Study on Temperature-Enabling Dynamic Liquid Chromatography and Its Application in Uranium Isotope Separation

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Abstract

Separation of uranium isotopes is not only a difficult scientific project, but also an engineering problem. A temperature-enabling dynamics liquid chromatography was designed for uranium isotopes separation based on dynamics liquid chromatography and liquid membrane diffusion model. This work prepared 'organic' and 'inorganic' chromatography columns filled ABS pellets and SiO2 pellets, respectively. In order to improve the efficiency of separation, the injection-outflow self-control system and temperature-enabling cells were equipped to chromatography columns. The organic column optimal working conditions obtained by experiments were pH=2, enabling temperature=70°C and injection flow rate=15mL/min. Meanwhile, multi-stage separation experiment verified feasibility of uranium isotopes using organic column, the separation factor can reach 1.0184 and needed over 79 stages to enrich 235U abundance to 3%. The optimal conditions for inorganic column, determined through prior experiments, were pH=2, enabling temperature=50°C and injection flow rate=15mL/min. Multi-stage separation experiments using inorganic columns achieved a separation factor of 1.0110, requiring over 112 stages to enrich 235U abundance to 3%. Moreover, a series of mechanism experiments illustrated the mechanism of chromatography and confirmed liquid membrane and silica hydroxyl groups involvement in separation process. These studies identified the temperature-enabling dynamics liquid chromatography can effectively separate 235U from 238U, which provided a new research idea in the field of chromatography and isotope separation.

Full Text

Preamble

Separation of uranium isotopes represents both a formidable scientific challenge and a complex engineering problem. This study presents a temperature-enabling dynamics liquid chromatography system designed for uranium isotope separation, built upon principles of dynamics liquid chromatography and the liquid membrane diffusion model. Two types of chromatographic columns were prepared: an "organic" column packed with ABS pellets and an "inorganic" column filled with SiO_2 pellets. To enhance separation efficiency, the system incorporated an injection-outflow self-control mechanism and temperature-enabling cells integrated with the columns. Experimental optimization revealed that the organic column performed best under the following conditions: pH = 2, enabling temperature = 70°C, and injection flow rate = 15 mL/min. Multi-stage separation experiments validated the feasibility of uranium isotope separation using the organic column, achieving a separation factor of 1.0184, though requiring over 79 stages to enrich ^{235}U abundance to 3%. For the inorganic column, prior experiments established optimal conditions of pH = 2, enabling temperature = 50°C, and injection flow rate = 15 mL/min, which yielded a separation factor of 1.0110 and required over 112 stages to reach the same enrichment level. Mechanistic studies elucidated the separation process, confirming the involvement of both liquid membrane dynamics and silica hydroxyl groups. These findings demonstrate that temperature-enabling dynamics liquid chromatography can effectively separate ^{235}U from ^{238}U, offering a novel approach for research in chromatography and isotope separation.

Keywords: Uranium isotopes separation; Dynamics chromatography; Temperature enabling; Maximum front enrichment value; Separation factor

Introduction

Nuclear energy represents one of the most critical solutions to global energy shortages. Nuclear power plants utilize enriched uranium as fuel, harnessing the immense energy released from nuclear fission reactions to generate electricity, thereby addressing regional power demands. However, the ^{235}U abundance in nuclear fuel must exceed 3% before it can be used in commercial reactors, making uranium isotope separation and enrichment essential for fuel production. As the heaviest naturally occurring element, uranium presents a unique challenge: the mass difference between ^{235}U and ^{238}U is merely 1%, rendering isotopic separation exceptionally difficult.

Historically, researchers have developed several uranium isotope separation methods, including gas diffusion, gas centrifugation, nozzle separation, laser enrichment, chemical separation, electromagnetic isotope separation, and plasma separation [**?**, **?**, **?**]. The gaseous diffusion method, the first to be historically developed and implemented, has been phased out due to its low separation

factor (1.0043), large facility footprint, and high energy consumption and costs [?, ?]. Gas centrifugation currently offers the lowest energy consumption ratio among industrial methods and remains the only commercially viable technique, achieving a separation factor of 1.01. However, it requires over 2000 separation stages and involves inconvenient, polluting operations [?, ?].

