Supplementary Information (SI) for Analyst.
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Supporting information for

Two-step seed swelling polymerization to prepare poly(glycidyl methacrylate-divinylbenzene) microspheres and their sulfonation for chromatographic separation of rare earth elements

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Contents

1. Chemicals and reagents

Styrene, azobisisobutyronitrile (AIBN), polyvinylpyrrolidone (PVP-30), isopropanol, anhydrous Methanol, anhydrous sodium sulfate, sodium bisulfate were provided by Aladdin Chemistry Co., Ltd. (Shanghai, China). Divinylbenzene (DVB), polyvinyl alcohol (PVA, 1750±50), dibutyl phthalate (DBP) were purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Toluene, ammonia solution or aqueous ammonia, 1,3-propane sultone (1,3-PS), α-hydroxyisobutyric acid (α-HIBA) were purchased from Xilong Biochemical Technology Co., Ltd. (Shantou, China).

2. Instruments

The high-performance liquid chromatography (HPLC) experiments were conducted using an EasySep 4060 chromatography system (Shanghai Tongwei, China), with the derivatization solution delivered by the EasySep 1020 pump. Fourier-transform infrared spectroscopy (FT-IR) data were collected using a Beifen-Ruili WQF-510A/520A FT-IR spectrometer (Beifen-Ruili Technology, China). The morphology of the materials was characterized using a JSM-IT800 scanning electron microscope (SEM) (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS SUPRA+ spectrometer (Shimadzu Corporation, UK). The water contact angle was measured using a JY-82B Kruss DSA optical contact angle goniometer (Chengde DingSheng Testing Equipment Co., Ltd.). Pore size distribution and Brunauer-Emmett-Teller (BET) surface area analysis were conducted using an ASAP 2460 analyzer (Micromeritics Instrument Corp., USA).

3. Syntheses of PS

Uniform polystyrene (PS) seed microspheres were synthesized via dispersion polymerization. A 250 mL three-neck round-bottom flask equipped with a mechanical stirrer and a condenser was charged with 100 mL of a dispersion medium (ethanol/water) and PVP K25-35. Subsequently, styrene monomer and an appropriate amount of AIBN were added to the mixture. The system was stirred at 150 rpm and purged with argon gas for 15 minutes before being heated to 70°C and maintained for 24 hours. After the reaction was completed, the resulting polystyrene microspheres were collected by centrifugation and thoroughly washed with ethanol and water multiple times. The PS seed microspheres were then dried overnight in a vacuum oven at 35°C. The dried PS microspheres were subsequently dispersed in a 1% (m/v) sodium dodecyl sulfate (SDS) aqueous solution for storage.

4. Syntheses of PGMA-DVB

A 50 mL beaker was charged with 2.6 mL of dibutyl phthalate (DBP) and 30 mL of 0.25% (m/v) sodium dodecyl sulfate (SDS) aqueous solution. The mixture was ultrasonicated using an ultrasonic cell disruptor for 30 minutes. Subsequently, polystyrene (PS) seed microspheres dispersed in 1% (m/v) SDS aqueous solution were introduced into the emulsified solution and stirred at 400 rpm at room temperature for 24 hours using a magnetic stirrer. A mixture consisting of 50 mL of 1% (m/m) polyvinyl alcohol (PVA) stabilizer solution, 5 mL of glycidyl methacrylate (GMA), 10 mL of divinylbenzene (DVB), 16 mL of toluene, 0.2 g of azobisisobutyronitrile (AIBN), and 1 g of SDS was added to 200 mL of water. The solution was ultrasonicated using an ultrasonic cell disruptor for 2 hours. After ultrasonication, the mixture was added to the swollen seed suspension. The resulting mixture was stirred at 400 rpm at room temperature for 24 hours, followed by polymerization at 70°C for 24 hours under continuous stirring. Upon completion of the reaction, the product was washed several times with anhydrous ethanol and vacuum-dried at 80°C.

