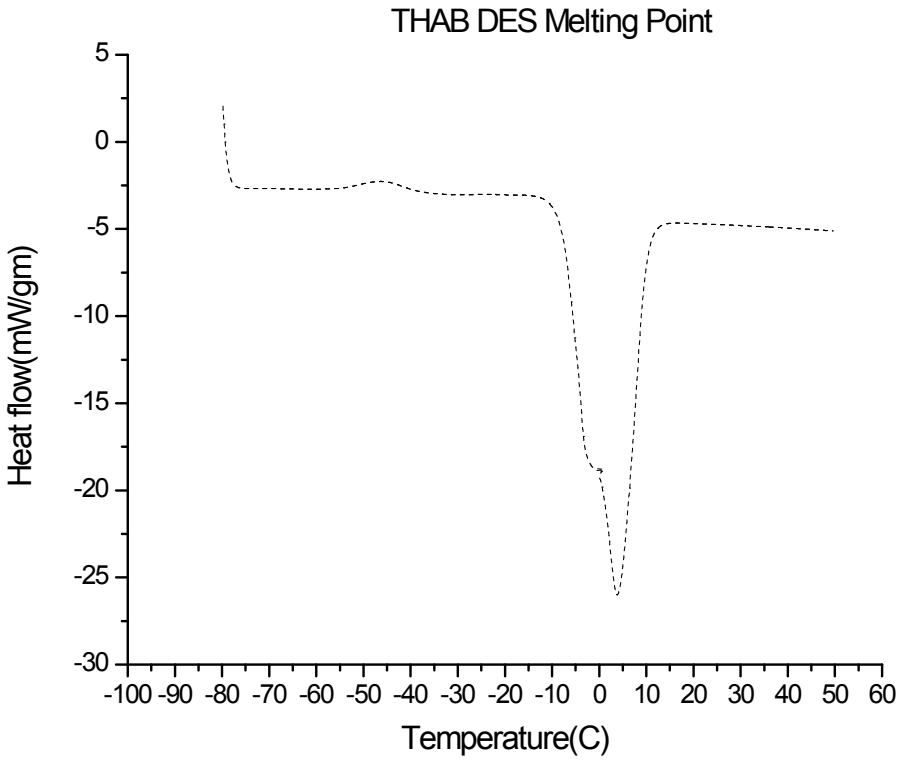
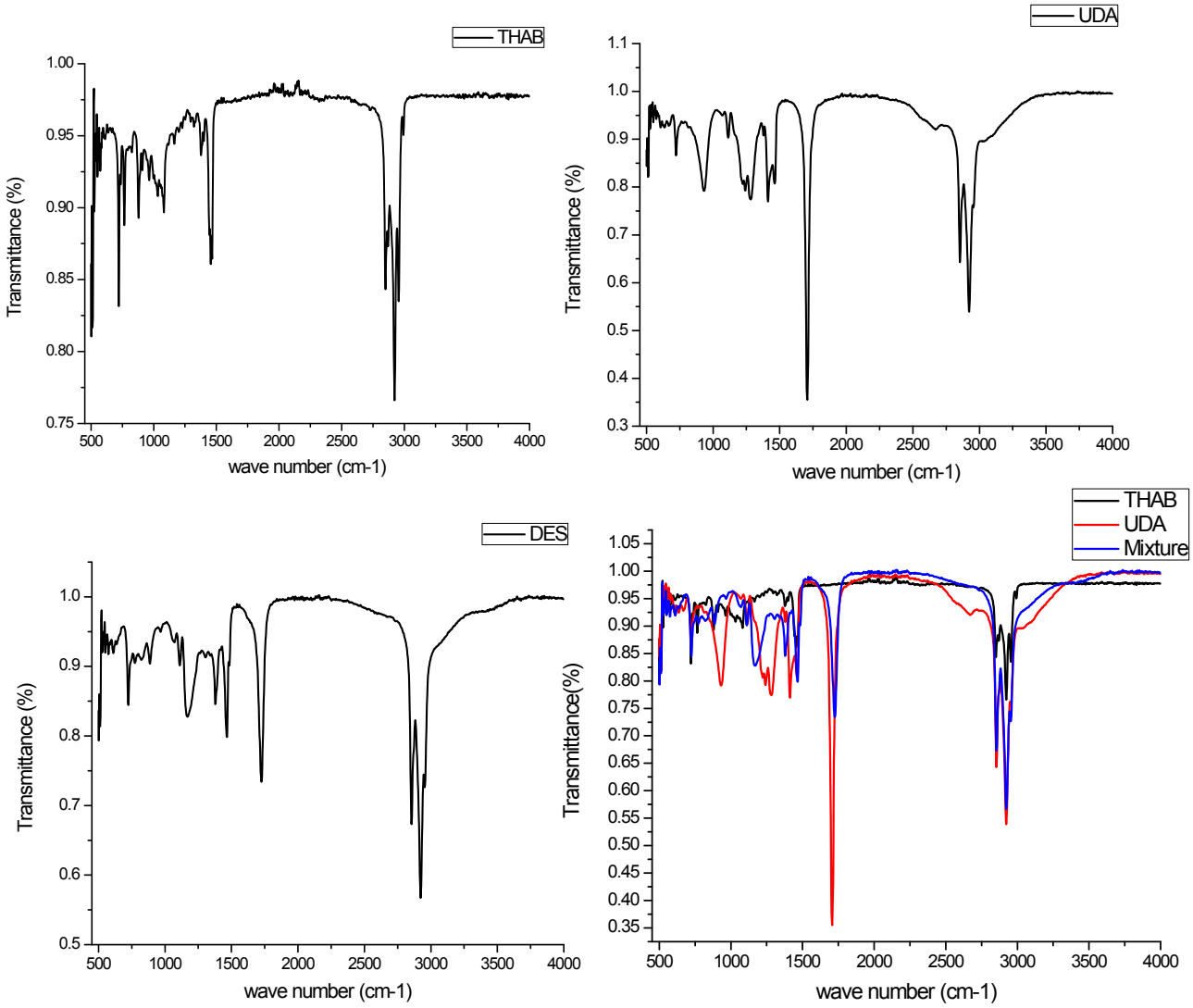