Chemical methods, including chromatographic and extraction techniques, were developed by Japan and France, respectively. The chromatographic method, known as the Asahi Chemical Enrichment Process (ACEP), employed isotope exchange chromatography for uranium enrichment. ACEP utilized a specialized anion exchange resin; as uranyl ions passed through the column, they adsorbed at the resin front where isotope exchange reactions occurred, with subsequent elution using a reducing agent. This method achieved a separation factor of 1.003. A key advantage was that depleted solution could be recirculated, eliminating the need for large-scale cascade equipment [?, ?]. The extraction method, termed Chemical Exchange (CHEMEX), relied on isotope exchange reactions between two immiscible liquid phases, achieving a separation factor of approximately 1.0015. Due to this low efficiency, thousands of stages were required for industrial-level enrichment. Both chemical processes have gradually been supplanted by more efficient methods like gas centrifugation because of high energy consumption and complex equipment requirements [?, ?].

Laser methods exploit spectral differences between ^{235}U and ^{238}U. Using uranium as feed material, a precisely tuned laser ionizes ^{235}U to $^{235}U^{6+}$, which is then collected. While this approach offers an extremely high separation factor with minimal stages, it involves complex technology, high costs, and demanding operating conditions [?]. Uranium isotope separation technology has remained stagnant for years, necessitating a new enrichment scheme that is safe, efficient, environmentally friendly, industrially scalable, and characterized by low separation energy [?, ?].

Since the early 20th century, chromatography has evolved continuously into a vital separation and analytical tool with applications in organic chemistry, analytical chemistry, medicine, biochemistry, and environmental protection. Dynamics liquid chromatography represents a major branch of this field and has proven highly effective for separating natural macromolecules [?, ?]. This technique divides into two primary categories: hydrodynamic chromatography (HDC) and slalom chromatography (SC). Both rely on fluid dynamic phenomena within the chromatographic system to separate solutes, typically without chemical reactions [?, ?, ?, ?].

This work fabricated two types of dynamics liquid chromatography columns for uranium isotope separation, packed with ABS (acrylonitrile-butadiene-styrene copolymer) plastic and SiO_2, respectively. A complete separation device system was constructed to enable automated operation and collection with these columns. Temperature-enabling methods were employed to improve separation efficiency, and multi-stage separation experiments determined the uranium isotope separation factor. The key innovation of this manuscript is the pulse chro-

matography method, which leverages chromatographic principles to position lighter, lower-valence species at the column front and heavier, higher-valence species at the rear, enabling separation through diversion. Pulse injection allows this process to be repeated sequentially, with each pulse constituting a separation cycle. Additionally, the effects of liquid membranes and functional groups on separation performance were investigated to elucidate the underlying mechanism.

II. Theory

2.1 Liquid Membrane Tidal Diffusion Model

Horvath and Lin (1978) proposed that a stagnant layer of nearly stationary mobile phase forms on filling surfaces in liquid chromatography, facilitating mass transfer and exchange [**?**]. Previous studies indicated that adsorption volumes often exhibited sharp transitions and minor fluctuations over time (Supplementary file Fig. 1 [Figure 1: see original paper]). During Eu adsorption on D231 resin, triply charged functional groups or cations ionized from the resin exchanged with Eu in solution. Hydrogen ion concentration influenced this ionization: at pH = 4, high hydrogen ion concentration inhibited cation ionization, reducing Eu adsorption and enhancing desorption. Supporting information Fig. 1 shows Eu adsorption by D231 resin as a function of time, where the vertical coordinate represents the ratio of Eu concentration at time t to its initial concentration [**?**].

Yu et al. [**?**] proposed a hypothesis for adsorbent adsorption/desorption, suggesting that beyond binding/separation within internal pores, the liquid membrane on the adsorbent surface also affected substance diffusion. This process was termed the "liquid membrane tidal diffusion model (LMTD)." LMTD comprises two steps, as illustrated in Fig 1. First, particles primarily diffuse into the liquid membrane on the filling surfaces; these particles are subsequently released into the bulk solution. Second, particles attached to the liquid membrane further diffuse into the solid internal pores, then release from the solid internal pores back into the liquid membrane. Haoqi Yu et al. [**?**] further investigated this model, combining it with non-homogeneous isothermal adsorption to develop new kinetic equations that successfully described concentration fluctuations during adsorption/desorption processes.

