INL/CON-24-81523-Revision-0

Investigating Radiation-Induced Actinide Species in Solution

February 2025

Changing the World's Energy Future

Amy Elizabeth Kynman, Gregory Peter Holmbeck

Idaho National Laboratory

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Postdoctoral Research Associate

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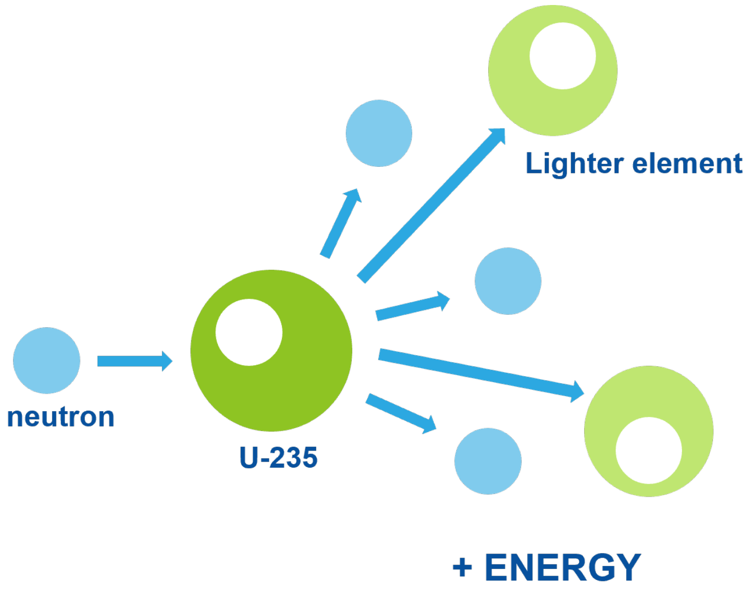
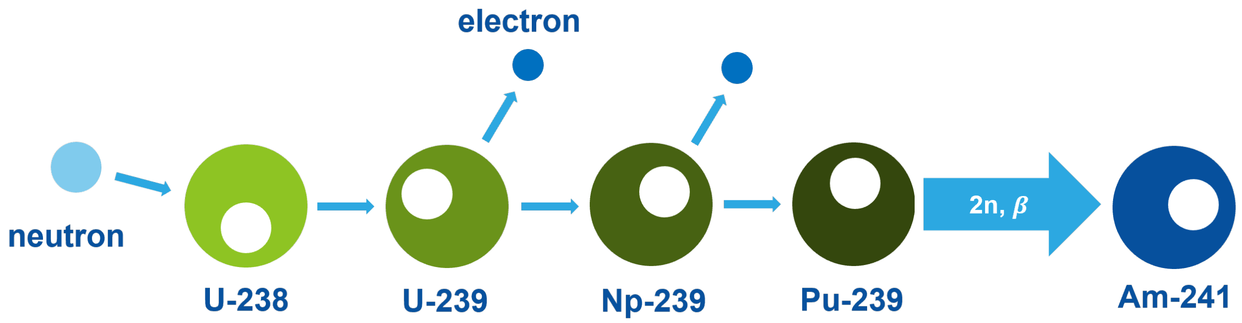
NEA Rising Stars Workshop 2024

Formation of Americium and Plutonium in Nuclear Reactors

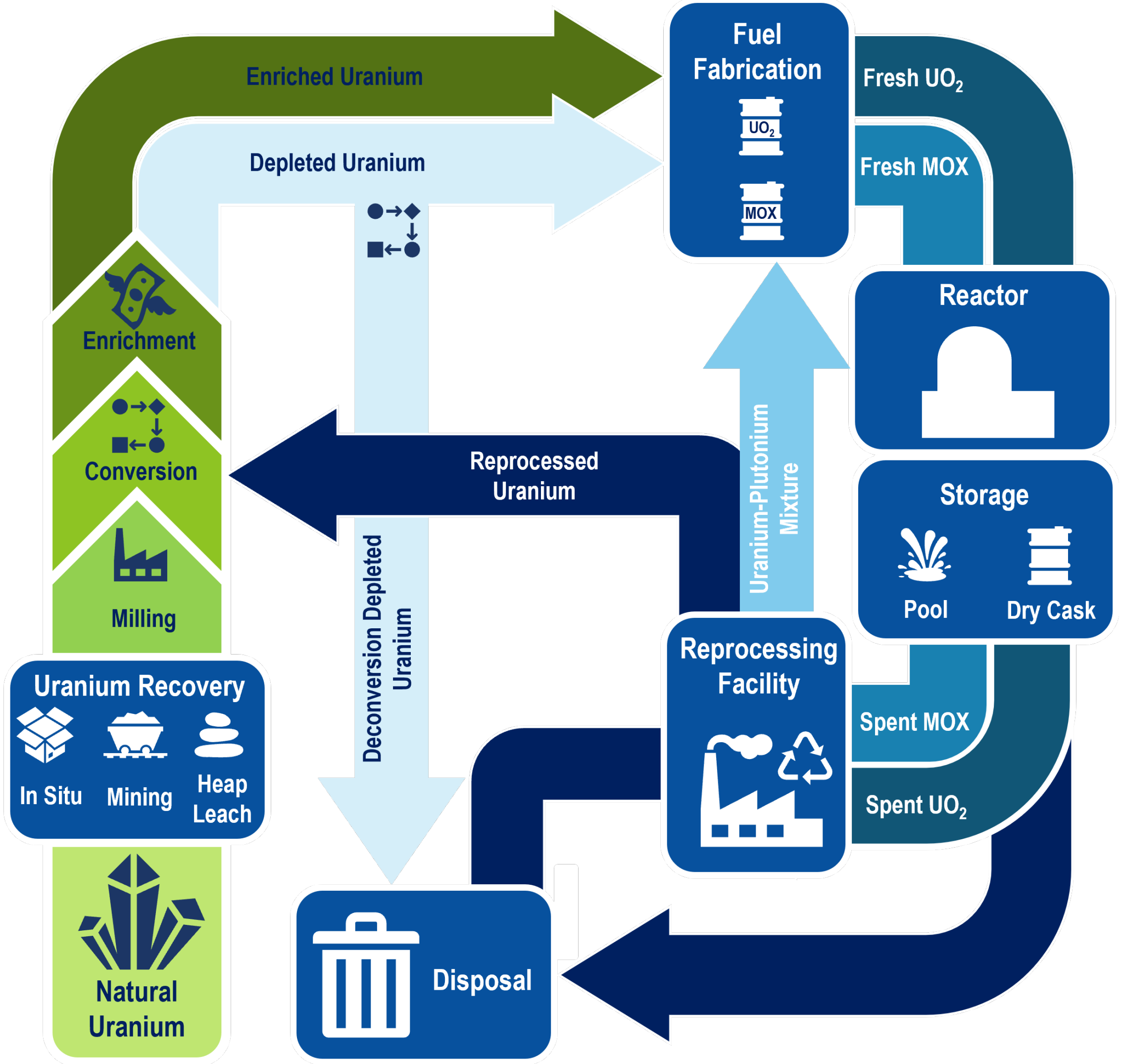




- Nuclear energy supplies over 70% of the clean, non-carbon emitting electricity in the United States.
- Reliant on the fundamental radiolytic instability of U-235.

- Americium and plutonium formed by neutron absorption.
- Highly radioactive with long half-lives.

Closing the Nuclear Fuel Cycle



- Closing the nuclear fuel cycle has several benefits:
  - ✓ Minimize final high-level waste for disposal or storage.
  - ✓ Recover additional energy from fuel.
  - ✓ Reduce impact on the environment and natural resources.

- To make reprocessing more cost-effective, greater fundamental understanding of actinide behaviour under radiation fields is needed.

Part I: Predicting Radiation-Induced Plutonium Redox Chemistry using Multiscale Modeling Methods

Radiation Chemistry under Reprocessing Conditions

Water Radiolysis

H_2O

Direct Radiation Effects

Indire

HNO

NO_3

NO_3

NO_3

$NO_2^{\bullet} + NO_2^{\bullet} \rightleftharpoons N_2O_4$

$N_2O_4 \rightarrow HNO_2 + HNO_3$

Key Radiolysis Products

e_{aq}^{-}, $H^{\bullet}$, $^{\bullet}OH$, and H_2O_2 from H_2O

$NO_3^{\bullet}$ and HNO_2 from HNO_3

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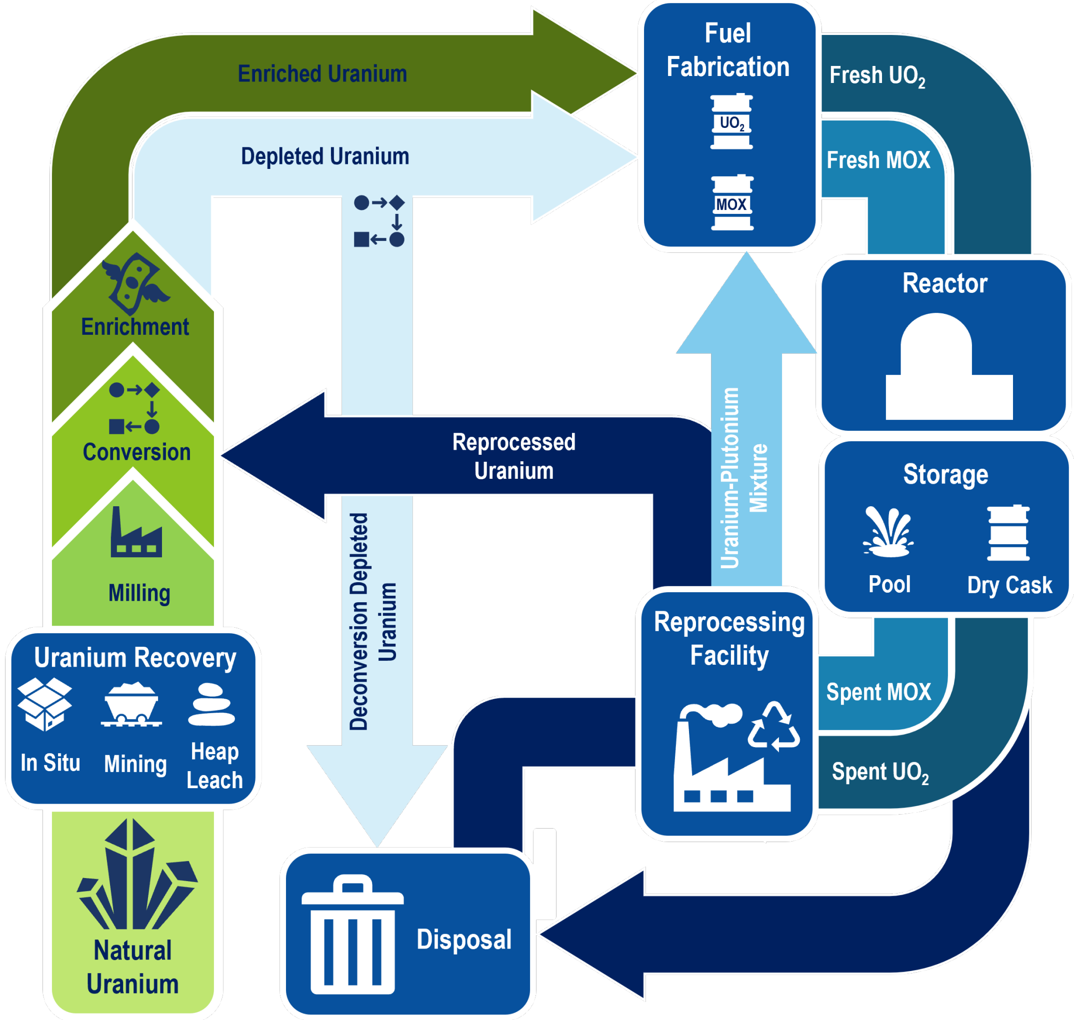
Plutonium in the Nuclear Fuel Cycle



