Development of a separation procedure for a mock ^{224}Ra pigment sample for future nuclear forensic analyses

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[3]Los Alamos National Laboratory, Nuclear and Radiochemistry (C-NR) Group

NSSC Fall Workshop and Advisory Board Review
October 17-18, 2023

Introduction

Outline

Department: Chemistry at Texas A&M University
Academic Advisor: Prof. Charles M. Folden III
NSSC Research Focus Areas: Nuclear Forensics/Radiochemistry
Planned Graduation Date: December 2024
Lab Mentor and Partner Laboratory: Dr. Evelyn Bond at LANL

This work aims to bring awareness to ^{226}Ra pigments and paints potential usage in nuclear terrorism attacks

- ^{226}Ra was used in pigments and paints in the early 1900's
  - IAEA identifies ^{226}Ra as a potential threat
    - Threat of nuclear terrorism events
    - Dirty bombs (RDDs)
- Nuclear forensics analysis
  - Pioneer nuclear forensics for ^{226}Ra materials
  - Nuclear forensic "signatures"

D. I. Harvie, Endeavour **23**, 100 (1999). doi:10.1016/S0160-9327(99)01201-6
S. Friedrich, R. Stan, and Z. Lyudmila, AIP Conf. Proc. **1034**, 3 (2008). doi:10.1063/1.2991254

Goals of my thesis project

Outline

<u>Developing a nuclear forensic database</u>

- Radiochronometry
  - Developing radiochemical analysis procedures
    - Dissolution of pigment
    - Separation of elements
  - Gamma spectrometry
  - Alpha spectrometry
  - ICP-MS
- Trace metal analysis
  - Developing radiochemical analysis procedures
  - ICP-MS

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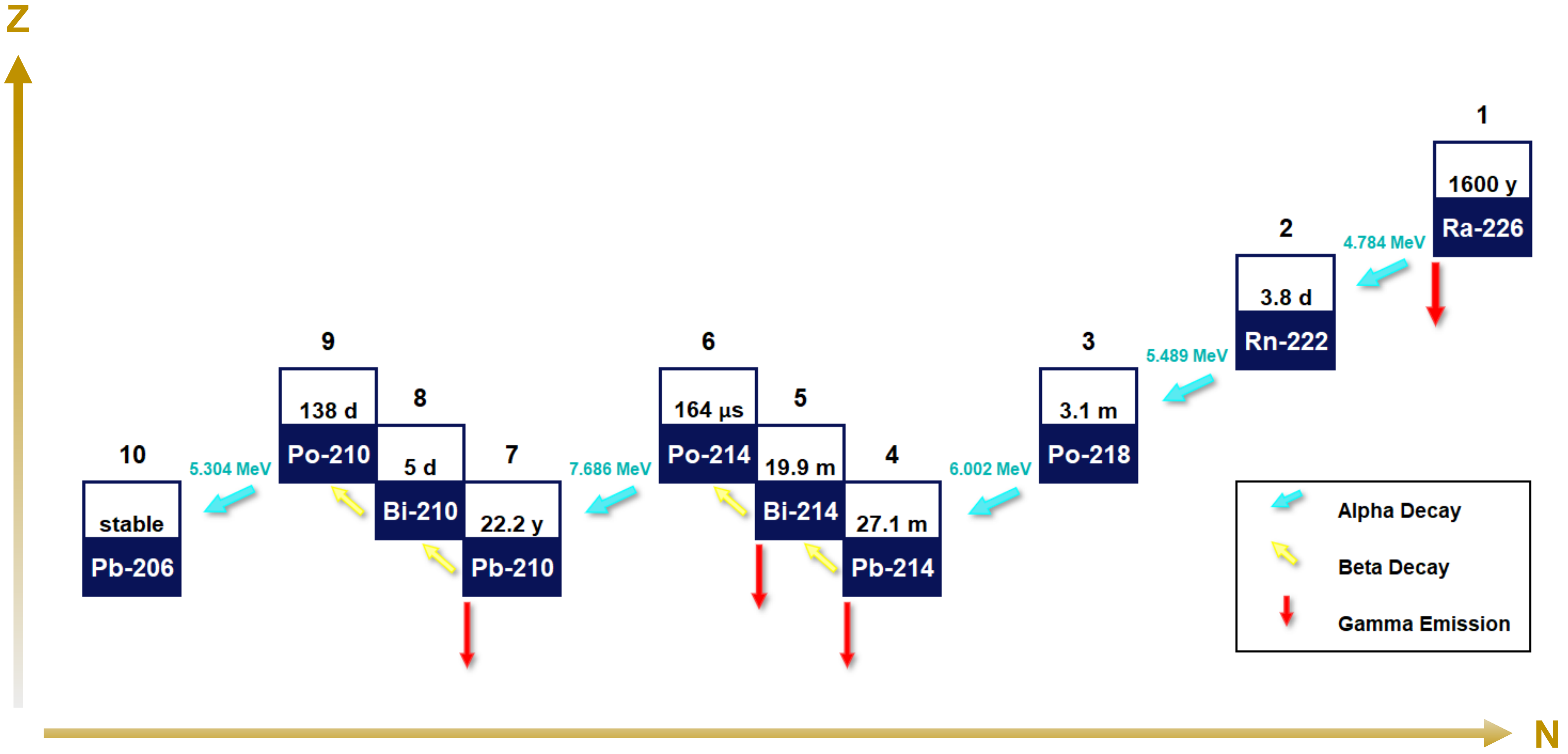
Selecting chronometers from the ^{226}Ra decay scheme

Outline



Selecting chronometers from the ^{226}Ra decay scheme

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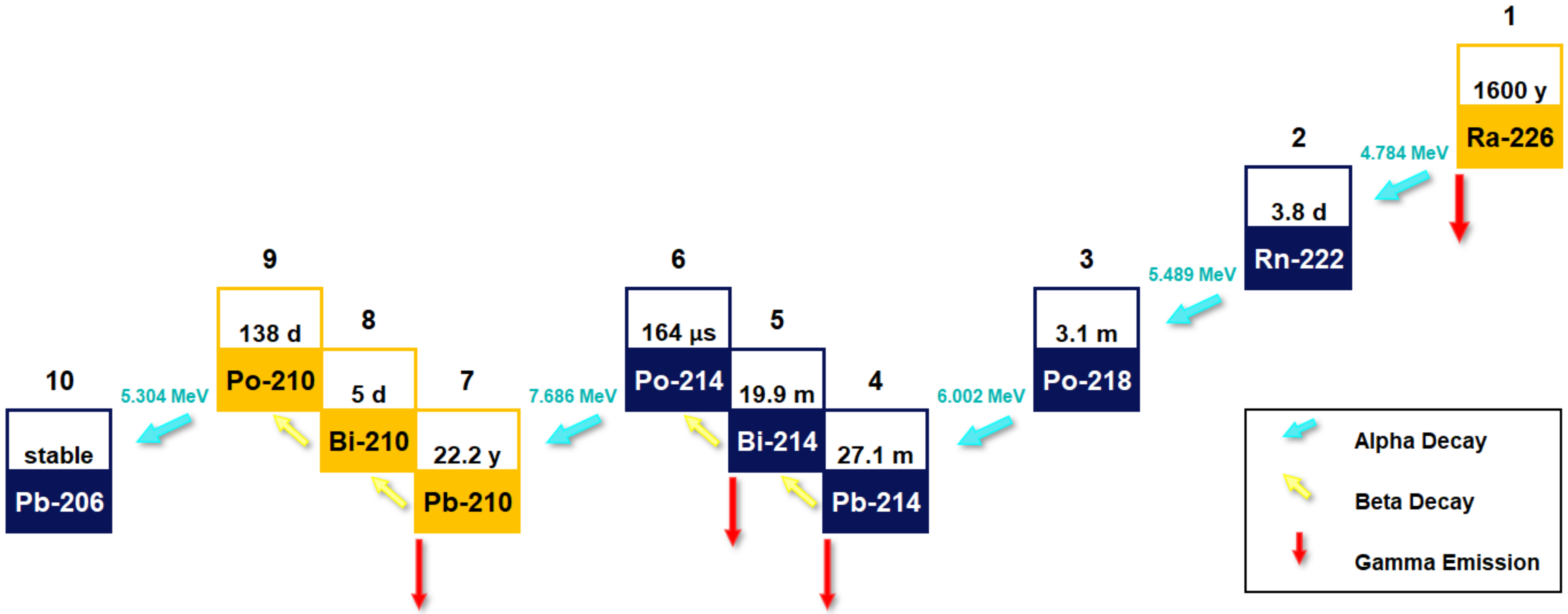


Conclusions from last report (UPR 2023)

Outline

Towards a radiochronometric analysis on the ^{226}Ra pigment sample

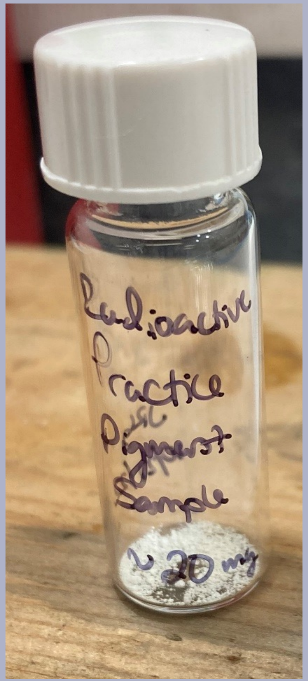
^{224}Ra Mock Pigment Sample

Based on Historical Components

~99% ZnS
~1% RaX_2

X = Cl or Br

^{226}Ra is subbed with ^{224}Ra



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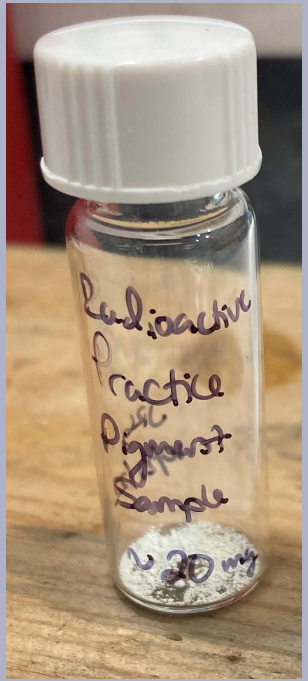
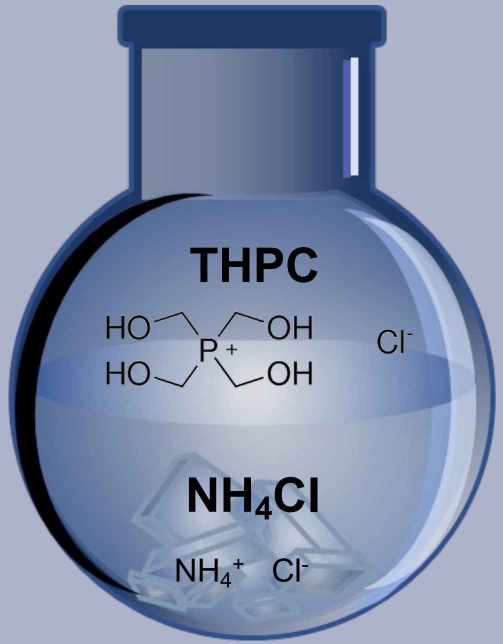