Based on previous research, this work proposes the following hypothesis: as the mobile phase flows through the chromatography column, a liquid membrane forms on filling surfaces. Uranyl ions enter and are retained within this liquid membrane. The flowing solution carries away some retained uranyl ions while continuously delivering new ions into the liquid membrane. Meanwhile, $^{235}UO_2^{2+}$ in the liquid membrane would more easily transfer into the mobile phase because $^{235}UO_2^{2+}$ is lighter than $^{238}UO_2^{2+}$, causing gradual separation of $^{235}UO_2^{2+}$ from $^{238}UO_2^{2+}$ in the chromatography column.

2.2 Determination of Optimal Separation Conditions

Each pulse involves injecting a sample solution, switching to an air segment, then injecting the next pulse' s sample solution. Optimal conditions for uranium isotope separation by the two chromatographic columns were determined through systematic experiments.

The mobile phase flow rate, pH value, and enabling temperature of dynamics chromatography all influence separation performance. To identify optimal conditions, researchers prepared ten test tubes to collect equal volumes of chromatographic effluent. The concentrations of ^{235}U and ^{238}U in each tube were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, iCAP PROX, Germany), and the separation performance was analyzed. To better describe column performance for U isotope separation, this paper employs the front maximum enrichment value (β) to evaluate chromatographic separation capability with different filling materials under various operating conditions [**?**], as defined in Eq (1):

$$\beta = \frac{^{235}\mathrm{U}/^{238}\mathrm{U}}{^{235}\mathrm{U}_0/^{238}\mathrm{U}_0}$$

where ^{235}U/^{238}U represents the isotopic abundance ratio in chromatographic effluents and $^{235}\mathrm{U}_0/^{238}\mathrm{U}_0$ represents that in the original $UO_2(NO_3)_2$ solution. β values exceeding 1.000 indicate that ^{238}U is preferentially enriched in the liquid phase at the front band region while ^{235}U enriches in the membrane.

The average enrichment value ($\bar{\beta}$) was used to evaluate chromatographic separation efficiency, defined in Eq (2):

$$\bar{\beta} = \frac{\sum_{i=1}^{n} \beta_i}{n}$$

where β_i represents the enrichment value ($\beta_i > 1$) in chromatographic effluents when ^{235}U abundance exceeds the mean value. The experimental approach consisted of three phases: first, conducting separation experiments under various conditions; second, using front maximum and average enrichment values to identify optimal separation conditions; third, performing U isotope separation under these optimal conditions, where the $\beta > 1$ portion of effluent constituted the "gold separation section." This section was collected from each chromatographic effluent for subsequent separation stages, with the process cycled to achieve multi-stage separation. Finally, based on multi-stage separation experiments, the chromatographic separation factor was calculated using Eq (3):

$$A\alpha^n = B$$

where A represents the mass ratio of ^{235}U to total U in the initial solution, α is the separation factor, n is the number of separation stages, and B is the mass ratio of ^{235}U to total U in the separated solution [**?**].

III. Experimental

3.1 Reagents and Materials

The following reagents and materials were used: polyvinyl chloride (PVC) plastic tubes, 1 mm diameter SiO_2 pellets, 1 mm diameter ABS plastic pellets, hydrochloric acid, absolute ethanol, uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$), zinc uranyl acetate ($ZnUO_2(CH_3COO)_4 \cdot 7H_2O$), and cationic surfactant (hexadecyl trimethyl ammonium bromide, $C_{19}H_{42}ClN$). All reagents were analytical grade.

3.2 Chromatographic Column Design

Two types of dynamics liquid chromatography columns were employed, designated as organic and inorganic columns. Their parameters are listed in supplementary file Table 1 , and column structures are shown in Fig 2 [Figure 2: see original paper].

