INL/CON-24-79909-Revision-0

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

August 2024

Amy Elizabeth Kynman, Gregory Peter Holmbeck, Travis S Grimes, Brian Matthew Rotermund, Andrew Cook, Bobby Layne, Stephen Mezyk

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Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517, DE-AC07-05ID14517

August 2024

Amy Kynman
Glenn T. Seaborg Distinguished
Postdoctoral Research Associate

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4th International Conference on Ionizing Processes

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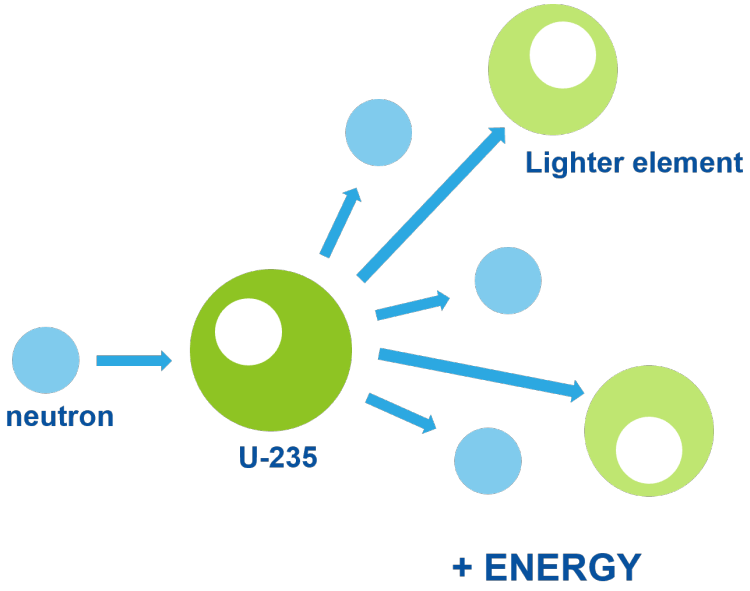
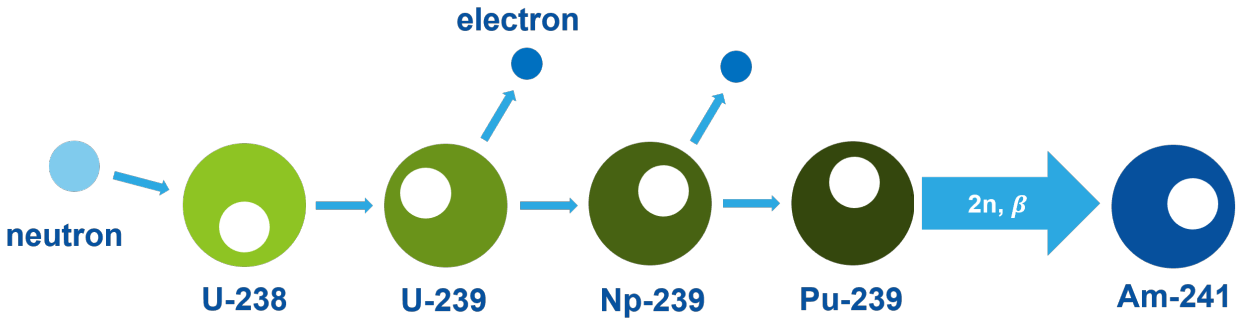
Generation of Americium by Nuclear Fission

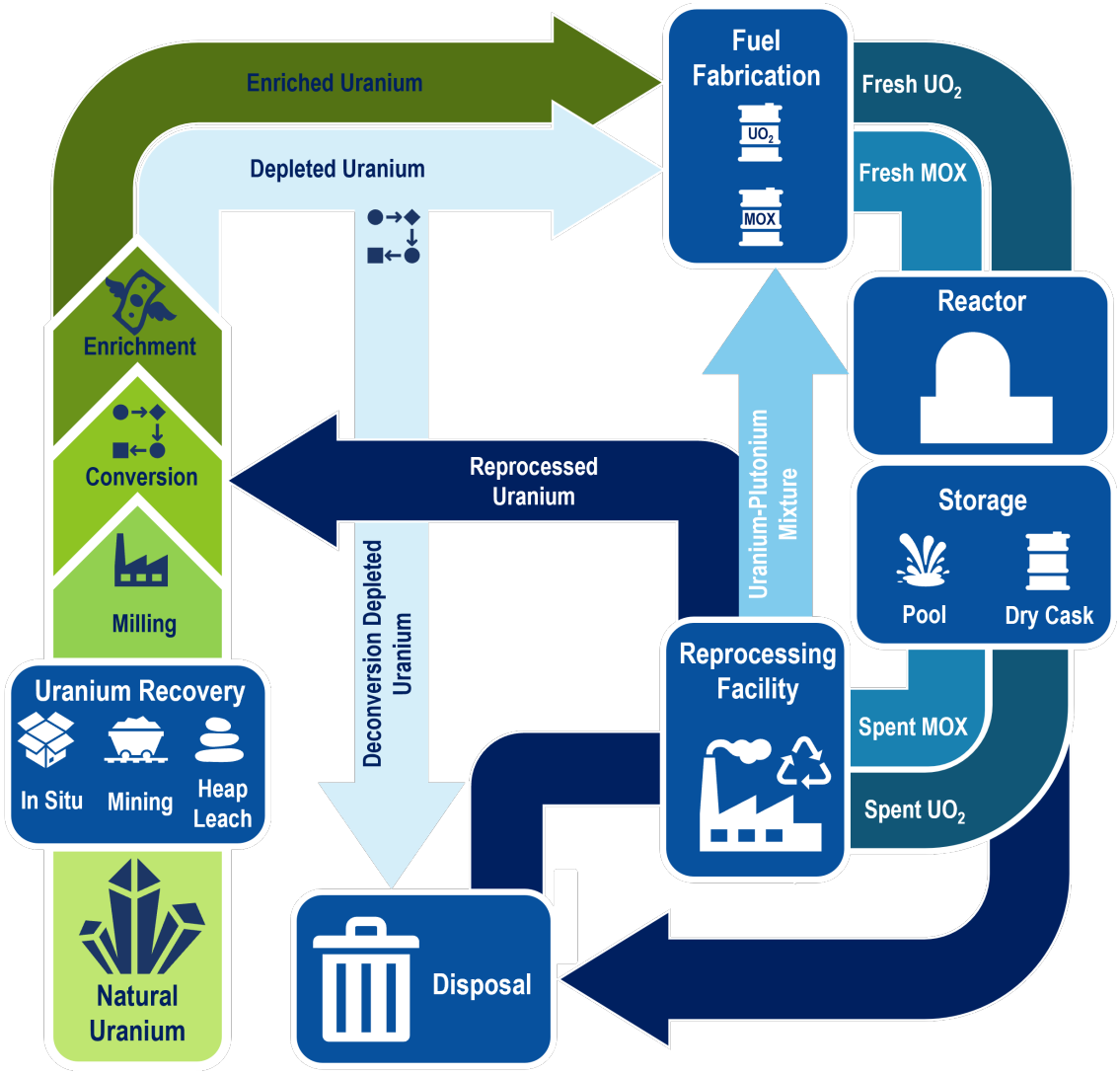




- Nuclear energy supplies over 70% of the clean, non-carbon emitting electricity in the United States.
- Reliant on the fundamental instability of U-235.