Dissolution using THPC & NH_4Cl



Dissolution Efficiency

100%

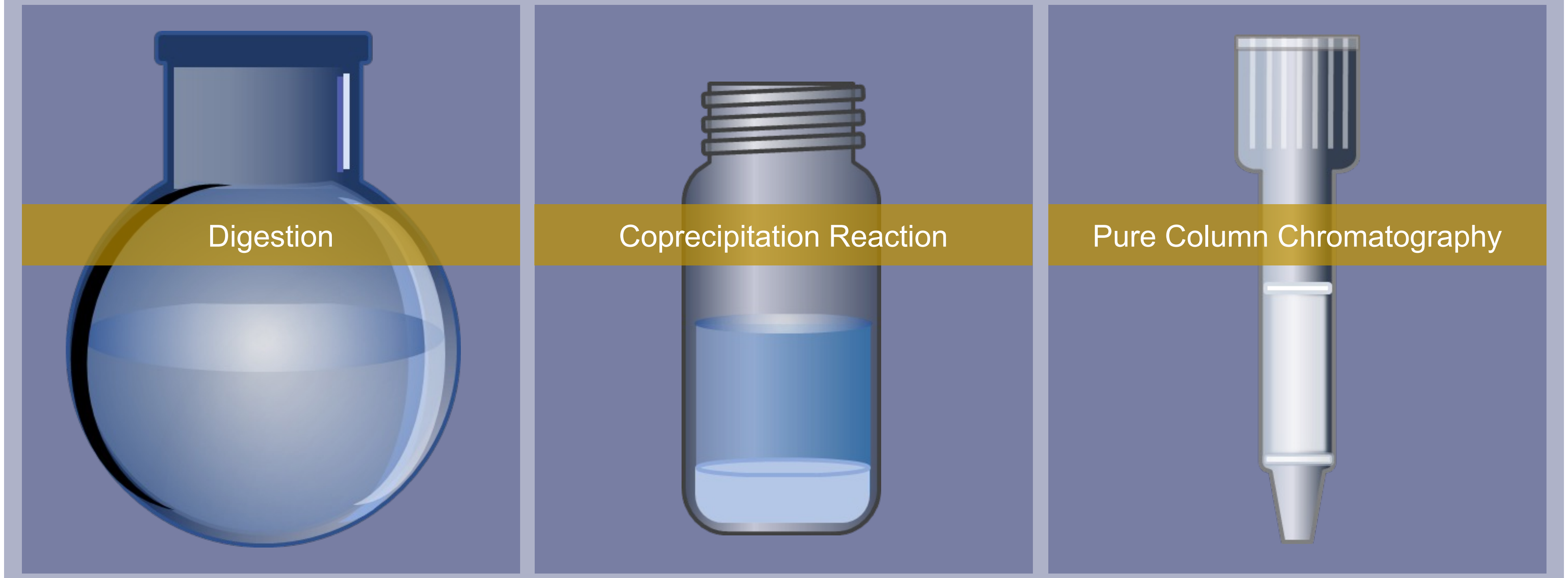
ZnS
$BaCl_2$
$RaCl_2$
$PbCl_2$

Progress outline towards a separation procedure

Outline

Towards a radiochronometric analysis on the ^{226}Ra pigment sample

Separation of Elements within the Pigment Sample



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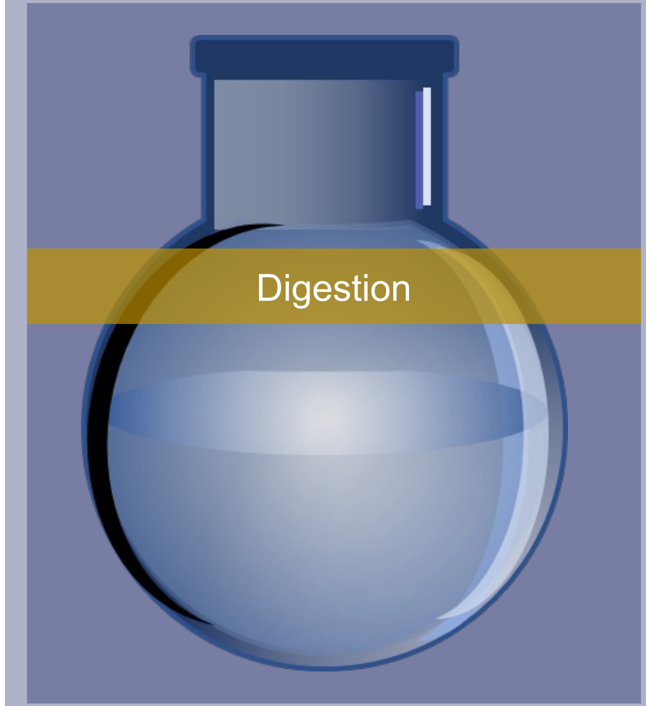
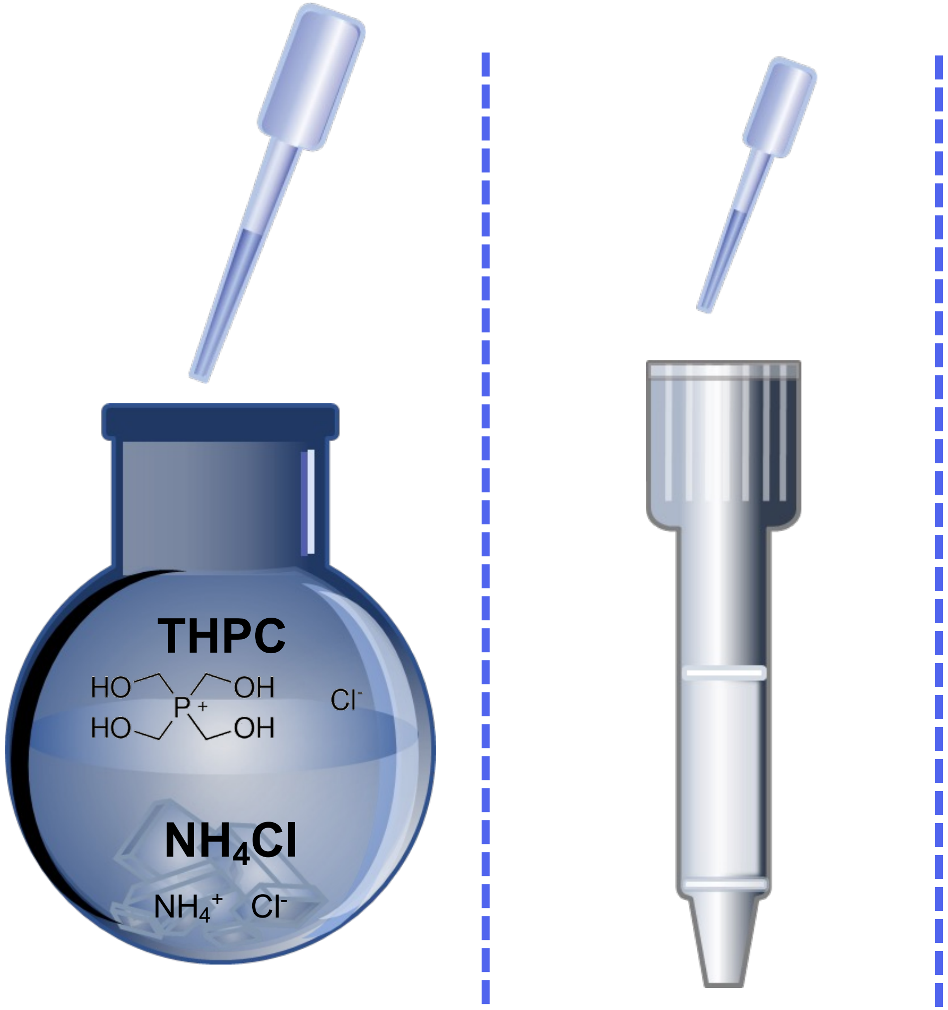


An ideal world for a separation pathway

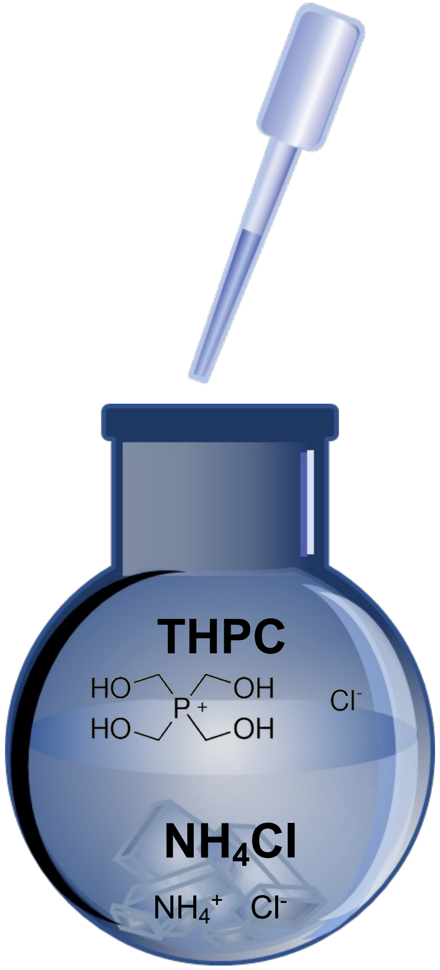
Outline

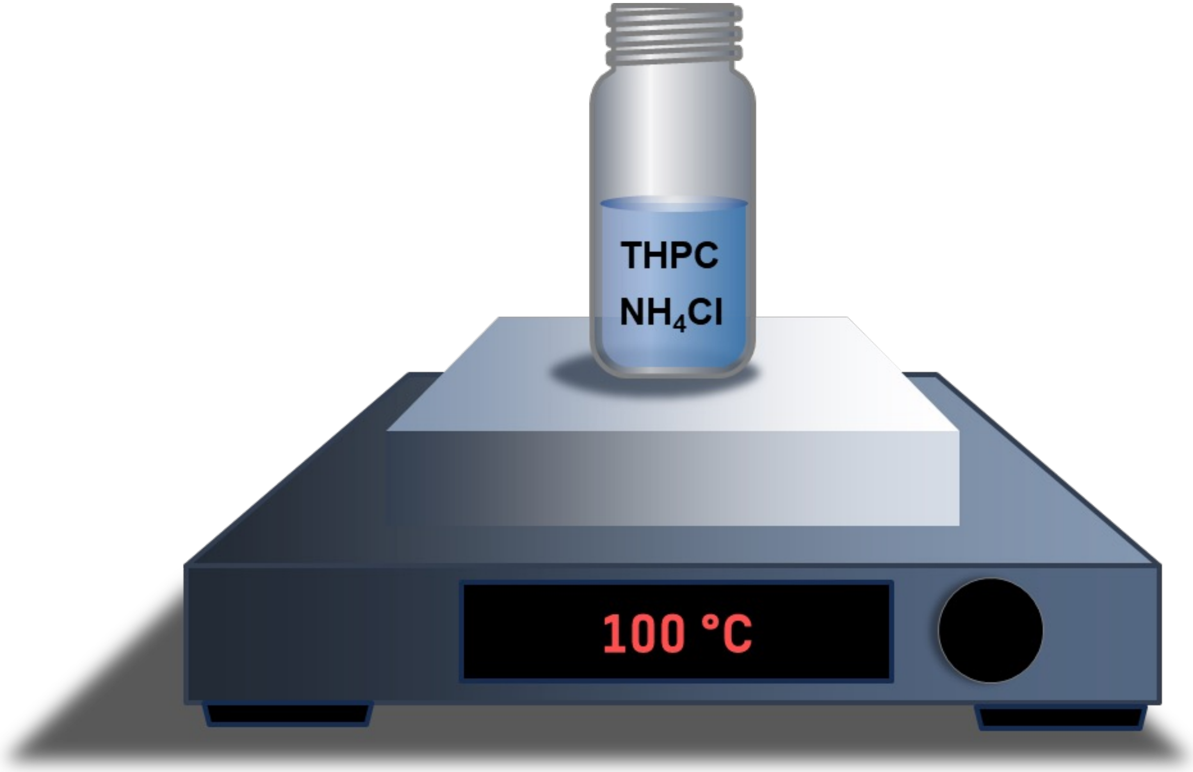


- Ideally, I take an aliquot from the dissolved solution and load onto a column
- There is NO literature regarding elemental behavior in THPC & NH_4Cl
- The long way is to measure this behavior…
- Can I convert this solution to what is known?
  - HCl solutions
  - HNO_3 solutions

