OAK RIDGE National Laboratory

Electrodeposition or Micro-Precipitation? With or Without Hydrofluoric Acid? ~Consideration of Alpha Source Preparation

Hiromu Kurosaki, Ph.D.

Dosimetry Services

Nuclear and Radiological Protection Division

Oak Ridge National Laboratory

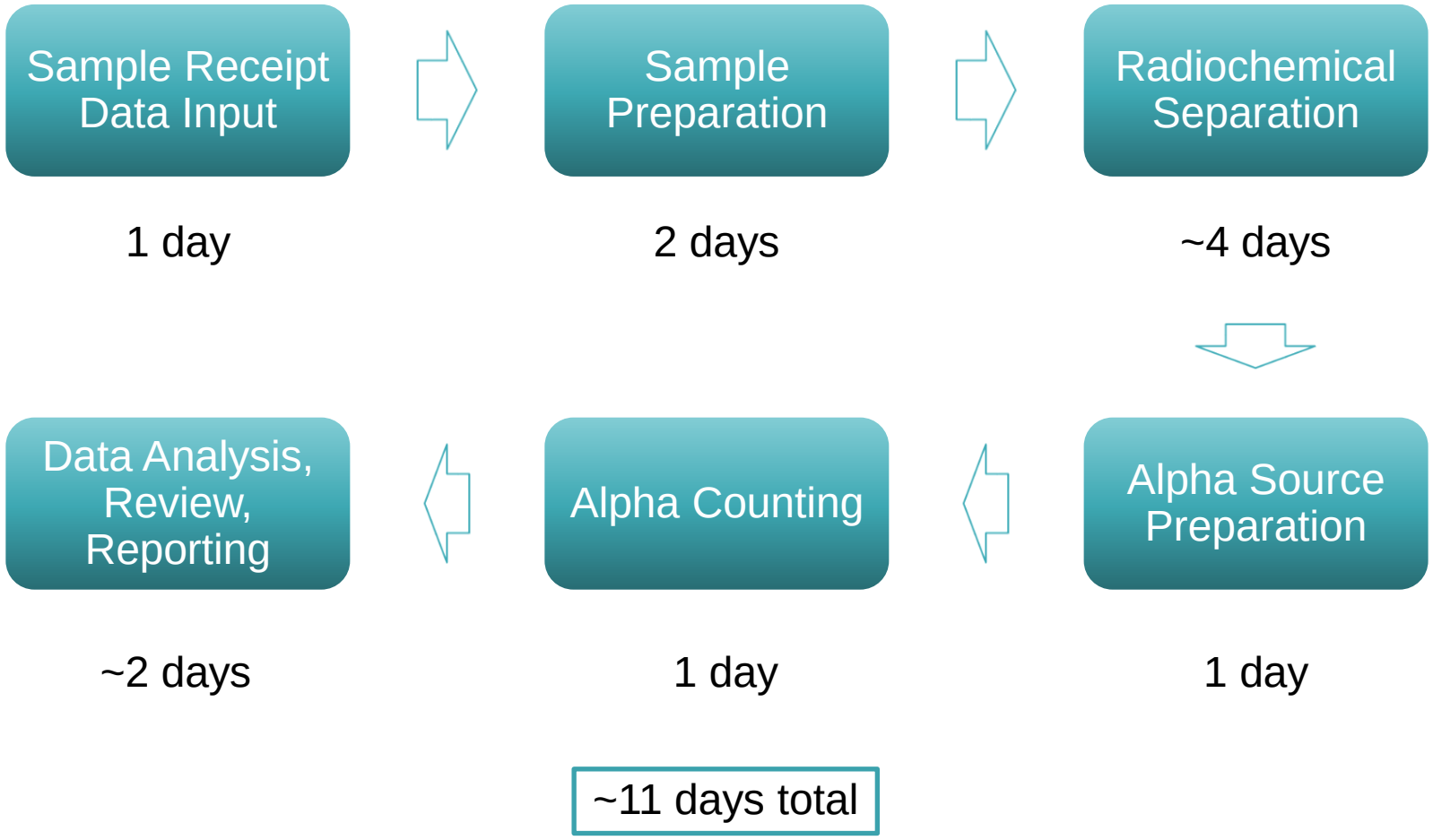
ORNL is managed by UT-Battelle LLC
for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

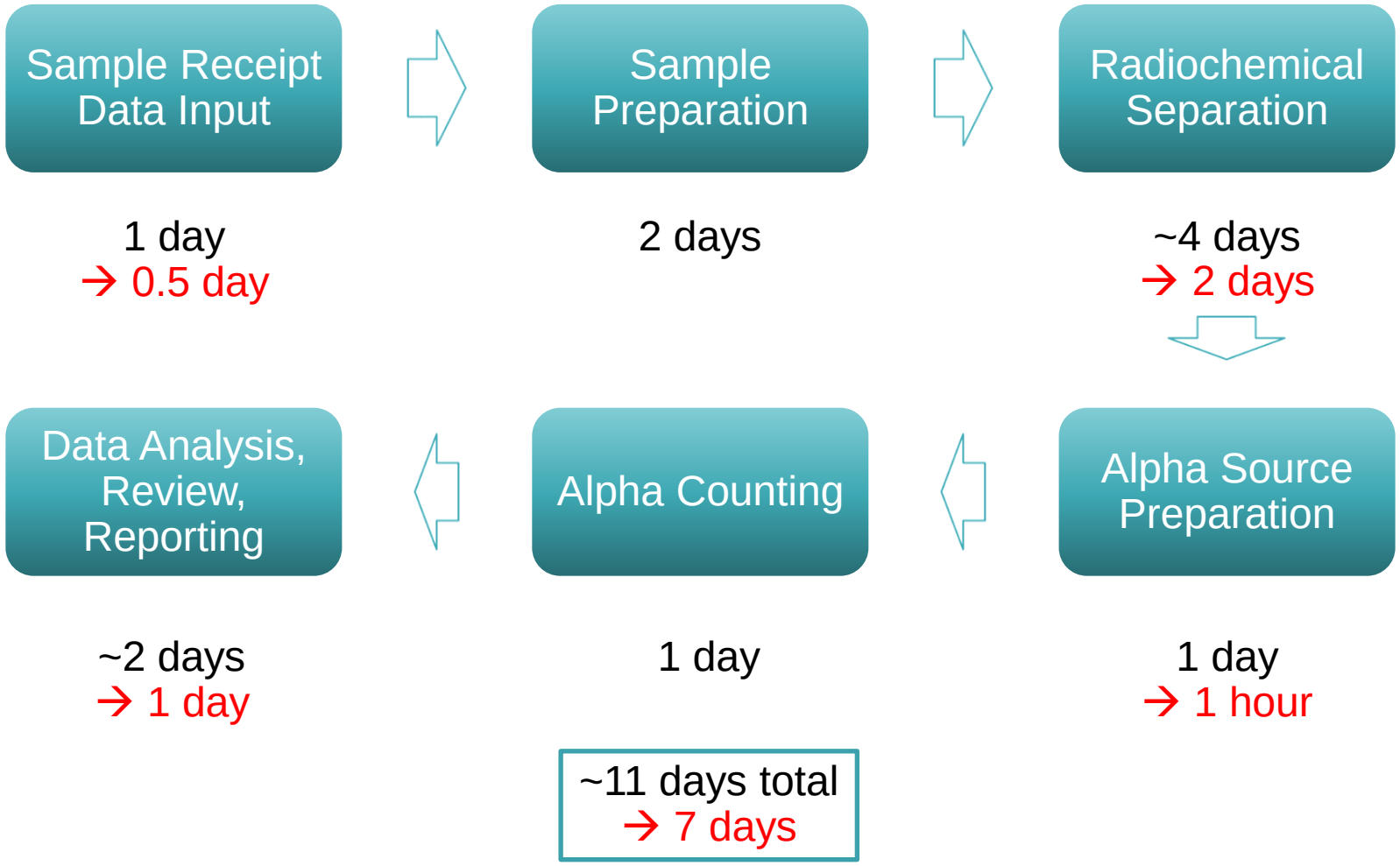
In-Vitro Radiobioassay Program at ORNL

- Routine Analysis ~4000 analytes per year
  - 24 Hour Void Urine
- Incident (Emergency) Analysis
  - Urine
  - Fecal, Nasal Swabs, Air Filters, etc.
- Analytes of Interest
  - Alpha ($^{225, 227}$Ac, $^{241, 243}$Am, $^{242, 244, 248}$Cm, ^{252}Cf, ^{237}Np, ^{210}Po, $^{238, 239+240, 242, 244}$Pu, $^{223, 226}$Ra, $^{228, 229, 230, 232}$Th, $^{232, 233, 234, 235, 236, 238}$U)
  - Beta (^{3}H, ^{14}C, ^{36}Cl, ^{63}Ni, $^{89/90}$Sr, ^{99}Tc, ^{241}Pu, ^{249}Bk)
  - Gamma Emitters
  - ICP-MS ($^{235, 238}$U, Ratio)

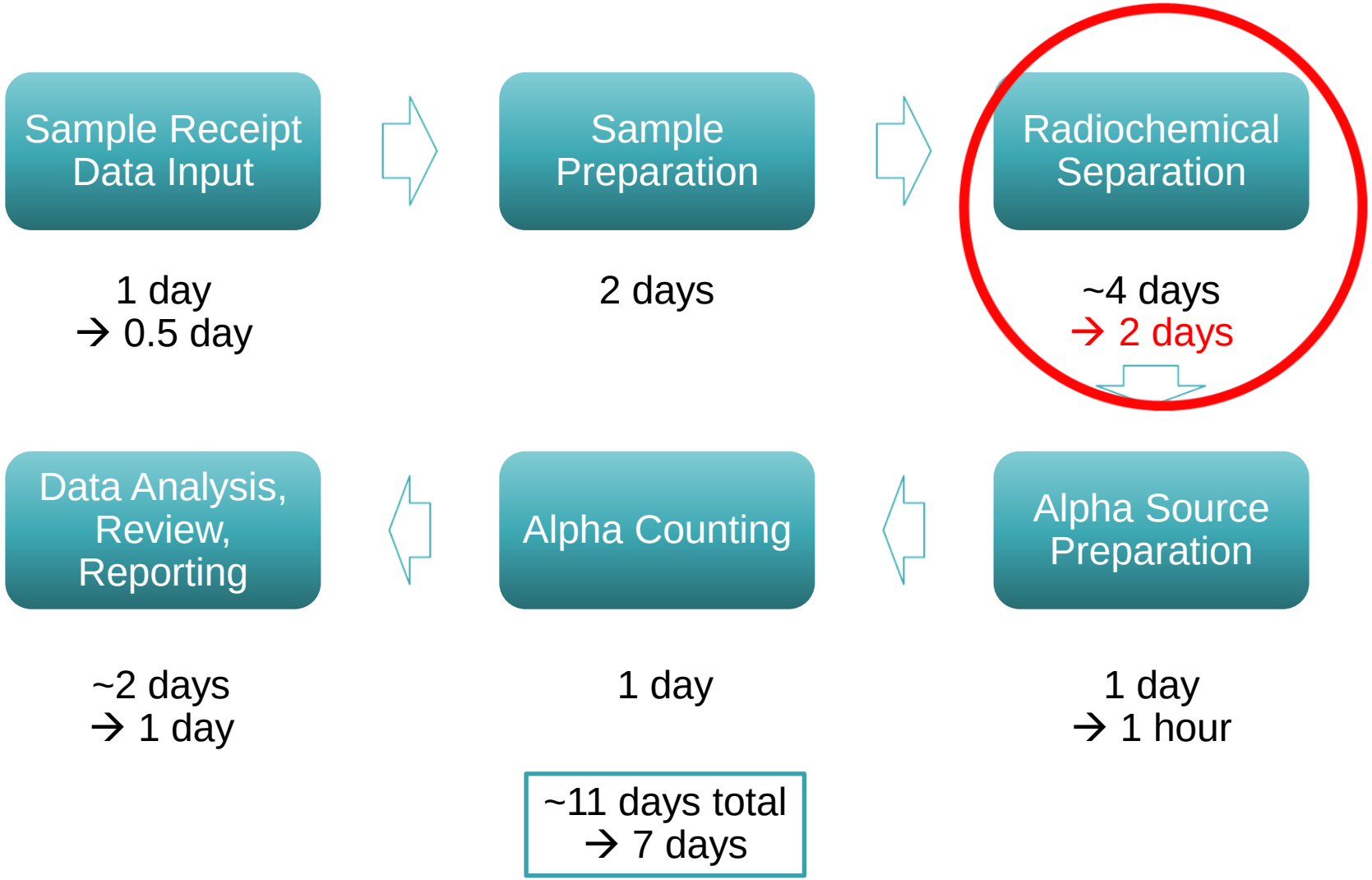
Routine Analysis for Alpha Emitters (Before)



