INL/CON-24-79906-Revision-0

Purification Techniques for Actinide Radiolysis Studies

August 2024

Changing the World's Energy Future

Amy Elizabeth Kynman, Travis S Grimes, Gregory Peter Holmbeck

Idaho National Laboratory

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Purification Techniques for Actinide Radiation Chemistry Experiments

4th International Conference on Ionizing Processes

Young Investigator Workshop

INL/CON-24-79906

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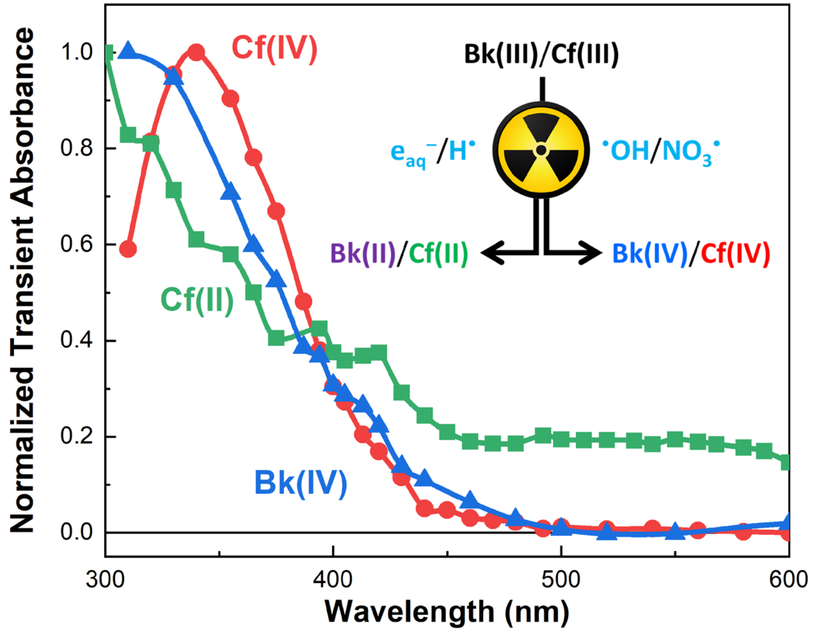
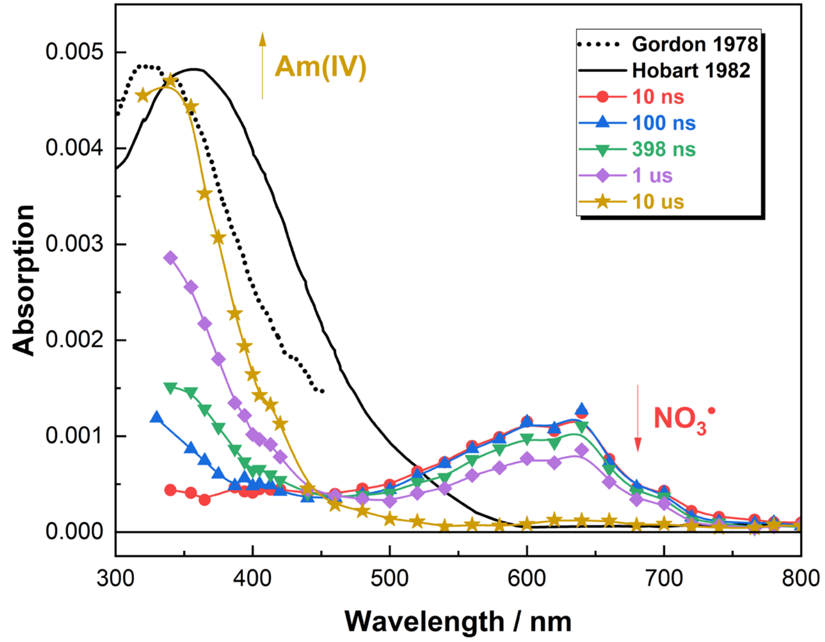
Radiation-Induced Actinide Redox Chemistry