- Approximately 2.5 kg of americium (Am) is generated by a pressurized water reactor each year.
- Am-243 formed under high flux conditions (4n + β decay).

Closing the Nuclear Fuel Cycle

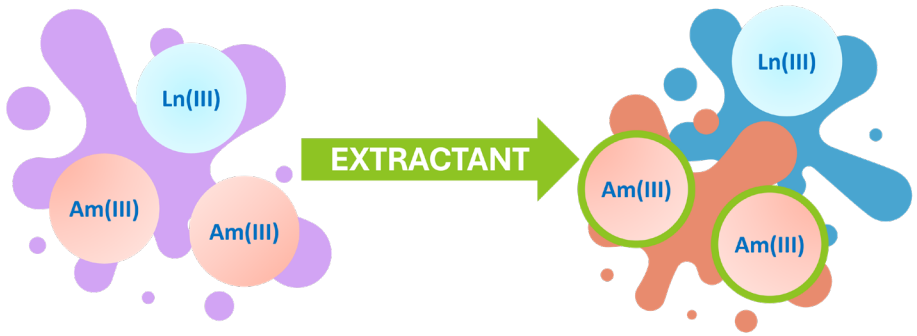


- Americium is a major contributor to the long-term radiotoxicity of used nuclear fuel (UNF).
- Closing the nuclear fuel cycle has several benefits:
  - ✓ Minimize final high-level waste for disposal or storage.
  - ✓ Recover additional energy from fuel.
  - ✓ Reduce impact on the environment and natural resources.
- Transmutation of americium is hindered by the high neutron cross section of lanthanide fission products.

Separation of Americium from Trivalent Lanthanide Fission Products

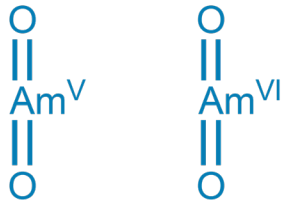
Trivalent Americium

- 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.

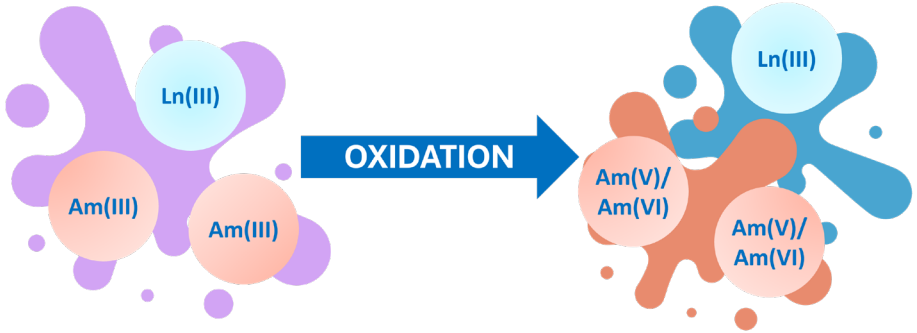


High Valent Americium

- 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.



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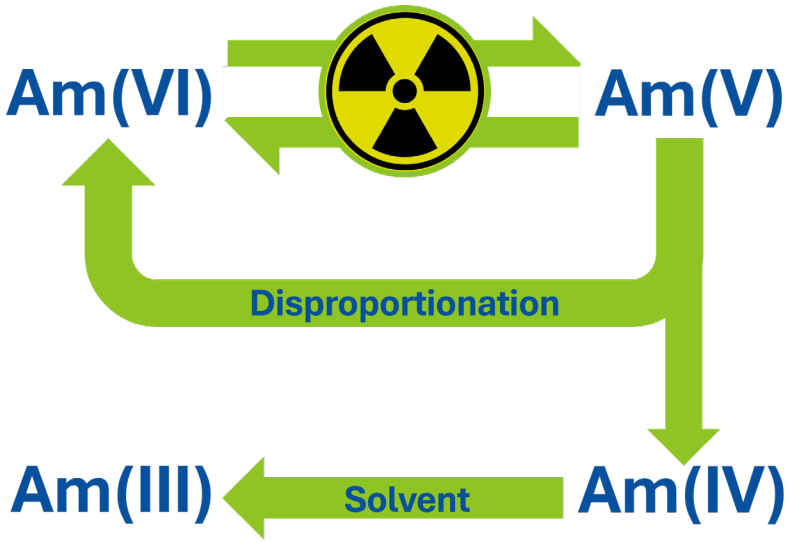
- Runde and Mincher, *Chemical Reviews* **2011**, *111*, 5723.

Radiation-Induced Americium Redox Chemistry

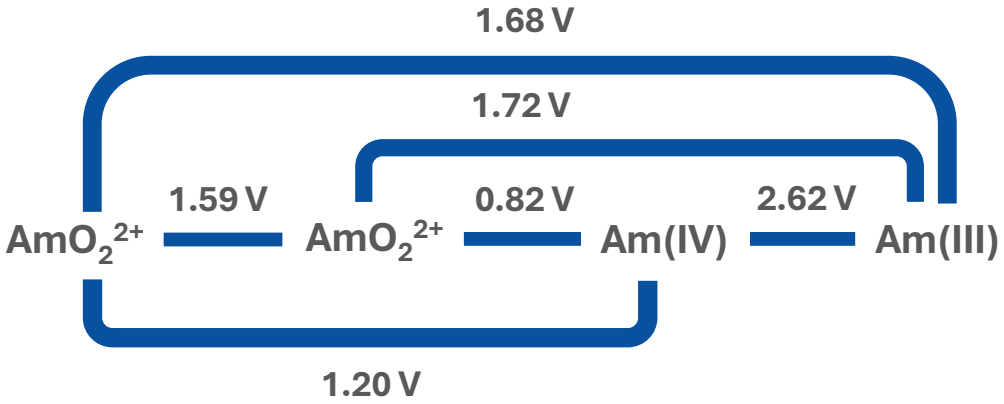


- The lifetime of the americyl states are dictated by a combination of chemical and radiolytic processes.
- Under alpha and gamma irradiation, Am(VI) is converted to Am(V) by nitric acid radiolysis products (HNO_2, H_2O_2, $HO_2^{\bullet}$).
- Disproportionation of Am(V)/Am(III) system eventually leads to the reduction of Am(V) and quantitative ingrowth of Am(III).