$$Pu^{4+} + PuO_2^{+} \rightleftharpoons Pu^{3+} + PuO_2^{2+}$$

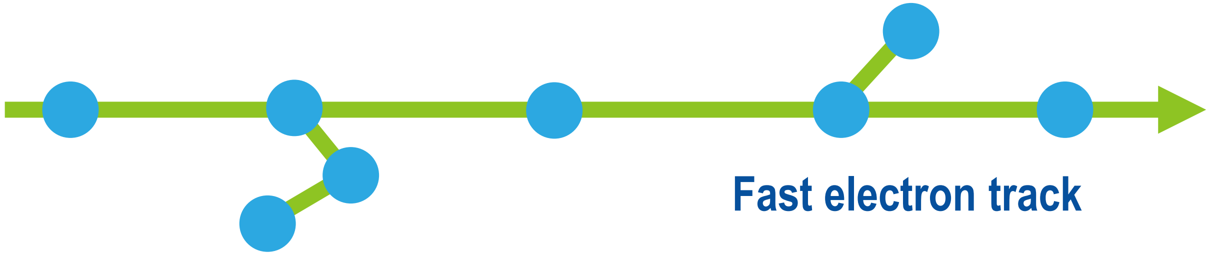
PUREX Chemistry

- Pu(IV) and U(VI) co-extracted as neutral nitrate complexes by TBP.
- Pu(III) generated via reduction and retained in aqueous phase while U(VI) remains in organic phase.
- Understanding and optimizing Pu redox and radiation chemistry is crucial for efficient separation and recovery.

In-Situ Alpha and Ex-Situ Gamma Irradiations

Gamma / Beta

- Actinide-containing solutions irradiated and changes in oxidation state monitored over time.
- Absorbed dose calculated from the irradiator dose rate.
- Radical products dominate.



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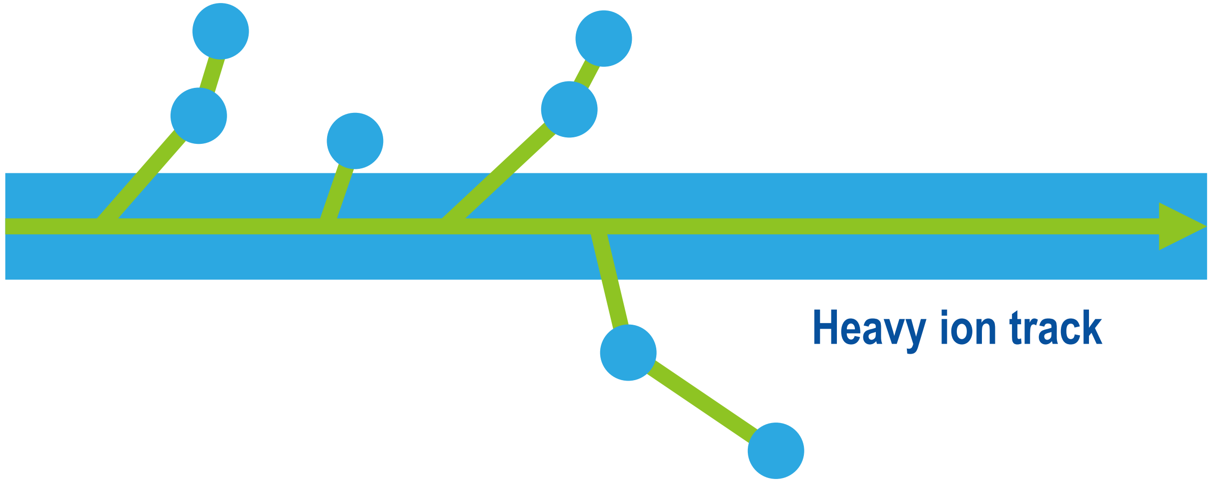
In-Situ Alpha and Ex-Situ Gamma Irradiations

Alpha

- Source of radiation is the inherent decay of the actinide element.
- Absorbed dose calculated from quantity and specific activity of alpha emitter, and time exposed.
- Molecular products dominate.



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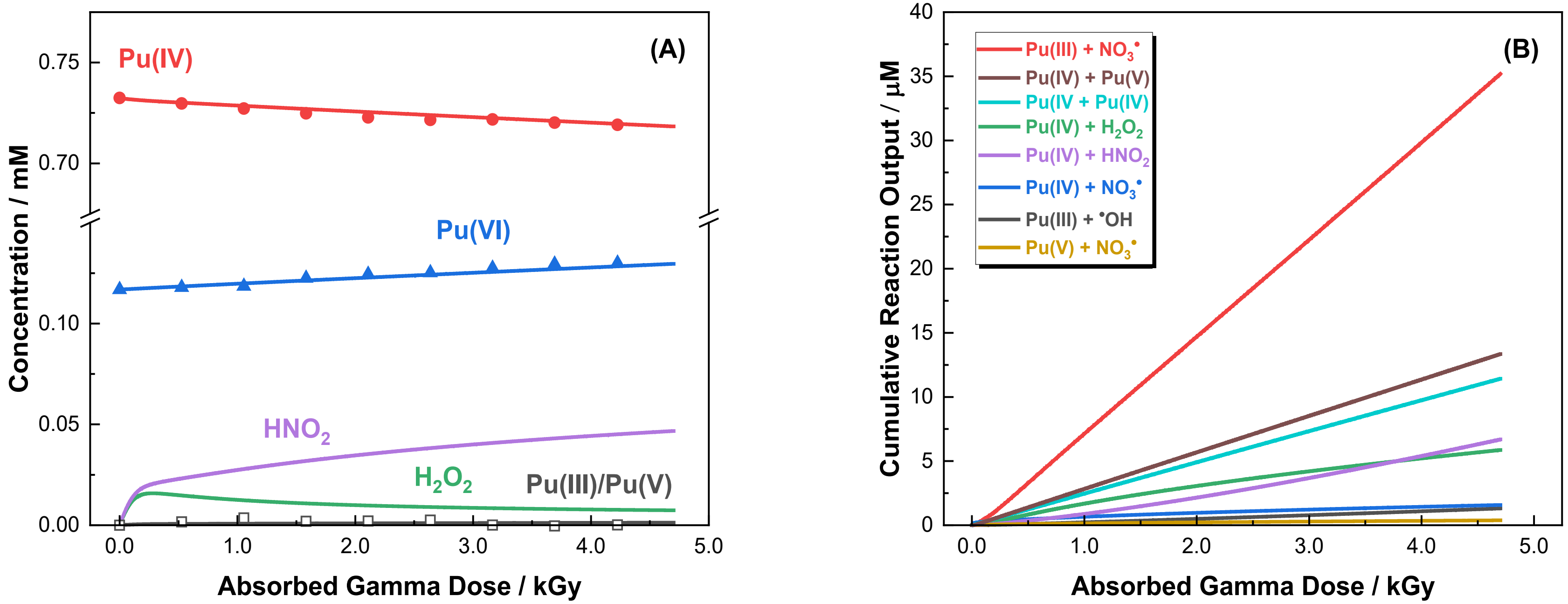
The Role of Radiation-Induced Plutonium Oxidation States in Solution (1.0 M HNO_3)



- **Pu(IV)** is transiently reduced to **Pu(III)** by its reactions with **H_2O_2** and **HNO_2**.
- Oxidation of **Pu(IV)** is in competition with the scavenging of **$NO_3^•$** radicals by **Pu(III)**.
- Remaining G(**$NO_3^•$**) partially accounts for the accumulation of **Pu(VI)** via the oxidation of **Pu(V)**.