Typical procedure to convert between salts

Outline





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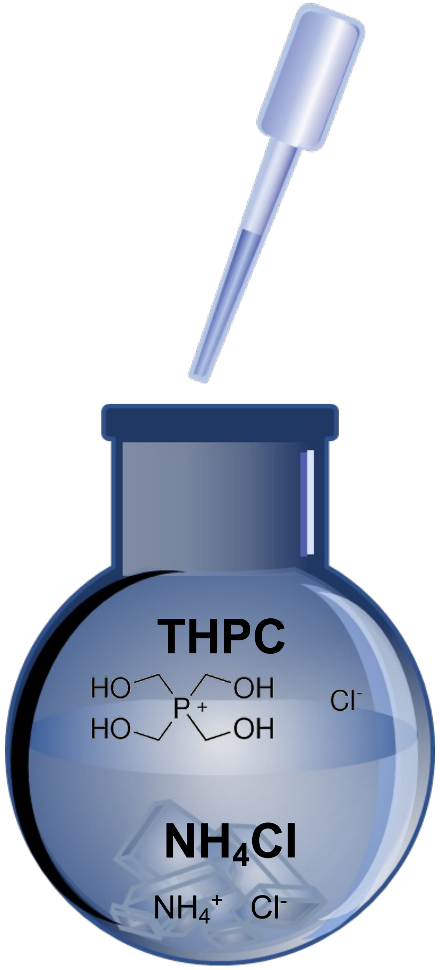

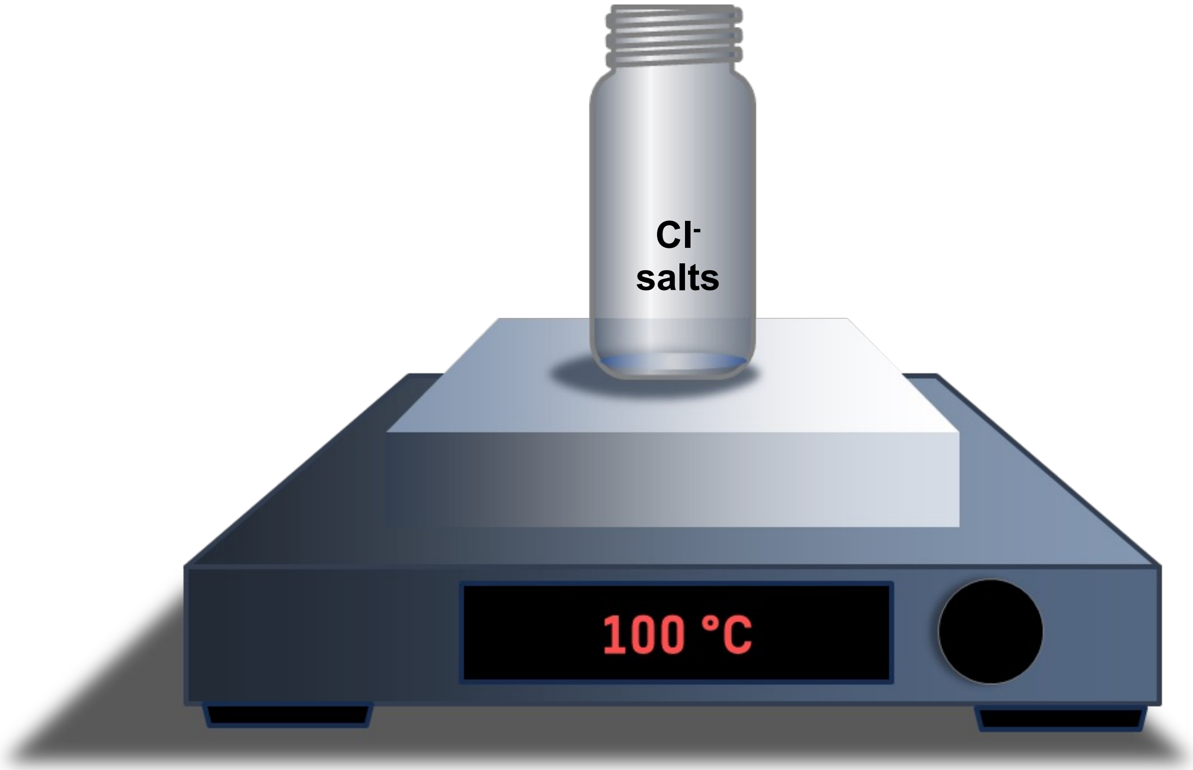

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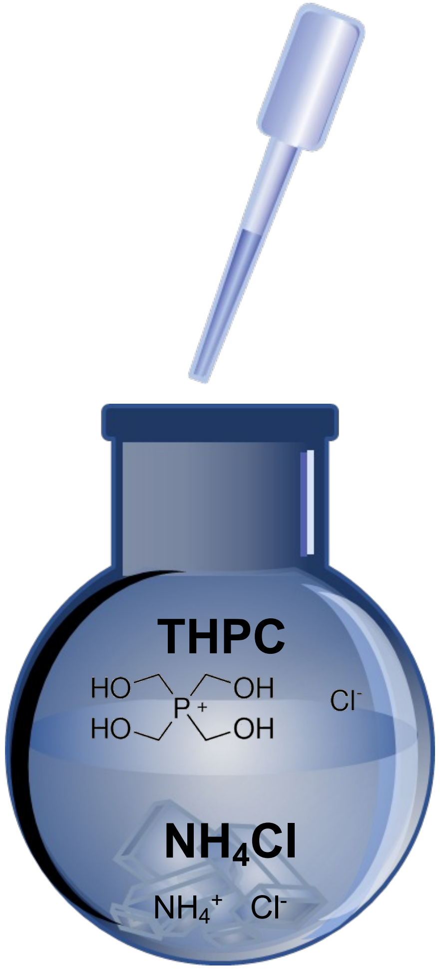

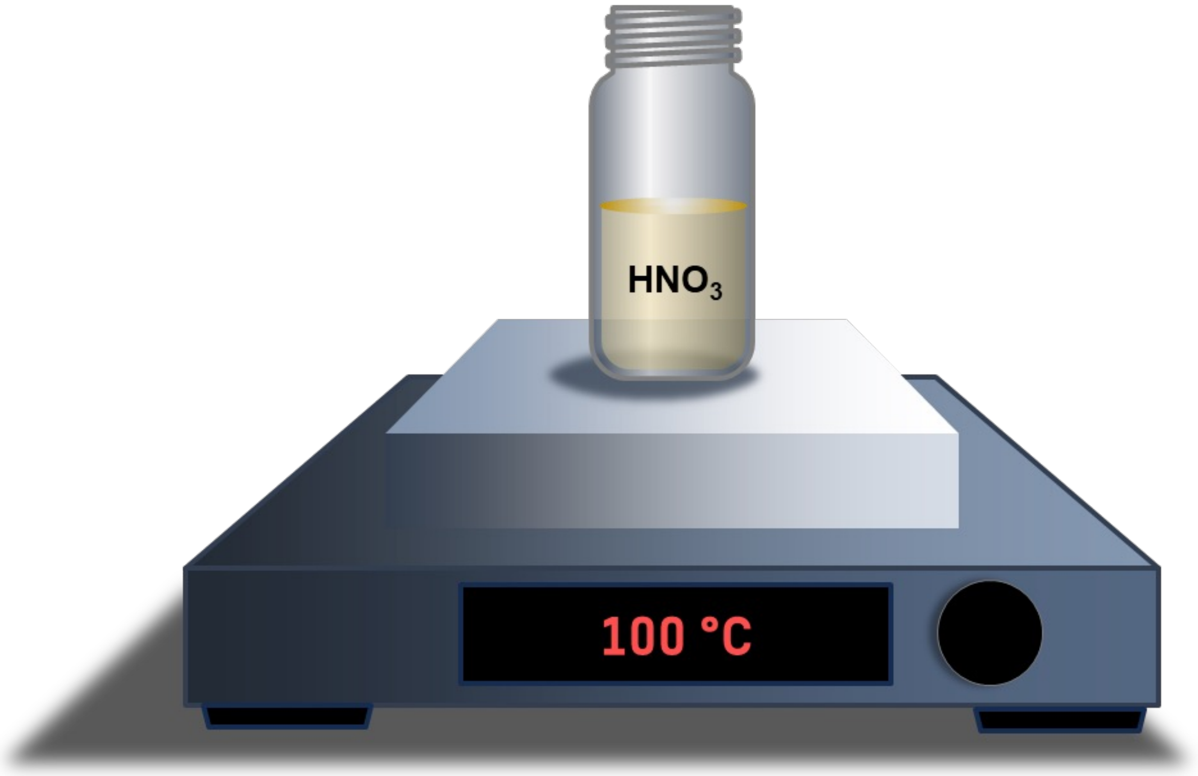

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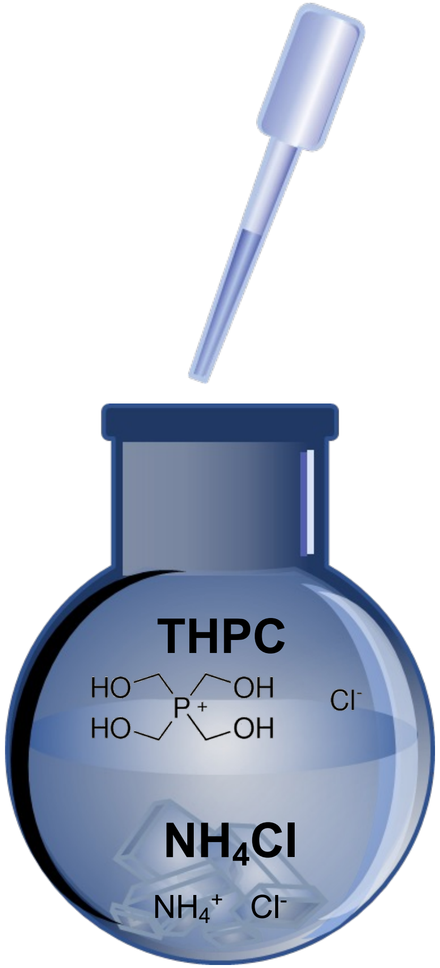
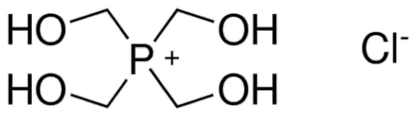


Why consider a digestion pathway to separation?

Outline

- Unfortunately, evaporation leaves behind this residue
- THPC is highly hygroscopic
- Higher temperatures cause decomposition and leave a viscous syrup
- I need a way to destroy THPC

- Digestion is a chemical technique used to break down large molecules
- THPC is an organic molecule



- Solutions of HNO_3 are most relevant

Progress outline towards a separation procedure

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    - Goals
    - Digestion
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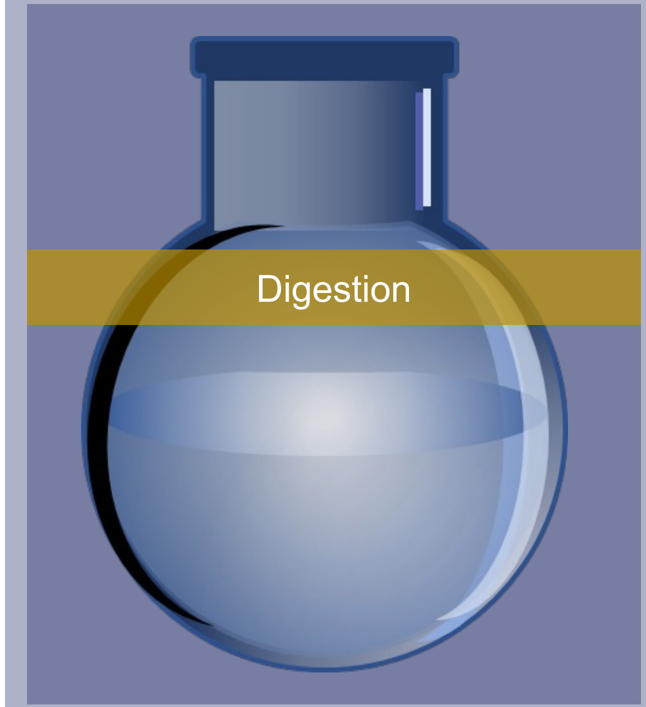
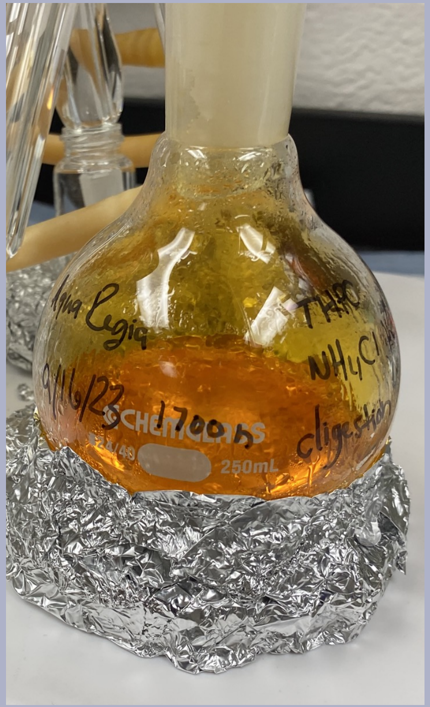
    - Column Chrom.
- Conclusion
- NSSC Experience
- Acknowledgement
- Questions?