$$2Am^{V}O_2^{+} + 4H_{aq}^{+} \rightarrow Am^{IV} + Am^{VI}O_2^{2+} + H_2O$$

$$Am^{V}O_2^{+} + Am^{IV} \rightarrow Am^{VI}O_2^{2+} + Am^{III}$$

$$2Am^{IV} + H_2O \rightarrow Am^{V}O_2^{+} + Am^{III} + 4H_{aq}^{+}$$



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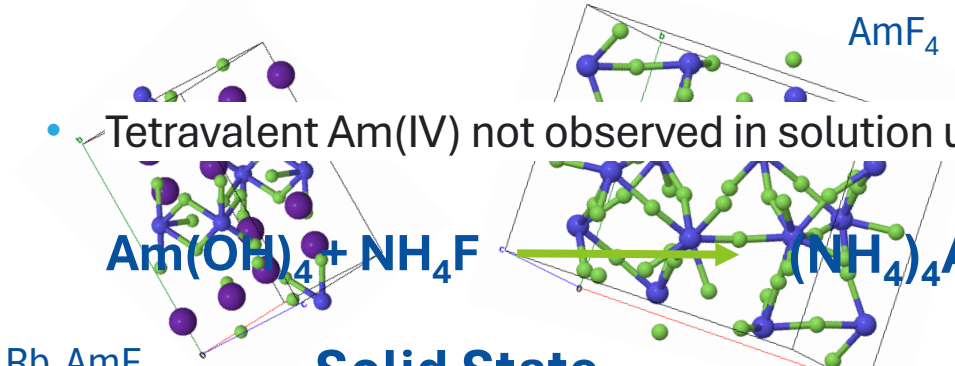
- Horne, Grimes, Bauer, Dares, Pimblott, Mezyk and Mincher, *Inorganic Chemistry* **2019**, *58*, 8551.

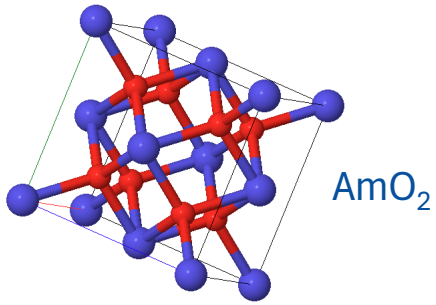
Tetravalent Americium

- Tetravalent Am(IV) not observed in solution until the 196

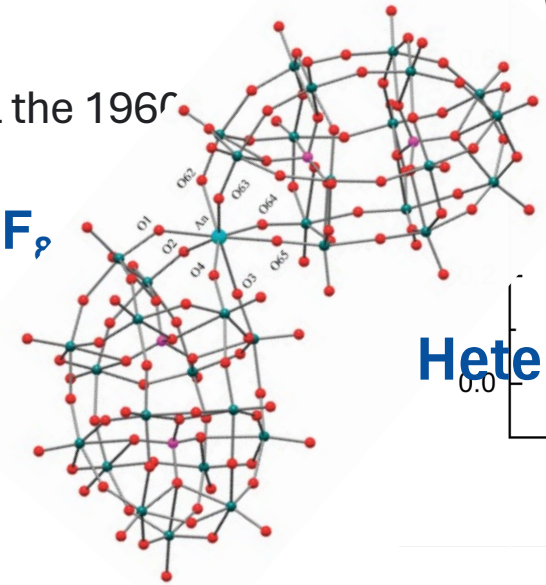


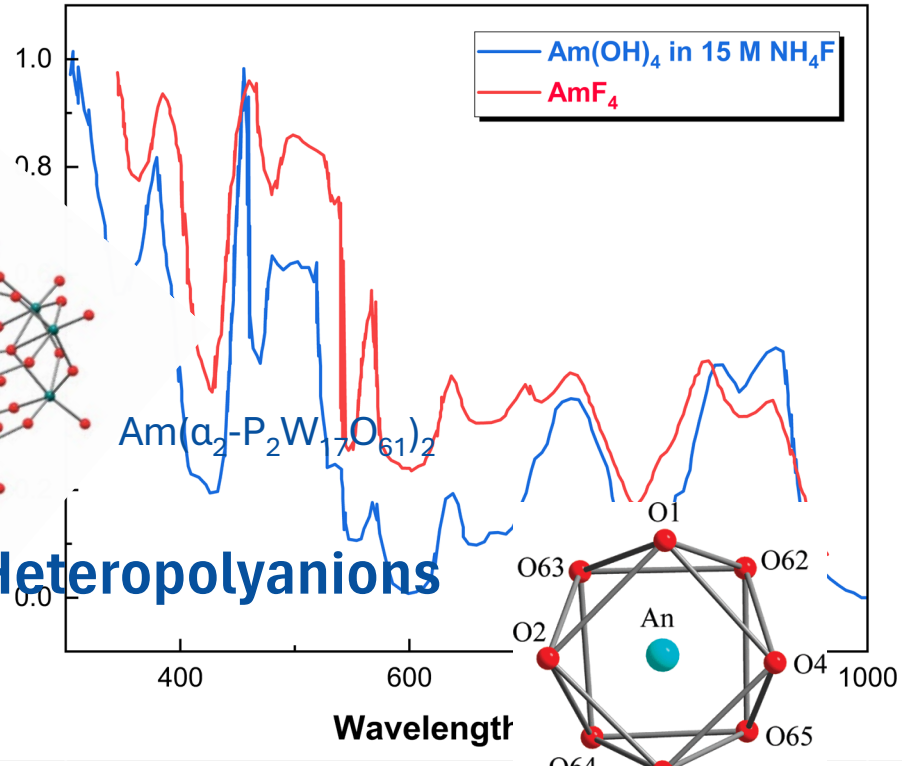
$Am(OH)_4 + NH_4F \rightarrow (NH_4)_4AmF_8$