5. Syntheses of PGMA-DVB-S1 and PGMA-DVB-S2

5.1. Syntheses of PGMA-DVB-S1

PGMA-DVB polymer microspheres were sulfonated using 1,3-propane sultone. PGMA-DVB microspheres were dispersed in 50 mL of 0.1 M dilute sulfuric acid solution and refluxed at 60°C for 12 hours. After hydrolysis, 5 g of dried hydrolyzed PGMA-DVB microspheres were transferred into a three-neck flask containing 30 mL of toluene and stirred at 200 rpm at 80°C for 2 hours. Then, 1.5 mL of 1,3-propane sultone was slowly added dropwise over 10 minutes. Upon completion of the addition, the reaction temperature was increased to 120°C, and the reaction proceeded for 48 hours. After completion, the reaction mixture was cooled to room temperature and dried overnight in a vacuum oven at 80°C. The sulfonated microspheres were designated as PGMA-DVB-S1.

5.1. Syntheses of PGMA-DVB-S2

PGMA-DVB polymer microspheres were also sulfonated using sodium sulfite. 10 g of sodium sulfite and 5 g of sodium bisulfite were dissolved in a mixture of isopropanol and water (10:75, v/v). Subsequently, 5 g of PGMA-DVB microspheres were added to the solution. The mixture was stirred at 60°C for 4 hours, followed by the addition of 5 mL of 0.2 M H_2SO_4, and the reaction was continued at 70°C for another 6 hours. Upon completion, the reaction mixture was cooled to room temperature and washed thoroughly with an excess of hot ultrapure water and anhydrous ethanol to remove any unreacted sodium sulfite. The product was then dried overnight in a vacuum oven at 80 °C. The sulfonated microspheres were designated as PGMA-DVB-S2.

6. Column packing

The chromatographic column was packed using a high-pressure slurry packing method. The packing material was suspended in a suitable slurry solvent to form a homogeneous suspension. Before sedimentation occurred, the slurry was rapidly introduced into the column at a high flow rate using a high-pressure pump, ensuring uniform column packing. The specific steps are as follows: 2.5 g of dried sulfonic acid-functionalized polymer microspheres were placed into a solution of methanol and isobutanol (1:1, 60 mL). The mixture was subjected to ultrasonication for 15 minutes, followed by stirring for another 15 minutes, and this process was repeated at least twice. The well-dispersed slurry was then quickly transferred into the slurry reservoir of the column packing system and properly connected to the tubing. Methanol was used as the displacement solvent. The system was maintained at 50 MPa for 40 minutes, followed by a pressure reduction to 25 MPa for an additional 20 minutes. After the packing process was completed, a frit was placed on top and secured with a nut. Finally, the column was flushed with deionized water at a flow rate of 1 mL/min for 24 hours to remove any residual impurities within the column.

7. Preparation of mobile phase and derivatization reagent

Preparation of mobile phase: Chromatographic analysis was performed under different elution conditions (isocratic and gradient) using appropriate mobile phases. Precisely measured amounts of eluent were dissolved in ultrapure water to achieve the desired concentration. The pH of the mobile phase was adjusted using aqueous ammonia or hydrochloric acid solution to obtain the required pH range.

Preparation of post-column derivatization reagent: The post-column derivatization solution was prepared by dissolving Arsenazo III (2,7-bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid) and urea in water. The final solution contained 1.5×10^{-4} M Arsenazo III, 0.01 M urea, and 0.1 M glacial acetic acid. The flow rate of the post-column

reagent was set to 0.6 mL/min. Photometric detection of the colored rare earth element complexes was performed using a UV-Vis variable wavelength detector at 658 nm.

8. SEM images of PS, PGMA-DVB-S1, and PGMA-DVB-S2; elemental analysis of PGMA-DVB-S1 and PGMA-DVB-S2; and adsorption/desorption measurements and static water contact angle results of PGMA-DVB, PGMA-DVB-S1, and PGMA-DVB-S2.