<u>Towards a radiochronometric analysis on the ^{226}Ra pigment sample</u>

Separation of Elements within the Pigment Sample





Progress outline towards a separation procedure

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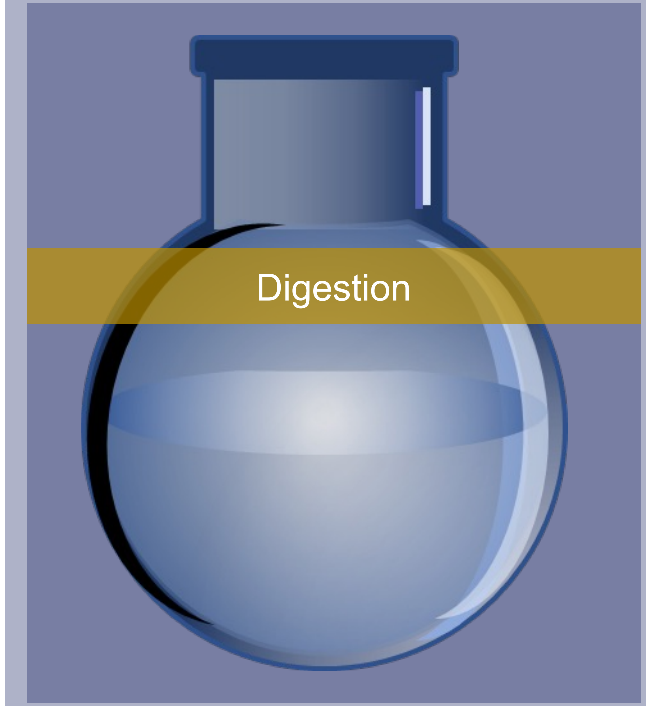
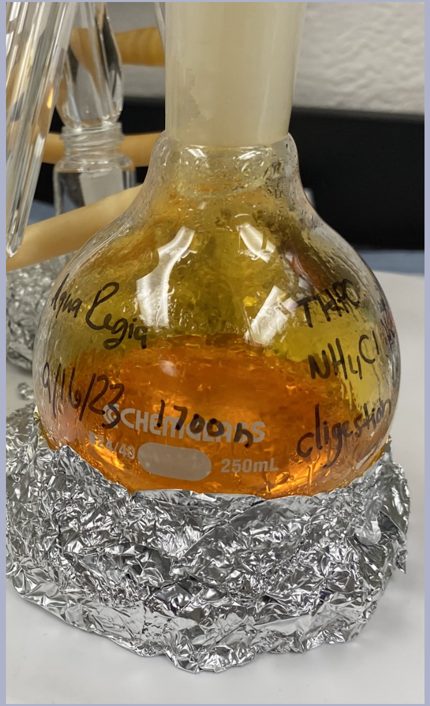
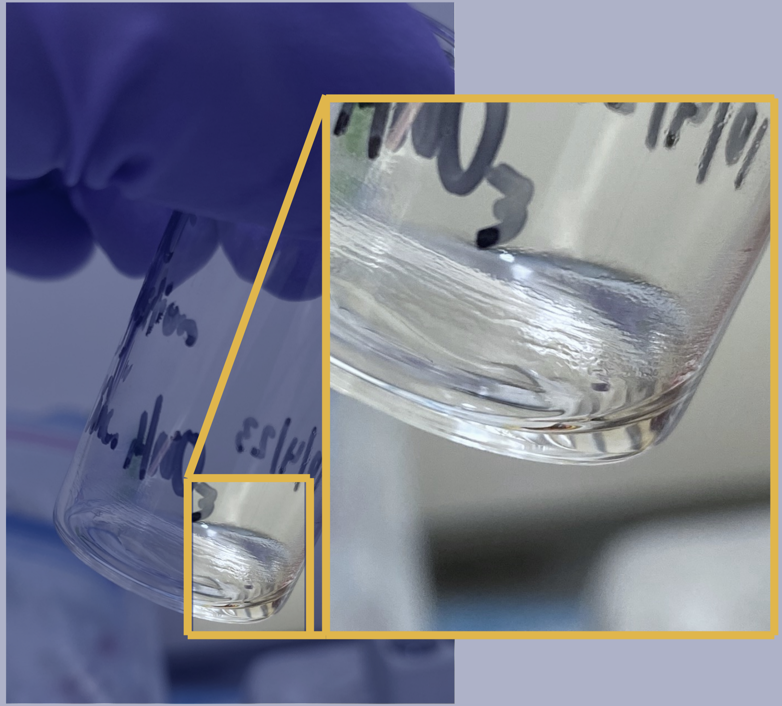


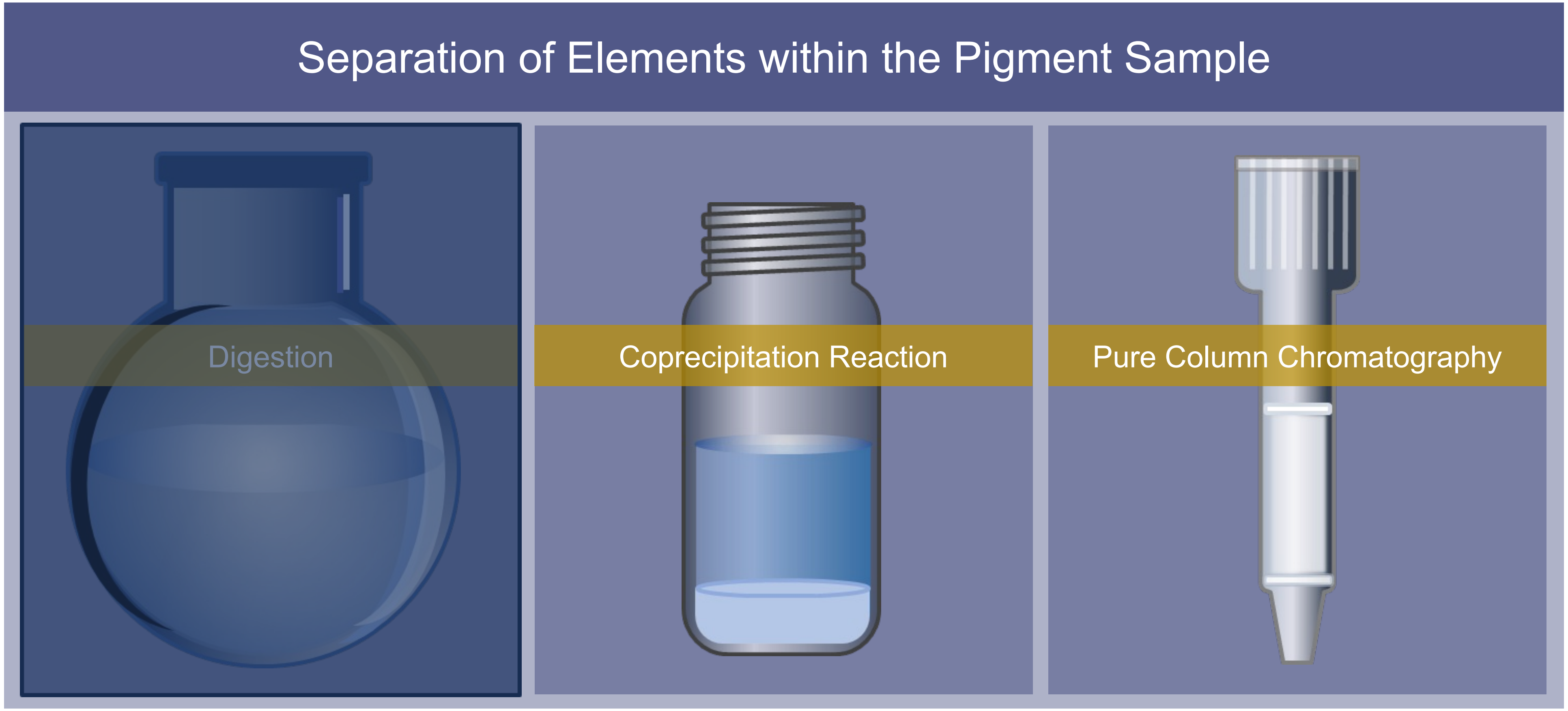




Progress outline towards a separation procedure

Outline

Towards a radiochronometric analysis on the ^{226}Ra pigment sample



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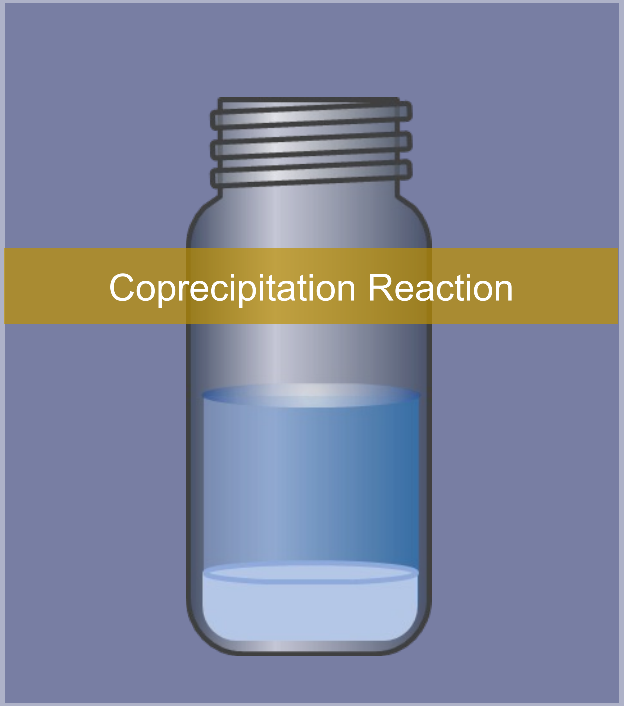
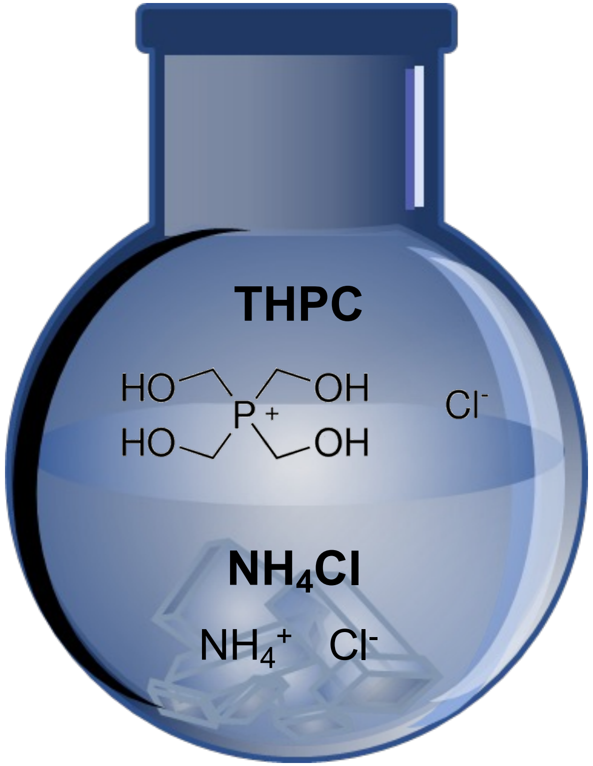