3.3 Characterization

Fourier Transform Infrared (FTIR) spectra of fillings before and after separation experiments were obtained using a Thermo Fisher Scientific Nicolet iS20 spectrophotometer (USA) across 4000–400 cm^{-1}. Energy Dispersive Spectrometer (EDS) and Scanning Electron Microscope (SEM) analyses of chromatographic fillings were performed on a Hitachi SU8100. X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific K-Alpha, USA) was used to analyze the chemical composition of fillings before and after experiments.

3.4 Design of Automatic Separation Device

To enable automated control of injection, diversion, and collection, a complete automatic separation device was designed, as shown in Fig 3 Figure 3: see original paper. The device comprises four components: adjustable flow systems, switching pulse injection systems, chromatographic separation systems (the column itself), and time-controlled automatic shunt systems.

The adjustable flow system, equipped with an SC-2556 peristaltic pump, provides the driving force for the entire apparatus, transporting sample liquid and controlling its flow rate. The switching pulse injection system uses a three-way valve to control gas/liquid switching feed, with injection times for liquid and gas determined experimentally. The chromatographic separation system is central to uranium isotope separation. The time-controlled automatic shunt at the column outlet operates through timing-based diversion controlled by a fluid sensor to achieve time-advancing shunt [**?**].

The switching pulse injection system has two internal parameters, T_1 and T_2. T_1 represents fluid injection time, while T_2 represents air injection time. This system feeds pre-treated sample into the column in an alternating air/liquid mode. Based on the assumption in Section 2.3, ^{235}U gradually separates from ^{238}U as it moves through the column and exits first. At this point, the time-controlled automatic shunt diverts a section of aqueous solution with higher ^{235}U abundance based on T_3 and T_4 values from prior conditional experiments. As shown in Fig 3(b), the time-controlled automatic shunt has two parameters: T_3 and T_4, both with initial values. When the air segment ends and solution flows from the column outlet, T_3 begins counting down, allowing solution with below-average ^{235}U abundance to exit through the T_3 outlet. After T_3 countdown completes, the three-way valve switches to the T_4 position, permitting higher-abundance ^{235}U solution to exit through the T_4 outlet while T_4 countdown begins. Once T_4 countdown ends, the valve resets to the T_3 position, and remaining solution continues exiting through T_3 until the next pulse' s air segment. In summary, solution collected from outlet T_4 constitutes the enrichment fraction, which flows into enrichment solution cells.

Since single-stage separation cannot achieve the ^{235}U abundance required for nuclear fuel, a reflux device was installed external to the chromatographic separation system to enable multi-stage separation. Generally, during the nth separation stage, the adjustable flow system returns the depleted stream to the (n-1)th stage sample cell while the enriched fraction flows into the cell awaiting (n+1)th stage separation, and so on [**?**], as illustrated in Fig 3(c).

IV. Results and Discussion

4.1 Organic Chromatographic Column for U Isotope Separation

ABS plastic is a ternary copolymer composed of varying proportions of acrylonitrile (A), butadiene (B), and styrene (S), offering advantages including strong corrosion resistance, high toughness, and readily available raw materials. This material finds wide applications in manufacturing and chemical industries, including mechanical, electrical, 3D printing, and other sectors [**?**, **?**, **?**]. To investigate the effect of organic functional groups on isotope separation while avoiding chemical reactions between uranyl nitrate and fillings and enabling long-term reuse, organic columns were packed with 1.0 mm diameter ABS plastic spheres.

Previous work by this research group [**?**, **?**] investigated temperature-enabling kinetic liquid chromatography. Since neither silica nor ABS fillings adsorb uranyl ions, many operational conditions from those studies could be adapted. The optimal flow rate in previous 10m-type columns was 5.698 mL/min, which was unsuitable for organic columns with larger internal diameters. Linear velocity of the sample in the column can be calculated using Eq (4), allowing inverse calculation of appropriate flow rates for organic columns:

$$l = \frac{Q}{V_{\text{column}} - V_{\text{fillings}}}$$

where l (cm/min) is the linear velocity of solution inside the column, Q (mL/min) is solution flow rate, H is column length, V_{column} is column volume, and V_{fillings} is total filling volume. Calculation based on the previous column geometry indicated a sample flow rate of 15 mL/min.