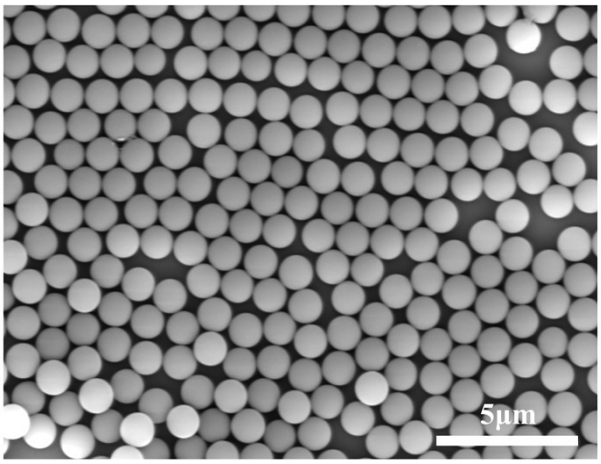

Fig. S1 The scanning electron microscope (SEM) images of polystyrene seed microspheres.

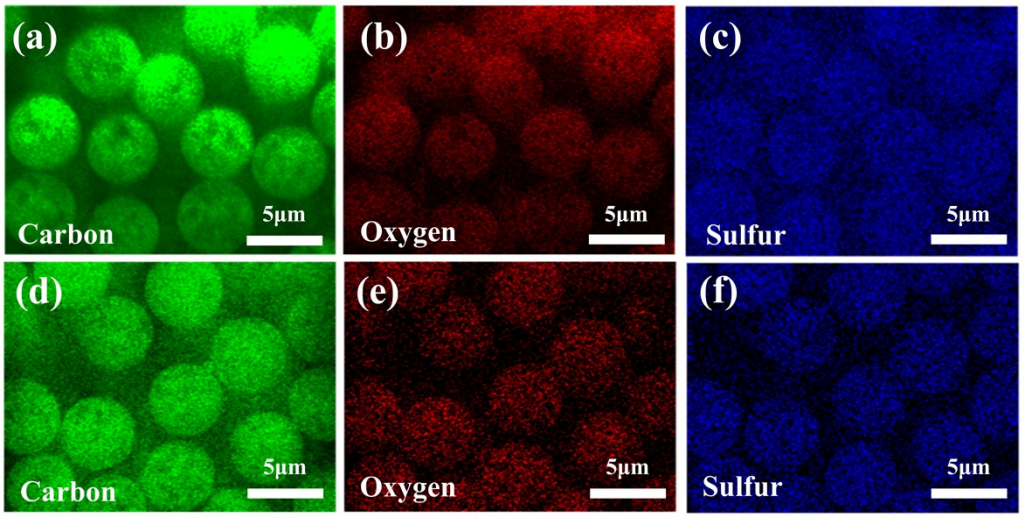

Fig. S2 Elemental mapping images of PGMA-DVB-S1: (a) C, (b) O, (c) S, and PGMA-DVB-S2: (d) C, (e) O, (f) S.