Identifying the precipitate for coprecipitation

Outline



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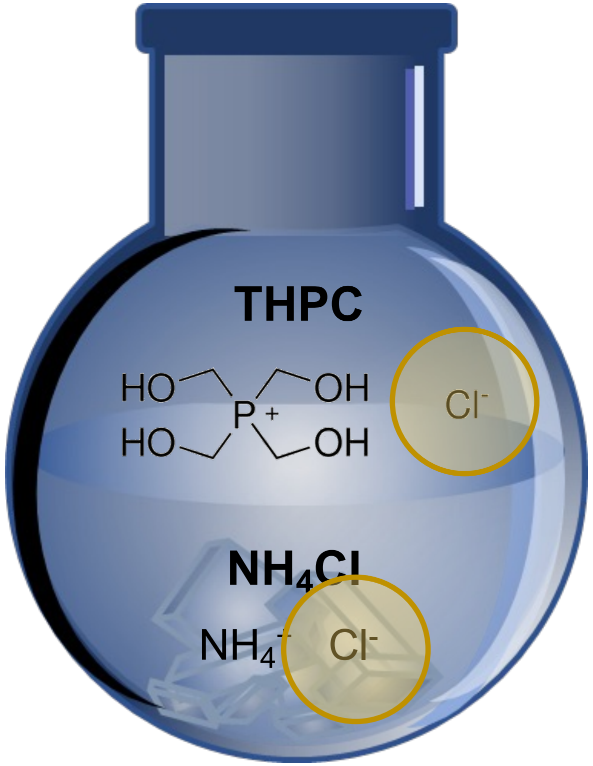

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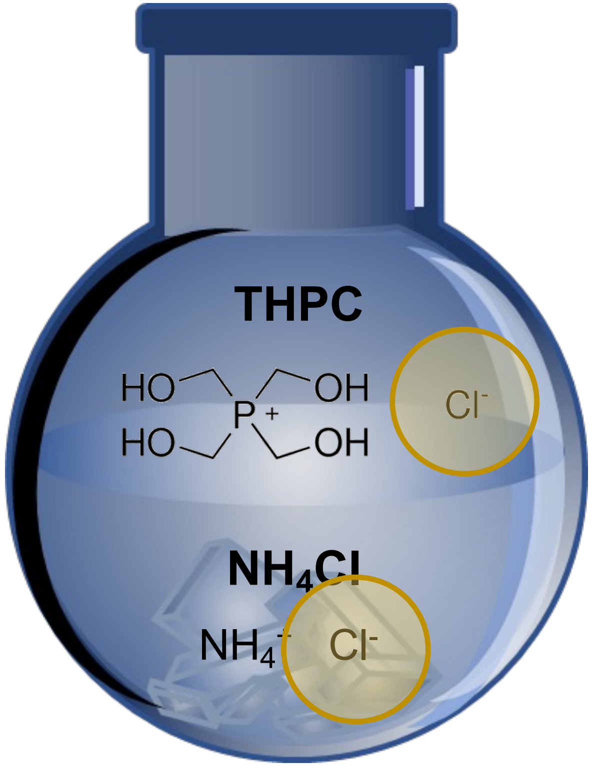

$AgNO_{3(s)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} + NO_{3}^{-}{}_{(aq)}$

- Adding silver nitrate could potentially precipitate silver chloride
- Activity could coprecipitate along with the silver chloride
- Silver chloride can be separated from the THPC & NH_4Cl solution

Coprecipitation experimental procedure

Outline

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  - Model Age
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    - Coprecipitation
    - Column Chrom.
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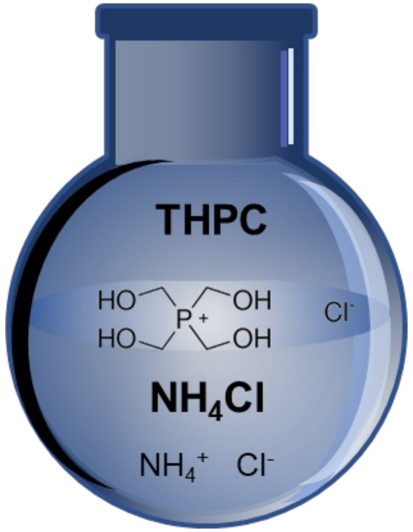
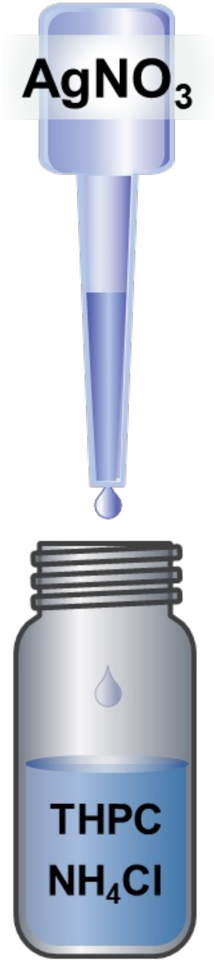
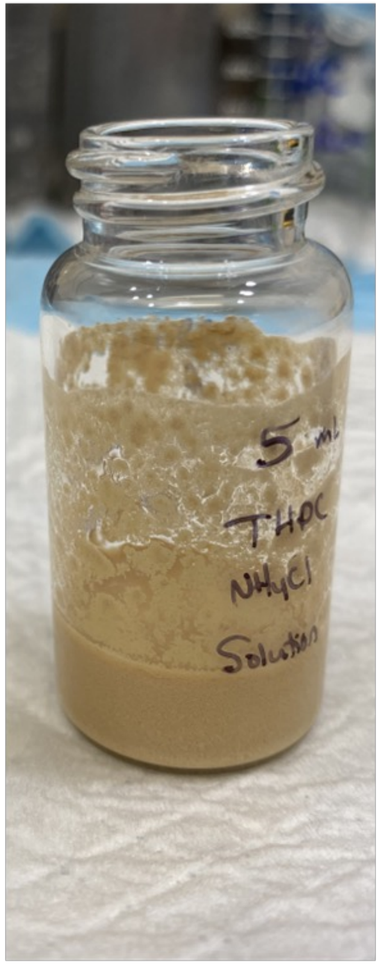
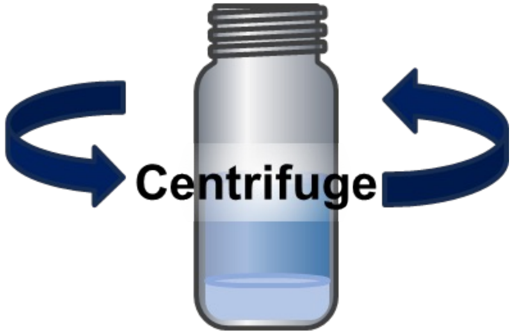
- Questions?