To maintain equivalent mobile phase flow rates through fillings in organic columns, this study also employed 15 mL/min. Building on prior experiments, the injection mode was set to 20 mL liquid injection for 80 s, then switched to gas (air). When solution flowed out in strands at the column outlet (approximately 100 s of gas injection), the inlet switched back to liquid injection, repeating this cycle. These timing parameters were programmed into the switching injection system (Fig 3(a)) to achieve automated gas/liquid switching injection.

4.1.1 Characterization of ABS Fillings Characterization was performed on chromatographic column fillings before and after separation experiments. SEM-EDS analysis revealed ABS plastic pellets as spherical with a slight layered surface structure; surface morphology remained essentially unchanged after experiments, with no detectable uranium adsorption observed at pH = 2. Although EDS did not detect uranium adsorption, XPS results indicated trace amounts of U(VI) remained on ABS plastic after experiments. Detailed characterization of ABS fillings is provided in the supplementary file.

4.1.2 Effect of pH on Separation Based on comprehensive prior experience, solution pH significantly influences separation. As ABS plastic pellets were used as chromatographic filling for the first time, determining optimal conditions was crucial. At pH = 2.5, uranium exists primarily as uranyl ions ($UO_2{}^{2+}$). When pH > 2.5, uranyl ions begin hydrolyzing with increasing pH, forming multinuclear or cage structures and eventually hydroxide precipitates [**?**]. To determine the most suitable acidity for organic columns, experiments used 15-200 ppb uranyl nitrate solutions divided into three groups at pH values of 2, 4, and 7. To exclude other interferences, columns were not temperature-enabled in these experiments; results are shown in Fig 5 [Figure 5: see original paper].

ICP-MS measurements of U isotope concentrations involve some uncertainty. In Fig. 9, the light-colored area indicates isotope concentration fluctuation ranges. Type-A uncertainty was used to analyze βmax quality and dispersion, defined in Eq (5):

$$u_A = \sqrt{\frac{\sum_{i=1}^{n}(s_i - \bar{s})^2}{n(n-1)}}$$

where u_A represents type-A uncertainty, s_i denotes the ith test result of a sample, $\bar{s}$ is the sample test average, and n is the number of tests per sample.

Results showed that at pH = 2, uranyl ions concentrated mainly at the front and back ends of column effluent, with optimal separation sections at 6–8 mL and 10–14 mL, yielding βmax = 1.0243, $u_A = 5.4419 \times 10^{-2}$, and $\bar{\beta} = 1.0150$. At pH = 4, uranyl ion concentration fluctuated continuously with effluent volume, with optimal separation at 2–6 mL and 8–10 mL, giving βmax = 1.0175, $u_A = 1.7082 \times 10^{-2}$, and $\bar{\beta} = 1.0093$, showing weaker separation than the other two conditions. At pH = 7, uranyl ions again concentrated at effluent ends, with optimal separation at 8–16 mL, yielding βmax = 1.0242, $u_A = 1.2595 \times 10^{-2}$, and $\bar{\beta} = 1.0148$. Overall results indicated pH = 2 as the most suitable acidity for organic columns.

At pH = 4, uranium species include both $UO_2{}^{2+}$ and $UO_2(OH)^+$, creating a complex internal column environment that produced irregular U isotope concentration trends (Fig 5(b)) and lower enrichment compared to pH = 2 and pH = 7. Due to liquid membrane formation and uranium adsorption by ABS fillings, solution uranium remained in residual liquid membranes on filling surfaces after each pass. Additionally, the gas/liquid switching injection method (Section 1.2) caused subsequent solution pulses to carry residue from previous pulses. At pH = 7, the main uranium species was $UO_2(OH)_2$, resulting in more regular concentration changes compared to pH = 4. Figures 5(a) and 5(c) clearly show U concentration decreasing then increasing with effluent volume, with generally higher concentrations in the first effluent fraction, indicating solution residue after column passage and U concentration in the latter half after chromatographic separation.