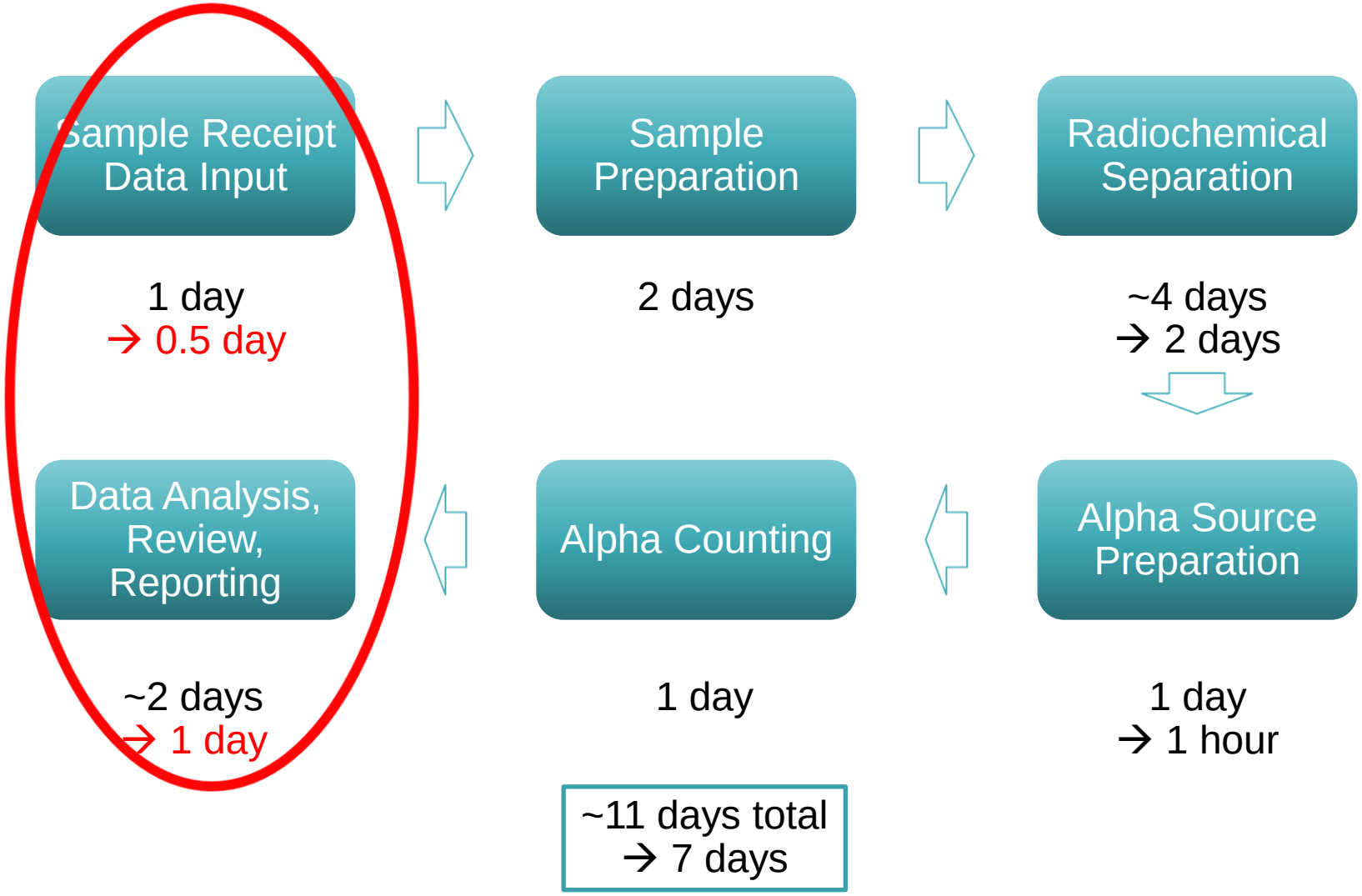
Routine Analysis for Alpha Emitters (After Improvement)



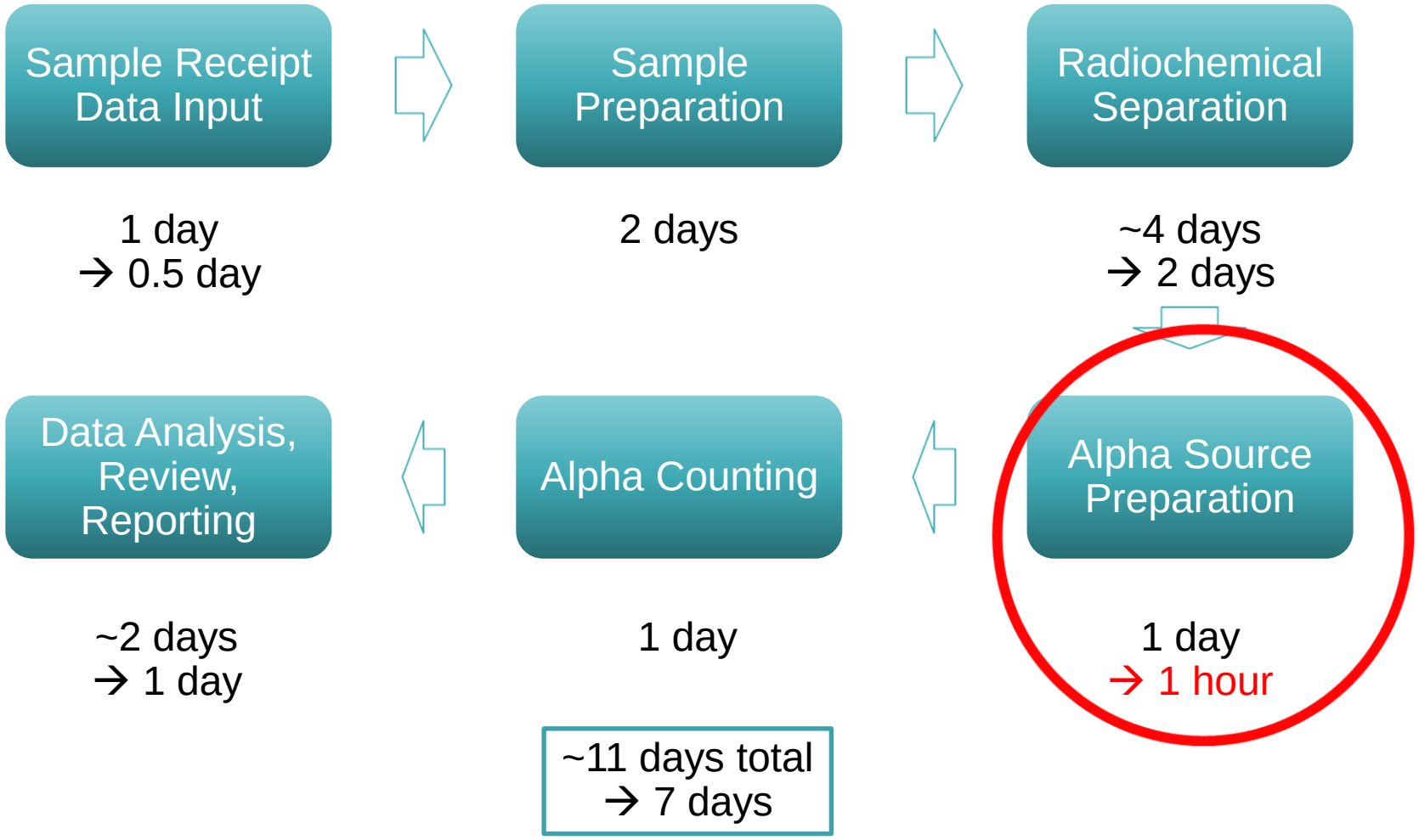
Ion Exchange to Extraction



Introduction of LIMS



Electrodeposition to Micro-Precipitation



Source Preparation for Alpha Spectrometry

Electrodeposition

- Well developed
- Good resolution
- Time consuming (8 hours)
- Tedious procedure

Micro-precipitation

- Well developed
- Simple procedure
- Quick (1 hour)
- Use of HF

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Source Preparation for Alpha Spectrometry

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Micro-precipitation

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- Simple procedure
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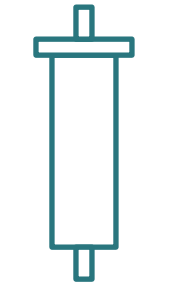
How about micro-precipitation without HF?

Lanthanide Hydroxide Micro-Precipitation

Elute

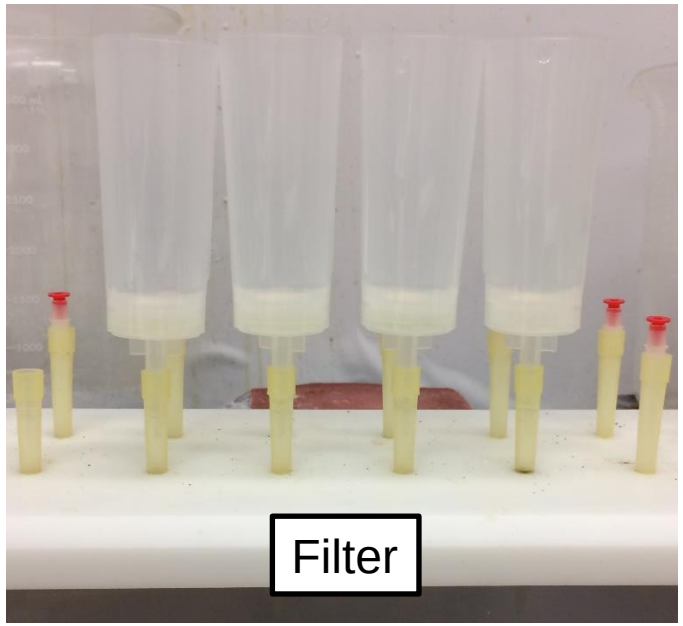


Add Carrier

Add H_2O_2

Add Indicator

Adjust pH



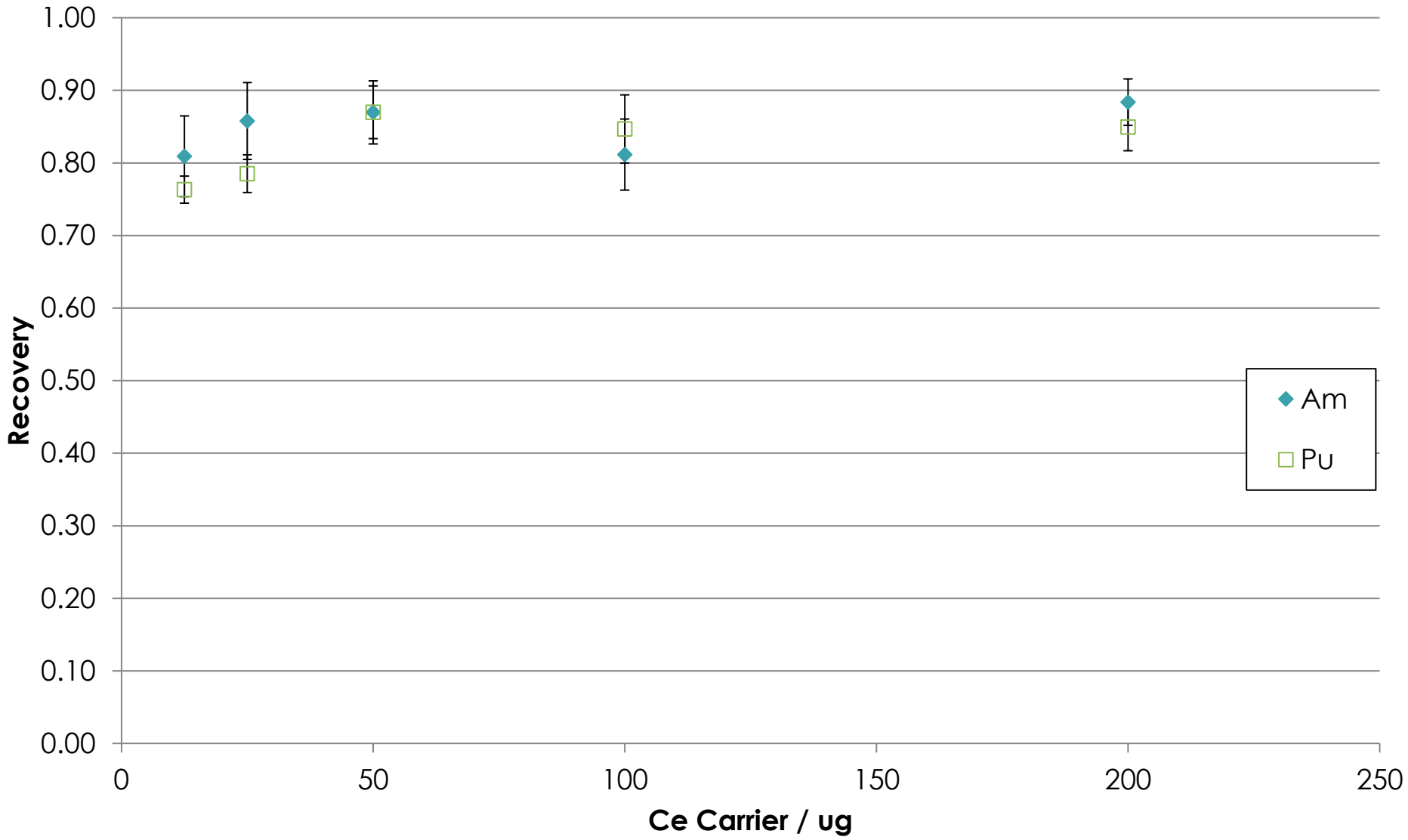
Filter

Alternate Method of Source Preparation for Alpha Spectrometry: No Electrodeposition, No Hydrofluoric Acid