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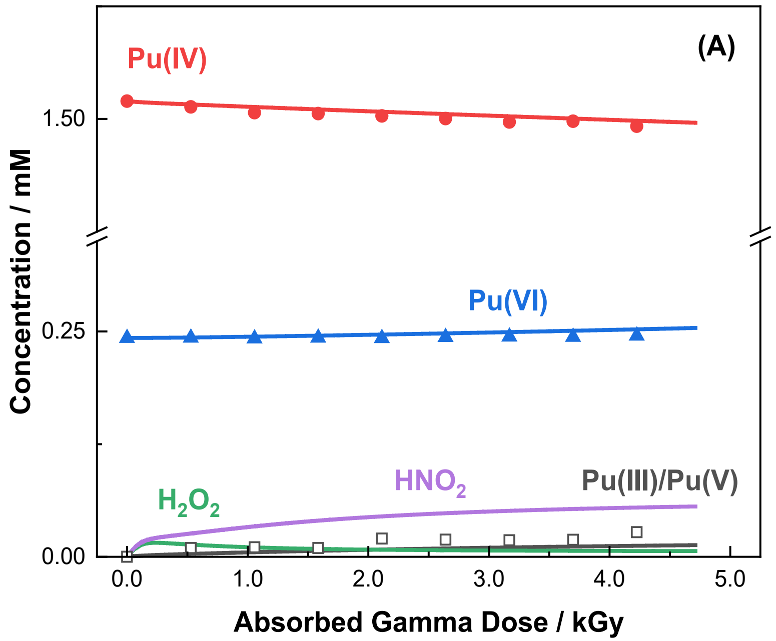
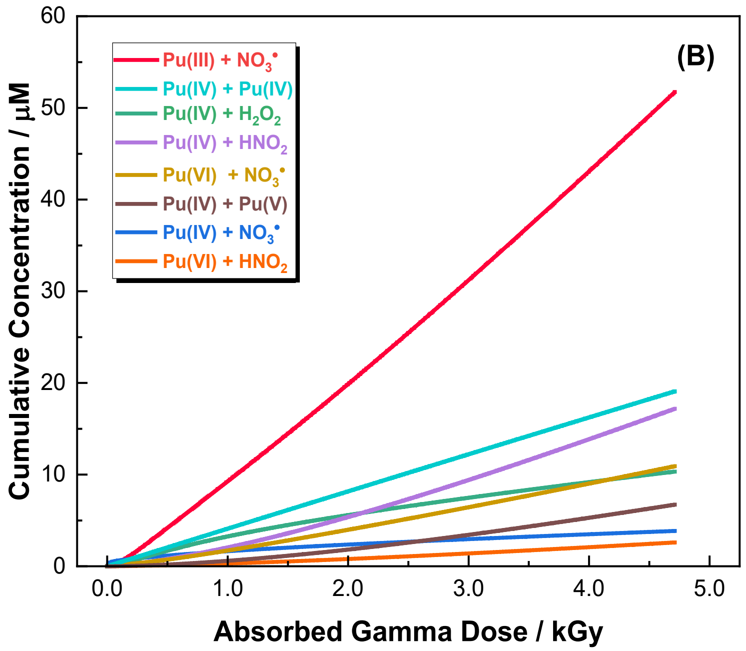
- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.*, **2024**, *68*, 18, 8092-8098.

The Role of Radiation-Induced Plutonium Oxidation States in Solution (3.0 M HNO_3)

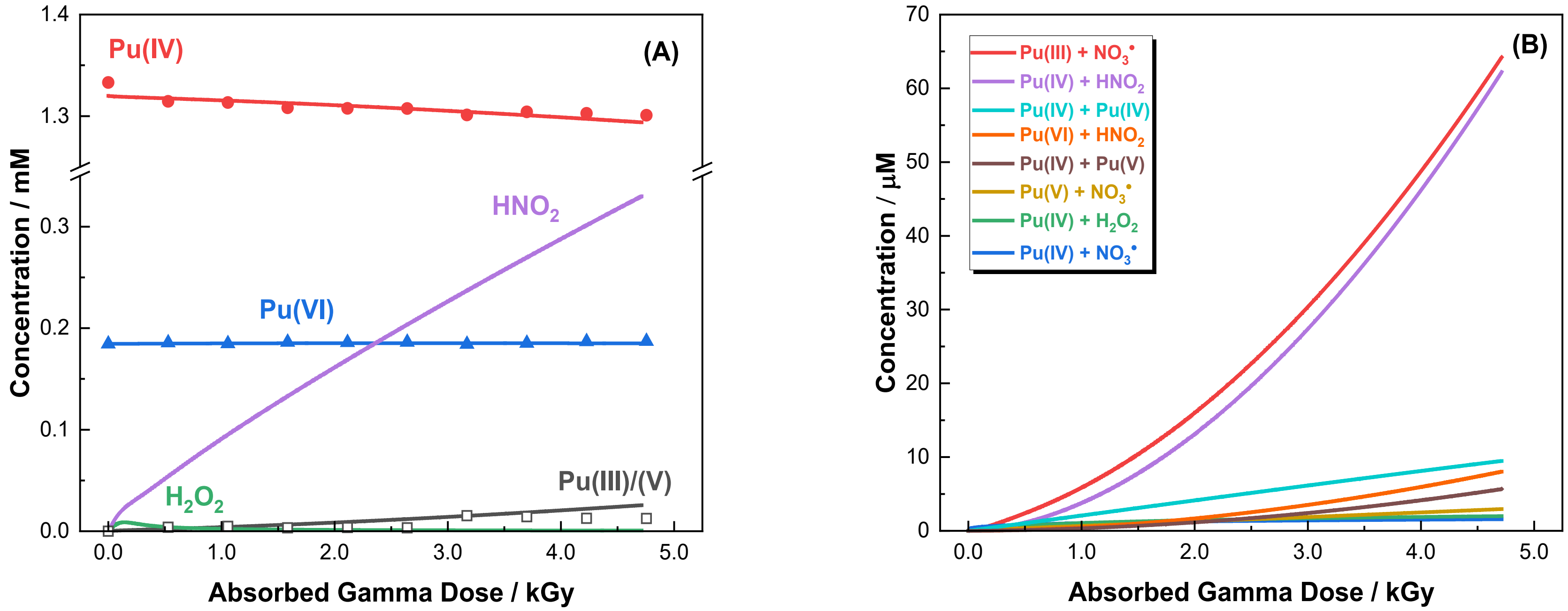




- Contribution of **HNO_2** to **Pu(IV)** reduction becomes greater than that afforded by **H_2O_2**.
- Less **Pu(VI)** is accumulated because of a shift in the position of the Pu-equilibria with acidity.
- Model predicts the formation of a low (µM), steady-state concentration of **Pu(III)** and **Pu(V)**.

- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.*, **2024**, *68*, 18, 8092-8098.

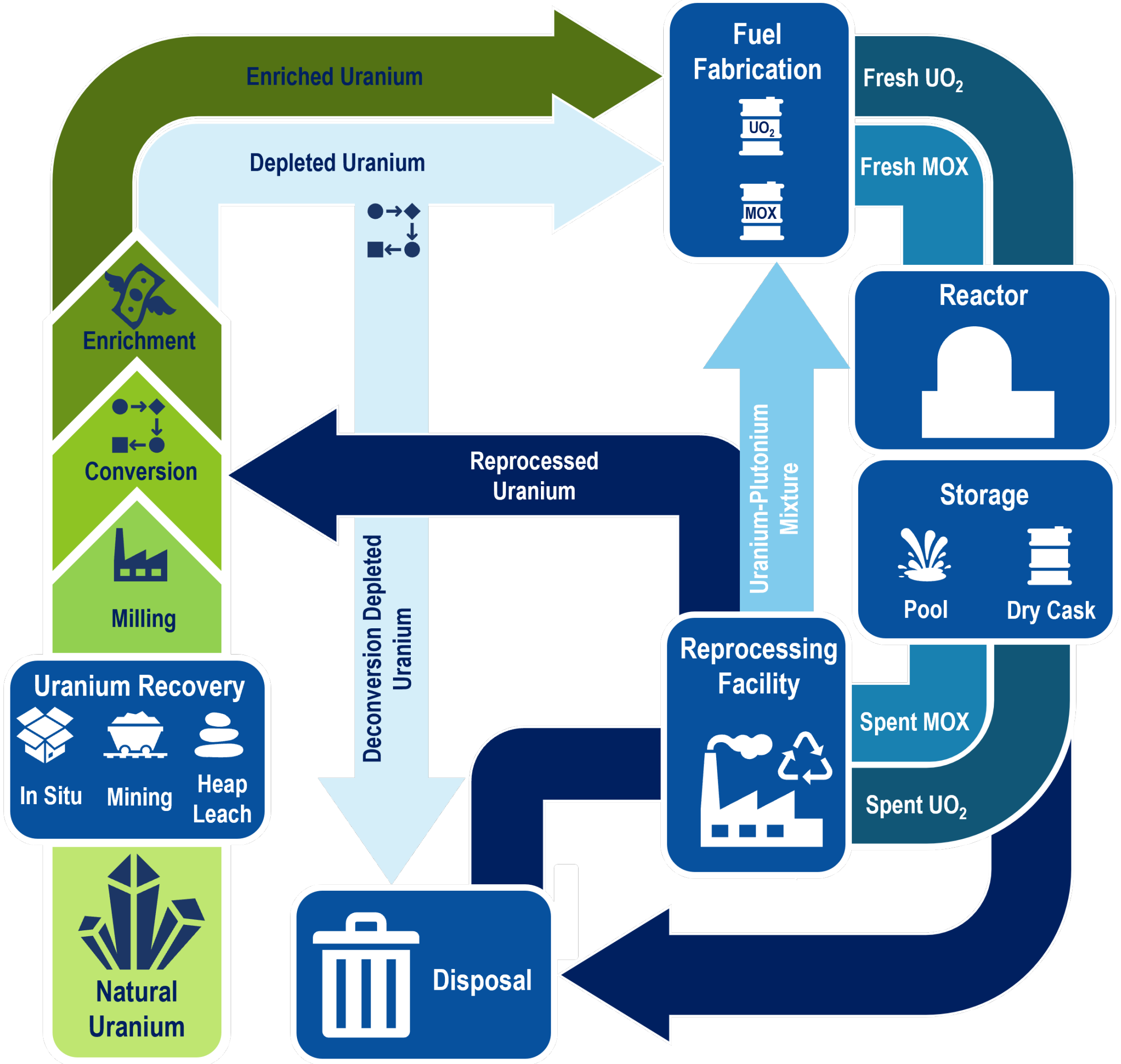
The Role of Radiation-Induced Plutonium Oxidation States in Solution ($6.0\ M\ HNO_3$)



- Radiation-induced redox chemistry of Pu is dominated by three processes: the reduction of **Pu(IV)** and **Pu(VI)** by HNO_2, and the oxidation of **Pu(III)** by $NO_3^{\bullet}$ radicals to regenerate **Pu(IV)**.
- Calculations again predict the accumulation (10s µM) of **Pu(III)** and **Pu(V)**.

- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.*, **2024**, *68*, 18, 8092-8098.

Part II: Conclusions & Future Work



- Developed the first experimentally verified multiscale model for radiation-induced plutonium redox chemistry.

- Alpha irradiation experiments.
- Study of other plutonium oxidation states.
- Continued development and validation of model.

