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Key Words

Ac-225

lanthanides

DGA resins

chromatographic separation

extraction chromatography

TODGA

TEHDGA

distribution coefficients (Kd)

Gibbs sorption energy

DFT

proton irradiation

thorium targets

radiolanthanides

HNO3

HCL

Objective

1. Increase Availability of Actinium-225 (225Ac): Support the production of 225Ac via irradiation of thorium metal targets to increase its availability for radiopharmaceutical applications.

2. Develop and Test Separation Methods: Develop and test separation methods for isolating quasi massless quantities of 225Ac from bulk thorium targets and co-produced fission products, particularly focusing on removing lanthanide isotopes that are chemically similar to actinium.

3. Evaluate Distribution Coefficients: Determine equilibrium distribution coefficients (Kd) for actinium

and lanthanide ions in nitric acid (HNO_3) and hydrochloric acid (HCl) media using diglycolamide (DGA) based extraction chromatography systems.

4. Conduct Dynamic Column Separation Experiments: Establish dynamic column separation conditions based on the measured equilibrium distribution coefficients for the separation of actinium from lanthanides.

5. Conduct Density Functional Theory (DFT) Studies: Perform DFT calculations to understand the selectivity of DGA based resins for actinium and lanthanides, supporting experimental observations with theoretical insights.

6. Optimize Actinium Recovery Process: Optimize the recovery process of actinium from irradiated thorium targets by integrating the separation methods into routine separation processes.

7. Understand Sorption Behavior: Investigate the sorption behavior of actinium and lanthanides on TODGA and TEHDGA resins in different acid media, aiming to provide a comprehensive understanding of their separation mechanisms.

Methodology

1. Chemical and Reagents

- Utilized Optima grade nitric acid (HNO_3) and hydrochloric acid (HCl) from Fisher Scientific.

Citric acid (99.9%) from Sigma Aldrich.

- Deionized water prepared on site.

- Cation exchange resin (AG 50WX8) and anion exchange resin (AG 1-X8) from Bio-Rad.

- Normal DGA resin (TODGA) and branched DGA resin (TEHDGA) from Eichrom Inc.

- Bio-Rad Econo-columns and glass columns for chromatography work

2. Gamma-Ray Soectrometry

- Conducted using an EG&G Ortec Model GMX-35200-S HPGe detector system with a Canberra

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Model 35-Plus multichannel analyzer.

- Used standards of radionuclide mixtures traceable to the National Institute of Standards and Technology (NIST) for detector response function determination and evaluation.

- Relative total source activity uncertainties ranged from 2.6% to 3.3%

3. Radionuclides

- Actinium-225 obtained from a 229Th generator.

- The 225Ra/225Ac eluent from the 229Th generator was further purified using TEHDGA resin.

- Additional radionuclides used for the study included 155Eu and 173Lu

4. Proton Irradiations

- Thorium metal targets irradiated at the Isotope Production Facility (IPF) and the Brookhaven Linac Isotope Producer (BLIP).

- Targets were irradiated with 90 and 190 MeV incident energy protons

5. Equilibrium Distribution Coefficients (Kd) Studies:

- Conducted by batch method in nitric and hydrochloric acid media.

- Approximately 50 mg of resin was placed in sample tubes with solutions of varying acid concentrations and radionuclide stock.

- Mixtures were stirred and allowed to equilibrate for 24 hours at room temperature.

- Gamma-ray spectrometric analysis was performed after filtration and equilibration

6. Dynamic Column Separation Experiments

- Established based on measured equilibrium distribution coefficients.

- Bio-Rad plastic columns filled with 1 mL of TODGA and TEHDGA resins.

- Columns preconditioned with water and 6 M HNO3.

- Solutions spiked with radionuclides were loaded onto the columns, followed by sequential elution with varying concentrations of HNO3 and HCl

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7. Irradiated Target Experiments and Actinium Separation

- Conducted in a hot cell at Oak Ridge National Laboratory (ORNL) under master-slave manipulator control.

- Involved two column-chromatographic steps: cation exchange column in a citrate matrix and further separation on a DGA column.

- Two studies: proof-of-principle and full-scale TEHDGA implementation.

- Recovery of actinium involved loading the DGA resin column with target solution, washing, and eluting actinium with HNO_3 .

8. Density Functional Theory (DFT) Studies

- Performed with Gaussian 09 software using B3LYP and M06 functionals.

- Included geometry optimization and Gibbs free energy calculations.

- Free energies of solvation calculated using IEF-PCM implicit solvation model.

- Aimed to understand the selectivity of DGA resins for actinium and lanthanides

Key Findings

Kd Studies

Actinium-225 in HNO_3

Kd Values and Sorption

- The study found that the Kd values for Ac in HNO_3 reach a maximum at 4 M for TODGA and 6 M for TEHDGA.

- Ac shows stronger sorption on TODGA (770 g/mL) compared to TEHDGA (226 g/mL) at these concentrations.