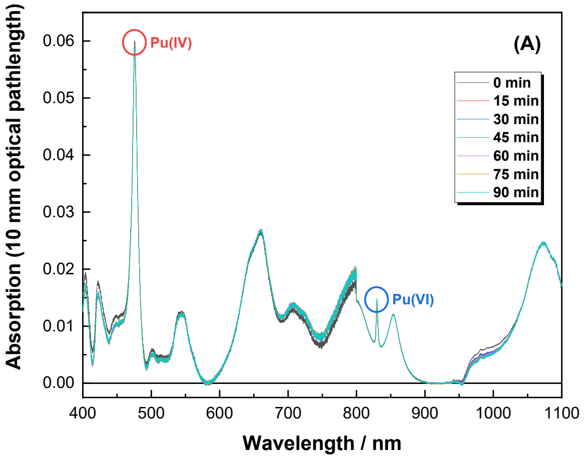
"Short-lived (≤ seconds) atoms or ions formed by the atomistic/molecular-level interaction of radiation-induced radical and molecular products with actinide ion oxidation states in aqueous solution."

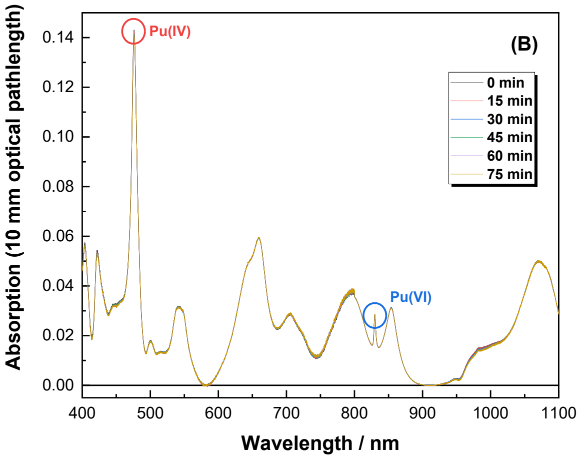




- Gordon, Sullivan, and Ross, J. Phys. Chem. Ref. Data **1986**, *15(4)*, 1357.
- Horne, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Trans.* **2021**, *50*, 10853.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Beck, Gomez Martinez *et al.*, *Inorg. Chem.* **2022**, *61(28)*, 10822.
- Rotermund, Mezyk, Sperling, Beck, Wineinger, Cook, Albrecht-Schönzart, and Horne, *J. Phys. Chem. A* **2024**, *128(3)*, 590.
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Trans.* **2024**, *53*, 9262..

Alpha vs. Gamma Irradiations





Gamma

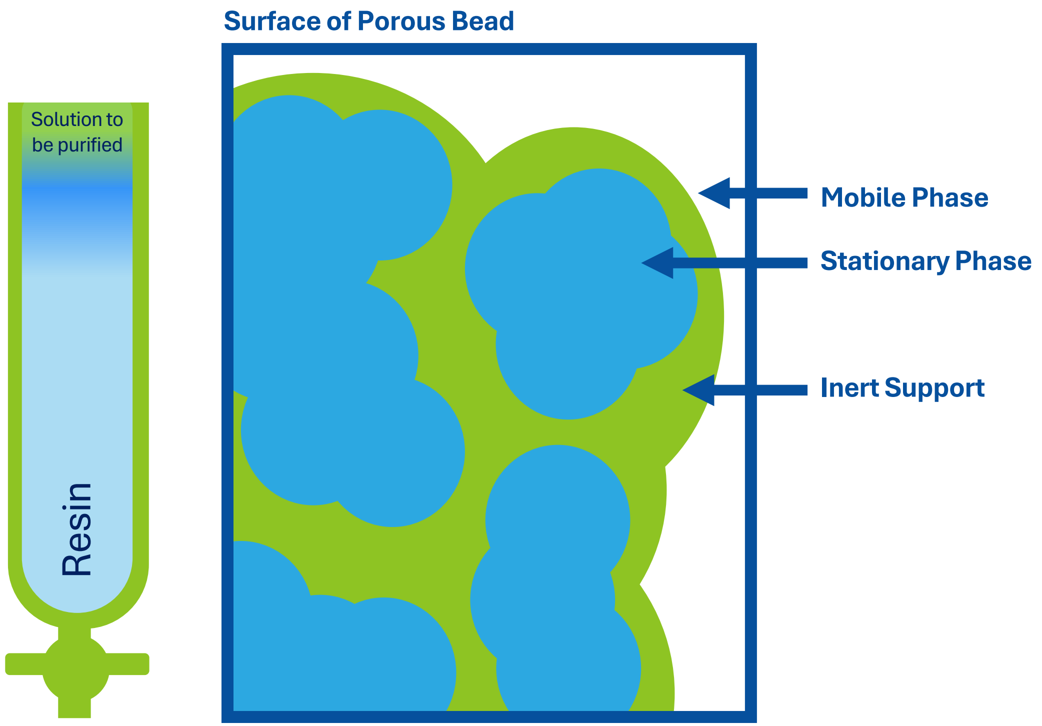
- Actinide-containing solutions irradiated and analyzed by UV-Visible spectroscopy
- Changes in oxidation state monitored over time.
- Absorbed dose calculated from the irradiator dose rate.