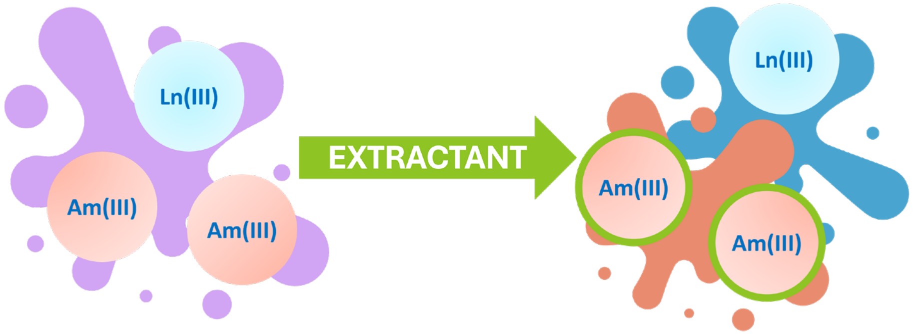
U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

Part II: Generation and Study of Am(IV) by Temperature-Controlled Electron Pulse Radiolysis

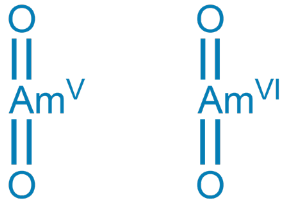
Separation of Americium from Fission Products

Trivalent Americium

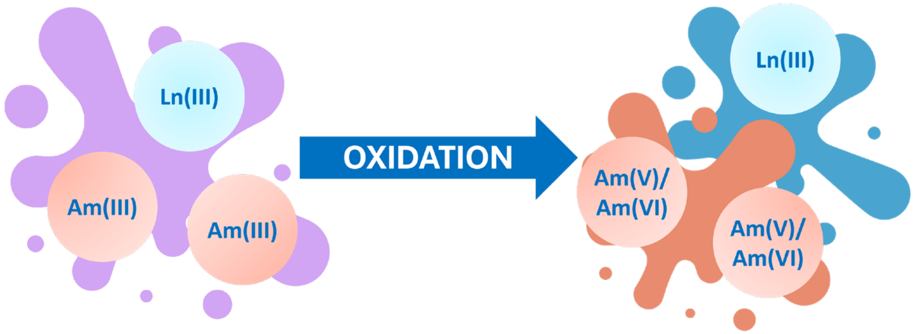
- Separation achieved by preferential binding of organic ligands to Am(III) or Ln(III).
- Exploits chemical bonding differences between Am(III) and Ln(III)
- Difficult because Am(III) and Ln(III) are very chemically similar.



High Valent Americium



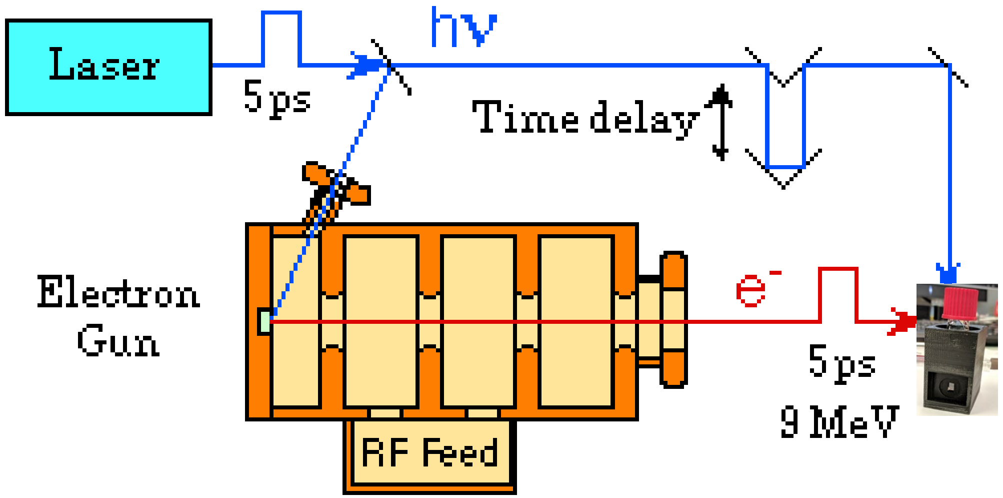
- Penta- and hexavalent oxidation states are not accessible for Ln.
- Am(V) and Am(VI) are not easily extracted by organic ligands.
- The chemistry of Am(V) and Am(VI) need to be better understood.



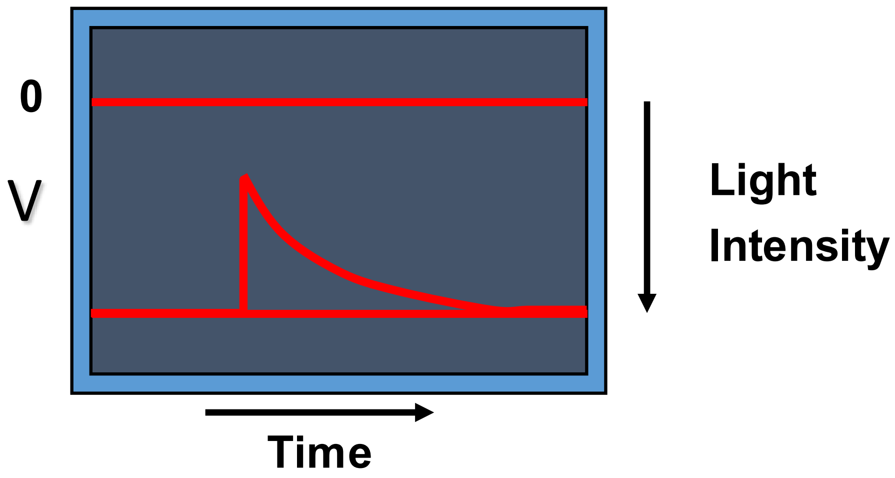
- Zsabka, Wilden, Van Hecke, Modolo, Verwerft and Cardinaels, *Journal of Nuclear Materials* **2023**, *581*, 154445.
- Runde and Mincher, *Chemical Reviews* **2011**, *111*, 5723.

Temperature Controlled Electron Pulse Radiolysis

$Am(III) + NO_3^{\bullet} \rightarrow Am(IV) + NO_3^{-}$

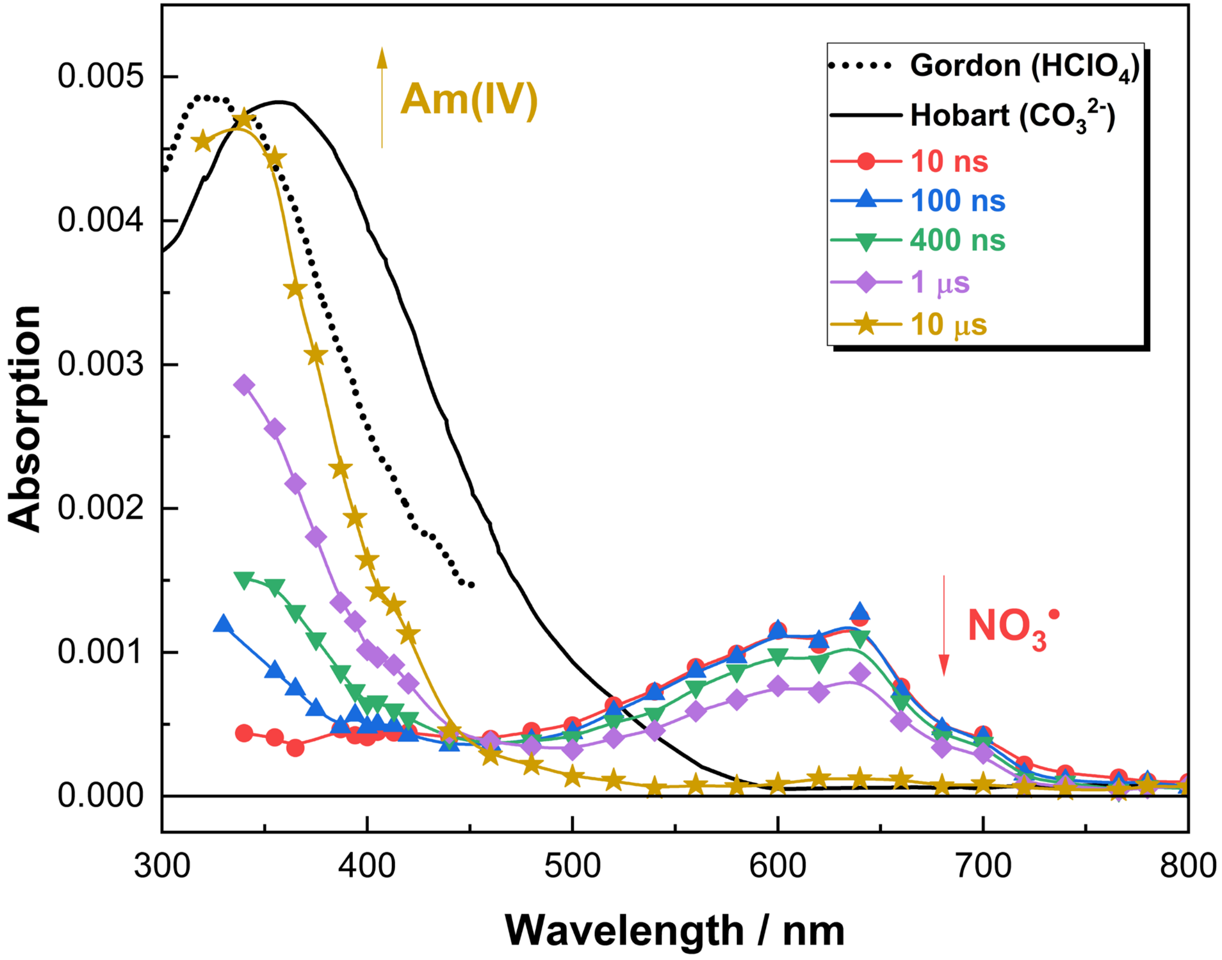


Transients are detected by optical absorption changes.