Hiromu Kurosaki, Rebecca J. Mueller, Susan B. Lambert, and Govind R Rao

J Radioanal Nucl Chem (2017) 311:323-329

Carrier Amount vs Recovery



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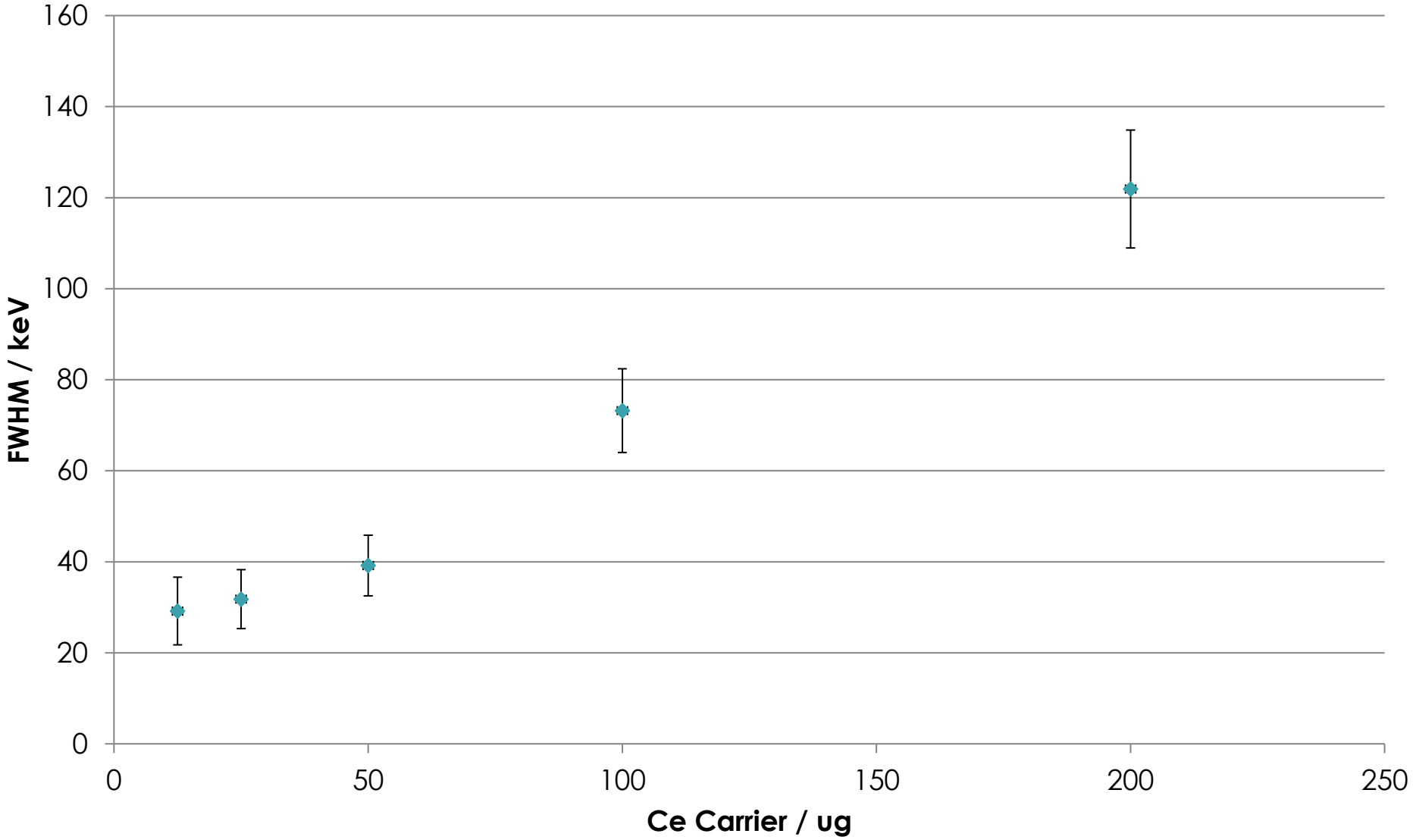
Carrier Amount vs Resolution (Am)



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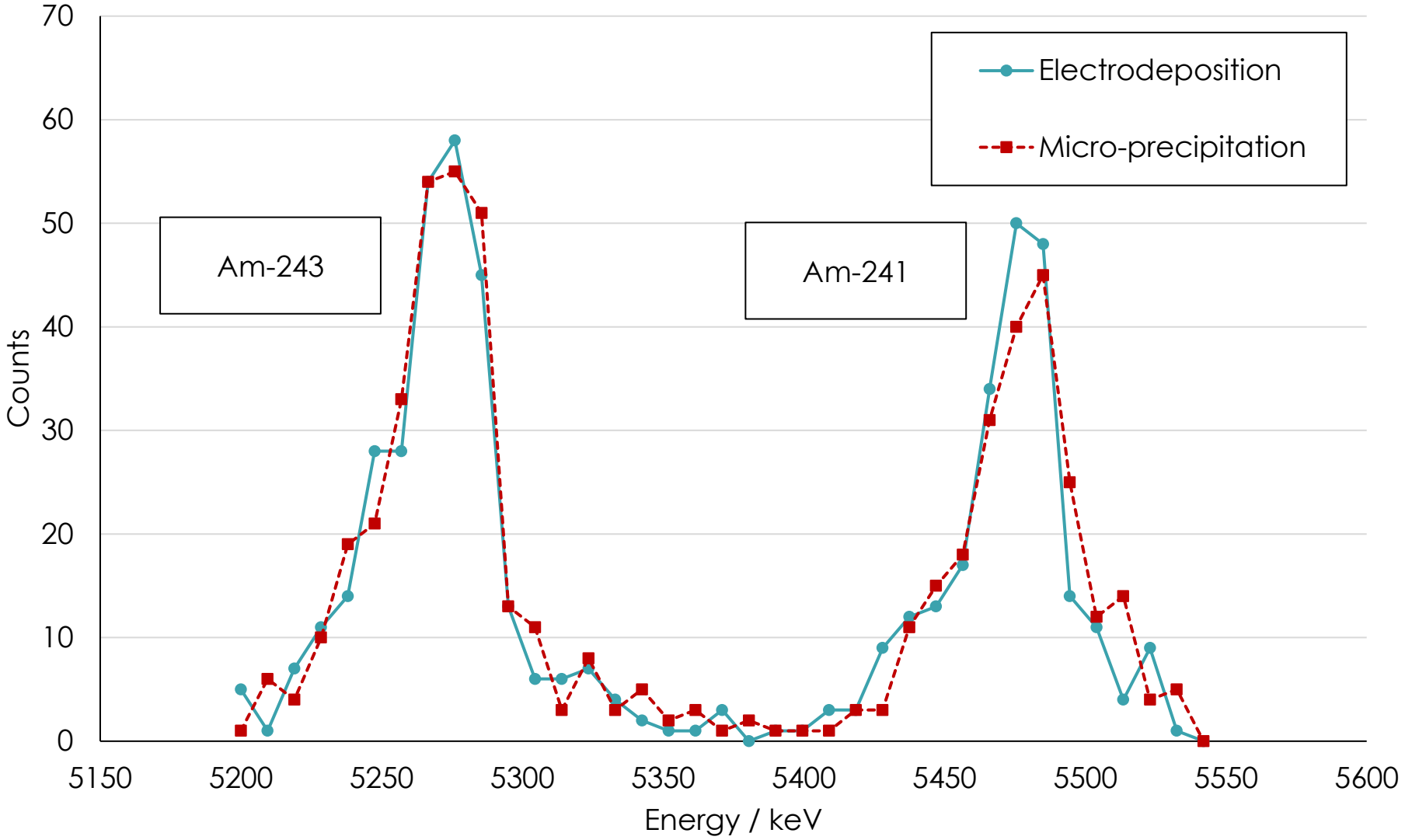
Electrodeposition vs Micro-Precipitation (50 ug carrier)



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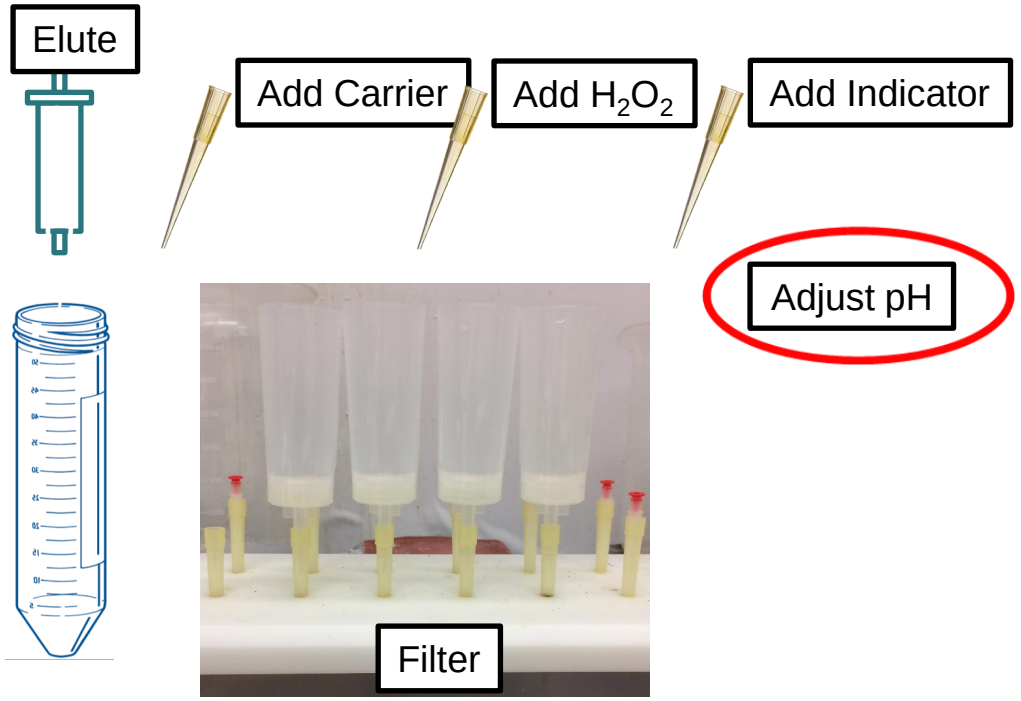
How to Adjust the pH?

- Using pH meter
  - Possible to adjust pH precisely
  - Time consuming

- Using pH indicator
  - pH end point may have larger uncertainty
  - Quick



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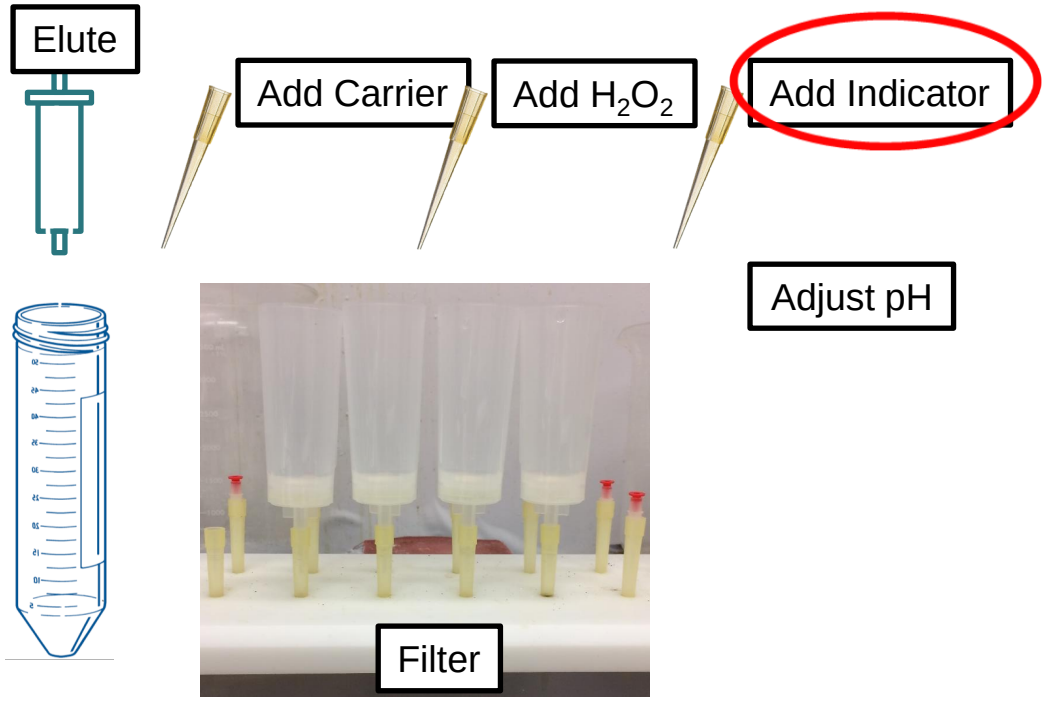

Thymol Blue : Yellow → Blue at pH9

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Lanthanide Hydroxide Micro-Precipitation