Alpha

- Source of radiation is the inherent alpha decay of the actinide element.
- Dose calculated from specific activity over time.

Purification by Extraction Chromatography

- Thorough purification and quantification of actinide elements is crucial for obtaining accurate data.

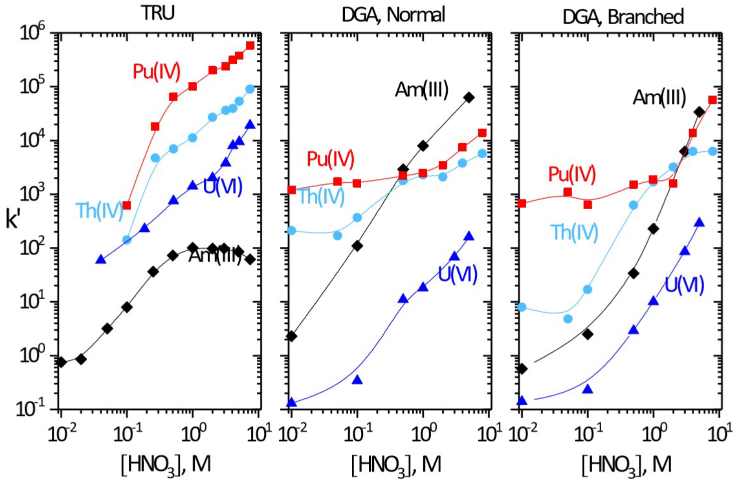


Stationary Phase

- Liquid extractant, diluent may be used.