- Wishart, Cook and Miller, *Review of Scientific Instruments* **2004**, *75*, 4359.
- Horne, Rotermind, Grimes, Sperling, Meeker, Zalupski, Beck, Huffman, Gomez Martinez, Beshay, Peterman, Layne, Johnson, Cook, Albrecht-Schönzart and Mezyk, *Journal of Physical Chemistry A* **2022**, *61*, 10822.
- Rotermund, Mezyk, Sperling, Beck, Wineinger, Cook, Albrecht-Schönzart and Horne, *Journal of Physical Chemistry A* **2024**, *128*, 590.
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

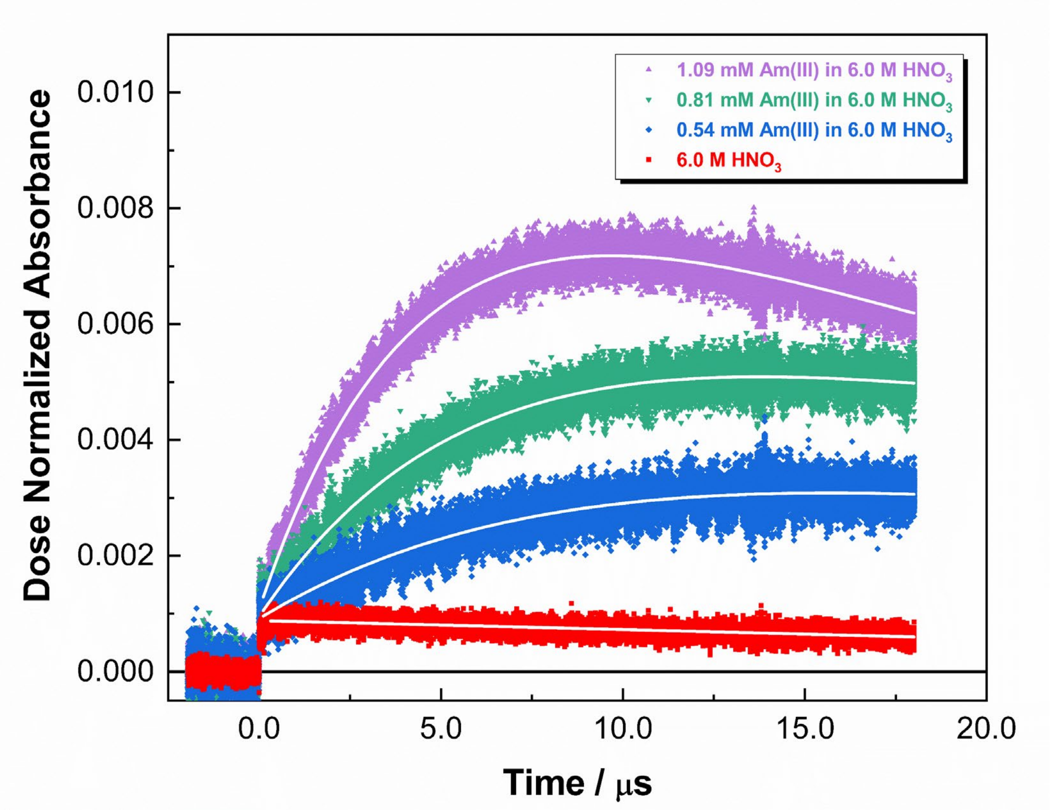
Transient Am(IV) Absorption

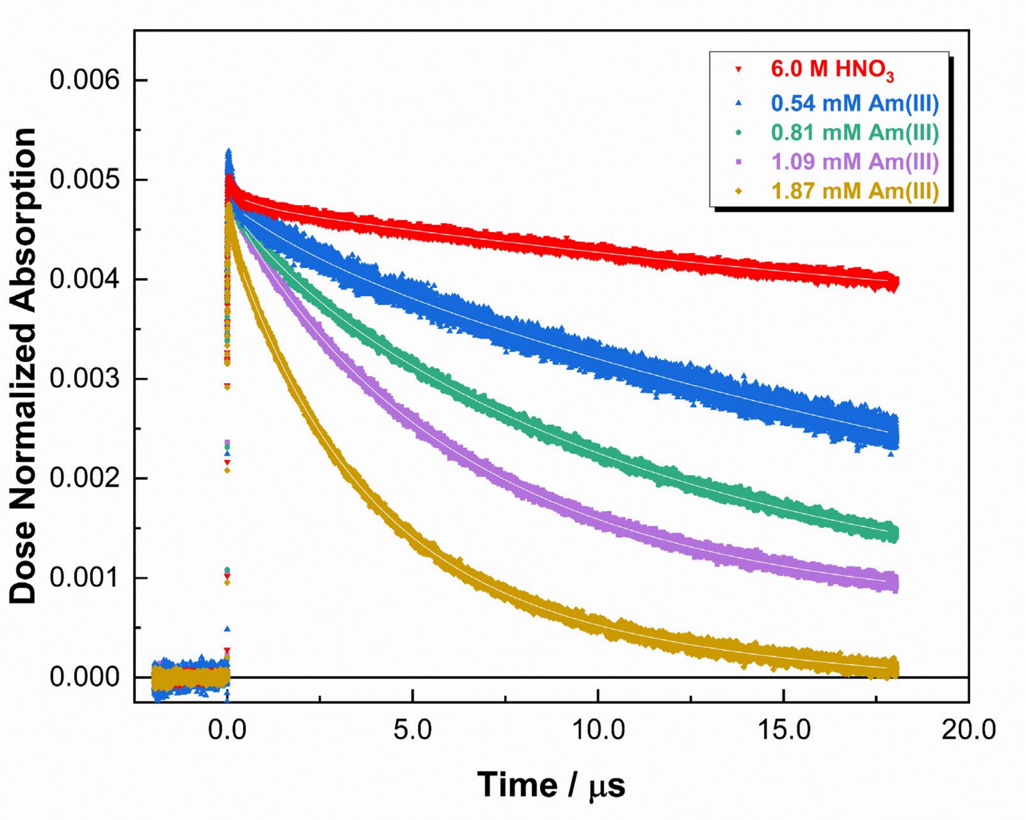


- Am(IV) in the absence of strong complexing agents observed in HNO_3 for the first time.
- Results consistent with previous reports of Am(IV) in solution and analogous reaction with other actinides.

- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

Ambient temperature Am(III) + $NO_3^{\bullet}$ kinetics





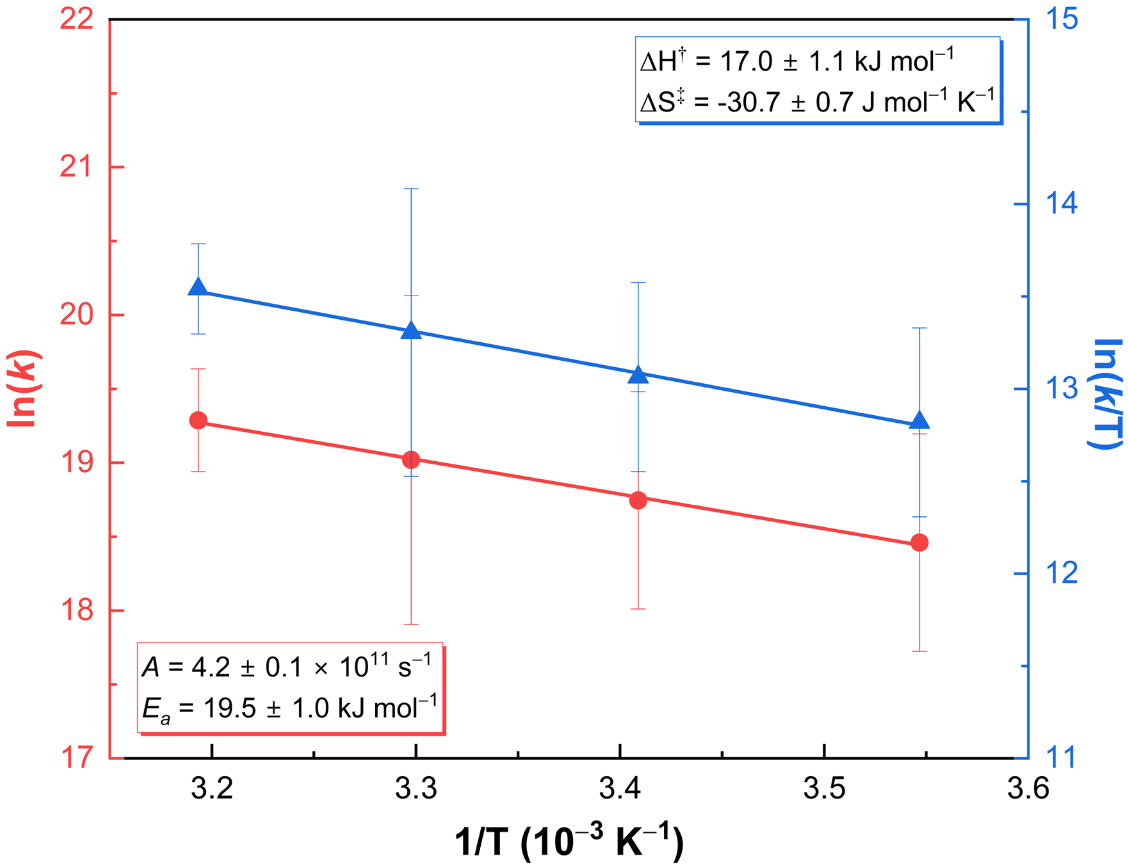
- Rate constant = $(1.35 \pm 0.05) \times 10^8\ M^{-1}\ s^{-1}$
- Am(IV) lifetime in 6 M HNO_3 is approximately 16 μs.