4.1.3 Effect of Enabling Temperature on Separation The chromatographic column tubing was constructed from PVC material, offering high toughness, transparency, and corrosion resistance with only 2 mm wall thickness, enabling effective temperature control. Solution temperature significantly affects functional groups on filling surfaces and liquid membrane formation. By heating and cooling the organic column using the temperature-enabling cell in Fig 3(a), uranyl ion flow blocked by column fillings changes periodically, facilitating U isotope separation. Theoretically, larger temperature differences between enabling and cooling cells yield more significant separation gains, but ABS plastic deforms at temperatures $ $75°C [**?**, **?**]. Therefore, this study used enabling temperatures of 30°C, 50°C, and 70°C. Experiments employed 50 ppb uranyl nitrate solution at pH = 2, with separation results shown in Fig 6 [Figure 6: see original paper].

Results demonstrated that optimal U isotope separation sections on the temperature-enabled organic column concentrated at effluent front and rear ends, with calculated values: βmax = 1.0150 and $\bar{\beta} = 1.0101$ at T = 30°C; βmax = 1.0231 and $\bar{\beta} = 1.0117$ at T = 50°C; and βmax = 1.0449 and $\bar{\beta} = 1.0373$ at T = 70°C. Separation efficiency increased with enabling temperature, with

maximum and average enrichments substantially higher at 70°C than other conditions. Therefore, 70°C was selected as the optimal enabling temperature, with 2–4 mL and 16–20 mL identified as the best separation sections in chromatographic effluent.

Section 2.1 theory indicated that $^{235}UO_2{}^{2+}$ is lighter than $^{238}UO_2{}^{2+}$ and would more easily transfer from the liquid membrane to the mobile phase, suggesting higher ^{235}U abundance in initial chromatography effluent. However, initial effluent data points (Fig 6) showed ^{235}U abundance below 0.72%. This phenomenon occurs because pulsed injection leaves previous pulse residue on column filling surfaces with lower ^{235}U and higher ^{238}U abundance, reflected in the sub-0.72% ^{235}U abundance in early data points.

4.1.4 Multi-Stage Separation Experiments Based on the above conditional experiments, optimal organic column working conditions were established as: solution flow rate = 15 mL/min, pH = 2, enabling temperature = 70°C, with optimal separation segments at 2–4 mL and 16–20 mL of chromatographic effluent. The time-controlled automatic shunt system in Fig 3(a) enabled precise effluent collection. Using natural abundance 50 ppb uranyl nitrate solution as feed, experimental results (Fig 7 [Figure 7: see original paper]) yielded separation factors: $\alpha_1 = 1.0287$, $\alpha_2 = 1.0084$, $\alpha_3 = 1.0259$, $\alpha_4 = 1.0106$, with average $\bar{\alpha} = 1.0184$ and type-A uncertainty of 5.4816×10^{-5}. Under these conditions, ^{235}U abundance could reach 3% after 79 separation stages. Results showed continuous ^{235}U abundance increase during stepwise separation, though stages 2 and 4 exhibited relatively lower separation factors. Moreover, these multi-stage factors were inferior to single-stage performance from Section 4.1.3, likely due to Bernoulli effects in the three-way valve of the time-controlled shunt system, which reduced solution flow rate, caused stagnation, and mixed front and back solutions, decreasing abundance. Table 1 summarizes all organic column experiments, including type-A uncertainty values.

4.2 Inorganic Chromatographic Column for U Isotope Separation

Previous work by researchers [**?**, **?**] used SiO_2-filled columns. This study followed those experimental conditions for inorganic column investigation, with working parameters: solution flow rate = 15 mL/min, pH = 2, and enabling cell temperature = 50°C.

4.2.1 Characterization of SiO_2 Before and After Experiments SEM-EDS characterization showed inorganic fillings (SiO_2) as smooth spheres that remained smooth after separation experiments, with no observable uranium adsorption. FTIR results indicated hydroxyl group formation on SiO_2 surfaces after experiments, while XPS detected trace uranium adsorption. Characterization results for SiO_2 fillings are presented in supplementary figure 2.