Dissolution with normal experimental conditions





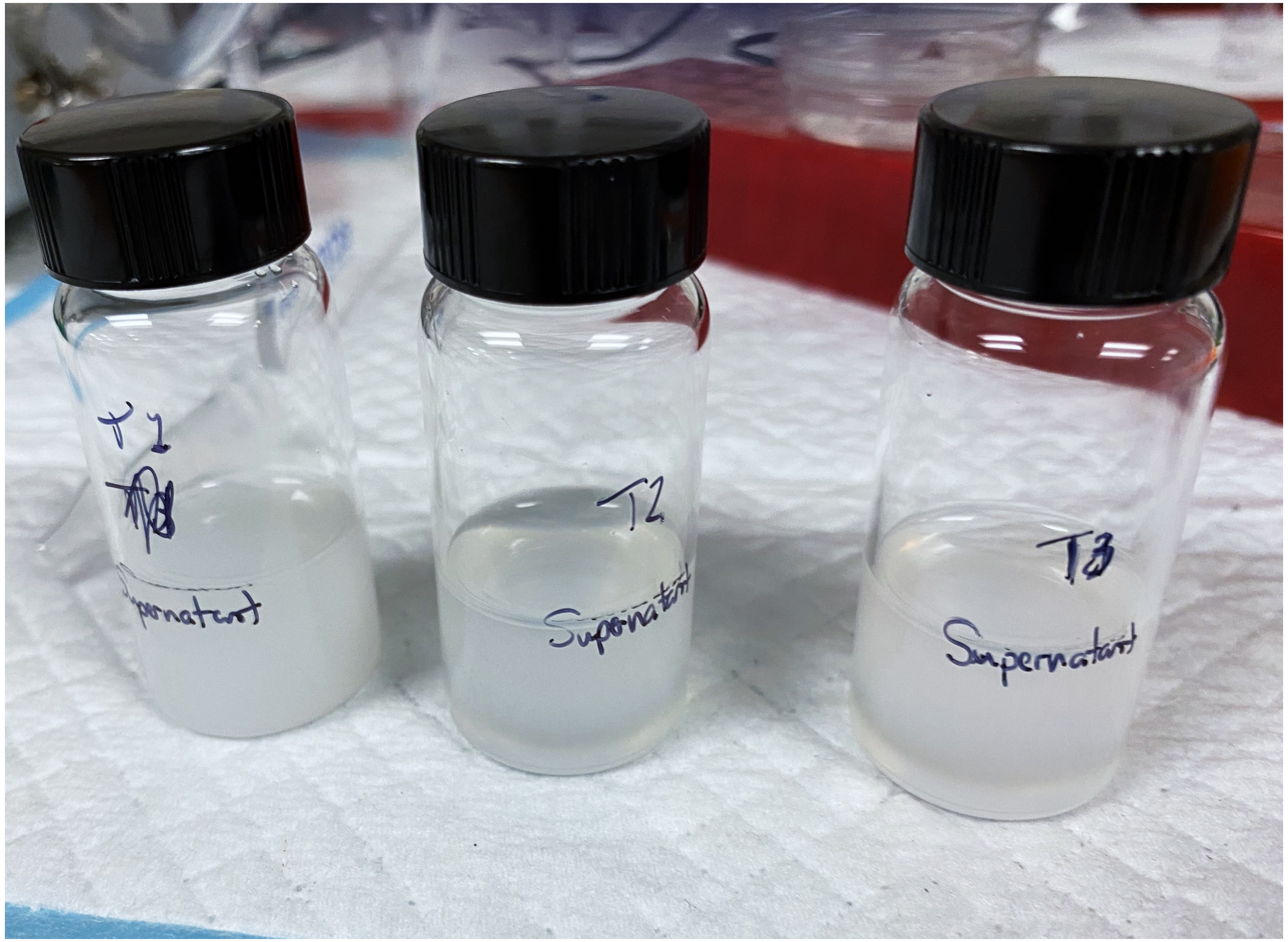




Collect supernatant and compare with initial activity

Coprecipitation experimental results and conclusions - Preliminary Data

Outline



Experimental Conclusions

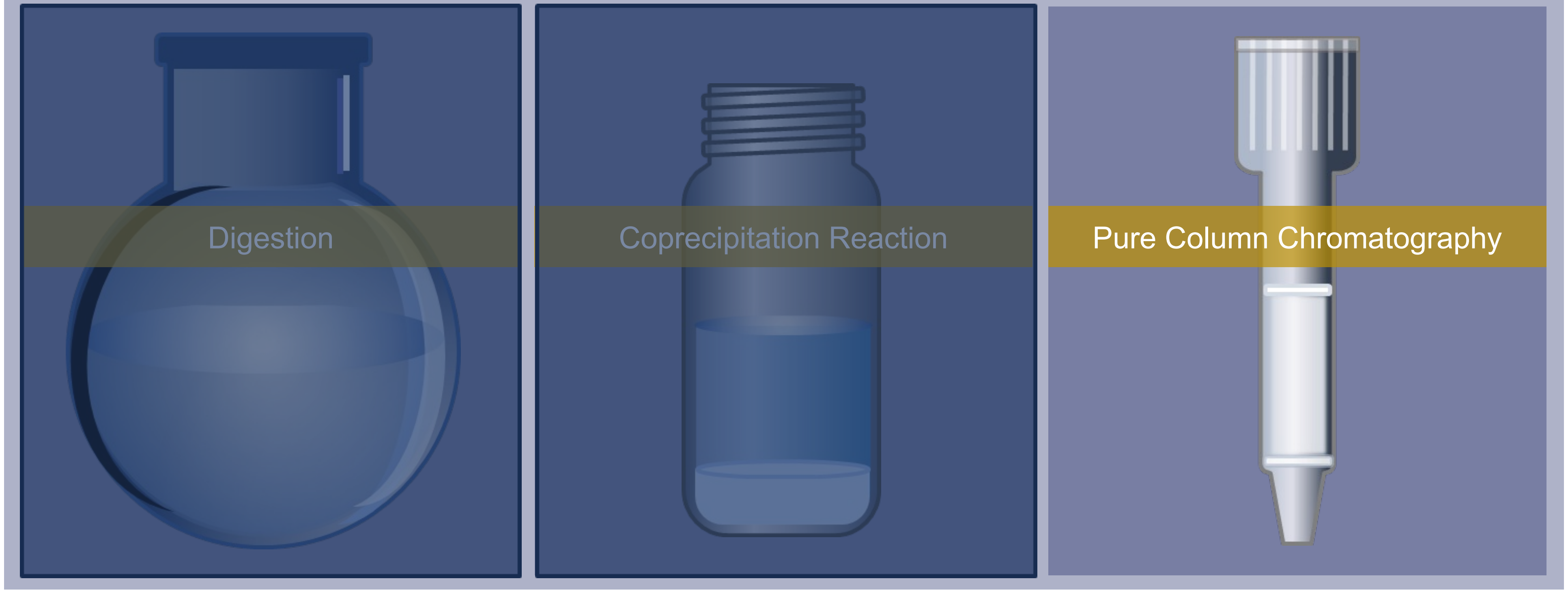
- Activity recovered in the supernatant was 79 ± 1%
- This means the amount coprecip-itated was 21 ± 1%
- Overall, this experiment was found ineffective for the recovery of activity

Progress outline towards a separation procedure

Outline

Towards a radiochronometric analysis on the ^{226}Ra pigment sample

Separation of Elements within the Pigment Sample



Progress outline towards a separation procedure

Outline

Towards a radiochronometric analysis on the ^{226}Ra pigment sample

Separation of Elements within the Pigment Sample

Pure Column Chromatography

Progress outline towards a separation procedure

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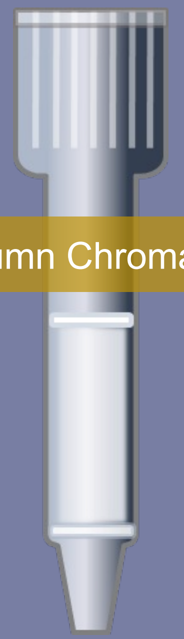
Towards a radiochronometric analysis on the ^{226}Ra pigment sample

Separation of Elements within the Pigment Sample

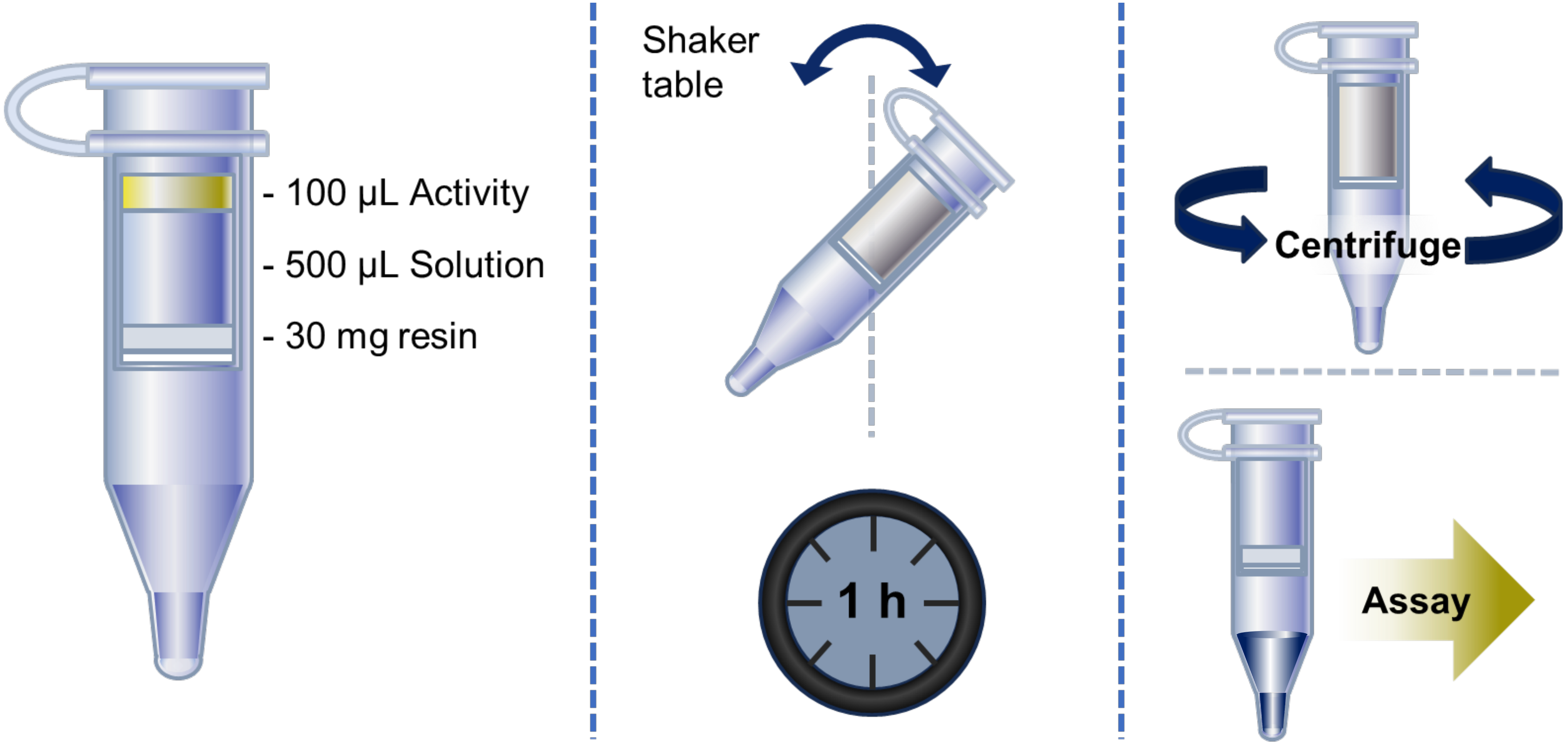
- Elemental behavior in the THPC/NH_4Cl matrix is unknown in all resins
- The weight distribution ratios (D_w) need to be measured to determine this behavior
- These values can be used to determine a separation pathway between elements
- D_w values are measured via batch study experiments



Pure Column Chromatography

Batch study experimental procedure

Outline

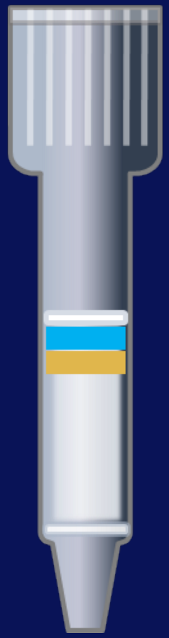


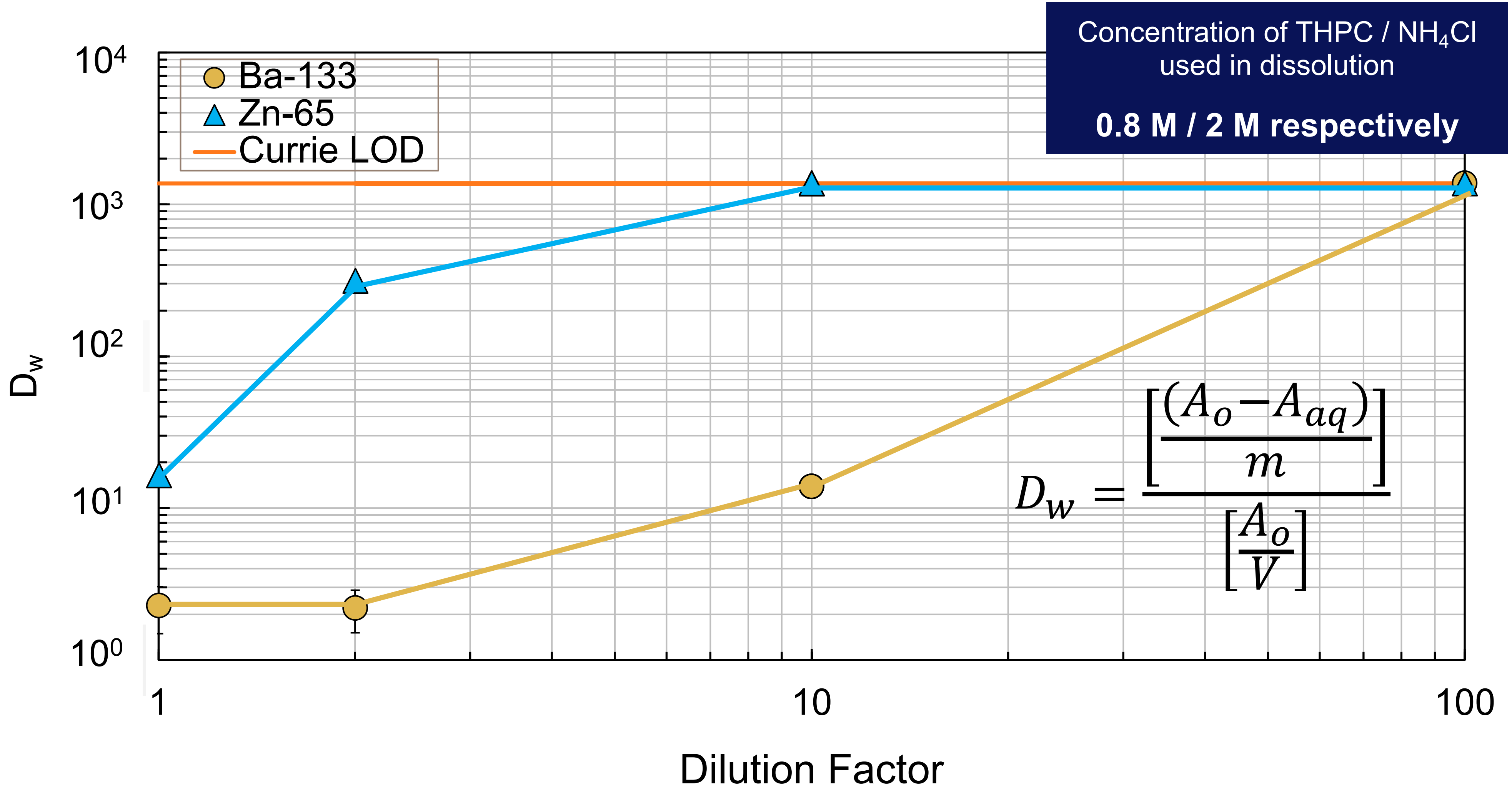
D_w values for Ba-133 and Zn-65 on Chelex-100 in THPC/NH_4Cl – Preliminary Data