- Faster than ED
  - (8 hours → 1 hour)
- Simpler than ED
- Safer than fluoride micro-precipitation
  - No need of hazardous HF

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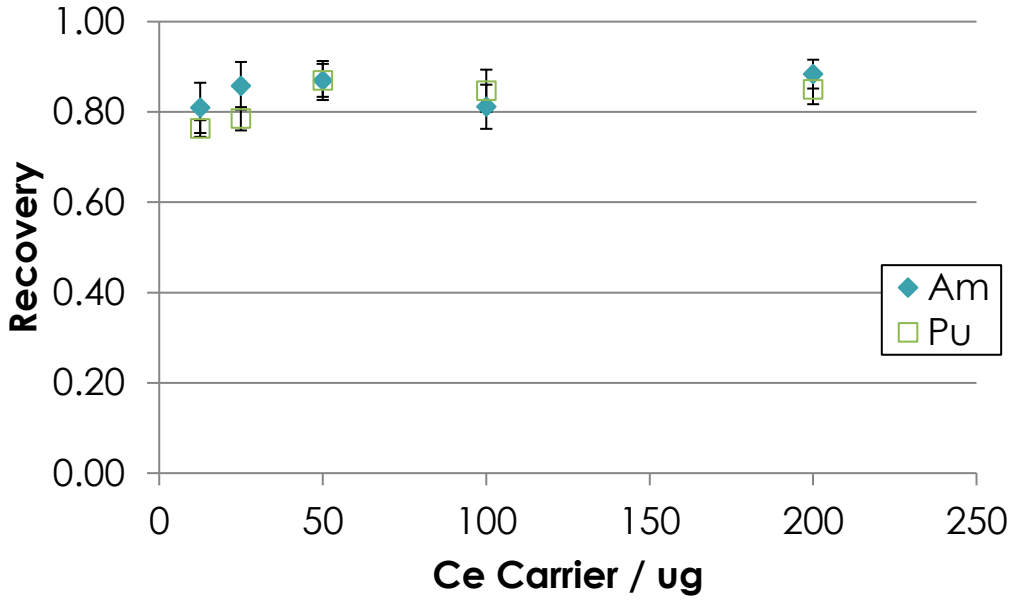
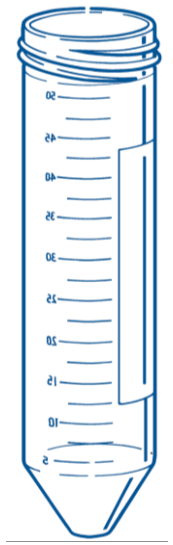
Lanthanide Hydroxide Micro-Precipitation

- Faster than ED
  - (8 hours → 1 hour)
- Simpler than ED
- Safer than fluoride micro-precipitation
  - No need of hazardous HF
- Sample Shelf Life?
- Lower Recovery?
  - Will talk later



Elute



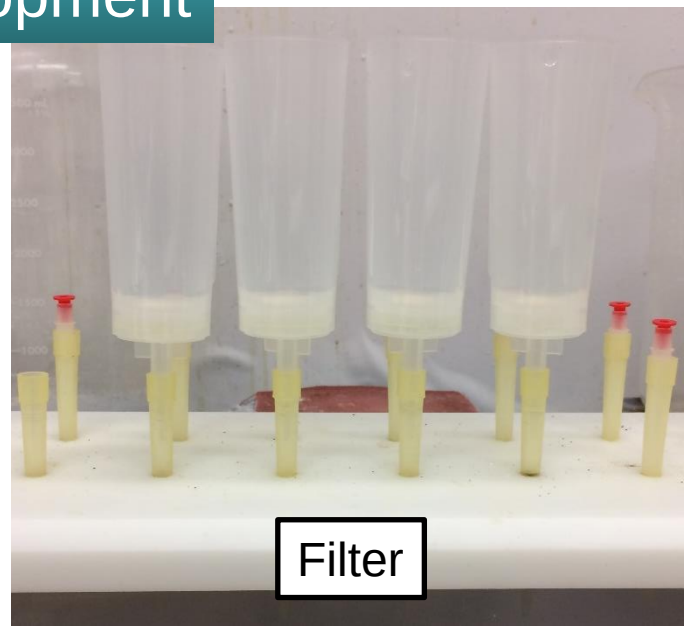
Add Carrier

Add H_2O_2

Add Indicator

Implemented for Tracer Verification Method Development

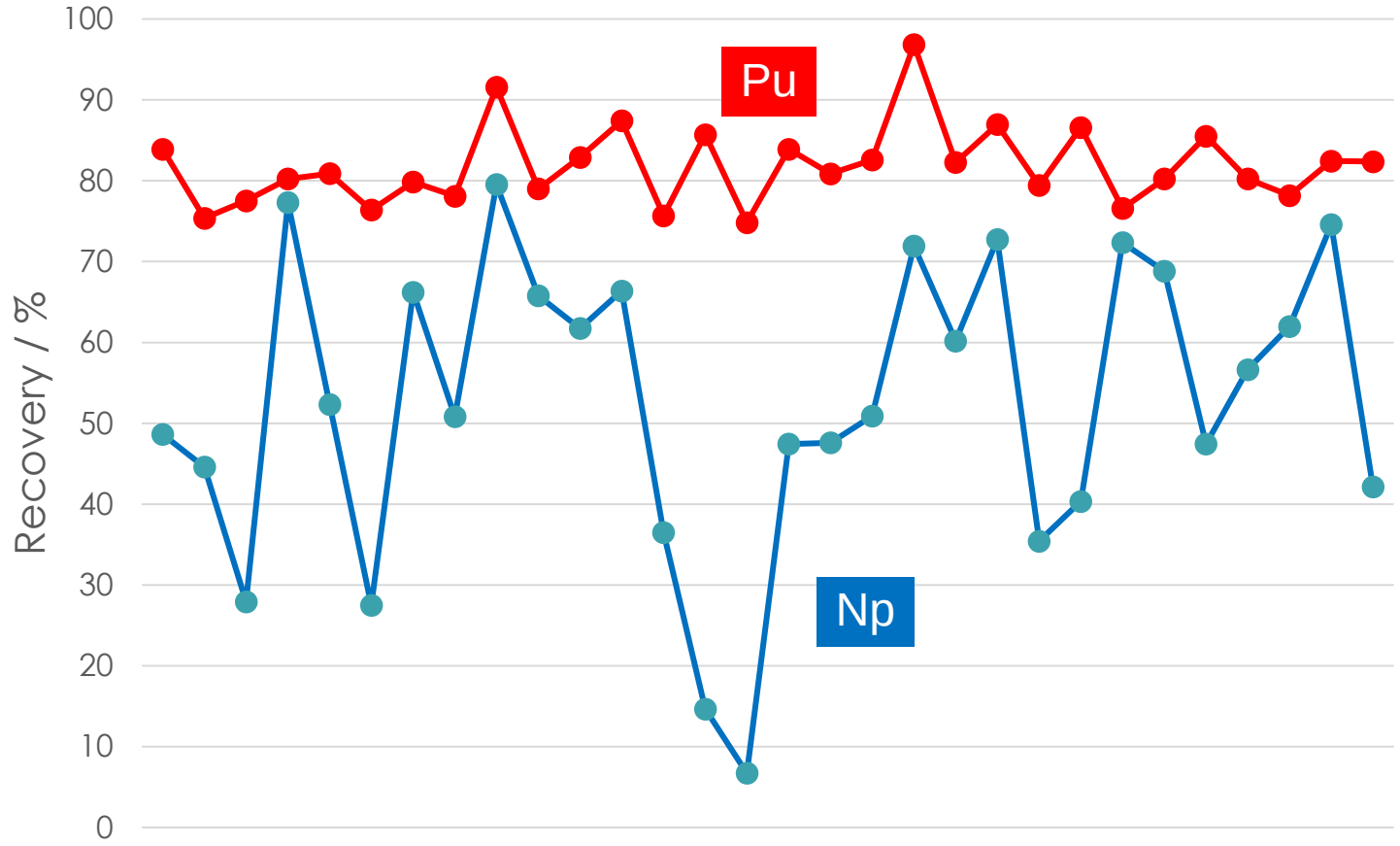
Adjust pH



Filter

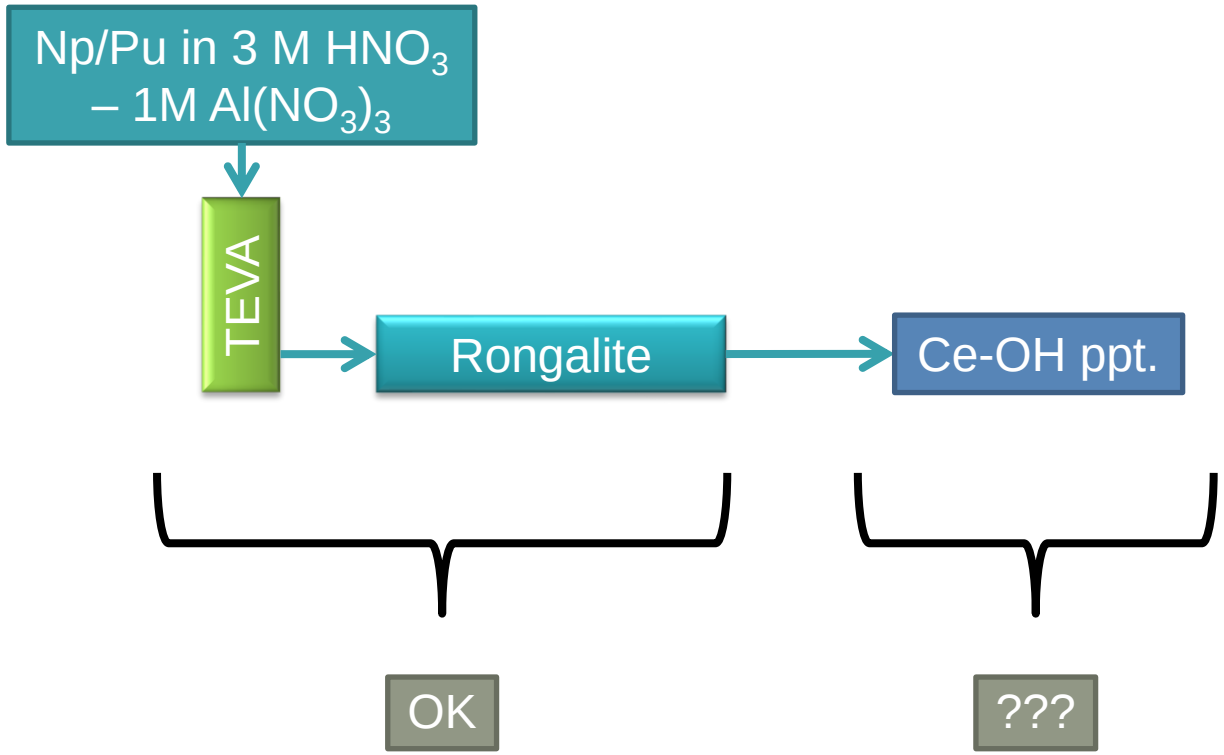
Problem Found

- Development of Np-237 procedure using TEVA
  Tracer: Np-239 → Pu-236
- Np recovery lower than Pu



Problem Found

- Assuming Pu follows Np during radiochemical separation, could this be during the micro-precipitation step?