Solid State



Heteropolyanions





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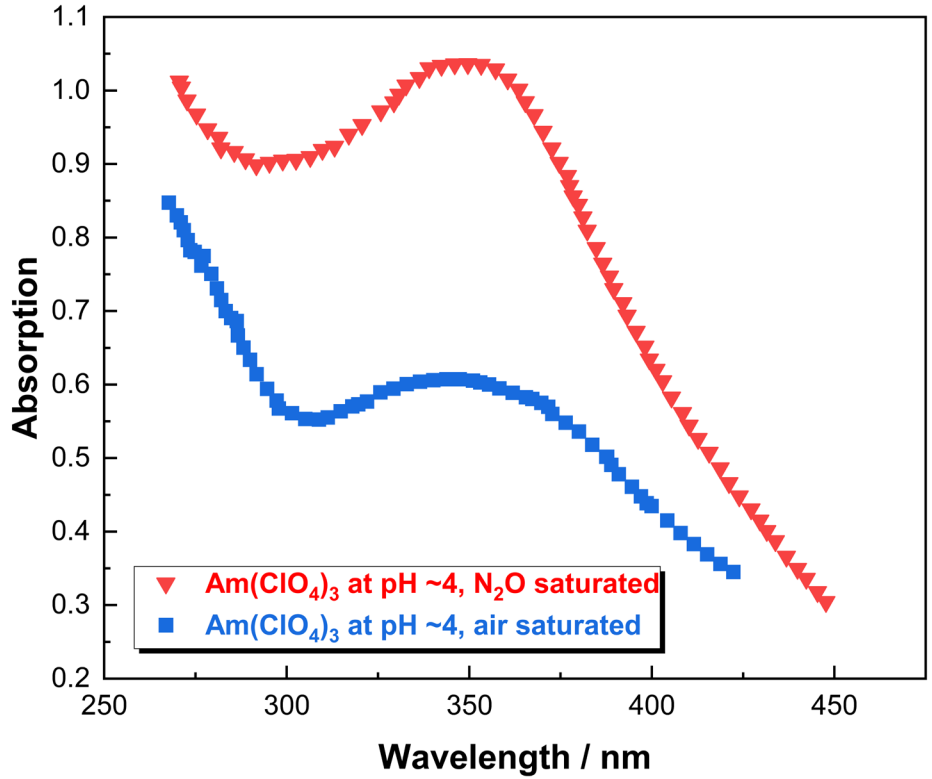
Using Pulse Radiolysis to Generate Am(IV)

- Use of accelerated electrons to create radical species in solution.

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

- Oxidizing $^{\bullet}OH$ radical used to generate Am(IV) in perchloric acid.
- Am(IV) characterized through changes in optical absorption.



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

- Gordon, Mulac, Schmidt, Sjoblom and Sullivan, *Inorganic Chemistry* **1978**, *17*, 294.
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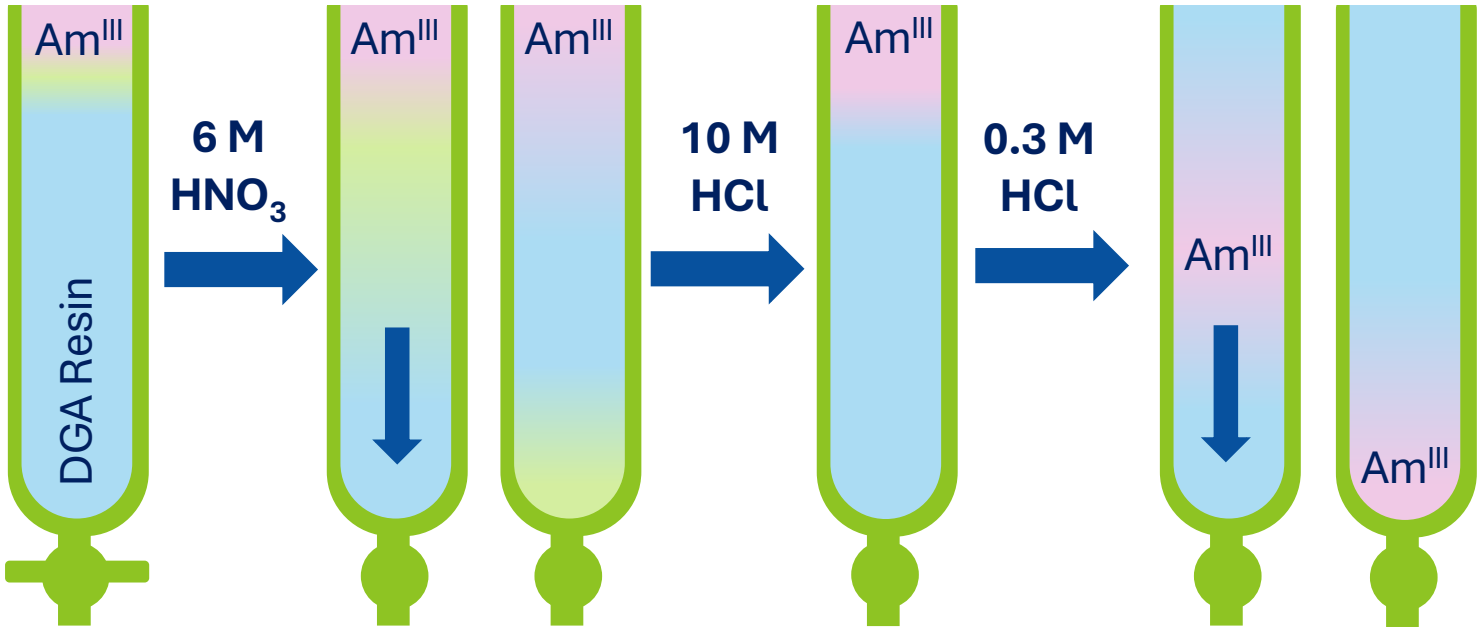
Americium-243 Purification

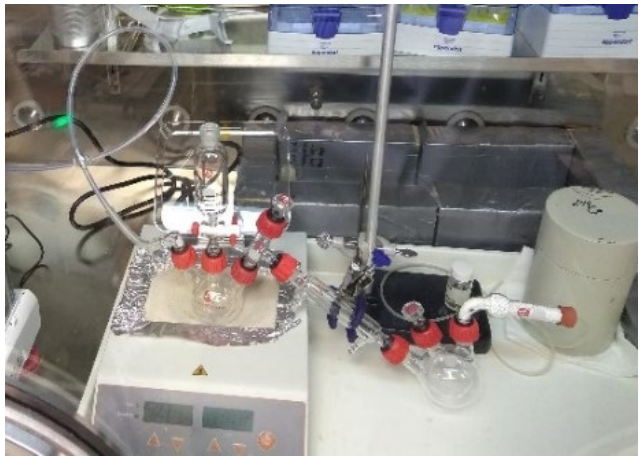


DGA Resin preequilibrated with 0.1 M HNO_3

Impurities removed with 6 M HNO_3

Conversion to chloride complex

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** —α-decay, $t_{½}$= 2.1 x 10^6 y→ **Pa-233**