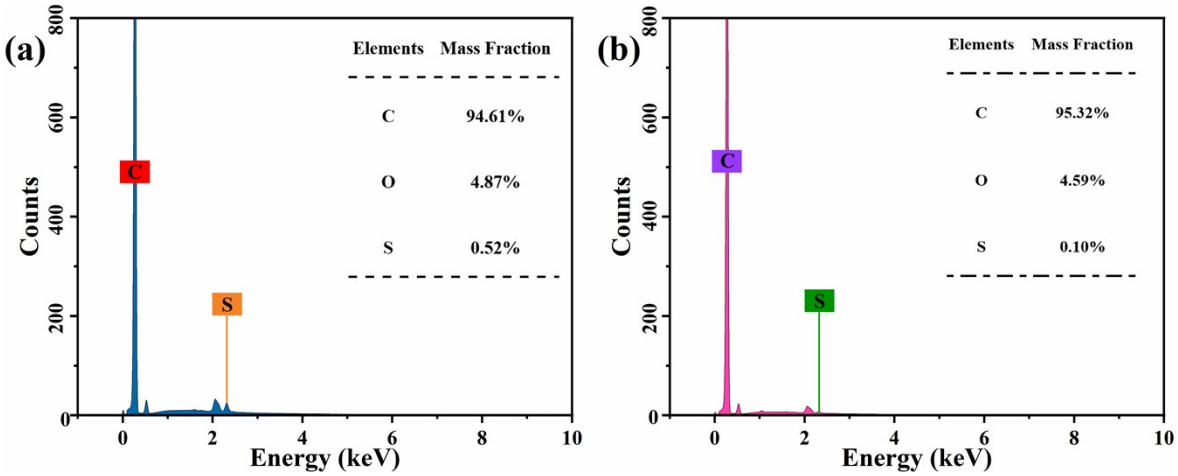

Fig. S3 EDS-calculated elemental composition of PGMA-DVB-S1 (a)and PGMA-DVB-S2(b).

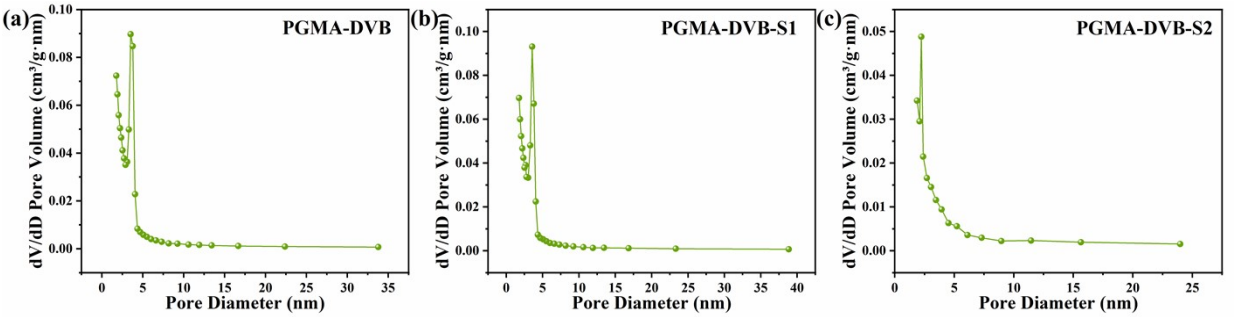

Fig. S4 The pore size distribution of PGMA-DVB (a), PGMA-DVB-S1 (b), and PGMA-DVB-S2 (c).

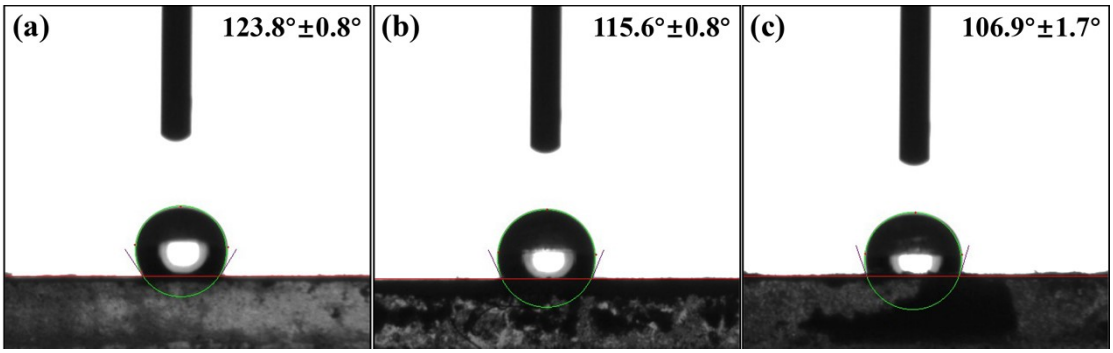

Fig. S5 Static water contact angle results of PGMA-DVB (a), PGMA-DVB-S1 (b), and PGMA-DVB-S2 (c).