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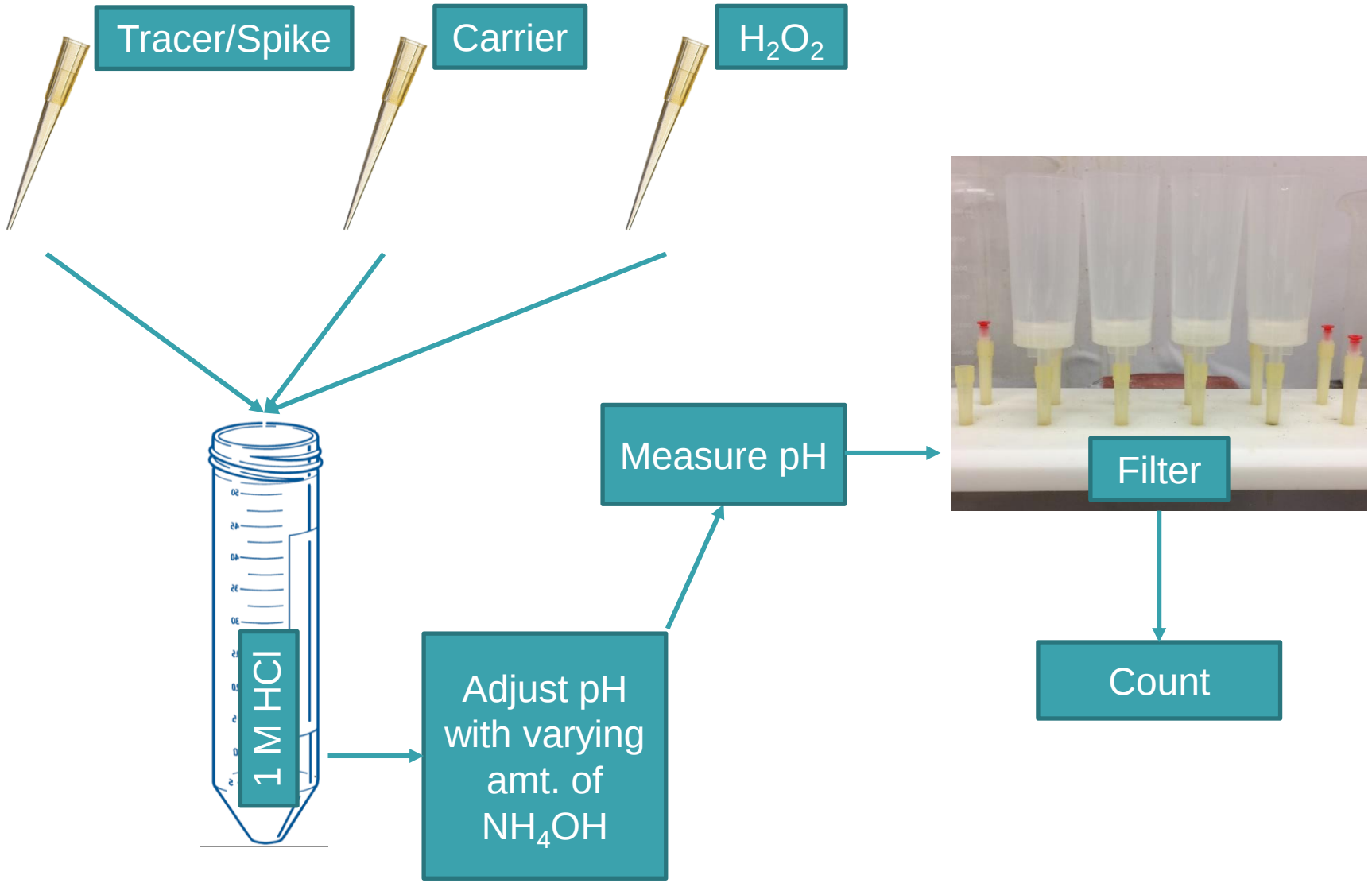
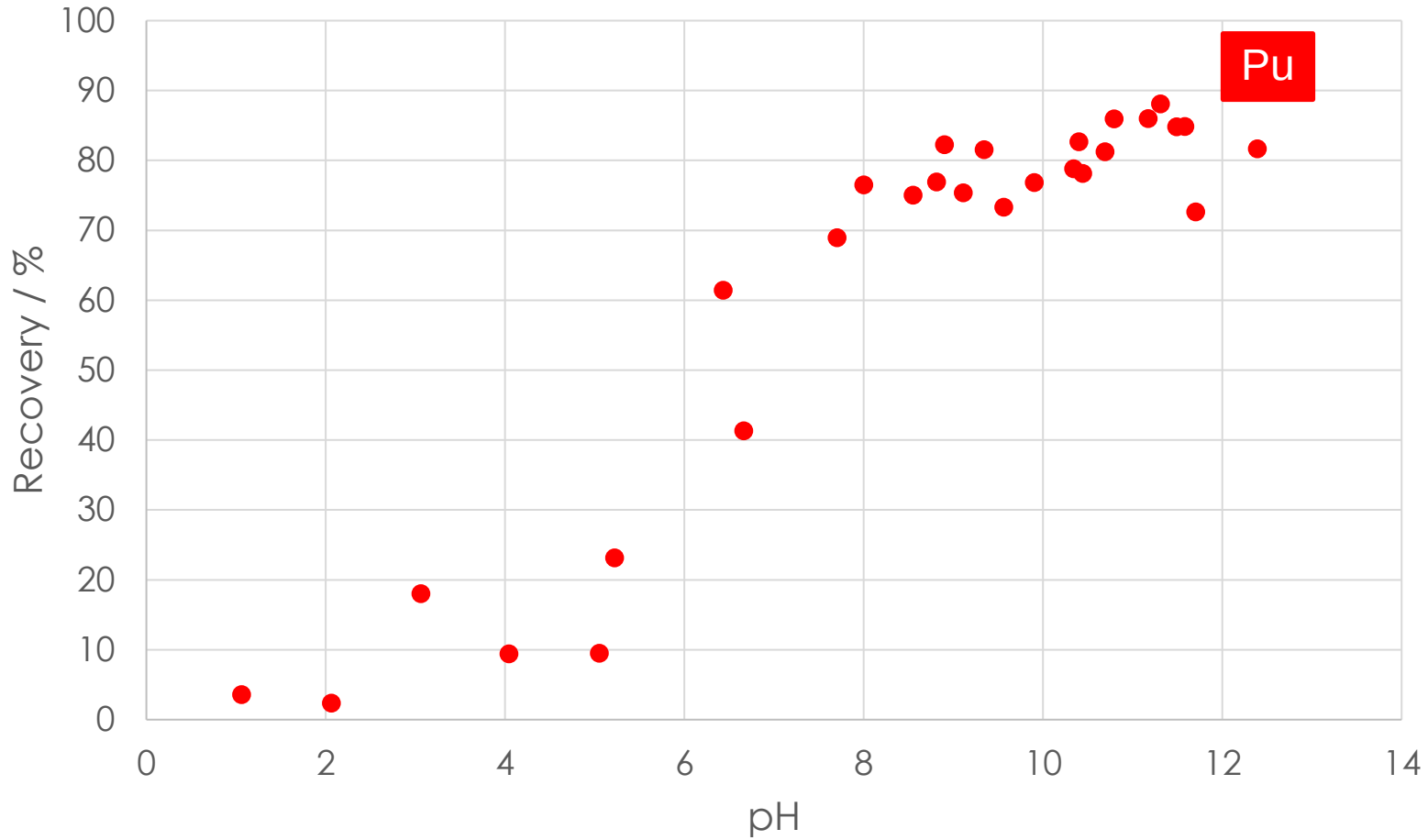
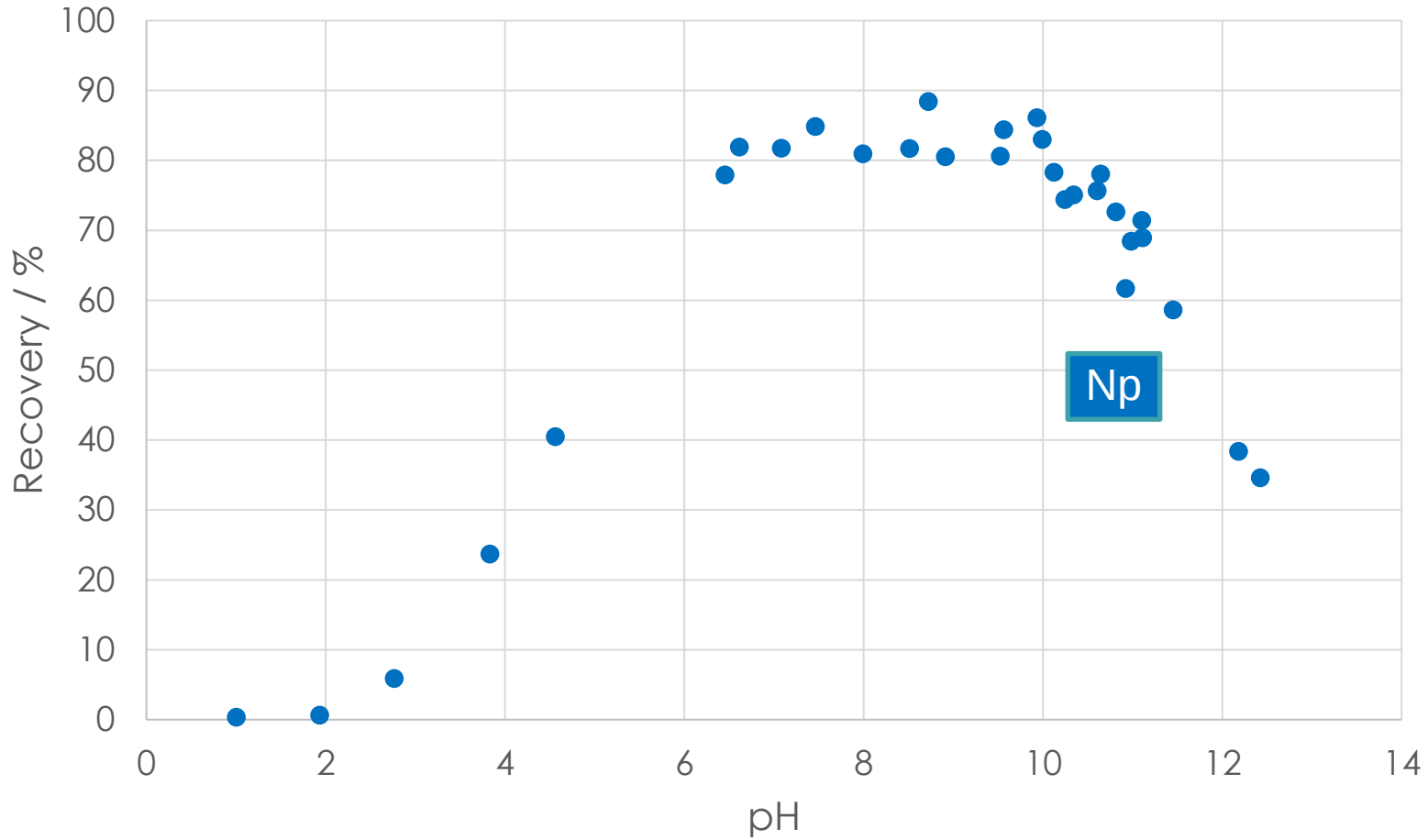
Experimental Set Up