- At lower and higher HNO_3 concentrations, no significant difference was observed between TODGA and TEHDGA, except at 0.1 M HNO_3, where Ac shows less sorption on TEHDGA.

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- In 10 M HNO_3, the Kd values for Ac decrease to roughly 50, enabling efficient separation of 225Ac from lanthanides.

- These findings suggest that either TODGA or TEHDGA resins can be used for effective separation of 225Ac from lanthanides at high HNO_3 concentrations

Actiumium-225 and Ln in HCl

Sorption Behvaior and Separation

- The study indicated that Ac exhibits the strongest sorption at 6 M HCl with TODGA, and at 4-10 M HCl with TEHDGA, with maximum Kd values observed at these concentrations.

- Lutetium (Lu) shows a maximum Kd value of >10,000 g/mL at HCl concentrations 4 M, and Europium (Eu) shows similar behavior at 6-10 M HCl.

- At lower acid concentrations (0.1 M HCl), both Lu and Eu exhibit significantly lower Kd values, indicating weaker sorption.

- These results demonstrate that HCl concentrations >4 M are effective for separating Ac from lanthanides using TODGA or TEHDGA resins, with both resins showing different sorption behaviors in varying HCl concentrations

Dyanmic Column Separations in HNO_3 Media

TODGA

- The elution profile for Ra, Ac, Eu, and Lu was established using TODGA resin in HNO_3 media.

- The first fraction (5 mL of 6 M HNO_3) contained more than 84% of the Ra activity, with the remaining Ra eluted using 4 M HNO_3.

- More than 98% of the Ac activity was recovered using 10 M HNO_3 (35 mL total), while lanthanides remained on the column and were eluted with 0.1 M HCl.

- This profile indicates that Ra can be efficiently removed with 6 M HNO_3, and Ac can be selectively

eluted with 10 M HNO_3, leaving lanthanides on the column for subsequent elution

TEHDGA

Elution Profile

- Similar to TODGA, the elution profile for Ra, Ac, Eu, and Lu was established using TEHDGA resin in HNO_3 media.
- The loading fraction (5 mL) contained more than 89% of the initial Ra activity.
- Ac was eluted with 35 mL of 10 M HNO_3, while Eu and Lu were eluted with 0.1 M HCl, achieving significant separation with minimal resin bed.
- The elution profile demonstrated that TEHDGA resin is also effective for separating Ra, Ac, and lanthanides in HNO_3 media

Irradiated Target Experiment and Ac Separation in GBq Quantities

Separation Process

- The process involved two column-chromatographic steps: an initial cation exchange column in a citrate matrix to separate bulk thorium, followed by a DGA column to separate Ac from lanthanides.
- In the proof-of-principle study, a small aliquot of irradiated thorium target solution was used to test the separation method.
- More than 99% of Ac was eluted within 50 bed volumes of 10 M HNO_3.
- In the full-scale implementation, the separation method was successfully integrated with routine processes for Ac recovery from irradiated thorium targets.
- The results confirmed the effectiveness of TEHDGA resin in separating Ac from lanthanides and other fission products at high acid concentrations

DFT Studies

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Complexation and Thermodynamic Analysis

- DFT calculations were performed to optimize the structures of [Ac(TMDGA)3]3+, [Eu(TMDGA)3]3+, and [Lu(TMDGA)3]3+ complexes.
- The calculations showed that Ac forms the weakest bonds with the donor oxygen atoms of TMDGA, as indicated by the longest bond lengths.
- The Gibbs free energy calculations (Gaq) confirmed significantly higher selectivity of TMDGA for LnIII over AcIII in the presence of nitrate ions.
- These theoretical results were in excellent agreement with experimental data, explaining the energetic differences underpinning the separation of Ac from lanthanides using DGA resins.
- The findings highlighted that Ac chemistry cannot be simply predicted from Ln behavior under comparable circumstances, emphasizing the need for specific studies on actinium separation

Conclusion

1. Efficiency of DGA Resins

- Diglycolamide (DGA) based resins, specifically TODGA and TEHDGA, are effective for the high-yield and high-purity separation of actinium (Ac) isotopes from radium (Ra) and fission product lanthanides in the context of Actinium-225 (225Ac) production via proton-induced nuclear reaction on thorium (232Th) targets

2. Sorption Behavior

- The sorption behavior of Ac and lanthanides (Ln) on DGA resins at higher nitric acid (HNO3) and hydrochloric acid (HCl) concentrations was studied. The equilibrium distribution coefficients (Kd) for Ac, Eu, and Lu cations on both resin types in HCl media and in HNO3 for Ac were measured over a wide concentration range for the first time. The data provided insights into the separation mechanism and efficiency

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3. Comparison with Previous Data

- The study confirmed some of the previously reported data but also revealed discrepancies. Specifically, for Ac in HNO3, the measured affinity was lower than previously reported, while a slightly higher affinity was observed in HCl media. These findings support the use of both TEHDGA and TODGA resins in HNO3 to separate Ac from Ln