Table S1 Elemental analysis of PGMA-DVB-S1 and PGMA-DVB-S2

Samples	C [%]	S [%]	Surface coverage (μmol/m^2)
PGMA-DVB-S1	66.7	1.83	1.62
PGMA-DVB-S2	92.8	1.35	1.19

Table S2 The adsorption/desorption measurement results of PGMA-DVB, PGMA-DVB-S1 and PGMA-DVB-S2

Samples	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
PGMA-DVB	353.06	0.19	3.51
PGMA-DVB-S1	379.86	0.11	4.85
PGMA-DVB-S2	365.04	0.19	3.76

9. Separation of REEs

Table S3 Retention factor, separation factor, resolution, asymmetry factor, and theoretical plate number of rare earth elements on PGMA-DVB-S1 and PGMA-DVB-S2 stationary phases.

Element	Retention Factor		Separation Factor		Degree of Separation		Asymmetry Factor		Theoretical Number of Plates	
	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2
Sc	4.35	4.31	3.10	3.49	3.9	11.9	2.83	1.36	199	244
Lu	13.49	15.02	1.37	1.18	1.3	2.2	0.01	1.06	342	2843
Yb	18.43	17.68	1.59	1.24	2.3	3.4	0.03	1.12	304	3563
Tm	29.36	22.00	1.23	1.2	1.6	3.3	1.35	1.19	586	5016
Er	36.01	26.40	1.15	1.19	1.7	3.5	2.31	1.15	1817	6228
Ho	41.48	31.39	1.11	1.12	1.5	2.3	0.03	1.17	3296	7757
Dy+Y	45.96	35.21	1.15	1.16	2.1	3.8	2.13	1.49	3622	6236
Tb	52.89	40.77	1.19	1.15	2.5	5.5	2.00	1.24	3513	23501
Gd	63.19	46.71	1.10	1.06	1.2	2.4	0.34	1.22	3074	30786
Nd	69.21	49.39	1.13	1.09	1.6	3.7	0.01	1.29	2911	31289
Sm	78.22	53.76	1.25	1.18	2.8	7.0	2.10	1.32	2969	30924
Nd	97.91	63.44	1.10	1.06	1.2	2.3	0.40	1.30	2324	28718
Pr	108.16	67.02	1.08	1.08	1.1	3.2	1.40	1.34	2794	28365
Ce	116.60	72.39	1.10	1.11	1.9	5.2	2.10	1.40	5128	26799
La	128.10	80.42					1.66	1.39	7999	62660

Table S4 Elution program for the separation of rare earth elements using PGMA-DVB-S1 as a liquid chromatography stationary phase. Chromatographic Conditions: Column temperature: 25 °C; Injection volume: 5 μL; Flow rate: 1 mL/min; Detection: Post-column reaction with Arsenazo III, Wavelength: 658 nm.

t/min	A% (Water)	B% (α-HIBA,800 mM, pH=3.26)
0	85%	15%
40	85%	15%
70	75%	25%
140	60%	40%
160	60%	40%
210	50%	50%

Table S5 Elution program for the separation of rare earth elements using PGMA-DVB-S2 as a liquid chromatography stationary phase. Chromatographic Conditions: Column temperature: 25°C; Injection volume: 5 μL; Flow rate: 1 mL/min; Detection: Post-column reaction with Arsenazo III, Wavelength: 658 nm.

t/min	A% (Water)	B% (α-HIBA, 800 mM, pH=3.26)
0	90%	10%
10	90%	10%
50	85%	15%
80	75%	25%
120	63%	37%
140	50%	50%
150	50%	50%

10. Chromatograms (a), retention time and peak area (b) of rare earth element separation on the PGMA-DVB-S2 column with different injection volumes.