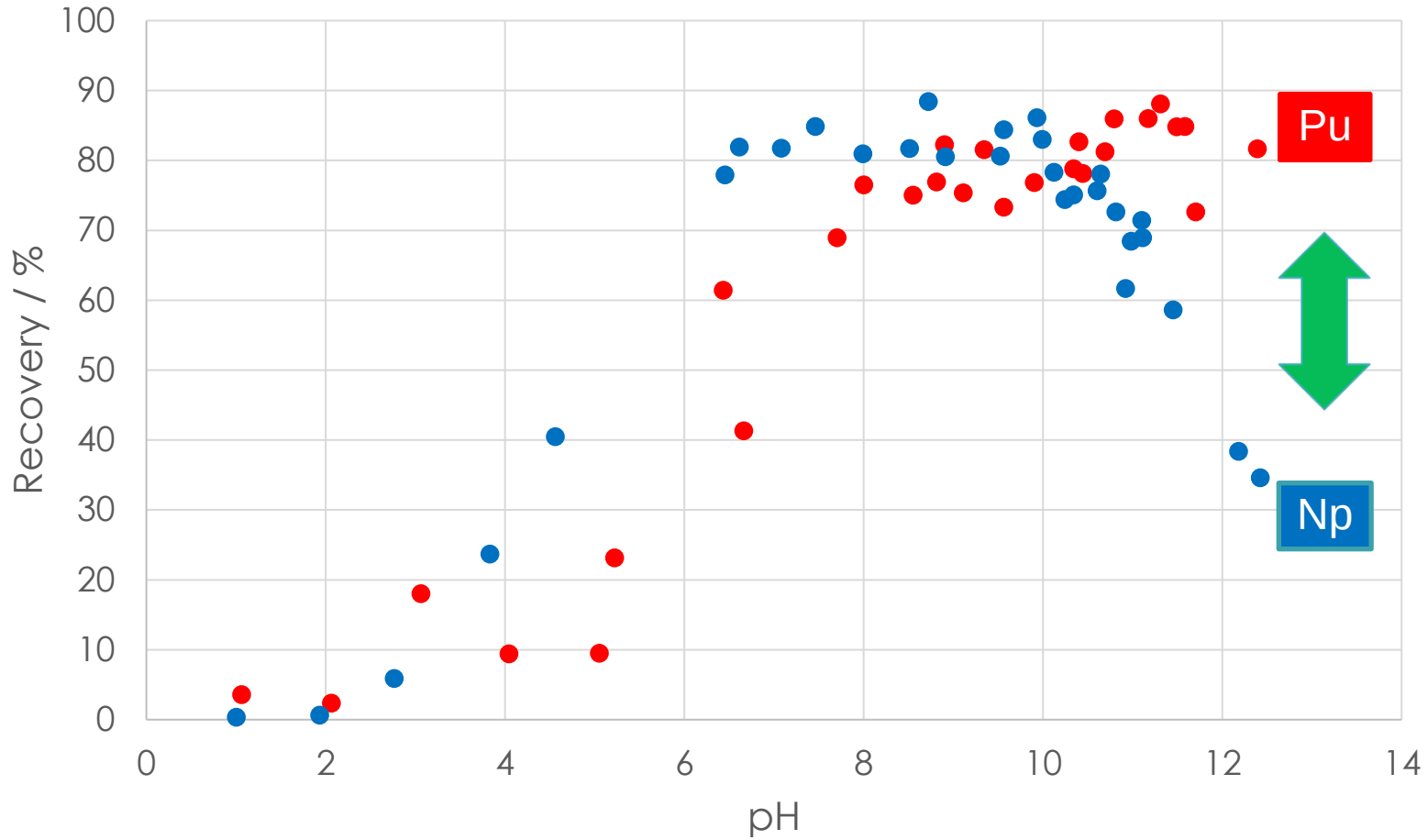
Pu Recovery Stays High at > pH 8

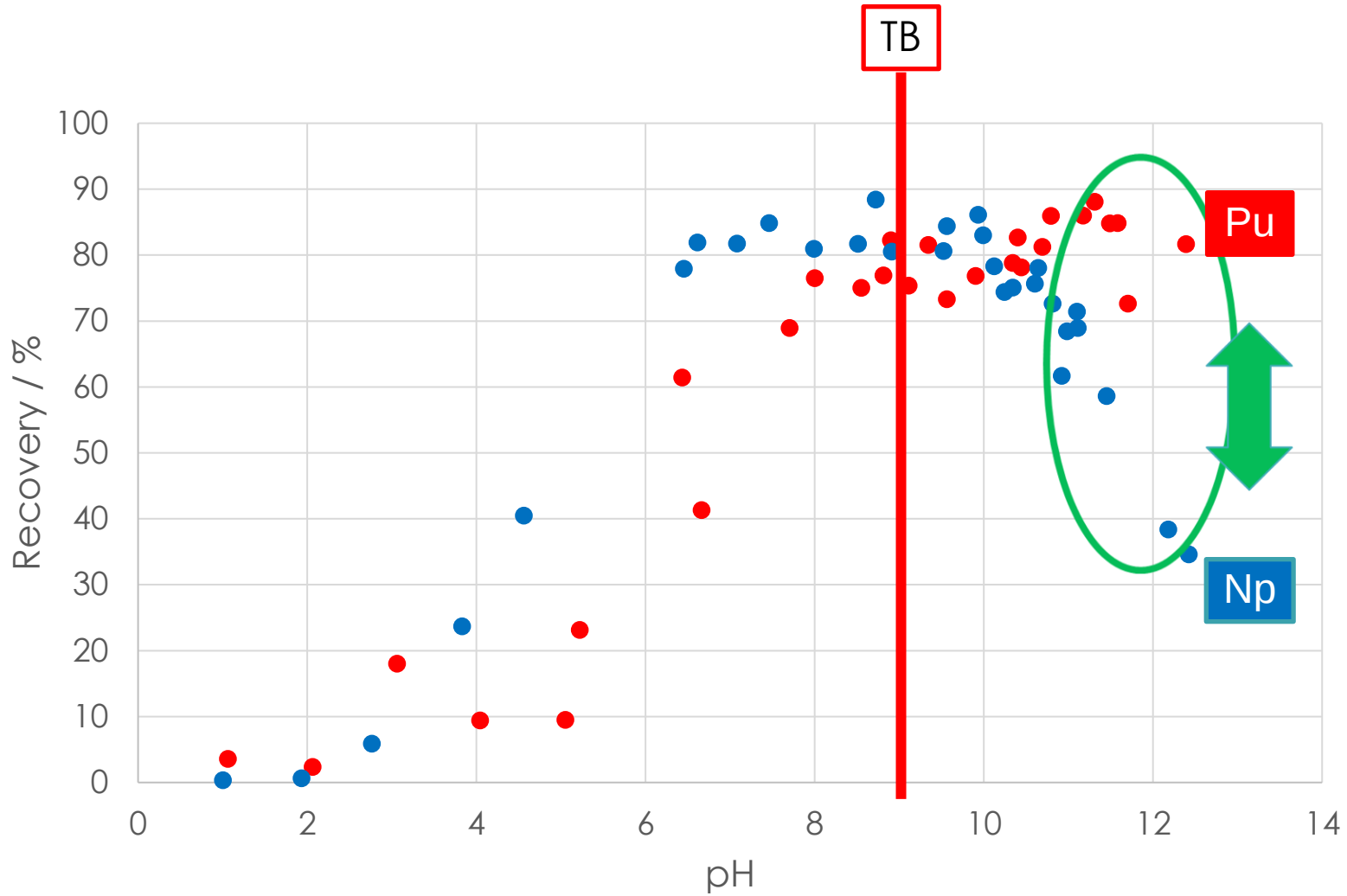


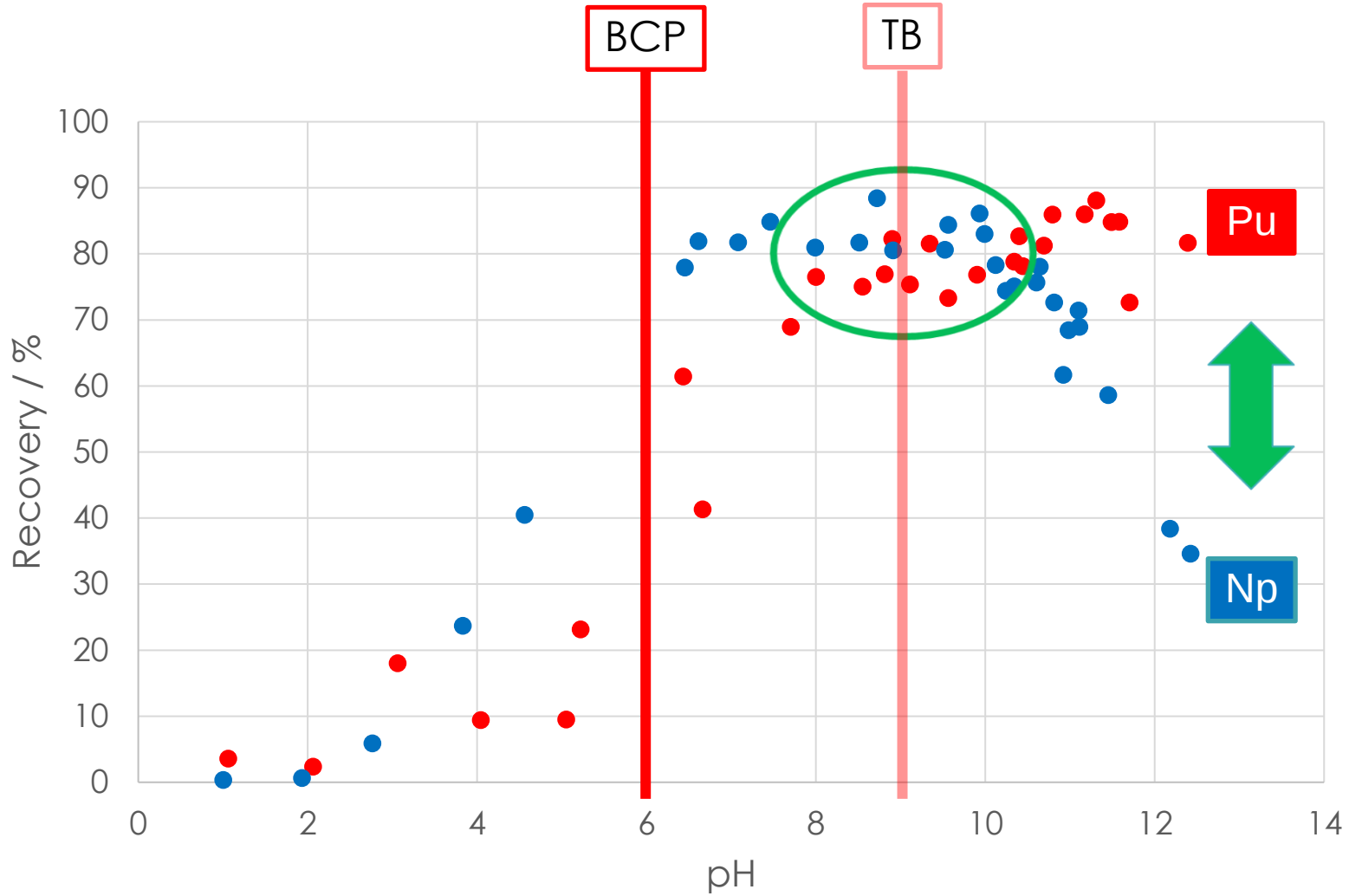
Np Recovery Decreases at > pH 10



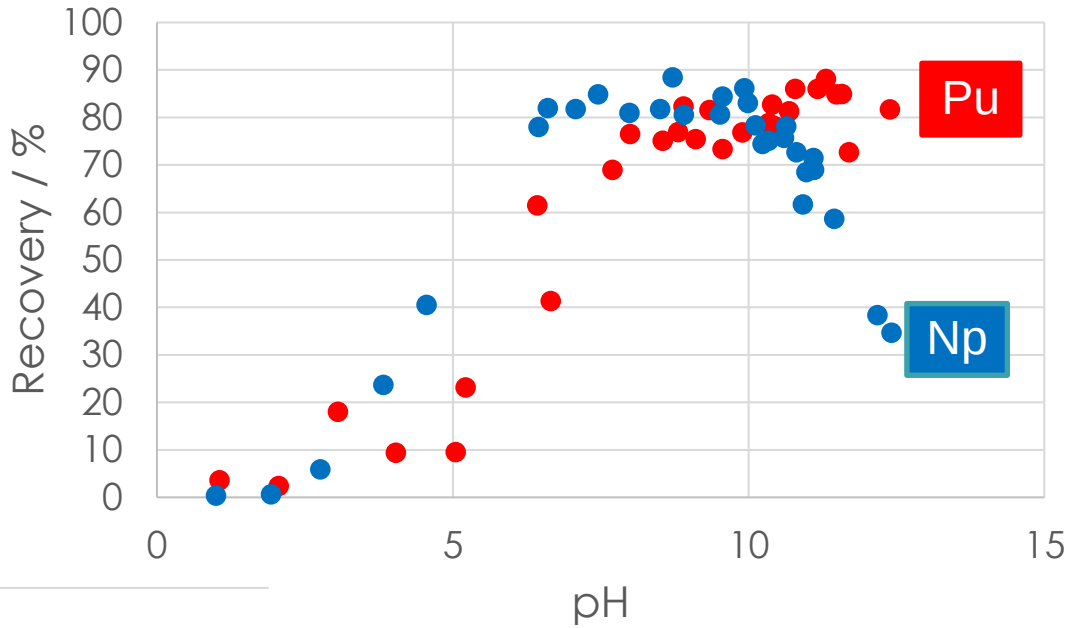
Micro-Precipitation that Needs Caution

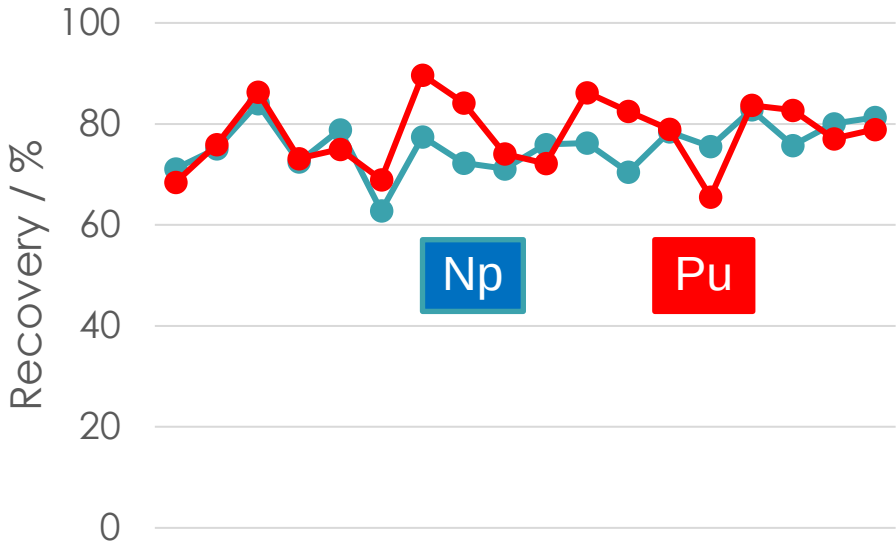



TB
Pu
Np
Recovery / %
pH
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14


BCP
TB
Pu
Np
Recovery / %
pH
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14

Consistent recoveries for Np and Pu

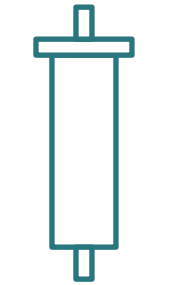




Np/Pu recoveries matched

Why H_2O_2 ??