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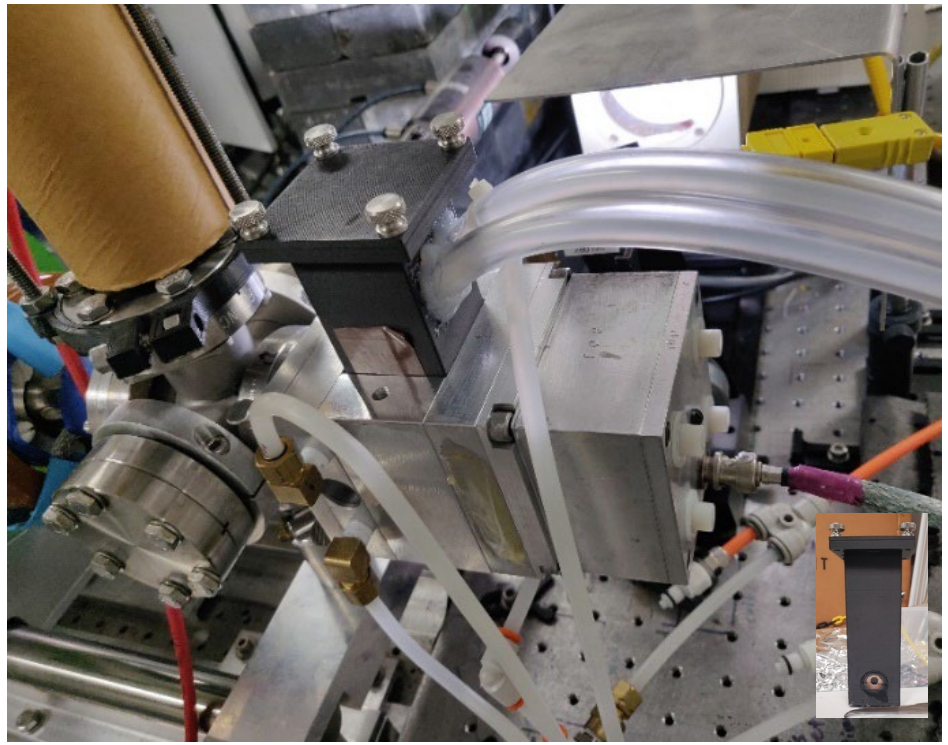
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

Temperature Controlled Actinide Sample Holder



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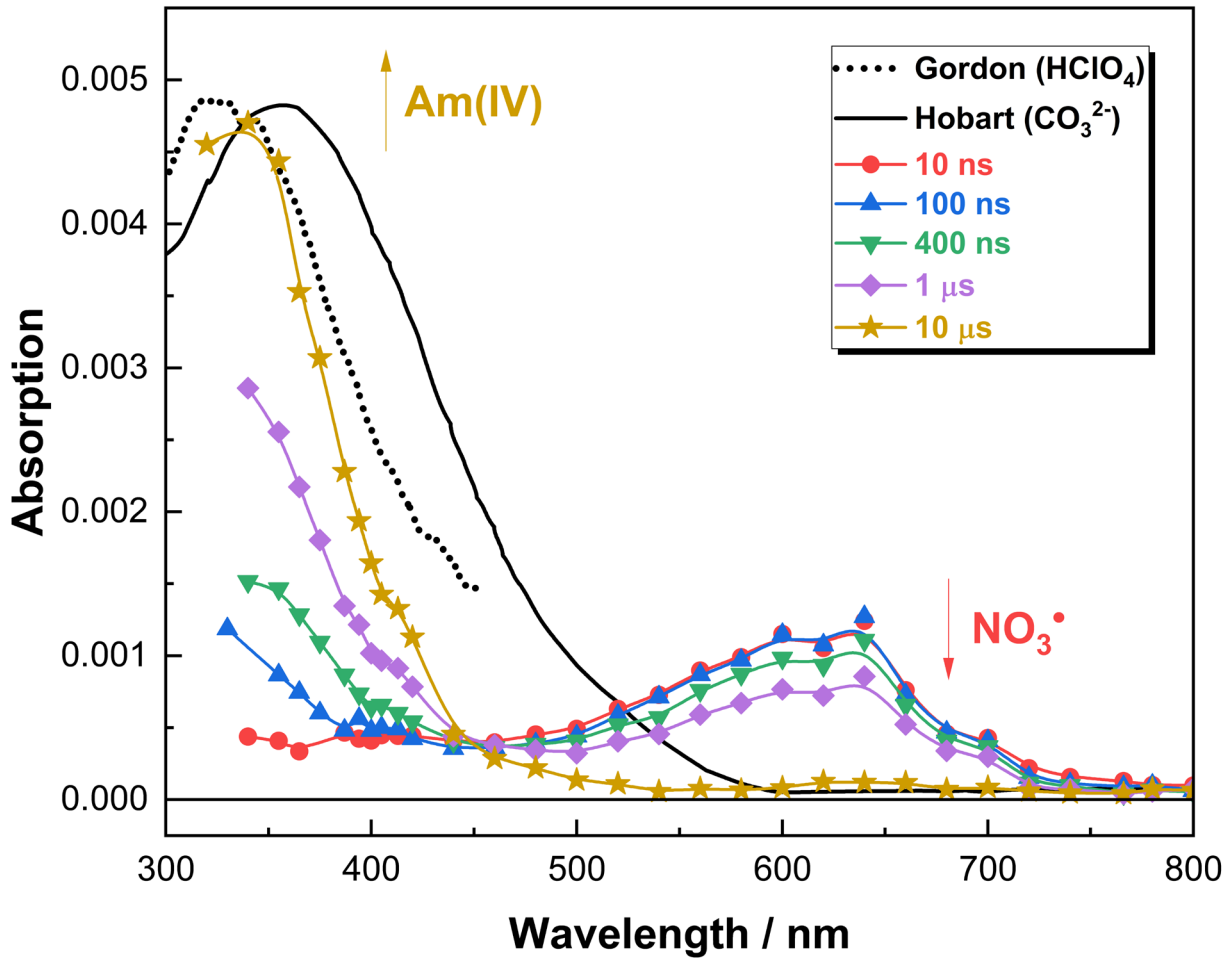
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.