Mobile Phase

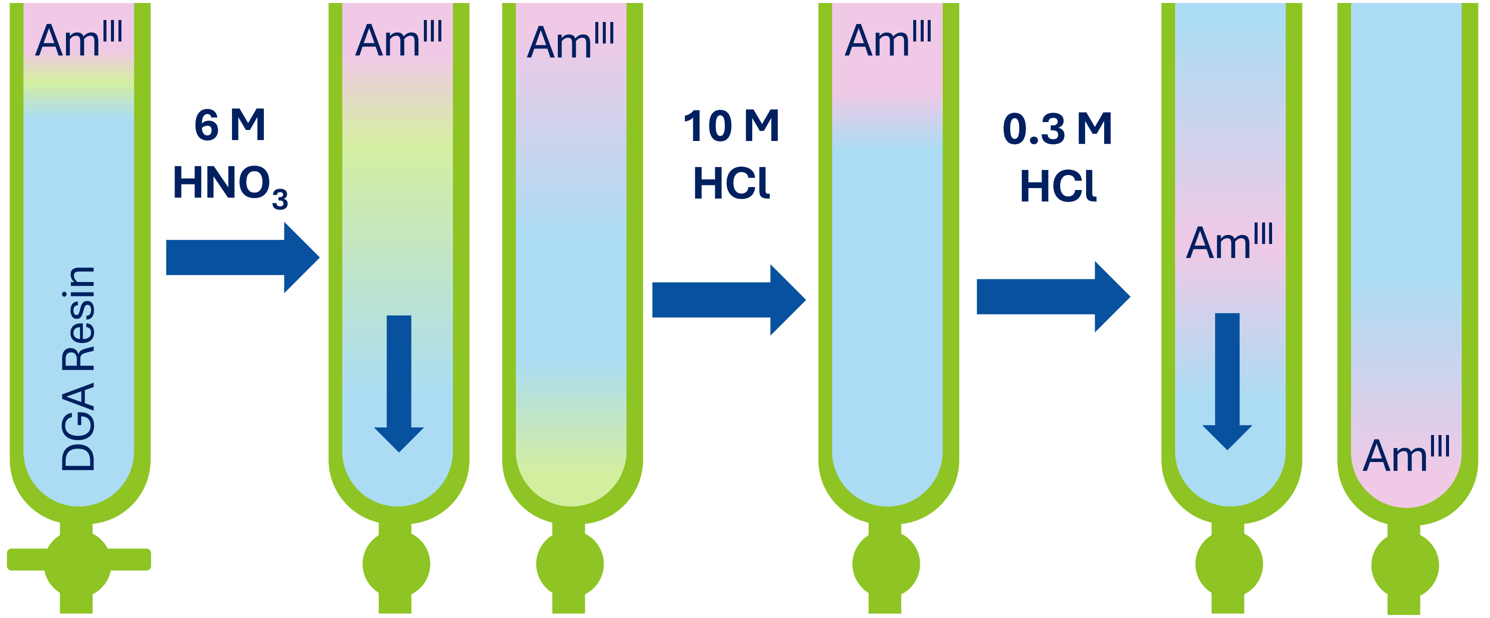
- Acidic solution of varying pH, complexants can be used to enhance properties.



- Important to consider the bed density and volume of the resin.
- Manipulations carried out in a radiological glovebox or fumehood.