Summary

Dilute THPC/NH_4Cl

Ba and Zn adsorb



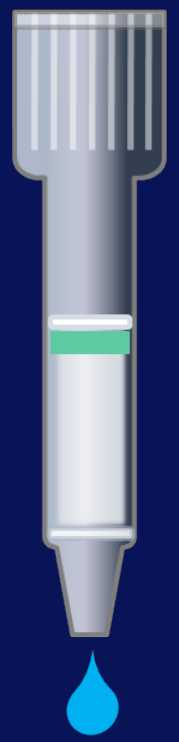


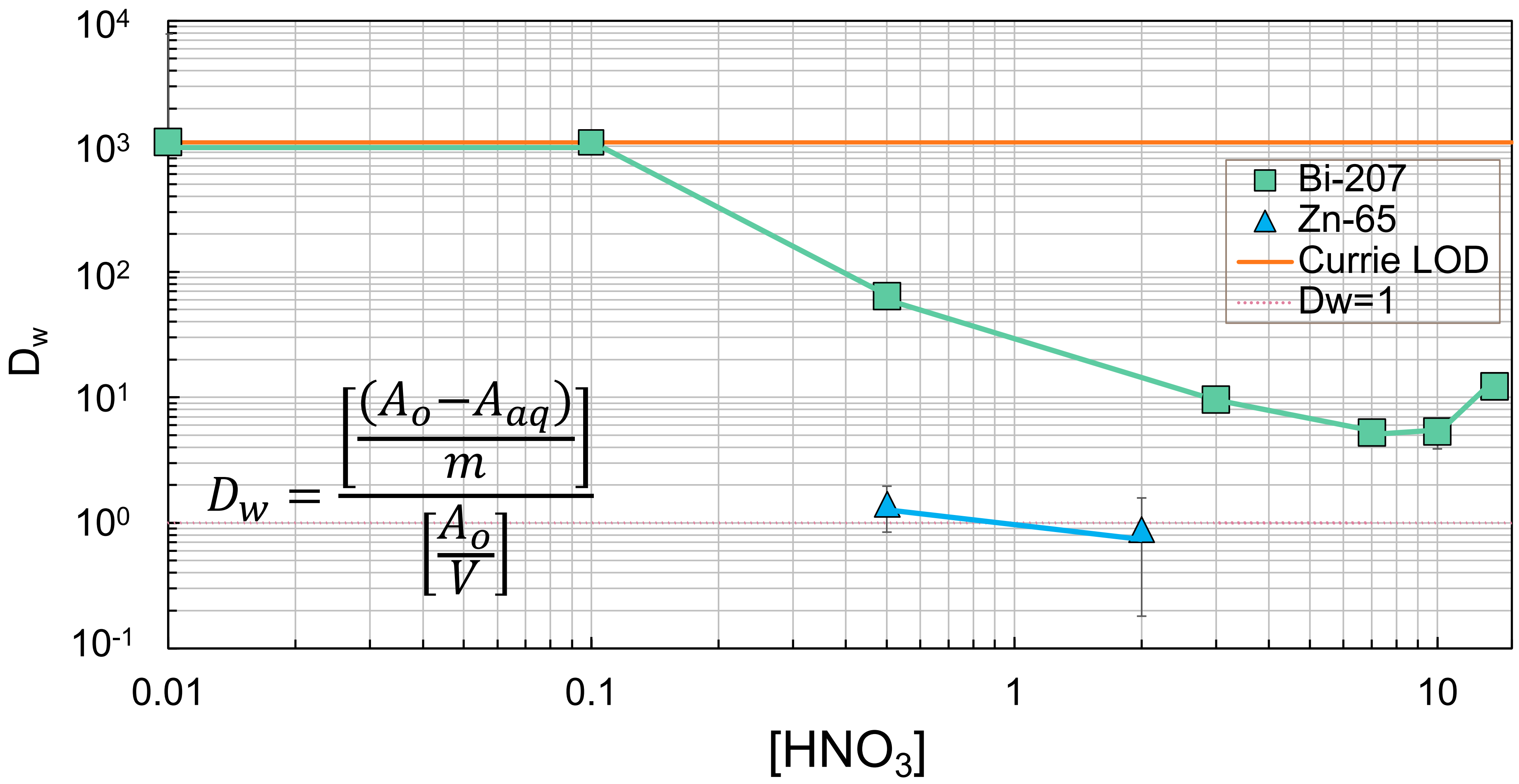
D_w values for Bi-207 and Zn-65 on Chelex-100 in HNO_3 – Preliminary Data

Summary

0.5 M HNO_3

Bi and Zn separation



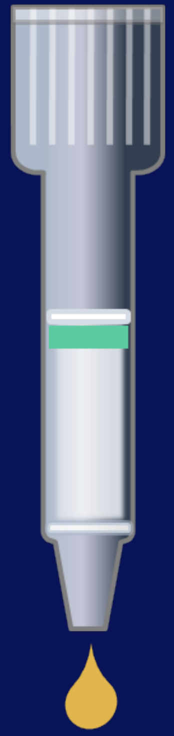


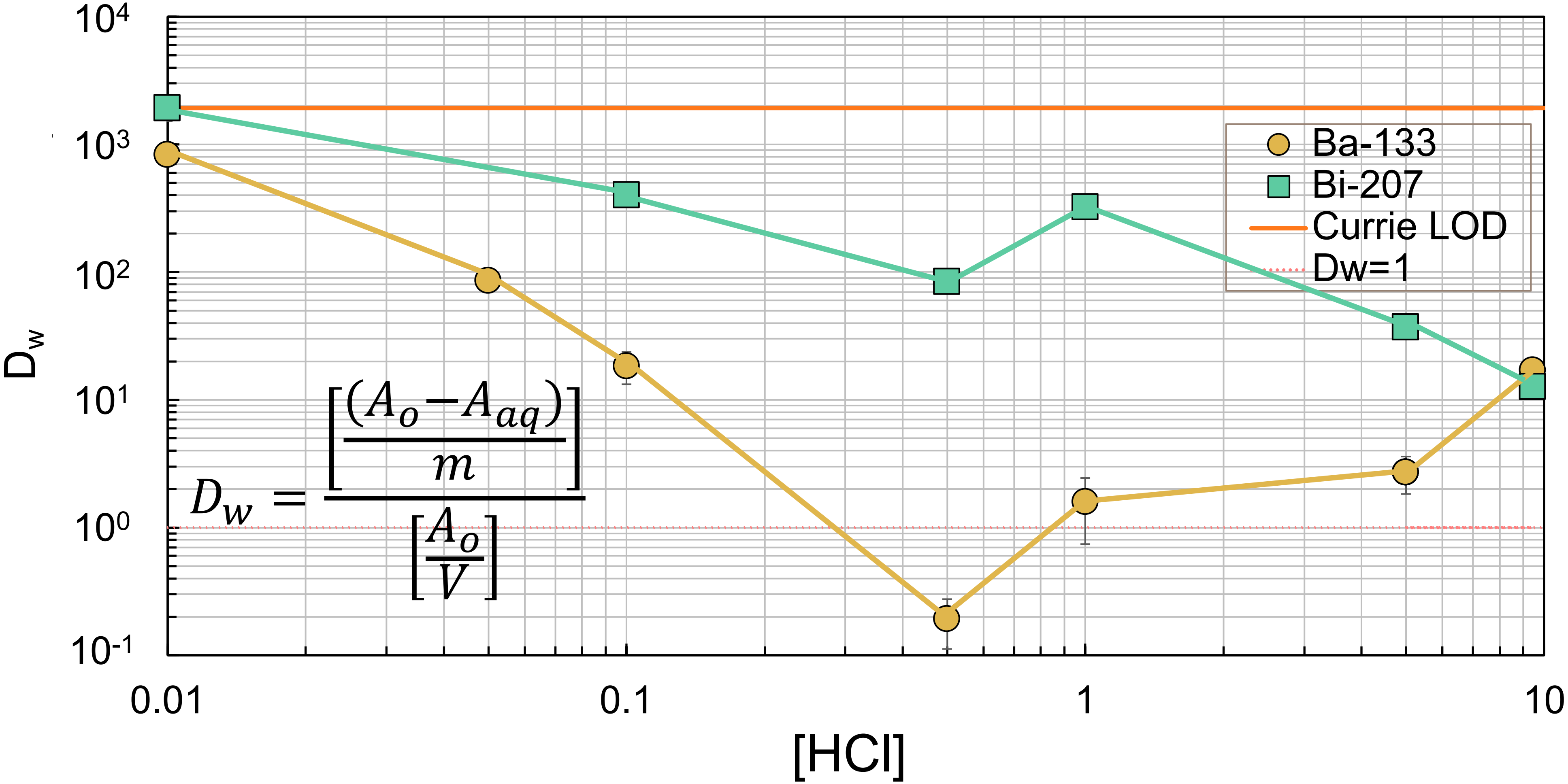
D_w values for Ba-133 and Bi-207 on Chelex-100 in HCl – Preliminary Data

Summary

0.5 M HCl

Bi and Ba separation





$$D_w = \frac{\left[\frac{(A_o - A_{aq})}{m}\right]}{\left[\frac{A_o}{V}\right]}$$

Conclusions / Future Work

Outline

Conclusions

- Three different separation pathways are currently being explored
- Thus far, digestion and coprecipitation are not viable pathways
- Separation via column chromatography can be achieved among different acids in Chelex-100 resin

Future Work at Texas A&M

Column chromatography will be the main focus

Finish collecting D_w values

More batch study experiments are underway

Bi-207 | Chelex-100 | THPC & NH_4Cl
Po-209 | Chelex-100 | THPC & NH_4Cl
Pb-212 | Chelex-100 | THPC & NH_4Cl
Ba-133 | Chelex-100 | HNO_3
Zn-65 | Chelex-100 | HCl
Etc…

Determine a proper separation scheme

Execute procedures on historical sample 2024

The NSSC Experience

Outline

- Radium forensics thesis project
- NSSC Keepin Program 2021
  - LANL: Dr. Evelyn Bond
  - Autoradiography of Ir-192/Ir-193
- GW Nuclear Policy Security Bootcamp 2021
- Seaborg Fellowship 2022
  - LANL: Dr. Evelyn Bond
  - Radium forensics
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  - LANL: Dr. Evelyn Bond
  - Radium forensics