Brookhaven National Laboratory

- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

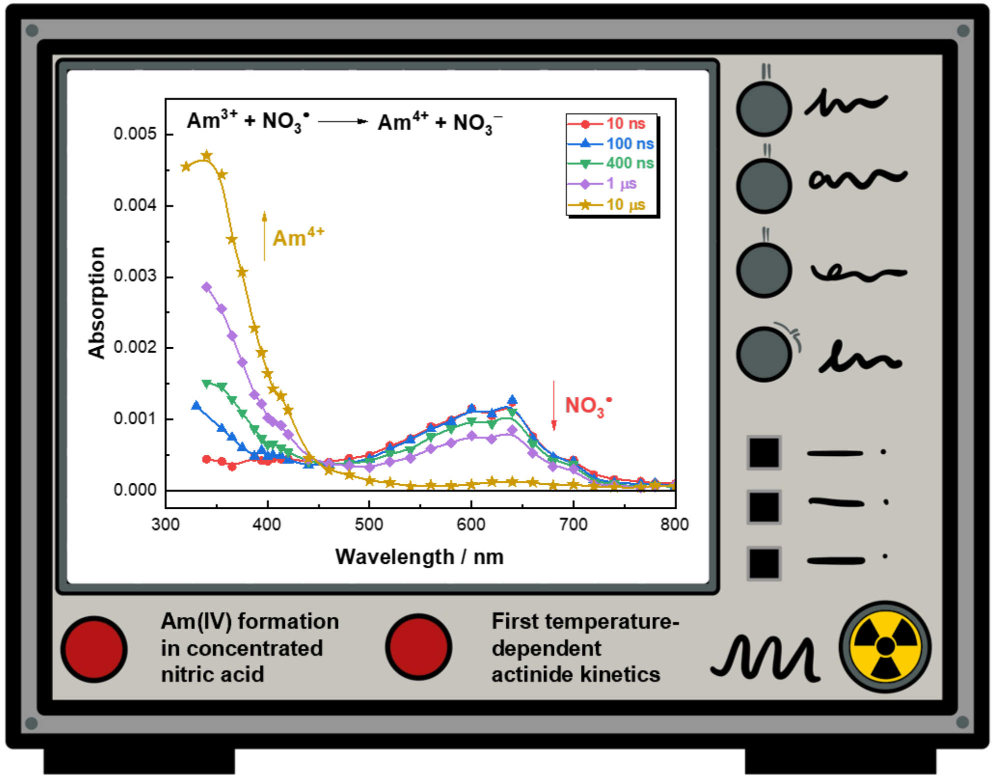
Temperature-dependent Am(III) + $NO_3^•$ kinetics

- First radiation-induced temperature-dependent kinetics for any actinide element.
- Unprecedented molecular level insight into Am chemistry.
- Oxidation of Am(III) to Am(IV) occurs via an associative mechanism with some perturbation of its coordination sphere by $NO_3^•$.



- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

Part II: Conclusions & Future Work



- Transient Am(IV) observed in nitric acid for the first time with a lifetime of 16 μs.
- First temperature-dependent radiation-induced kinetics of any actinide conducted.

- Further investigation of temperature-dependent actinide kinetics under varied conditions.
- Continued development of multiscale models to predict americium redox chemistry.

- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

Acknowledgements

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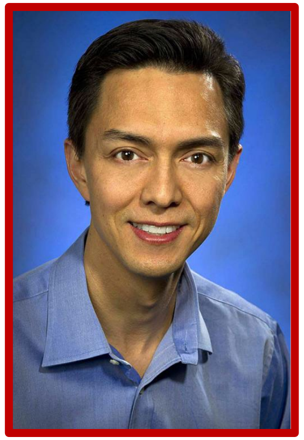

Bobby Layne

Stephen Mezyk

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Glenn T. Seaborg Institute — Idaho National Laboratory

Brookhaven National Laboratory

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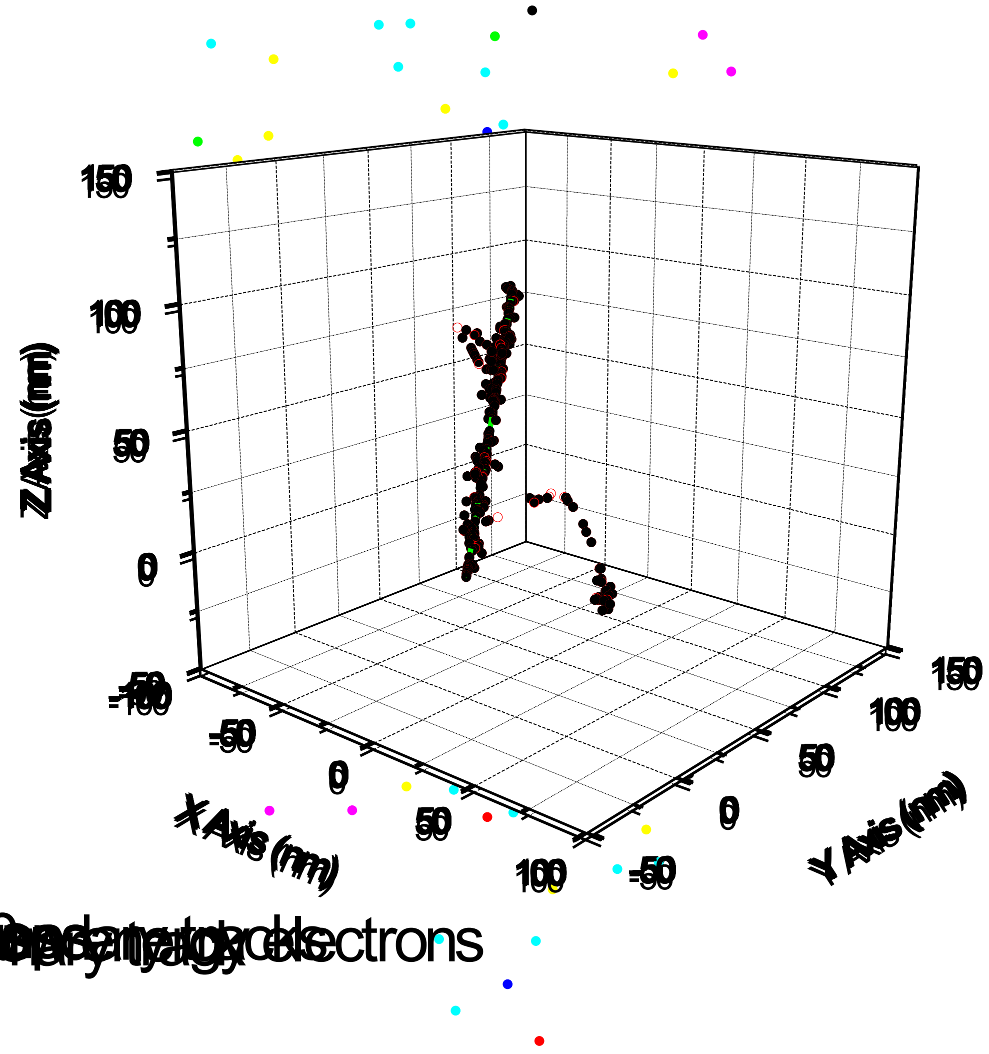
- U.S. DOE, SC, BES, Solar Photochemistry Program under award DE-SC0024191
- U.S. DOE, BES, Division of Chemical Sciences, Geosciences, and Biosciences under contract DE-SC0012704.

Idaho National Laboratory

Battelle Energy Alliance manages INL for the U.S. Department of Energy's Office of Nuclear Energy. INL is the nation's center for nuclear energy research and development, and also performs research in each of DOE's strategic goal areas: energy, national security, science and the environment.

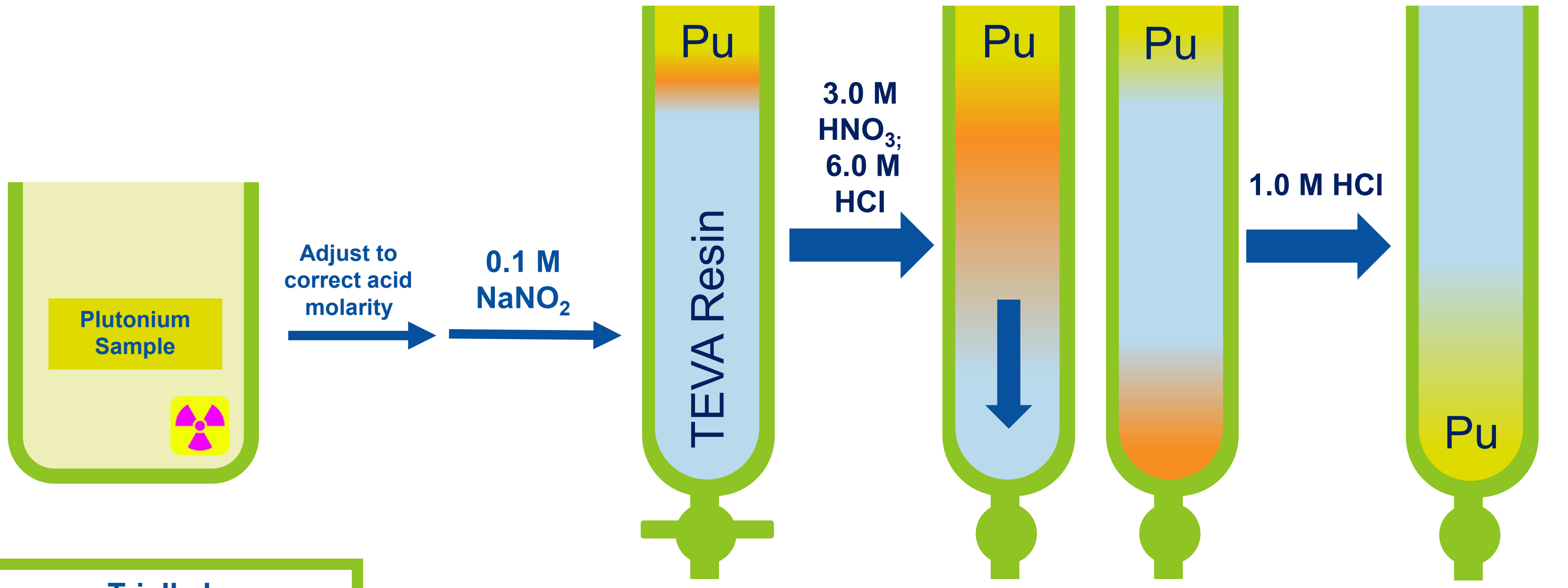
Multiscale Model Construction



Species	Radiolytic yield (G-value, molecules 100 eV^{-1})		
	1.0 M HNO_3	3.0 M HNO_3	6.0 M HNO_3
H_{aq}^{+}	4.2017	4.4706	4.3887
e_{aq}^{-}	0.0000	0.0000	0.0000
$^{\bullet}OH$	3.0583	0.0117	0.0000
$H^{\bullet}$	0.0000	0.0000	0.0000
H_2	0.1039	0.0909	0.0543
OH^{-}	0.0000	0.0000	0.0000
H_2O_2	0.6764	0.601	0.5418
$O(^3P)$	0.0173	0.0154	0.0073
O^{-}	0.0000	0.0000	0.0000
O_2	0.0043	0.0081	0.0036
$O_2^{\bullet-}$	0.0000	0.0000	0.0000
$HO_2^{\bullet}$	0.0427	0.4502	0.2997
HO_2^{-}	0.000	0.0000	0.0000
H_2O	0.1180	0.1715	0.1259
$NO_3^{\bullet 2-}$	3.9872	3.1975	3.2376
$NO_3^{\bullet}$	0.0000	3.0839	3.1534
$NO_2^{\bullet}$	0.2310	0.5087	0.6111

- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.*, **2024**, *68*, 18, 8092-8098.