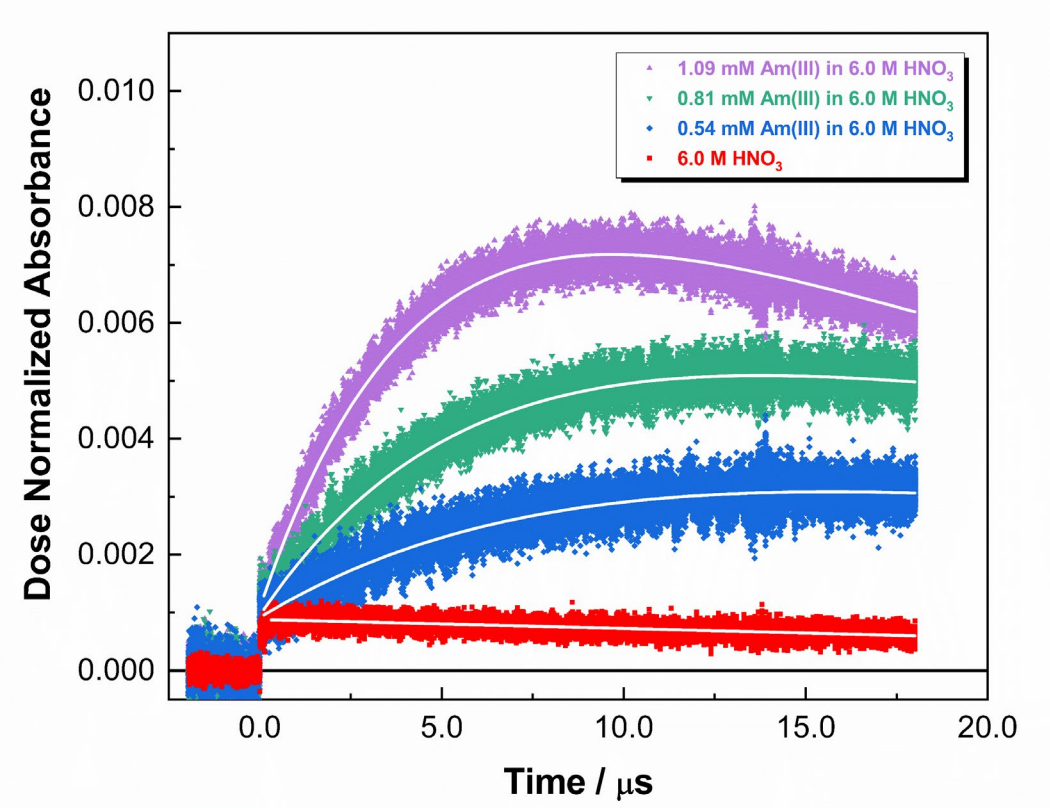
Transient Am(IV) Absorption

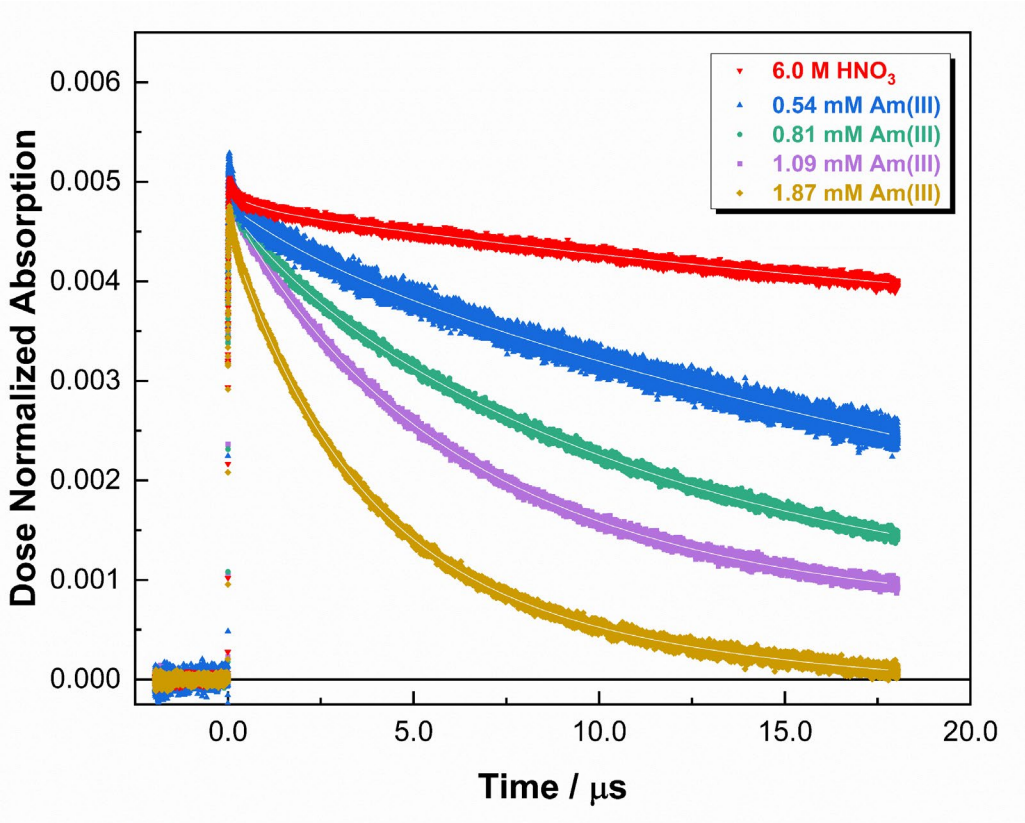


- Am(IV) in the absence of strong complexing agents observed in HNO_3 for the first time.
- Results consistent with previous reports of Am(IV) in solution.