- Eichrom Technologies

Americium-243 Purification

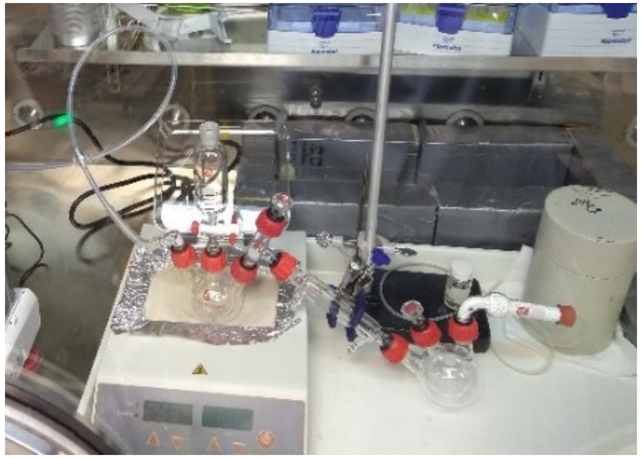


DGA Resin preequilibrated with 0.1 M HNO_3

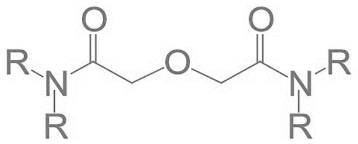
Impurities removed with 6 M HNO_3

Conversion to chloride complex

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



Multiple acid metathesis cycles required to change acid matrix



R = *n*-octyl or 2-ethyl-1-hexyl

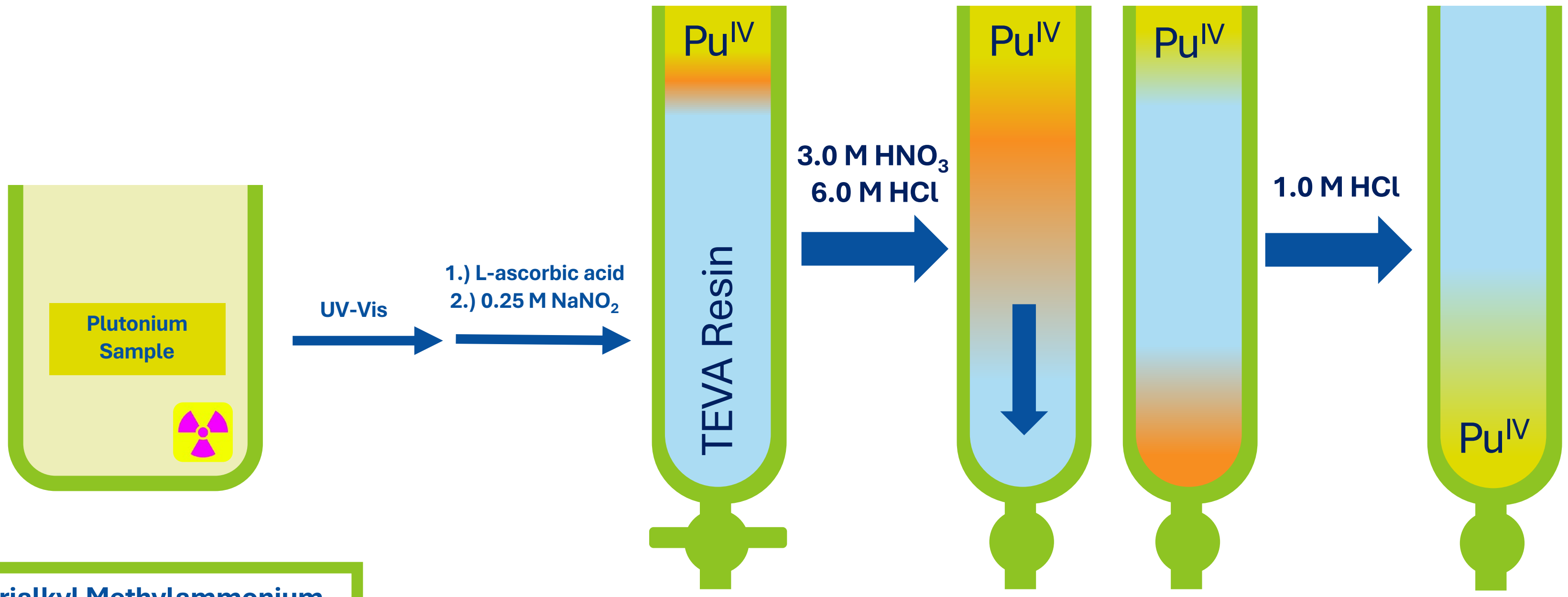
$M^{3+} + 3DGA + 3X^{-} \leftrightarrow M(DGA)_3X_3$

M = Ln(III) or An(III), X = NO_3^{-} or Cl^{-}

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

Plutonium-239 Purification

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



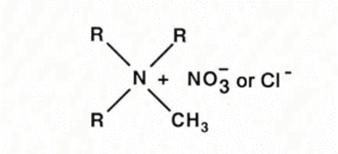
TEVA Resin preequilibrated with 0.1 M HNO_3

Background electrolytes and impurities removed

Pu(IV) eluted in HCl

- Anion exchange column needed to change background electrolyte.