Plutonium-239 Purification



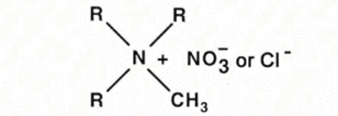
TEVA Resin preequilibrated with 0.1 M HNO_3

Background electrolytes and impurities removed

Pu eluted

- Anion exchange column needed to change background electrolyte.

Trialkyl Methylammonium Nitrate (or Chloride)

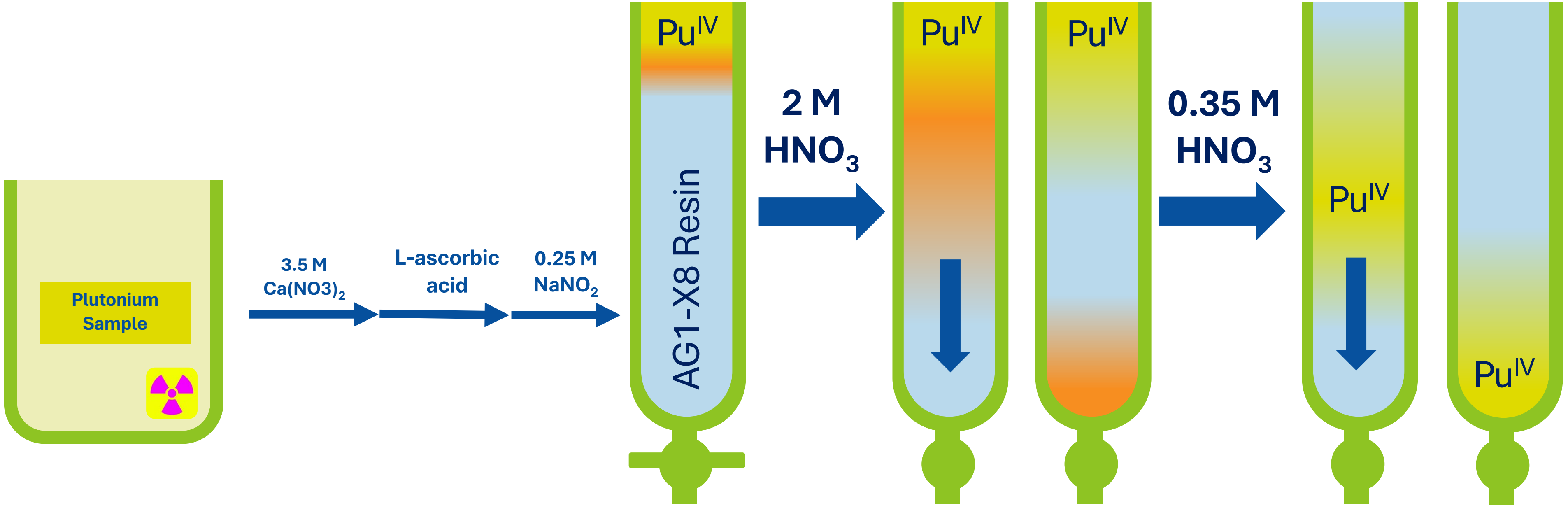


R = C_8H_{17} or $C_{10}H_{21}$

TEtraValent Actinides

- Ryan and Wheelright, *Industrial and Engineering Research* **1959**, *51*, 60.
- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorganic Chemistry* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

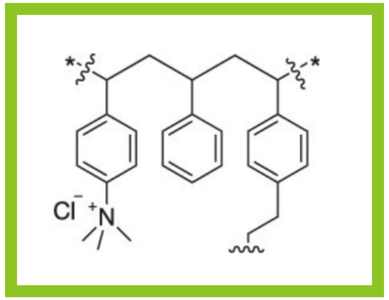
Plutonium-239 Purification



AG1-X8 Resin rinsed with $Ca(NO_3)_2$ in 2 M HNO_3

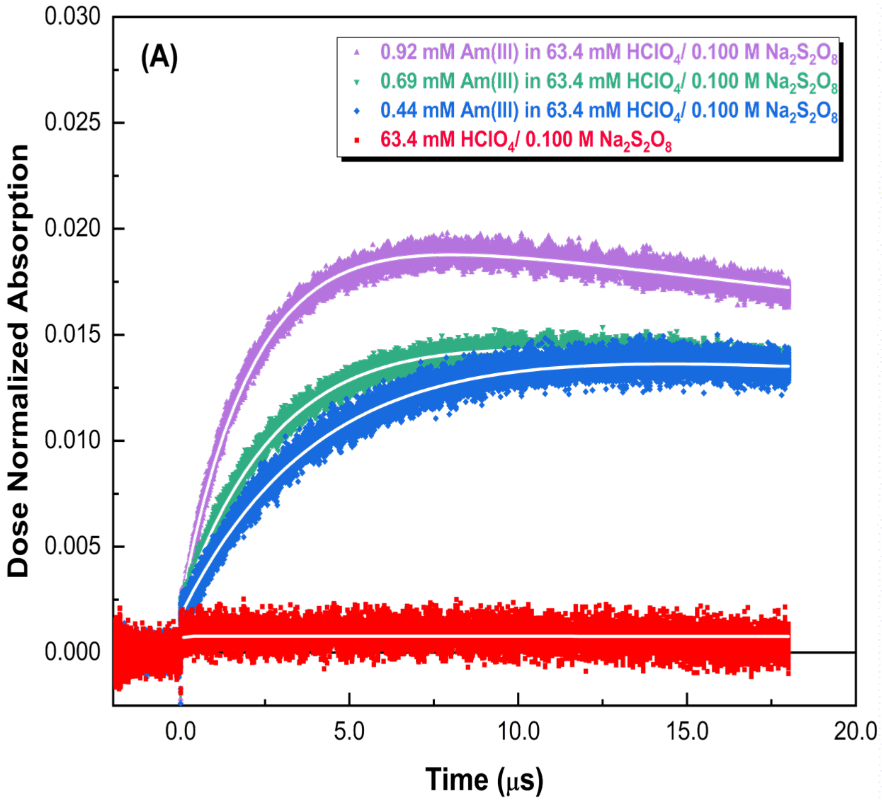
Converted to nitrate complex

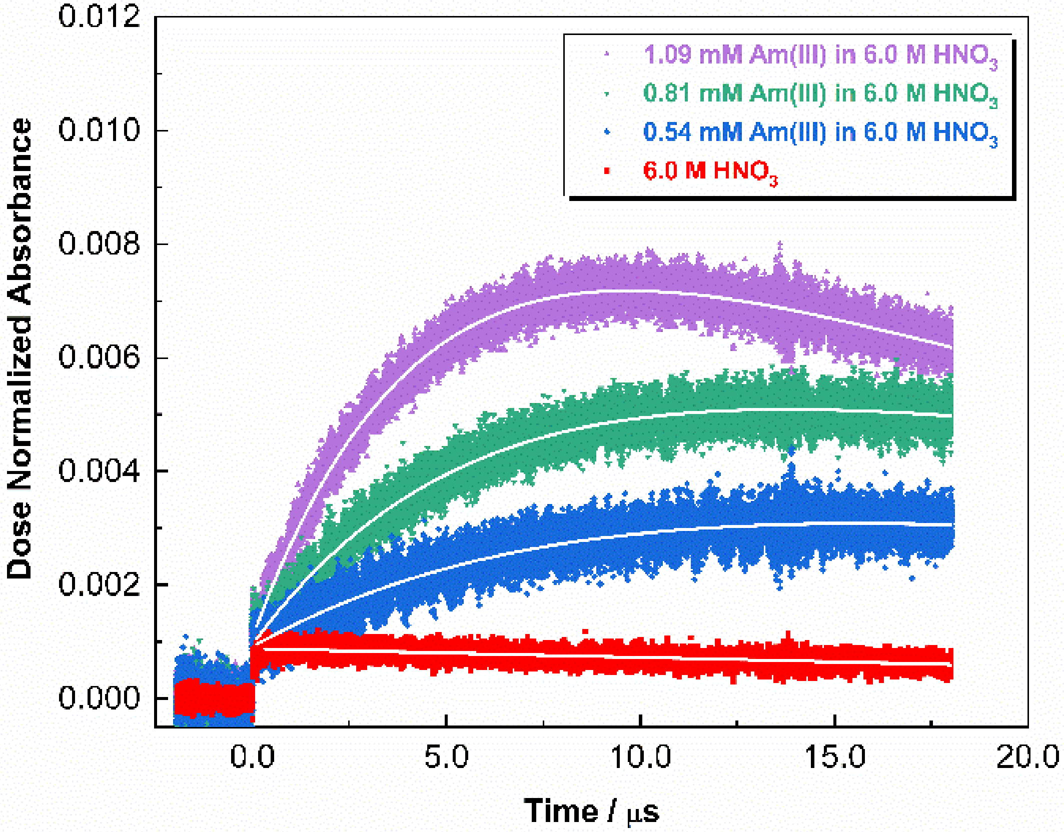
Pu(IV) eluted into HNO_3 reservoir



- Ryan and Wheelright, *Industrial and Engineering Research* **1959**, *51*, 60.
- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorganic Chemistry* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