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

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





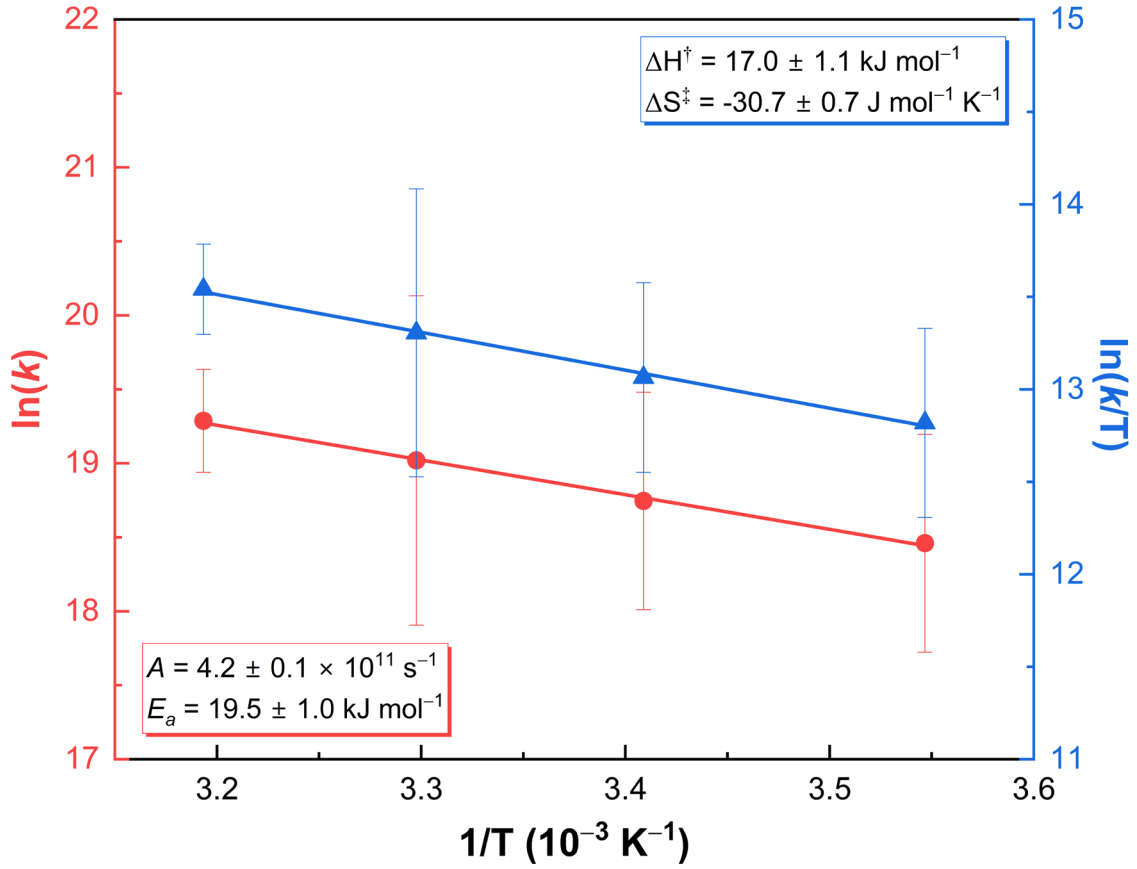
- Rate constant = (1.35 ± 0.05) × 10^8 M^{-1} s^{-1}
- Am(IV) lifetime in 6 M HNO_3 is approximately 16 μs.

Brookhaven National Laboratory

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

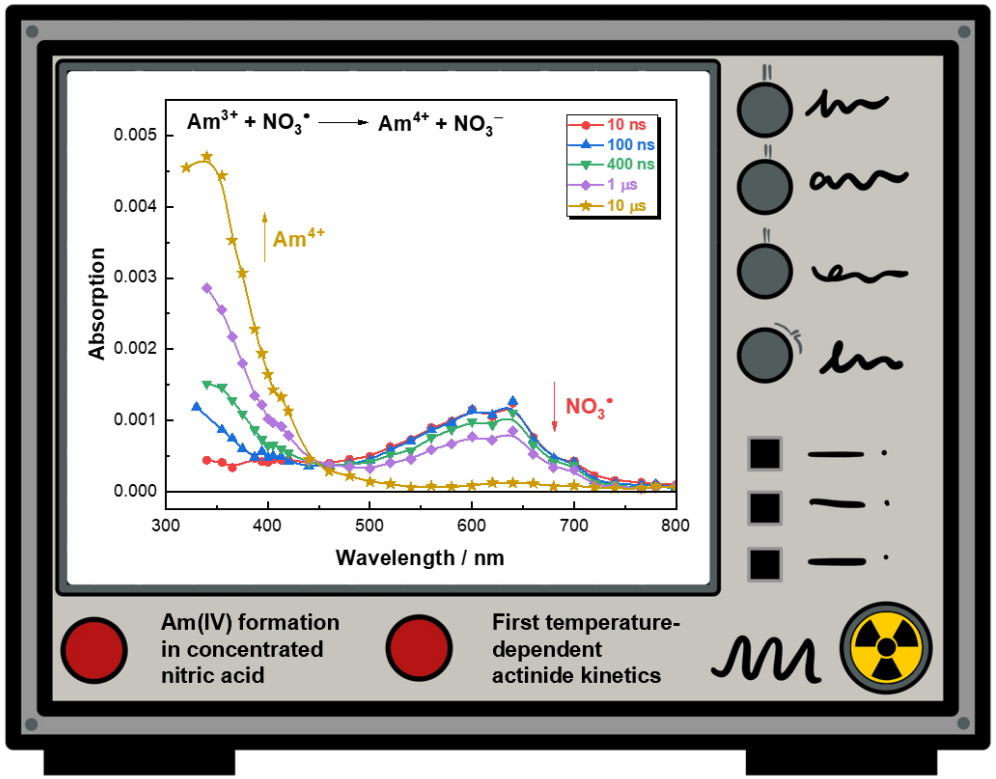
Temperature-dependent Am(III) + $NO_3^{\bullet}$ kinetics

- 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 $NO_3^{\bullet}$.



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

Conclusions and 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 Am chemistry.

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

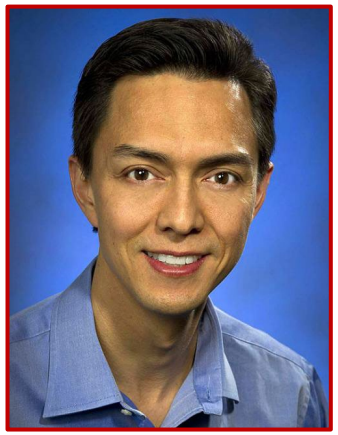
Acknowledgements

Brian Rotermund

Travis Grimes

Gregory Holmbeck

Stephen Mezyk



Bobby Layne

Andrew Cook

Graduate Students, INL Staff, and External Collaborators (California State University Long Beach, Brookhaven National Laboratory).