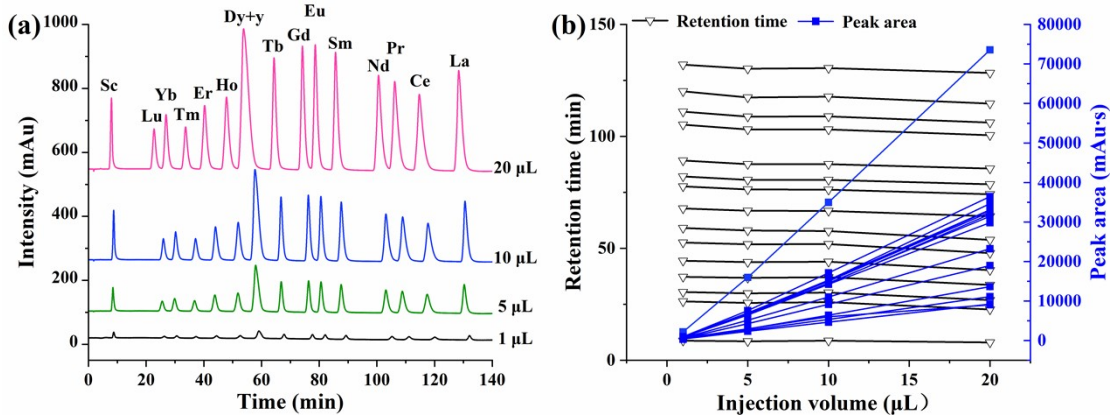

Fig. S6 (a) Chromatograms of rare earth element separation on the PGMA-DVB-S2 column with different injection volumes. (b) Retention time and peak area of rare earth element separation on the PGMA-DVB-S2 column under different injection volumes. Chromatographic conditions: column temperature: 25 °C; injection volume: 5–20 μL; flow rate: 1 mL/min with isocratic elution. Detection: post-column reaction with Arsenazo III, detection wavelength: 658 nm.

11. Effect of column temperature on separation

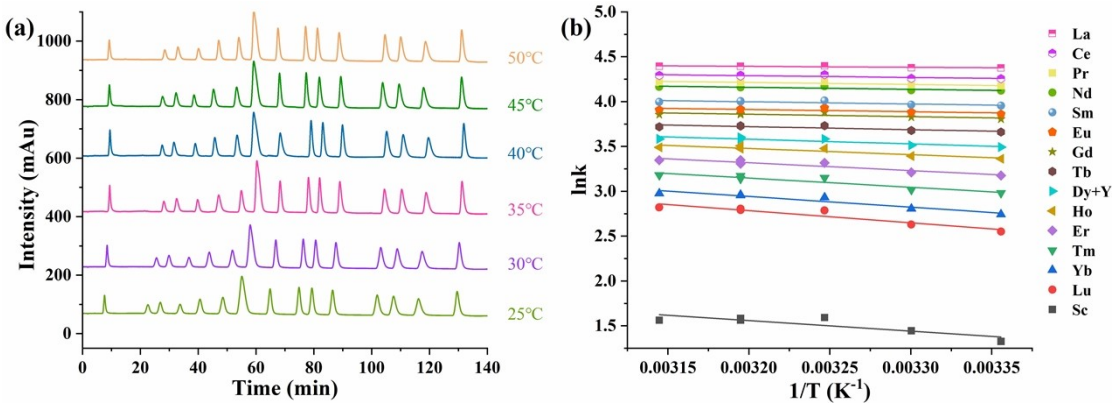

Fig. S7 (a) Chromatograms of rare earth element separation on the PGMA-DVB-S2 column at column temperatures ranging from 25 to 50 ℃. (b) Van't Hoff plot. Chromatographic conditions: Column temperature: 25–50 °C; injection volume: 5 μL; flow rate: 1 mL/min with isocratic elution. Detection: Post-column reaction with Arsenazo III, detection wavelength: 658 nm.