Trialkyl Methylammonium Nitrate (or Chloride)



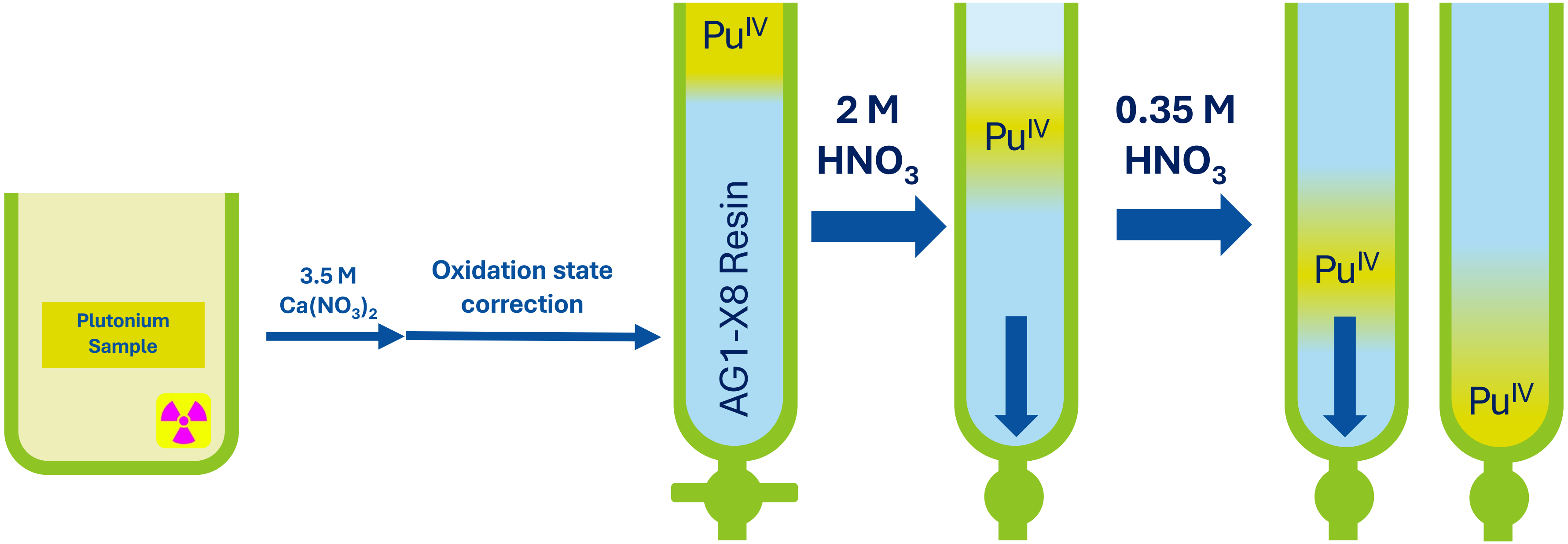
R = C_8H_{17} or $C_{10}H_{21}$

TEtraValent Actinides

- Ryan and Wheelright, *Industrial and Engineering Research* **1959**, *51*, 60.
- **Kynman**, Grimes, Conrad, Pimblott, and Horne, *Inorganic Chemistry* **2024**. DOI.

Plutonium-239 Purification

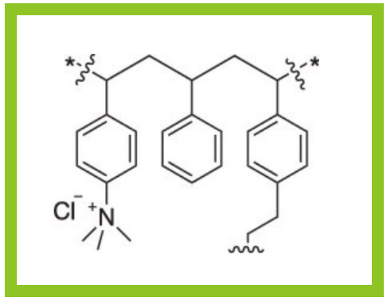
$Pu^{4+} + PuO_2^{+} \rightleftharpoons Pu^{3+} + PuO_2^{2+}$



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**.

Quantification: UV-Visible Spectroscopy

- Measures the amount of light absorbed or transmitted by a sample, characteristic oxidation states can be quantified based on the Beer-Lambert Law.