- **Idaho National Laboratory, Laboratory Directed Research & Development Program under Department of Energy Idaho Operations Office Contract DE-AC07-05ID14517.**
- 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.

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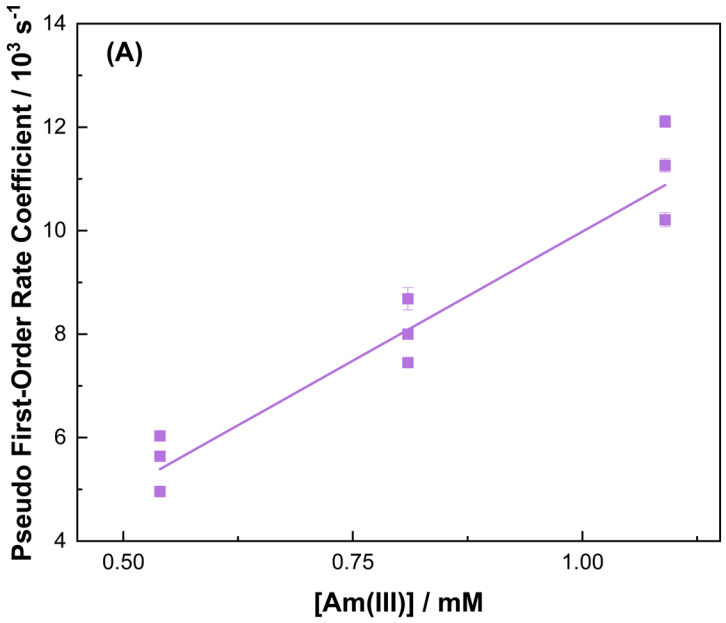

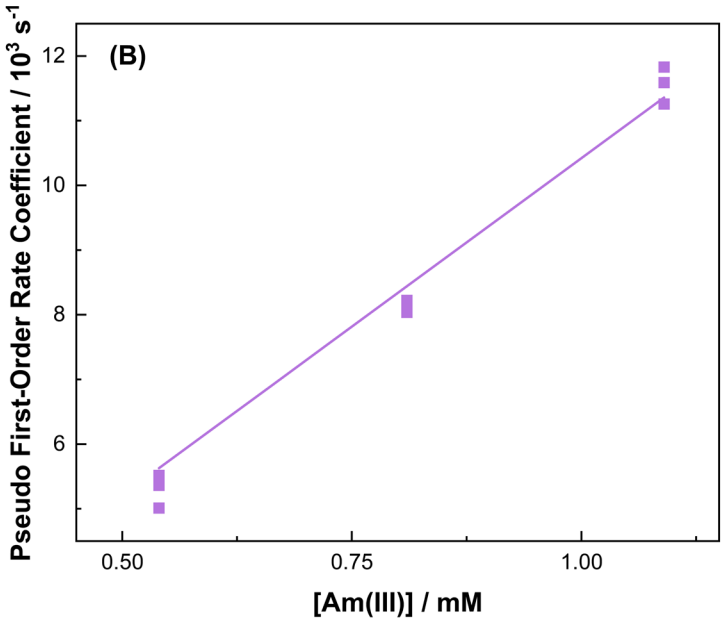

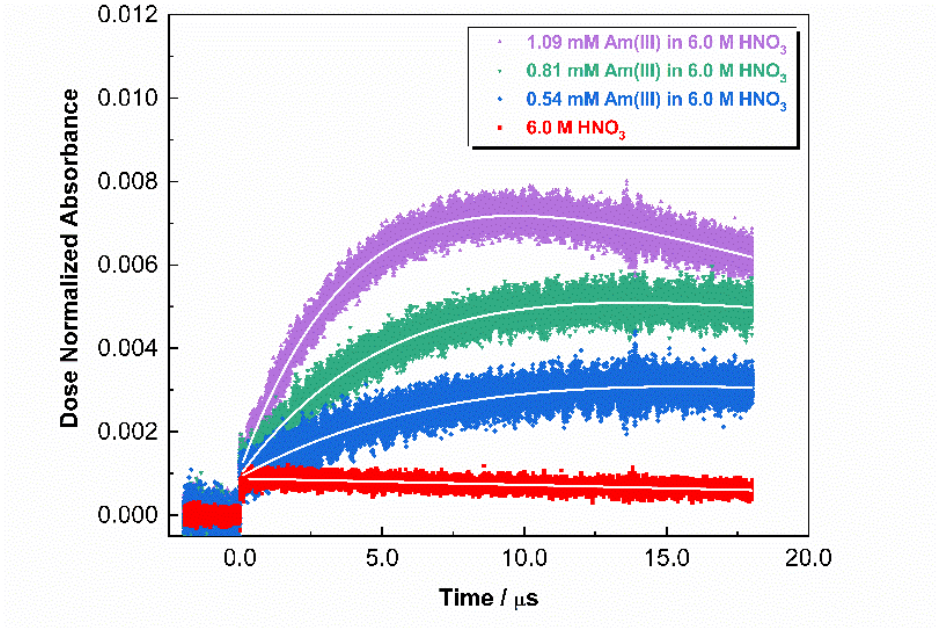

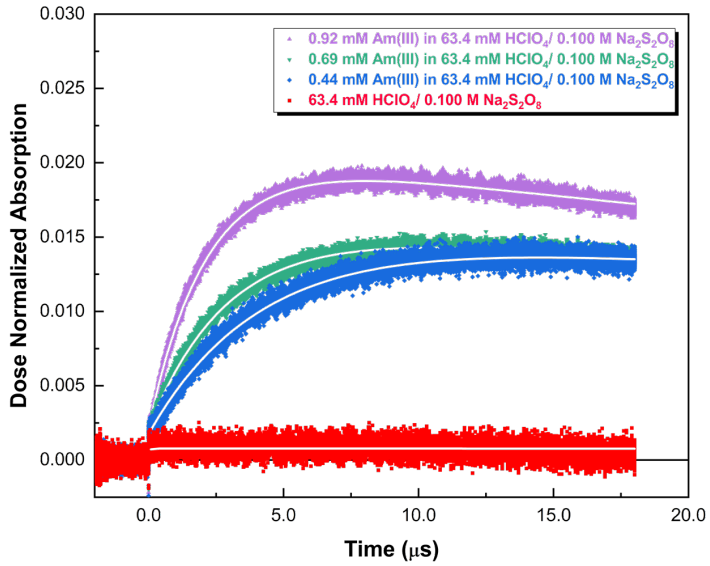

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