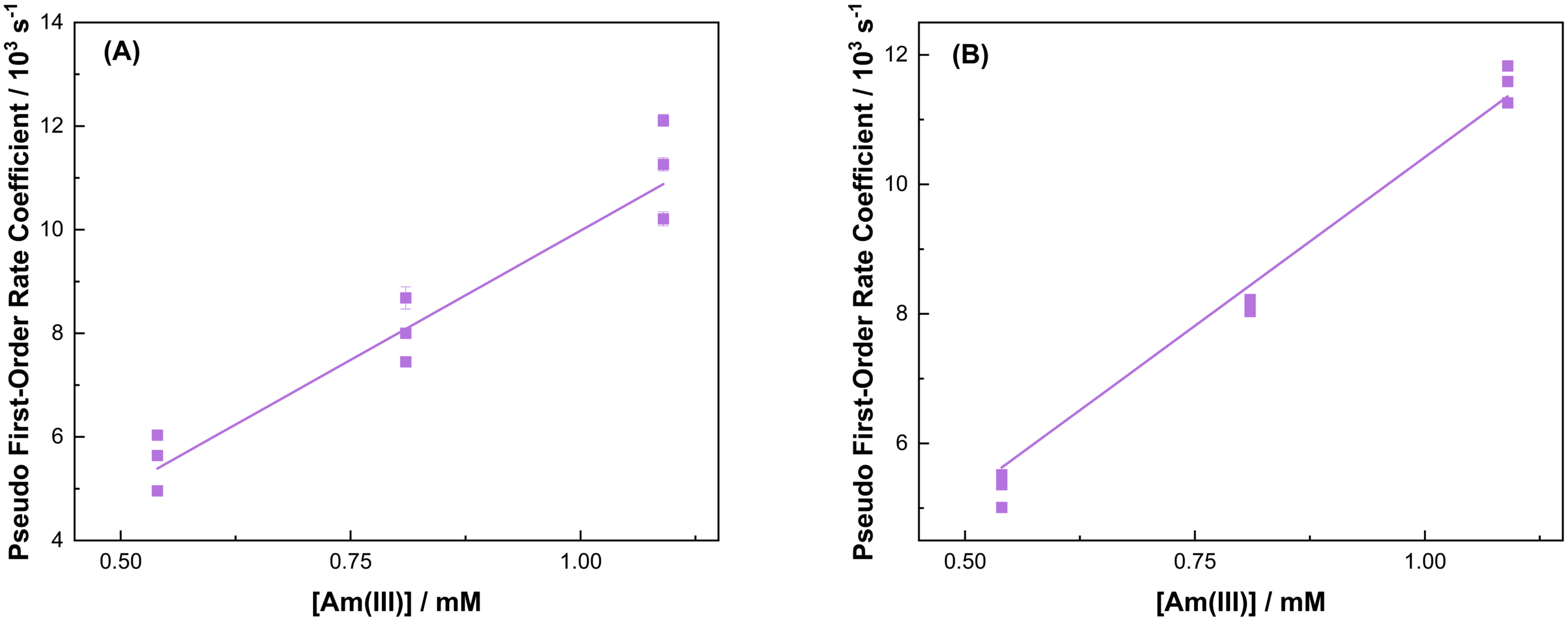
Americium Kinetic Data





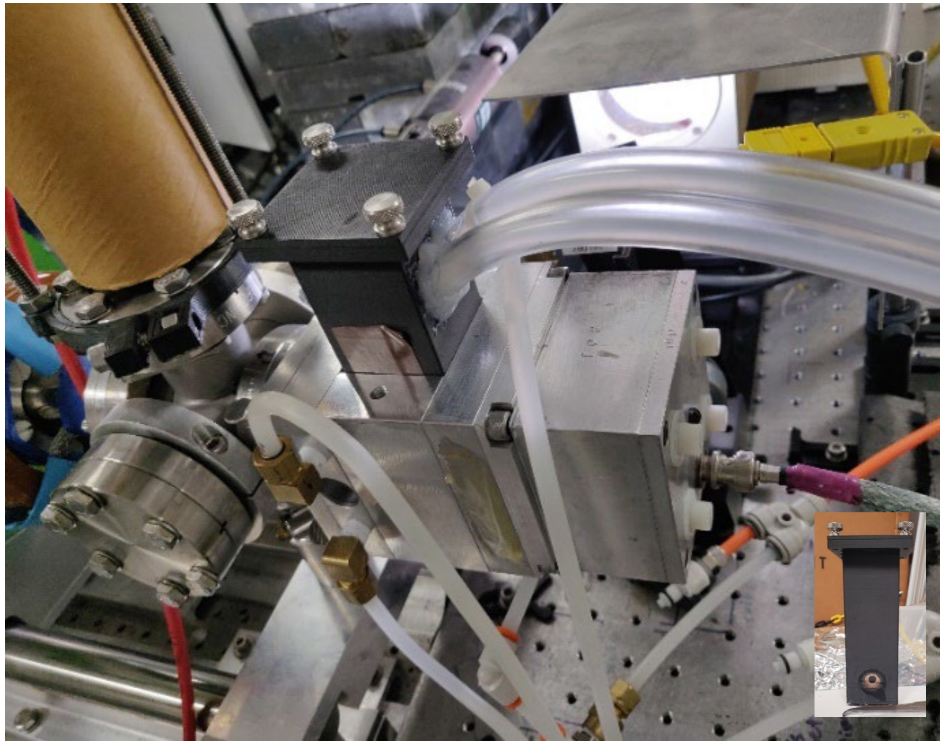
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

Americium Kinetic Data



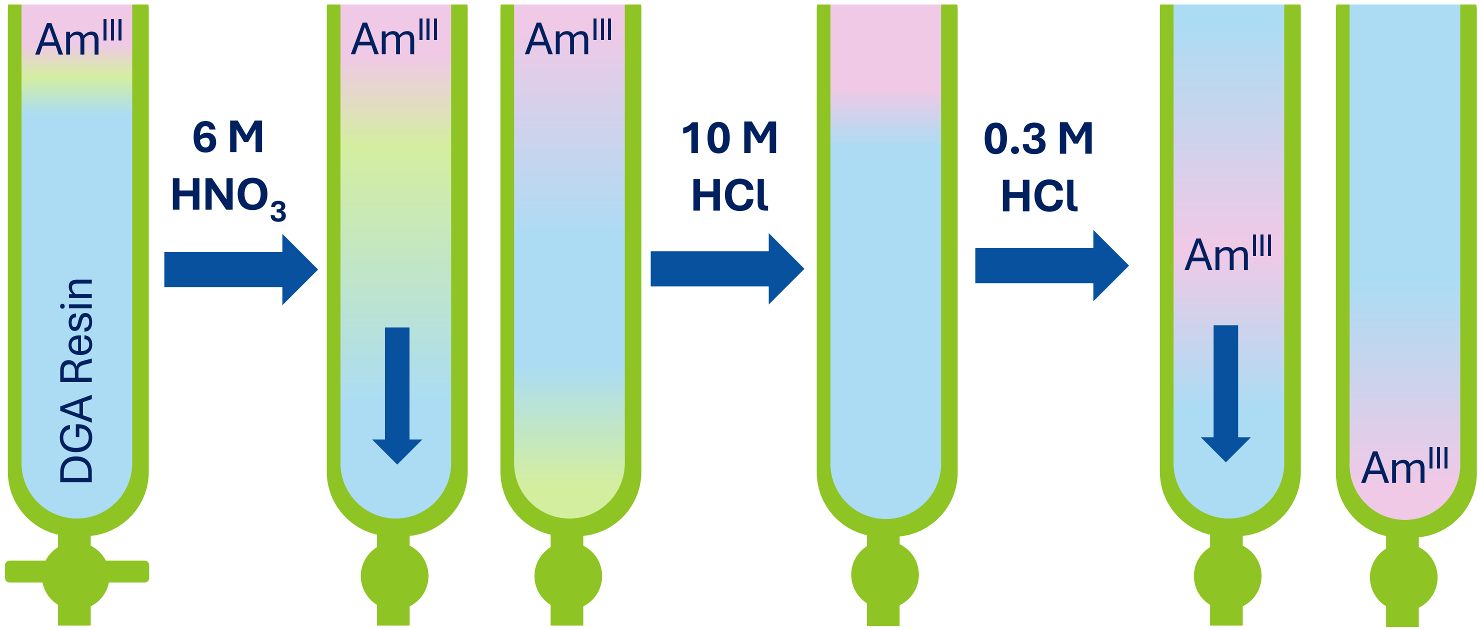
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

Temperature Controlled Actinide Sample Holder



- Wishart, Cook and Miller, *Review of Scientific Instruments* **2004**, *75*, 4359.
- Horne, Rotermind, Grimes, Sperling, Meeker, Zalupski, Beck, Huffman, Gomez Martinez, Beshay, Peterman, Layne, Johnson, Cook, Albrecht-Schönzart and Mezyk, *Journal of Physical Chemistry A* **2022**, *61*, 10822.
- Rotermund, Mezyk, Sperling, Beck, Wineinger, Cook, Albrecht-Schönzart and Horne, *Journal of Physical Chemistry A* **2024**, *128*, 590.
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

Americium-243 Purification

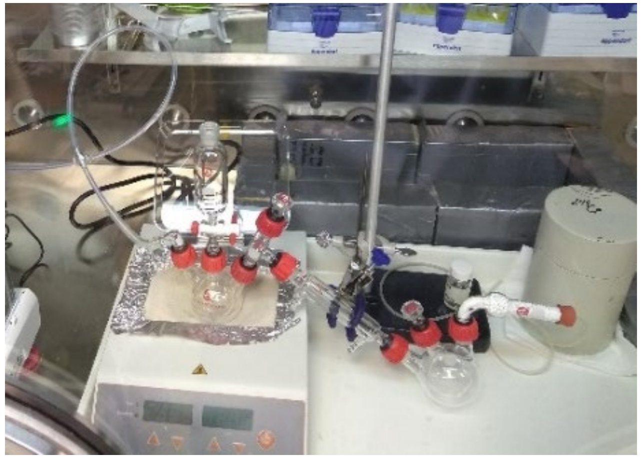


DGA Resin preequilibrated with 0.1 M HNO_3

Impurities removed with 6 M HNO_3

Conversion to $AmCl_3$

Am(III) eluted as hydrated $AmCl^{2+}/AmCl_2^+$



Multiple acid metathesis cycles required to convert to the nitrate complex used to generate samples.

Am-243 —α-decay, $t_{½}$= 7350 y→ **Np-239** —β-decay, $t_{½}$= 2.4 days→ **Pu-239**

Am-241 —α-decay, $t_{½}$= 433 y→ **Np-237** —β-decay, $t_{½}$= 2.4 days→ **Pu-239**

- Ryan and Wheelright, *Industrial and Engineering Research* **1959**, *51*, 60.
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.