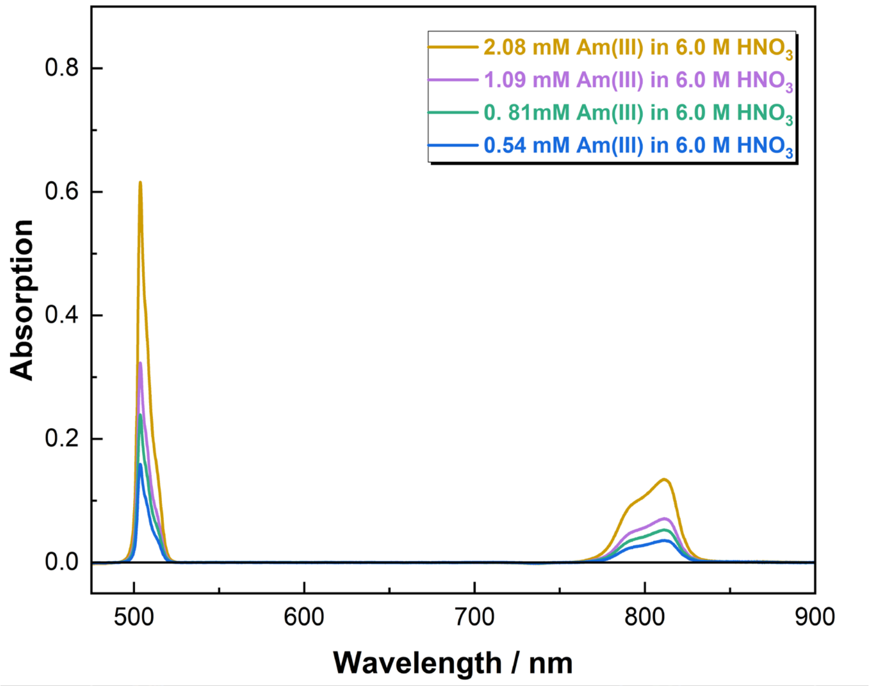


TABLE II

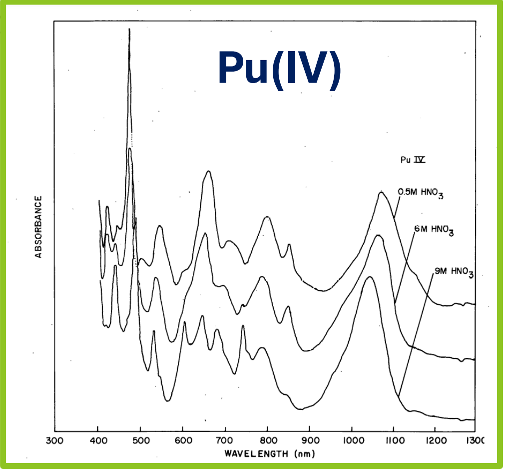
PuIV IN 0.6, 0.9, AND 5.0M NITRIC ACID

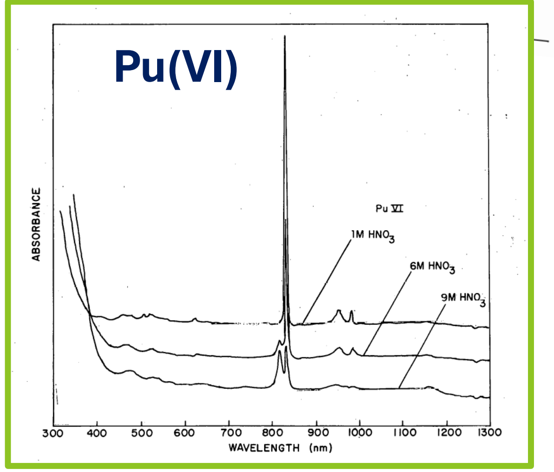
λ mμ	ε 0.6M HNO_3	ε 0.9M HNO_3	ε 5.0M HNO_3
400	20.7	-	31.3
438	13.8	14.0	20.9
476	66.5	70.0	67.7
564	5	6.3	5.5
569	2	4.4	4.0
602	0.6	3.3	6.0
660	29.5	30.1	32.1
710	13.3	14.0	15.7
775	12.5	13.1	17.0
832	10	10.1	8.8
952	2.9	2.4	5.0
982	[illegible]	7.2	10.

TABLE II. Relative Molar Absorptivity Values of Plutonium IV as a Function of HNO_3 Concentration.