The enthalpy change (ΔH) is given by the Van't Hoff isotherm：**1**

$$\Delta H = -R\frac{d\ln k}{d(1/T)}$$

Where T is the absolute temperature, and R is the gas constant (1.987 cal·K^{-1}·mol^{-1}).

12. Reproducibility and stability of the chromatographic column

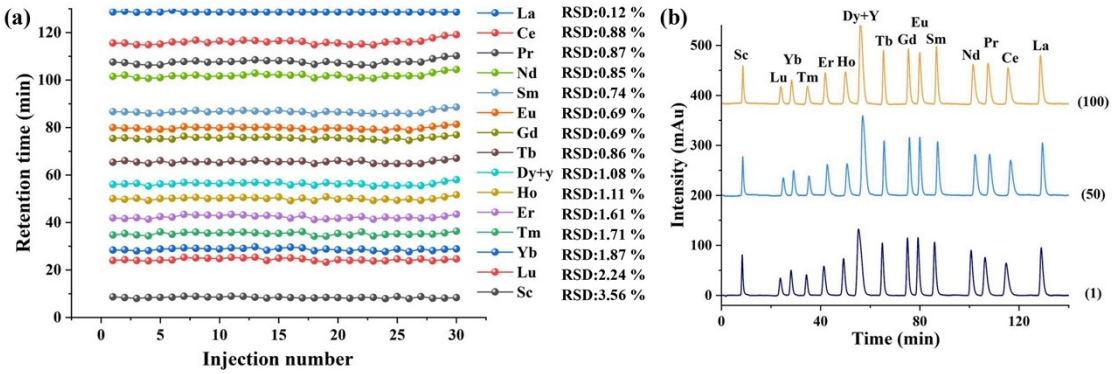

Fig. S8 (a) Variation in retention time of rare earth elements over 30 consecutive injections. (b) Chromatograms of the first, fiftieth, and hundredth injections. Chromatographic conditions: Column temperature: 25 °C; injection volume: 5 μL; flow rate: 1 mL/min with isocratic elution. Detection: Post-column reaction with Arsenazo III, detection wavelength: 658 nm.

13. Separation of REEs from impurity elements

Table S6 Retention factor, separation factor, resolution, asymmetry factor, and theoretical plate number of rare earth elements, iron, and uranium.

Elements	Retention Factor	Separation Factor	Degree of Separation	Asymmetry Factor	Theoretical Plates
Fe	1.436	3.94	7	2.37	367
Sc	5.664	2.32	7.8	1.53	1448
U	13.126	1.85	10.4	2.16	2187
Lu	24.269	1.1	2.7	1.43	11712
Yb	26.762	1.13	4	1.46	14345
Tm	30.295	1.1	3.7	1.44	23087
Er	33.194	1.09	3.9	1.36	33714

Ho	36.187	1.06	2.2	1.33	34185
Dy+Y	38.475	1.11	3.9	1.85	14128
Tb	42.559	1.12	6.3	1.47	53713
Gd	47.74	1.05	2.7	1.50	45877
Nd	50.21	1.08	4.1	1.56	51369
Sm	54.007	1.17	8.9	1.62	54022
Nd	63.348	1.06	2.8	1.64	48857
Pr	66.929	1.08	3.8	1.73	36423
Ce	72.365	1.11	6.1	1.84	42385
La	80.256		0	1.80	79004

Table S7 Elution program for the separation of Fe, U, and 16 rare earth elements using GMA-DVB-S2 as the chromatographic stationary phase. Chromatographic Conditions: Column temperature: 25°C; Injection volume: 5 μL; Flow rate: 1 mL/min; Detection: Post-column reaction with Arsenazo III, Wavelength: 658 nm.

t/min	A% (Water)	B% (α-HIBA, 800mM, pH=3.26)
0	91%	9%
26	91%	9%
50	85%	15%
80	75%	25%
120	63%	37%
130	50%	50%
140	50%	50%

References

S1. R. Dybczyński and K. Kulisa, Chem Anal (Warsaw), 2009, 54, 437-457.