4. DFT Modeling and Selectivity

- Density functional theory (DFT) modeling provided a theoretical basis for understanding the observed experimental results. The study revealed that the structures of Ac, Eu, and Lu nitrate complexes with a model ligand (TMDGA) showed that AcIII forms weaker bonds with the ligand donor atoms compared to EuIII and LuIII. The Gibbs free energy calculations confirmed higher selectivity of TMDGA for LnIII over AcIII in nitrate media, which was in line with the experimental observations

5. Experimental Observations and Theoretical Support

- The experimental observations of different DGA sorption behaviors for Ac and lanthanides were supported by DFT results, explaining the energetic differences underpinning the separation of Ac from Ln. The study demonstrated that Ac chemistry cannot be simply predicted from Ln behavior under similar conditions, highlighting the need for specific studies on actinium separation

6. Applicability for Ac225 Recovery

- The separation method using TEHDGA resin was successfully integrated with routine processes for Ac recovery from irradiated thorium targets. This demonstrated the practical applicability of the developed method for large-scale 225Ac production and purification

Relevance to Study

1. Effective Separation Methodologies

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- Demonstrates the efficiency of diglycolamide (DGA) based resins, specifically TODGA and TEHDGA, in selectively separating actinium (Ac) from lanthanides (Ln) and other fission products. This is critical for the reprocessing and purification of actinides in the nuclear fuel cycle

2. Distribution Coefficiencts (Kd) Analysis

- Provides detailed Kd values for Ac and Ln in varying concentrations of nitric acid (HNO3) and hydrochloric acid (HCl). These values are essential for understanding the behavior of these elements under different conditions, aiding in the design of more effective ligands for separation processes

3. Dynamic Column Separations

- Establishes effective dynamic column separation conditions using TODGA and TEHDGA resins. These methods can be applied to large-scale separation processes required in nuclear fuel reprocessing, ensuring high purity and yield of desired elements

4. Theoretical Support Through DFT Studies

- Density Functional Theory (DFT) calculations provide a theoretical foundation for understanding the selectivity and interaction mechanisms of DGA resins with actinides and lanthanides. This supports the experimental findings and guides the design of more efficient ligands

5. Application in Radiopharmaceuticals

- The methodologies developed for separating 225Ac are directly relevant to the production of targeted alpha therapy (TAT) isotopes. This links the nuclear fuel cycle processes with radiopharmaceutical applications, enhancing the practical utility of the findings

6. Insight into Sorption Behavior

- Provides experimental and theoretical insights into the sorption behavior of actinides and lanthanides on DGA resins at different acid concentrations. This information is crucial for optimizing ligand design and separation conditions in the nuclear fuel cycle

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Critical Parameters Identified

High Importance

Chemical Stability: The study emphasizes the efficiency of diglycolamide (DGA) resins (TODGA and TEHDGA) in maintaining their functionality under various chemical conditions, specifically high concentrations of nitric acid (HNO3) and hydrochloric acid (HCl). This suggests their chemical stability is suitable for nuclear fuel reprocessing

Radiolysis Resistance: The research indirectly addresses radiolysis resistance by focusing on the separation of radioactive actinium (225Ac) and lanthanides from fission products. The successful application of DGA resins in these processes indicates that the ligands are likely resistant to radiolytic degradation, maintaining their separation efficiency under radioactive conditions

Theromodynamics: Detailed equilibrium distribution coefficients (Kd) for Ac and Ln in varying acid concentrations and the supporting density functional theory (DFT) studies provide insights into the thermodynamics of the separation processes. These findings are crucial for understanding the selectivity and binding strength of the ligands towards specific metal ions, making the separation processes fundamentally feasible

Medium Importance

Kinetics (forward and reverse): While the study primarily focuses on equilibrium and thermodynamic aspects, the reported sorption behavior and elution profiles indicate that the kinetics of the separation process were considered to ensure efficient separation within practical time frames

Loading capacity: The dynamic column separation experiments and irradiated target experiments provide data on the loading capacity of the DGA resins. The ability to handle substantial quantities of actinium and lanthanides before reaching saturation highlights the efficiency of the ligands for large-scale processing

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Operational Condition Range: The study demonstrates the effectiveness of DGA resins under a wide range of acid concentrations (HNO3 and HCl), indicating their operational flexibility. This broad range of applicable conditions enhances the utility of these ligands in various nuclear fuel reprocessing scenarios

Low Importance

Solubility: The study does not specifically address the solubility of the ligands. However, the successful application of the resins in different acid media implies that solubility issues are managed through the selection of appropriate solvents and conditions

Dispersion Numbers: Dispersion numbers are not directly discussed in the study. The focus on equilibrium and dynamic separations suggests that mass transfer efficiency between phases was considered but not explicitly quantified

Phase Disengagement: While phase disengagement is critical for practical separation, the study does not provide detailed information on this aspect. The reported elution profiles and separation efficiency imply that phase disengagement was achieved effectively in the experimental setup used