HNO_3, M	A 475 – 495 nm $\bar{\epsilon}$	A 475 – 495 nm ±SD	A ~476* – 495 nm $\bar{\epsilon}$	A ~476* – 495 nm ±SD	A ~476* – Baseline nm $\bar{\epsilon}$	A ~476* – Baseline ±SD	A 660 – 690 nm $\bar{\epsilon}$	A 660 – 690 nm ±SD	A 1075 – 1200 nm $\bar{\epsilon}$	A 1075 – 1200 nm ±SD
1	61.5	3.3	68.1	1.3	77.2	3.0	19.3	0.7	28.7	2.2
2	62.8	3.3	70.1	1.1	82.0	5.4	19.6	0.4	28.9	0.9
3	56.8	4.8	66.7	2.3	78.5	3.5	18.9	1.3	29.8	0.5
4	53.8	1.2	60.5	1.0	73.1	0.4	18.6	0.5	30.5	0.2
5	42.0	1.6	51.2	0.3	64.4	1.7	17.0	0.2	30.8	0.2
6	28.3	1.3	35.1	0.9	55.1	1.0	13.1	0.6	29.6	0.2
7	11.6	2.8	18.3	1.4	44.2	1.4	8.0	0.5	27.1	0.2
8			10.8	0.5	45.7	1.3	2.7	0.2	24.2	0.4
9			12.0	1.2	59.7	8.5			22.7	1.7
10			11.8	1.2	56.8	3.3			22.0	1.2
Average RSD(%)	7.7		4.4		4.7		4.3		3.0	

* Peak shifts from 476 to 491. Readings taken at maximum peak height.
** This peak was evaluated but not used because of interference from

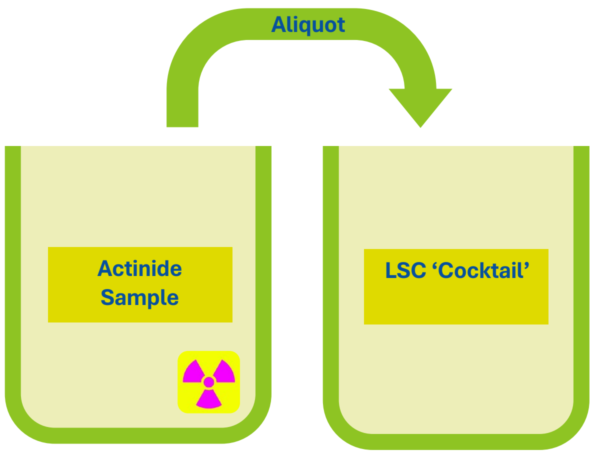




- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* **2024**, *53*, 9262.
- Hagan and Miner, The Dow Chemical Company RFP-1391, 1969.
- Hall, Herniman and Walter, Atomic Energy Research Establishment, 1951.

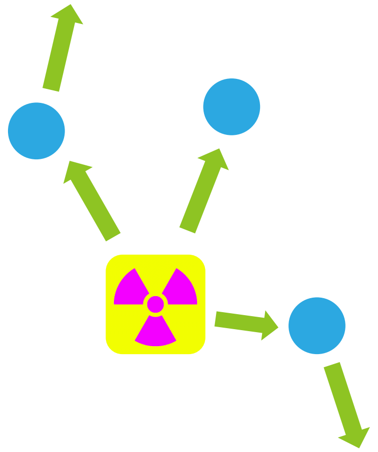
Quantification: Liquid Scintillation Counting

- Measure the radioactive activity of a sample via its decay (alpha/beta), which can then be used to quantify the element present.



Typically contains:

- **Aromatic organic solvent**
- **Surfactant**
- ***Scintillators***



Particles emitted by the sample transfer energy between solvent molecules until it reaches a phosphor.

Phosphor emits energy in the form of UV light into a photomultiplier tube.

Quantification: Gamma Spectroscopy

- Quantify radionuclides based on their characteristic gamma spectrum.

Acknowledgements

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Gregory Holmbeck

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