Elute



Add Carrier

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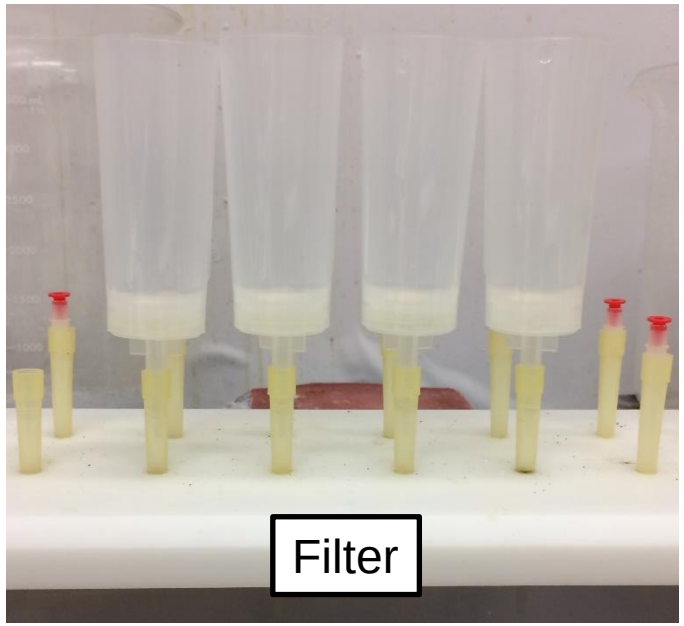
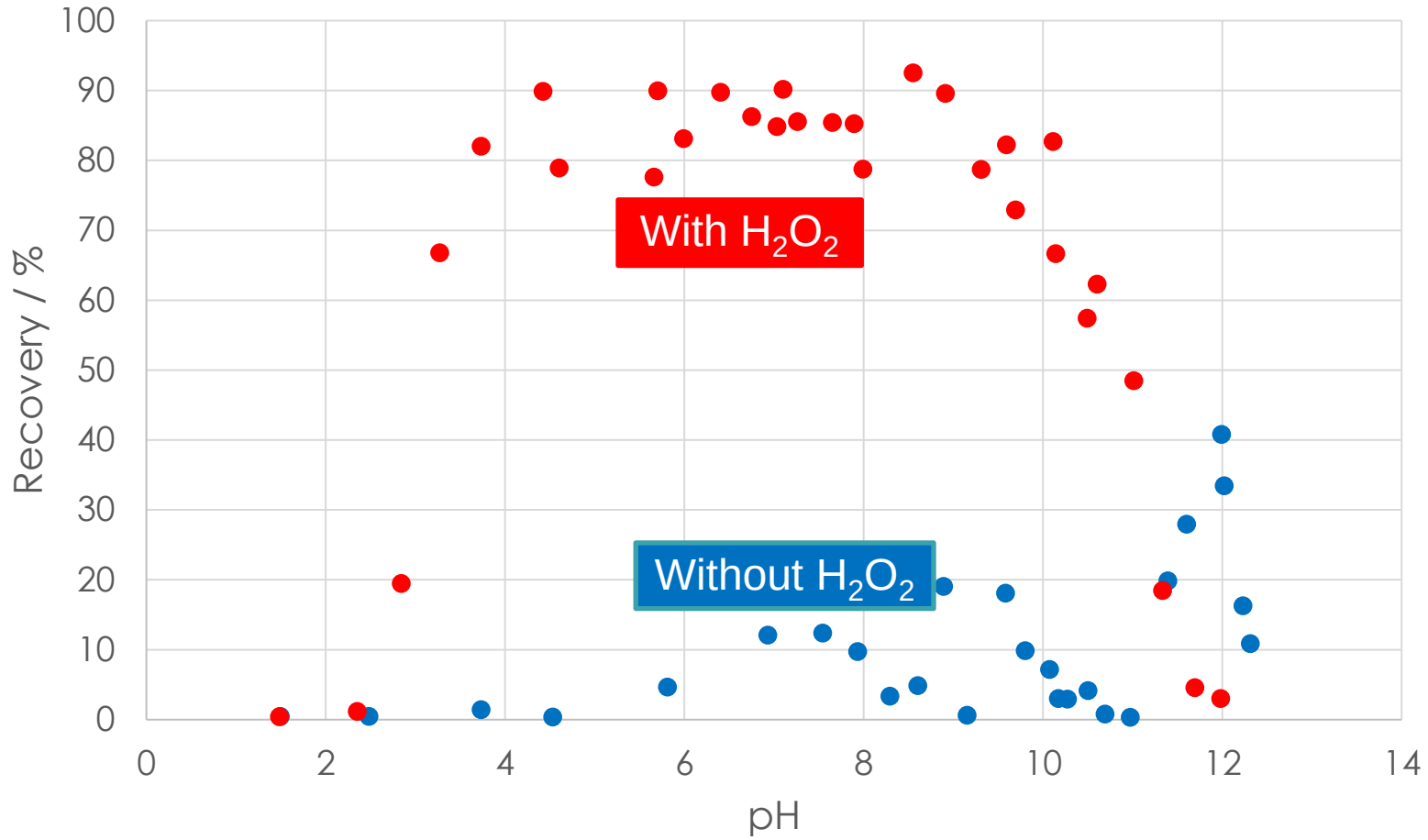
Add Indicator

Adjust pH

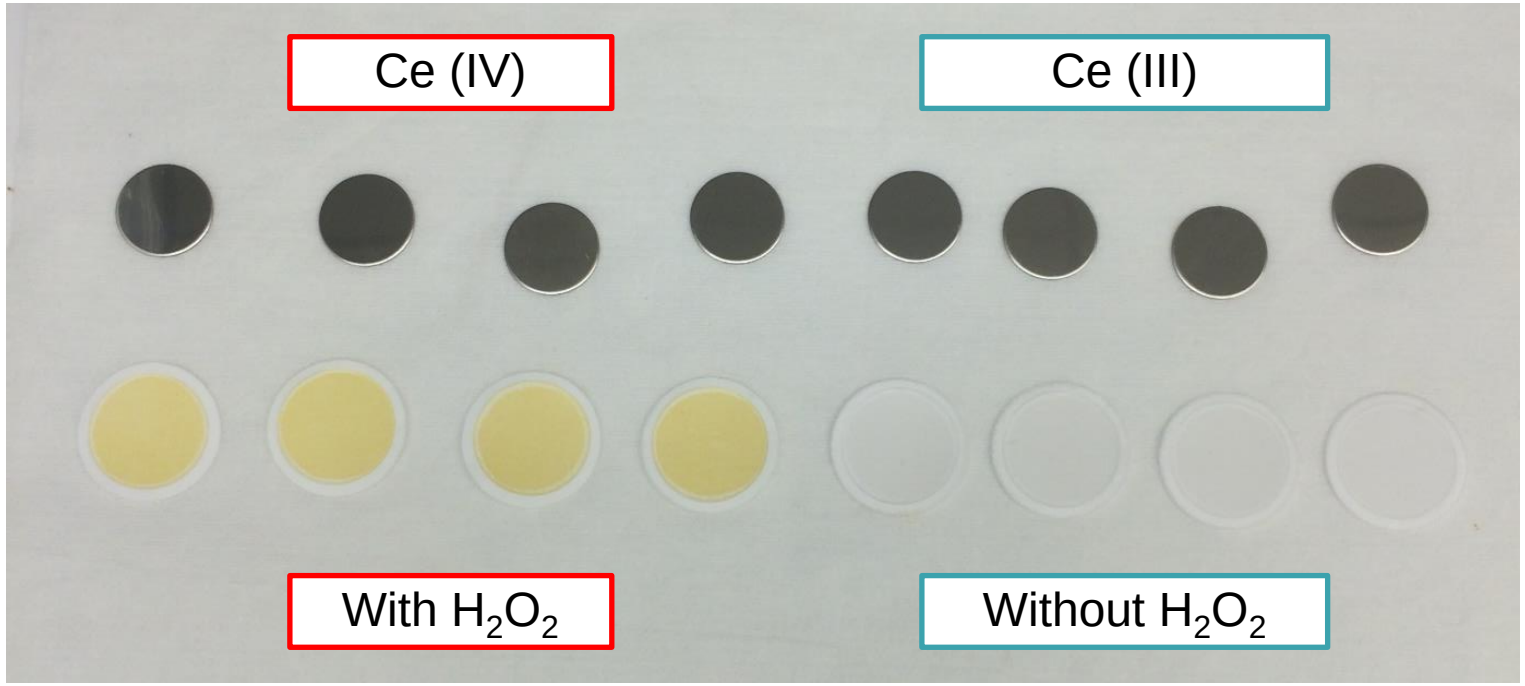


Filter

Adding H_2O_2 is Necessary for U Recovery



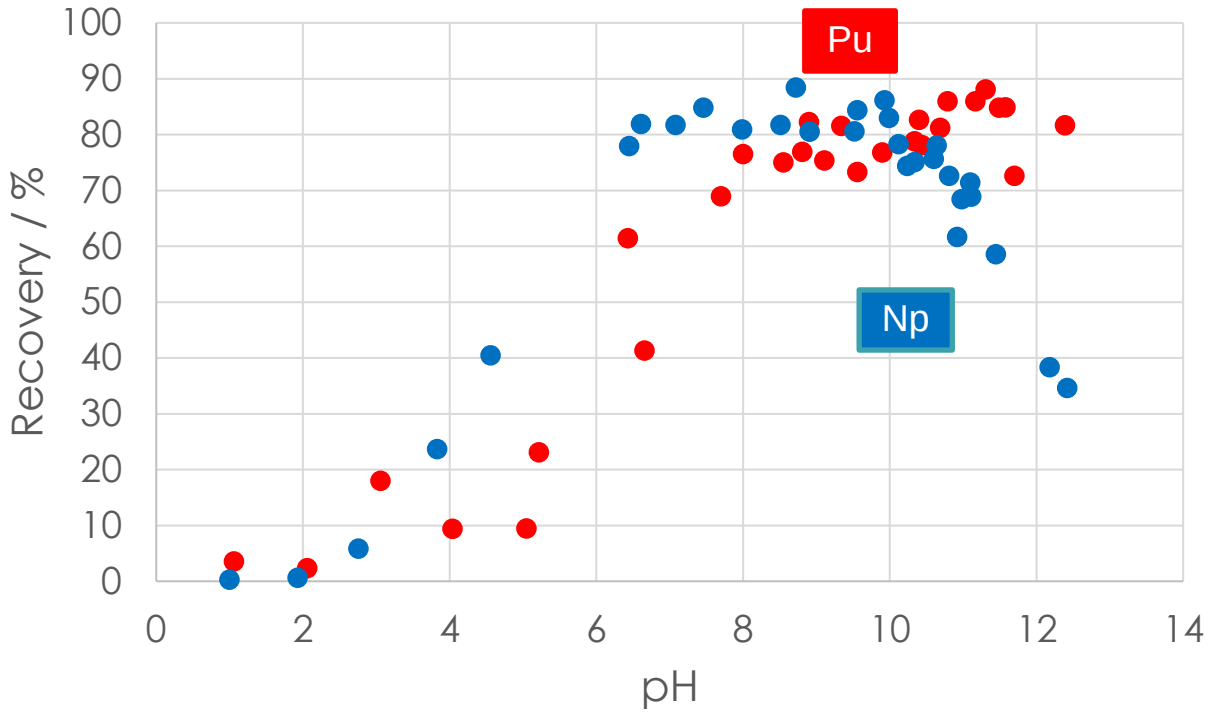
Adding H_2O_2 to Ce has Color Advantage



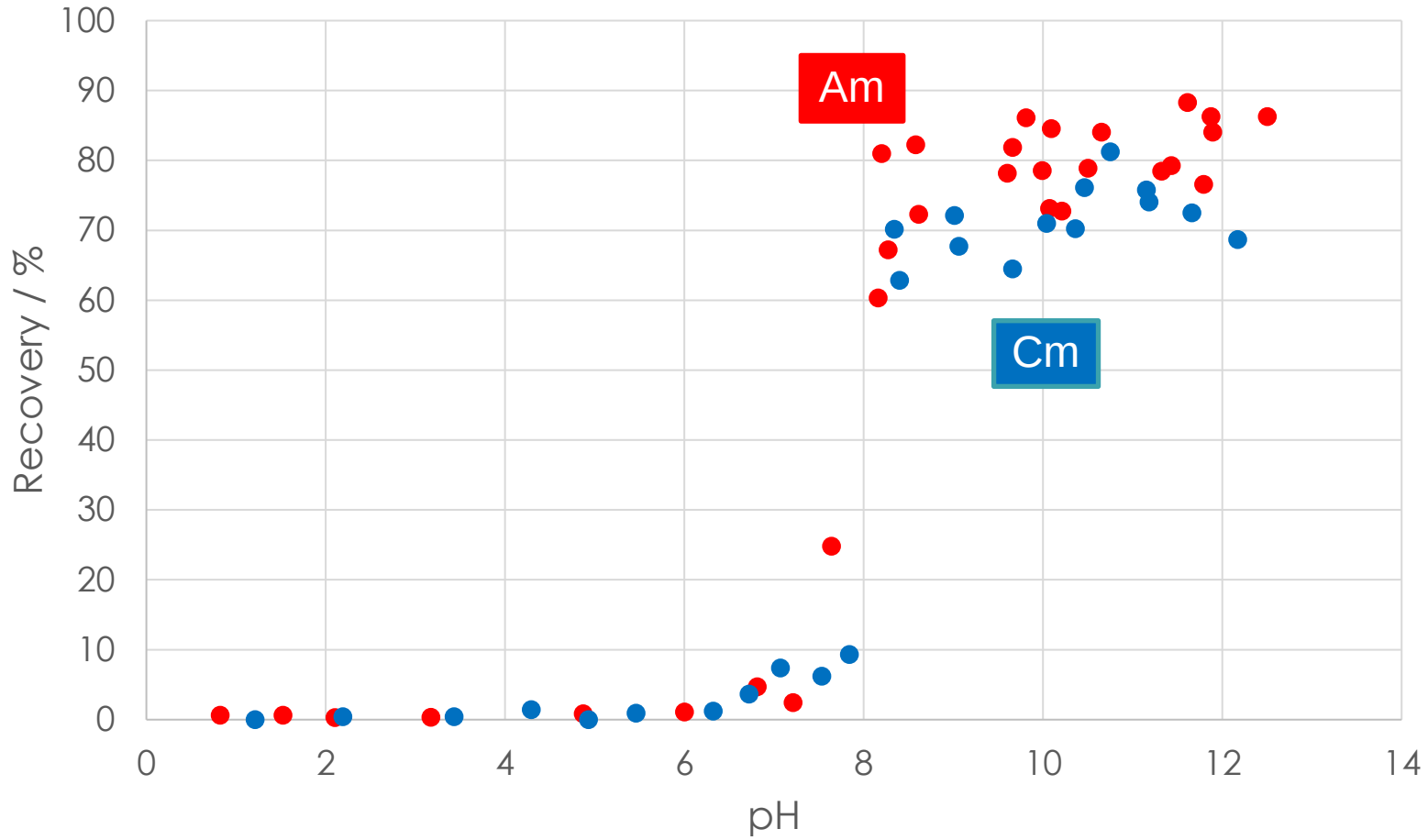
Using Different Elements as Tracers: More Options