Acknowledgements

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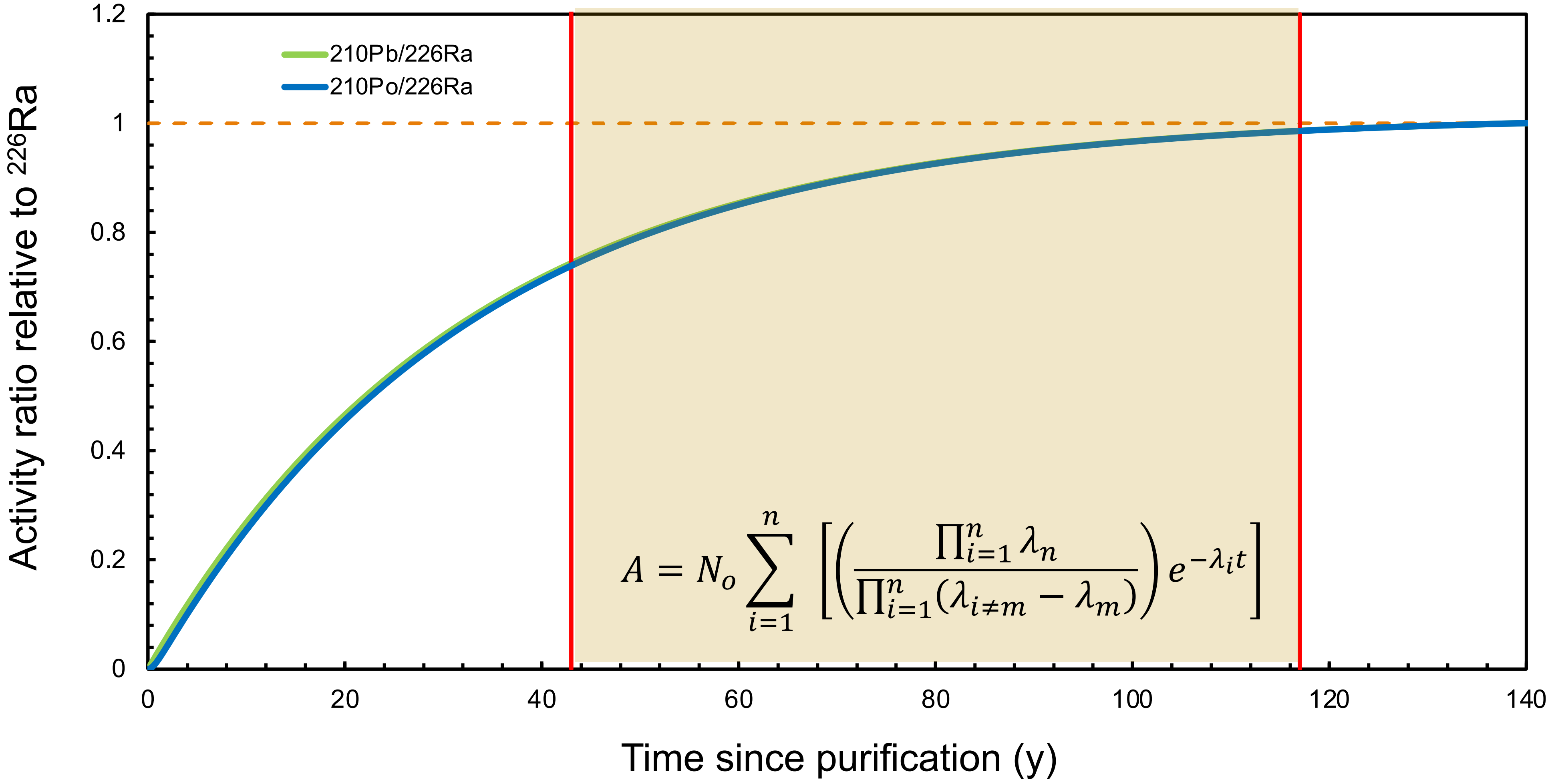
Questions?

Outline

Model age of ^{226}Ra pigments and paints

Outline

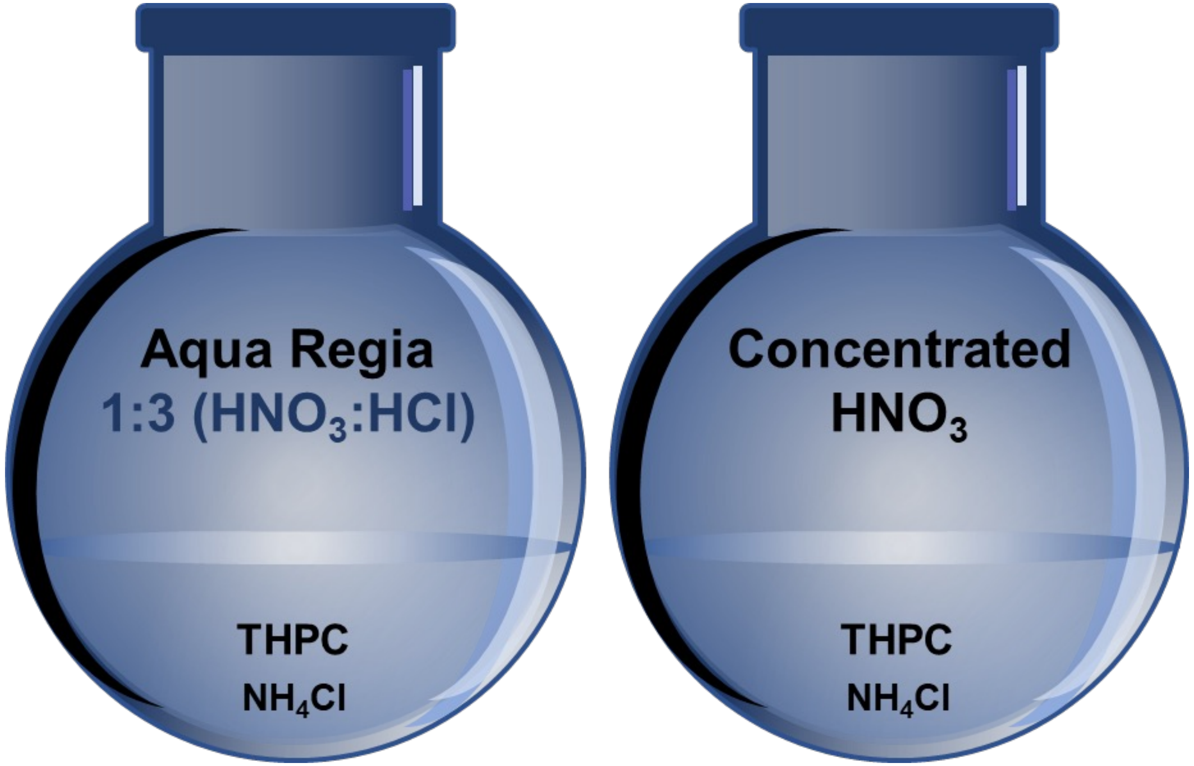


$$A = N_o \sum_{i=1}^{n} \left[\left(\frac{\prod_{i=1}^{n} \lambda_n}{\prod_{i=1}^{n} (\lambda_{i \neq m} - \lambda_m)} \right) e^{-\lambda_i t} \right]$$

M. Vobecký, Czechoslov. J. Phys. **49**, 35 (1999). doi:10.1007/s10582-999-0004-9
G. F. Kunz, (1905). patent number:789,811

Digestion experimental details

Outline



Experimental Details

- 10 mL THPC/NH_4Cl solution
- 40 mL of digestion solution
- 2 days refluxing

- If an aliquot evaporates to dryness, then we have success!

Digestion experimental results and conclusions - Preliminary Data

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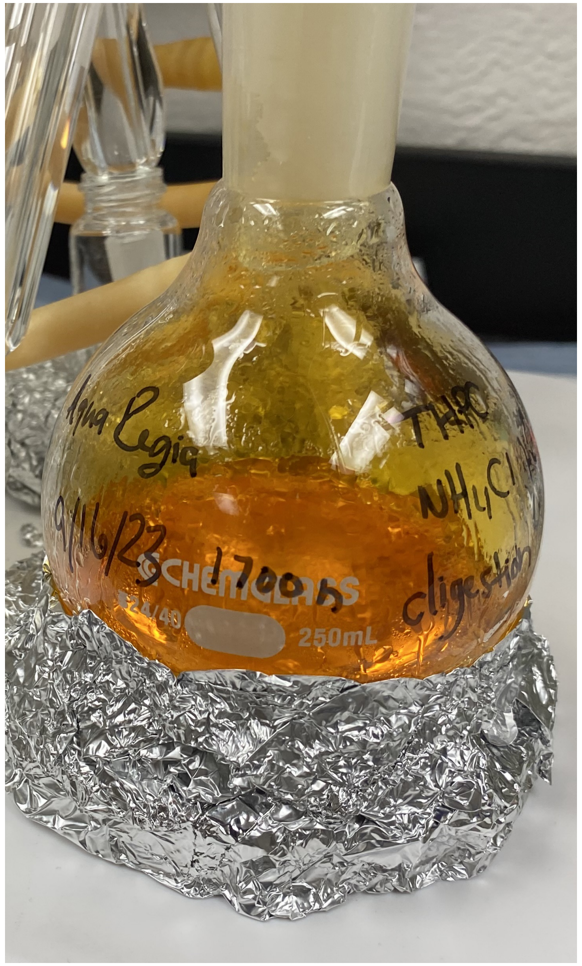
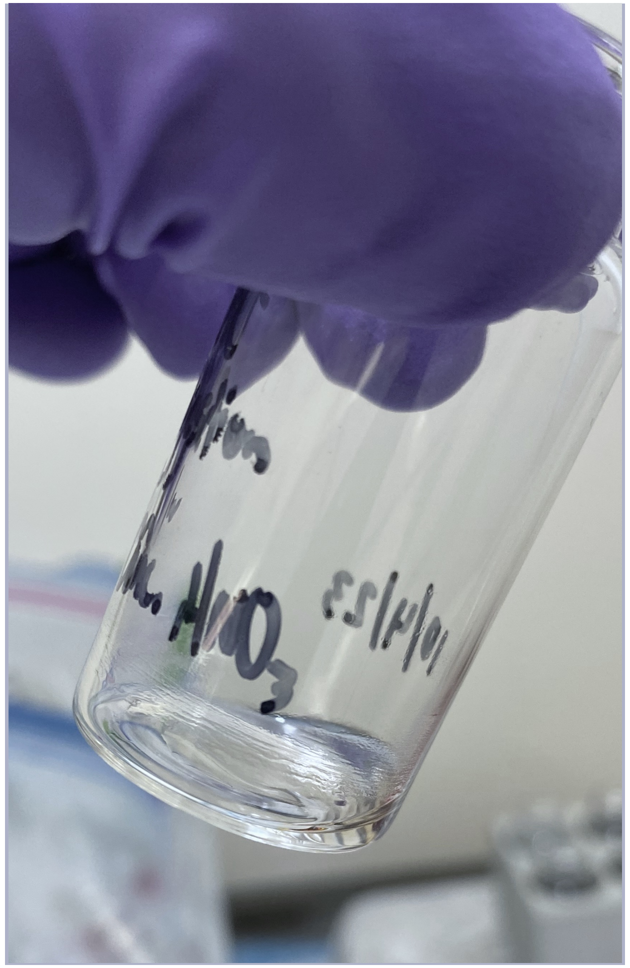


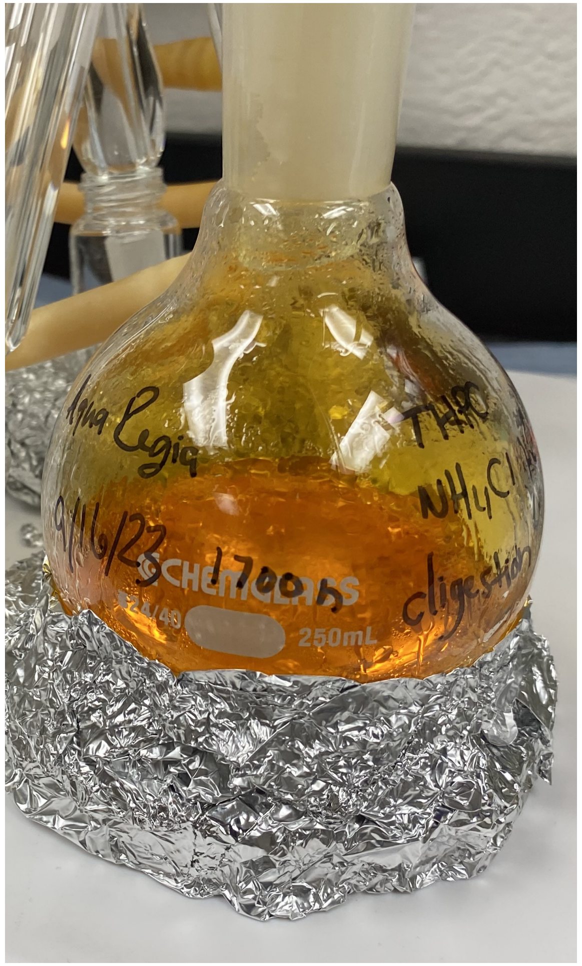


Experimental Conclusions

- For both aqua regia and purely nitric acid solutions, digestion was unsuccessful
- THPC residue is left behind after 2 days of refluxing
- Either find more digestion solvents, or close this door completely

Digestion experimental details

Outline



Experimental Details

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- If an aliquot evaporates to dryness, then we have success!

Why consider a digestion pathway to separation?

Outline

- Unfortunately, evaporation leaves behind this residue
- THPC is highly hygroscopic
- Higher temperatures cause decomposition and leave a viscous syrup
- I need a way to <u>destroy THPC</u>