4.2.2 Single Separation of Uranium Isotopes Using 50 ppb uranyl nitrate solution at pH = 2 as feed, with column enabling temperature at 50°C and injection rate of 15 mL/min, effluent was collected in 2 mL increments at the column exit. Eleven samples (including original solution) were analyzed by inductively coupled plasma mass spectrometer (model: ICAPRQ02625), with results shown in Fig 8 [Figure 8: see original paper]. Significant ^{235}U and ^{238}U separation occurred in the 5–11 mL effluent range, establishing this as the optimal separation section for the inorganic column. Maximum enrichment occurred at 10 mL effluent, with βmax = 1.0171 and $\bar{\beta} = 1.0142$ in the optimal section.

Regarding Fig 8(b), adsorption of uranyl ions by silanol groups on SiO_2 surfaces caused longer ^{235}U retention times, resulting in uranium abundance appearing in the middle-to-late effluent volume with overlapping double peaks.

4.2.3 Multi-Stage Separation Experiments Based on Section 4.2.2 results, the optimal U isotope separation section in the inorganic column was 5-11 mL of effluent, meaning the middle 3/10 of solution could be collected as enrichment fraction after each stage. The self-constructed automatic control shunt system successfully enabled automated separation of each effluent section, allowing continuous operation without manual intervention.

After four separation stages, results (Fig 9 [Figure 9: see original paper]) yielded separation factors: $\alpha_1 = 1.007$, $\alpha_2 = 1.004$, $\alpha_3 = 1.02$, $\alpha_4 = 1.009$, with average $\bar{\alpha} = 1.011$, comparable to the gas diffusion method though inferior to the organic column. Achieving 3% ^{235}U abundance required 112 separation stages. Results showed continuous ^{235}U abundance increase during stepwise separation, with the second stage again proving least effective.

4.2.4 Experiments in Strong Acid Environments Characterization (Section 4.2.1) revealed minor silica hydroxyl group formation on SiO_2 surfaces during separation (Fig 8). To verify the importance of these groups, solution pH was adjusted to 0.1, which strongly suppresses silica hydroxyl groups [**?**], to assess their effect on separation (Fig 10 [Figure 10: see original paper]). Using 15 ppb uranyl nitrate solution at pH = 0.1 as feed, with other conditions matching Section 4.2.2, results (Fig 11 [Figure 11: see original paper]) showed nearly identical concentration trends for ^{235}U and ^{238}U, with βmax = 1.0122 and $\bar{\beta} = 1.0056$. This markedly differed from Section 4.2.2 results, showing poor separation efficiency and irregular abundance peaks (Fig 11(b)). Thus, when silica hydroxyl groups were suppressed, separation became insignificant, proving their positive contribution to separation performance. Moderate acidity (pH 2) favors U isotope separation, while excessive acidity (pH $<$ 0.1) is detrimental.

4.3 Separation Mechanisms

Experiments in Sections 4.1 and 4.2 demonstrated that both organic and inorganic chromatographic columns efficiently separate U isotopes, but the under-

lying mechanisms require further exploration. The following experiments were designed to verify previous hypotheses: (1) a liquid membrane forms between fillings and mobile phase, exerting different blocking effects on particles of different masses; (2) functional groups generated on filling surfaces trap and release flowing particles.

To verify separation of other particles with different masses, a U-Zn separation experiment was designed using 50 ppb zinc uranyl acetate solution at pH = 2 as feed, under conditions identical to Section 4.1. The relative atomic mass of UO_2^{2+} is 270 while Zn^{2+} is 65.38; both have the same valence, neither reacts chemically within the chromatogram, and their mass difference is substantial, satisfying validation requirements. Zn and U distribution in effluent is shown in Fig 12 Figure 12: see original paper(b).

Eq (1) was modified to Eq (6) for describing chromatographic U-Zn separation capacity:

$$\beta = \frac{s_{\mathrm{Zn}}/s_{\mathrm{U}}}{o_{\mathrm{Zn}}/o_{\mathrm{U}}}$$

where $s_{\mathrm{Zn}}/s_{\mathrm{U}}$ is the mass concentration ratio of Zn-U in chromatographic effluent and $o_{\mathrm{Zn}}/o_{\mathrm{U}}$ is that in the original sample. Calculation yielded βmax = 1.3253, demonstrating much more pronounced separation than U isotopes due to the larger mass difference between UO_2^{2+} and Zn^{2+}, confirming that the liquid membrane effectively separates ions of different masses.