Fig. S5. DSC thermogram of the UDA-THAB DES.



The melting point temperature of the prepared DES was studied using differential scanning calorimetry (Mettler Toledo DSC1 STARe).

Fig. S6. FTIR spectra of THAB, UDA and UDA-THAB DES and corresponding overlapped spectra.



All Fourier transformed infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum Two spectrometer equipped with a Spectrum Two UATR (universal attenuated total reflectance) module. Allsamples were scanned over a wavenumber range of 450-4000 cm^{-1}.

Table S1. The UDA-THAB DES immobilization in the microporous poly(propylene) membrane (PPM). Dimensions of membrane samples used were5cm×5cm.

Sample No.	Wt. of PPM before loading (g)	Wt. of PP membrane after DES loading (g)	%Wt. Gain	Average % Wt. gain (± % RSD-3σ)
1	0.0569	0.3816	570	556 ± 3
2	0.0600	0.3853	542	
3	0.0592	0.3884	556	

Table S2. Isotopic Composition and concentration of Plutonium Spikes.

Isotope Ratio (± % RSD-3σ)	**^{239}Pu Spike**	**^{240}Pu Spike**
^{238}Pu/^{239}Pu	0.00123 ± 3	0.00273 ± 3
^{240}Pu/^{239}Pu	0.010860 ± 0.05	0.40382 ± 0.005
^{241}Pu/^{239}Pu	0.000114 ± 1	0.030748 ± 0.1
^{242}Pu/^{239}Pu	0.000026 ± 3	0.031786 ± 0.1
Concentration (µg/g) (± % RSD-1σ)	11.25 ± 0.1	18.91 ± 0.2

Determination of plutonium concentration using Isotope dilution mass spectrometry

A known weight W_{sp} of a pre-calibrated spike solution, having Pu concentration C_{sp}, is added to a known weight W_{sa} of the sample. From the change in the ^{240}Pu/^{239}Pu atom ratios in the spiked mixture (R_m) with respect to that in the sample (R_{sa}) and spike (R_{sp}),plutonium concentration is calculated using following equation:

$$C_{sa} = \frac{C_{sp} \times W_{sp}}{W_{sa} \times R_{sp}} \times \frac{(R_{sp} - R_m)}{(R_m - R_{sa})} \times \frac{A.F._{sp}}{A.F._{sa}} \times \frac{(Avg.At.Wt)_{sa}}{(Avg.At.Wt)_{sp}}$$

where, C_{sa} and C_{sp} are Pu concentrations in sample and spike, W_{sa} and W_{sp} are the weights of sample and spike in the mixture, R_{sa}, R_{sp} and R_m are the ^{240}Pu/^{239}Pu atom ratios in sample,spike and mixture, and A.F. and Avg.At.Wt. are the atom fractions and average atomic weights, respectively.