† Electronic Supplementary Information

Superparamagnetic bi-functional composite bead for thermal ionization mass spectrometry of plutonium(IV) ions

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**Scheme S1.** Chemical structures of 3-(acrylamido propyl) trimethylammonium chloride (a) and phosphoric acid 2-hydroxyethyl methacrylate ester (b) used for grafting on the PES beads.
Fig. S1 Comparison of elemental profiles of poly(HEMP-co-APTAC) grafted magnetic PES beads before and after subjecting to the equilibrations with 3 and 8 mol L\(^{-1}\) HNO\(_3\).
**Fig. S2** Attainment of sorption equilibrium of Pu(IV) and pseudo-second order rate of sorption of Pu(IV) by poly(HEMP-co-APTAC) grafted magnetic PES bead in 3 M HNO₃.

The sorption rate profile could be fitted to linearized pseudo-second order rate equation given below, which is normally observed in chemical sorption of ions at tracer concentration into the sorbent.

\[
\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}
\]

where \(Q_t\) and \(Q_e\) are the amounts of solute sorbed per unit weight of the sorbent at time \(t\) and at equilibrium, respectively, and \(K_2\) is the pseudo-second-order rate constant of sorption.
Fig. S3 Effect of volume on extraction efficiency of Pu(IV) by poly(HEMP-co-APTAC) grafted magnetic PES bead in 3 M HNO$_3$ medium.
**Fig. S4** Effect of degassing time prior to TIMS analysis on the standard deviation of observed isotope ratios.