To verify the liquid membrane' s role, experiments used 50 ppb zinc uranyl acetate solution at pH = 2 with varying concentrations of cationic surfactant (cetyltrimethylammonium chloride: $C_{19}H_{42}ClN$) added to observe liquid membrane changes on separation performance, with results shown in Fig 12(c).

Surfactant structure resembles a matchstick configuration (supplementary file Fig. 3(a)). The hydrophobic "matchstick" (R-alkyl) repels water molecules while the hydrophilic "match head" (-OH, $-NH_2$) attracts them. This structure makes surfactant molecules water-soluble at one end while tending to escape water at the other, reducing water molecule tension. When used in the mobile phase, surfactants affect the liquid membrane formed on filling surfaces [**?**], as shown in supplementary file Fig. 3(b).

Experimental results showed poor separation at 50 ppm surfactant concentration (βmax = 1.0773). At 300 ppm, separation improved (βmax = 1.1394), while at 600 ppm, separation decreased (βmax = 1.1519). Increased surfactant concentration promoted micelle formation in the mobile phase, substantially increasing flow impedance, with Zn affected more significantly than UO_2^{2+} and chromatographic peaks shifting backward. At 50 ppm, uneven water tension weakening created irregular, thin liquid films, greatly reducing separation and preventing distinct chromatographic peaks. At 300 ppm, surfactant groups covered the packing surface, increasing resistance to mobile phase ions; although

separation occurred, effluent curves failed to form regular peaks. At 600 ppm, surfactant micelles further increased flow resistance, producing obvious double chromatographic peaks. These experiments successfully confirmed liquid membrane participation in the separation process.

The inorganic column effectively separated U isotopes, with U isotope abundance increasing during multi-stage separation experiments, suggesting potential for industrial production. The liquid membrane model hypothesis was verified, and the chromatographic separation mechanism was explored. Table 2 summarizes relevant experimental parameters for inorganic column experiments.

V. Conclusion

This study prepared chromatographic columns with organic and inorganic fillings for U isotope separation, evaluated separation efficiency, and discussed the underlying mechanisms. ABS plastic fillings for organic columns are cost-effective and flexible, ideal for prolonged use, achieving higher separation factors than inorganic columns. However, they exhibit lower mechanical strength and limited surface modification options. SiO_2 pellets as inorganic column fillings offer high mechanical strength, excellent chemical stability, and large surface area, though they are potentially brittle and show lower separation efficiency than organic columns.

Organic column experiments identified optimal conditions: injection flow rate = 15 mL/min, pH = 2, enabling temperature = 70°C, with optimal separation segments at 3–5 mL and 17–20 mL of chromatographic effluent. Multi-stage separation experiments achieved a U isotope separation factor of 1.0184, requiring 79 stages to enrich ^{235}U abundance to 3%.

Inorganic column experiments, based on prior studies, established optimal conditions: injection flow rate = 15 mL/min, pH = 2, enabling temperature = 50°C, with optimal separation segments at 5–11 mL of effluent. Multi-stage separation experiments indicated a U isotope separation factor of 1.011, requiring 113 stages to achieve 3% ^{235}U abundance.

Characterization and mechanistic experiments confirmed that liquid membranes and surface functional groups on fillings participated in separation processes. For industrial production, uranyl nitrate feedstock could be applied directly, potentially eliminating UF_6 preparation required for gas centrifugation. SEM-EDS, XPS, and FTIR analyses showed SiO_2 and ABS adsorb only trace uranium without affecting filling properties, enabling long-term column reuse.

Therefore, combining organic and inorganic dynamic liquid chromatography provides a cost-effective, environmentally friendly, and efficient method for U isotope separation. This research also offers new perspectives for the fields of chromatography and isotope separation.

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Note: Figure translations are in progress. See original paper for figures.