- Np traced with Pu
  requires pH 8 – 10

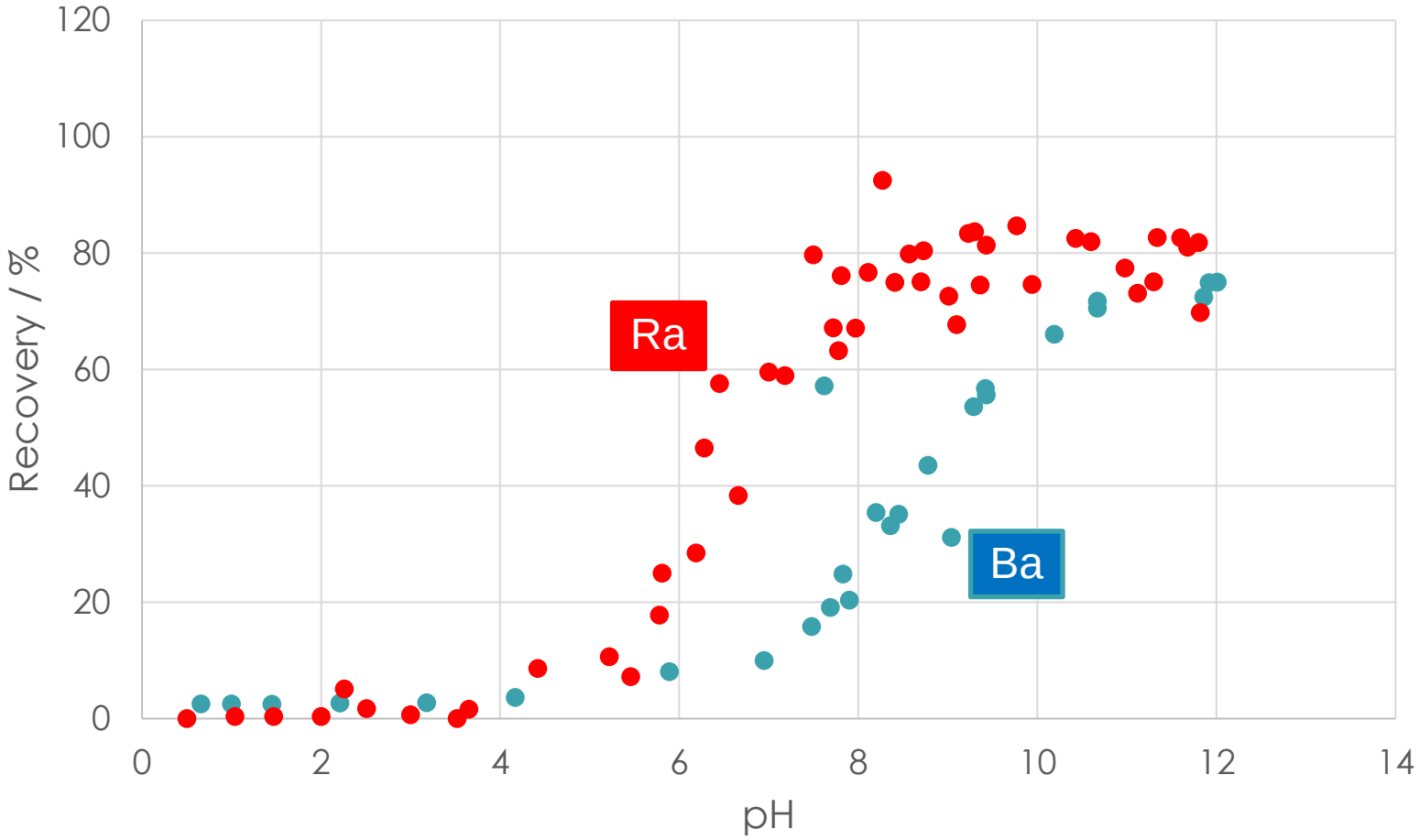
- How about
  - Cm / Am
  - Ra / Ba



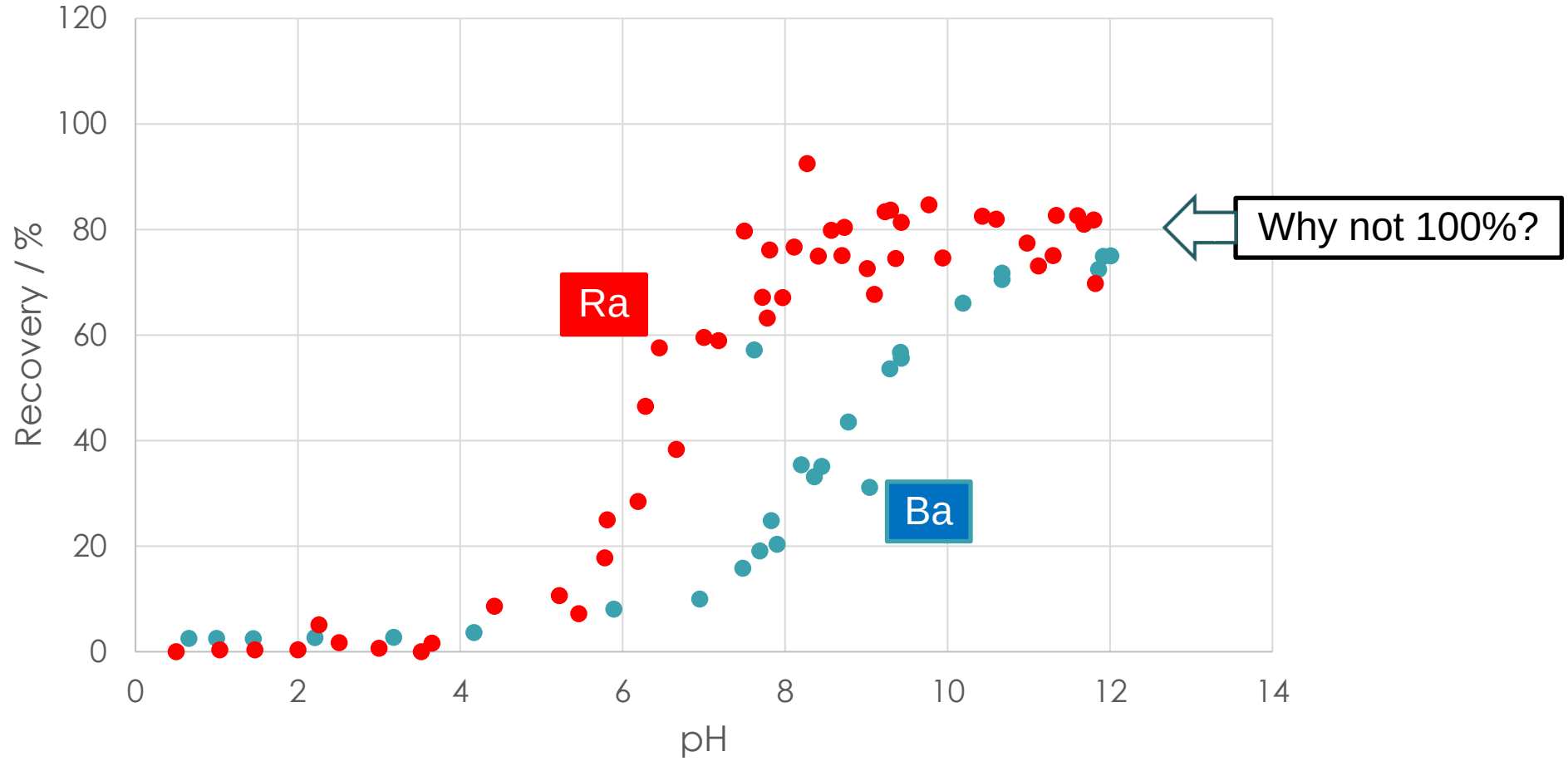
Am Follows Cm (pH 8 or higher)



Ba Lower than Ra



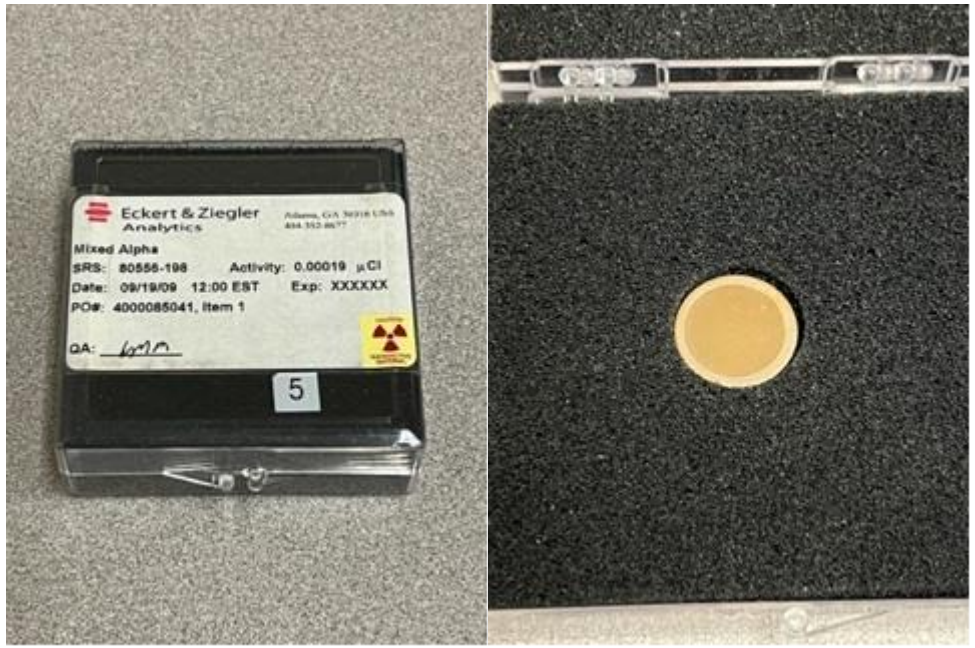
Why are Recoveries NOT 100%?



$$Recovery = \frac{Tracer\ Counts}{Count\ Time \times Efficiency \times Tracer\ Activity}$$

How do we determine alpha counting efficiencies?

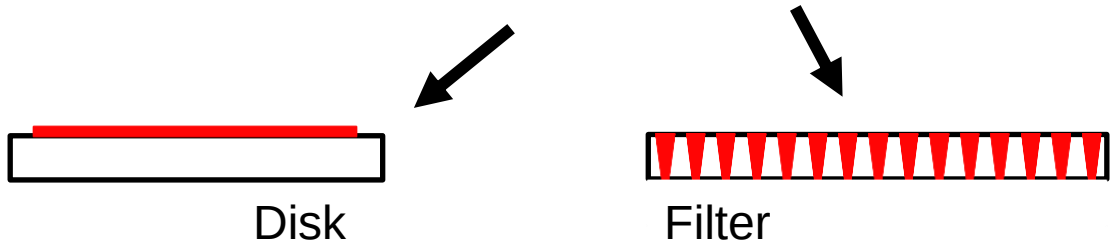
- Use NIST traceable source (Typically electroplated)
- Efficiency defined as $\frac{cpm}{dpm}$



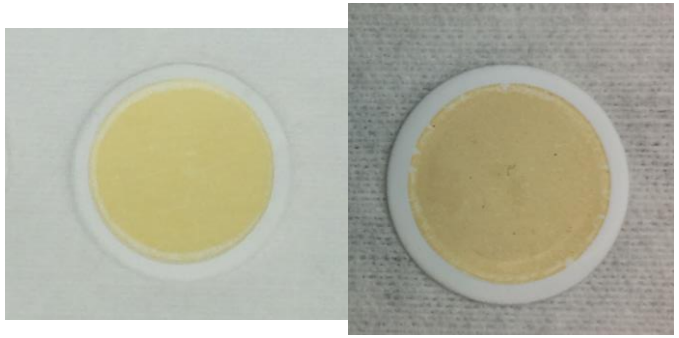
What if samples are prepared by Micro-PPT?

- Can we use the same efficiency?

- Are the efficiencies the same for ED and micro-PPT?

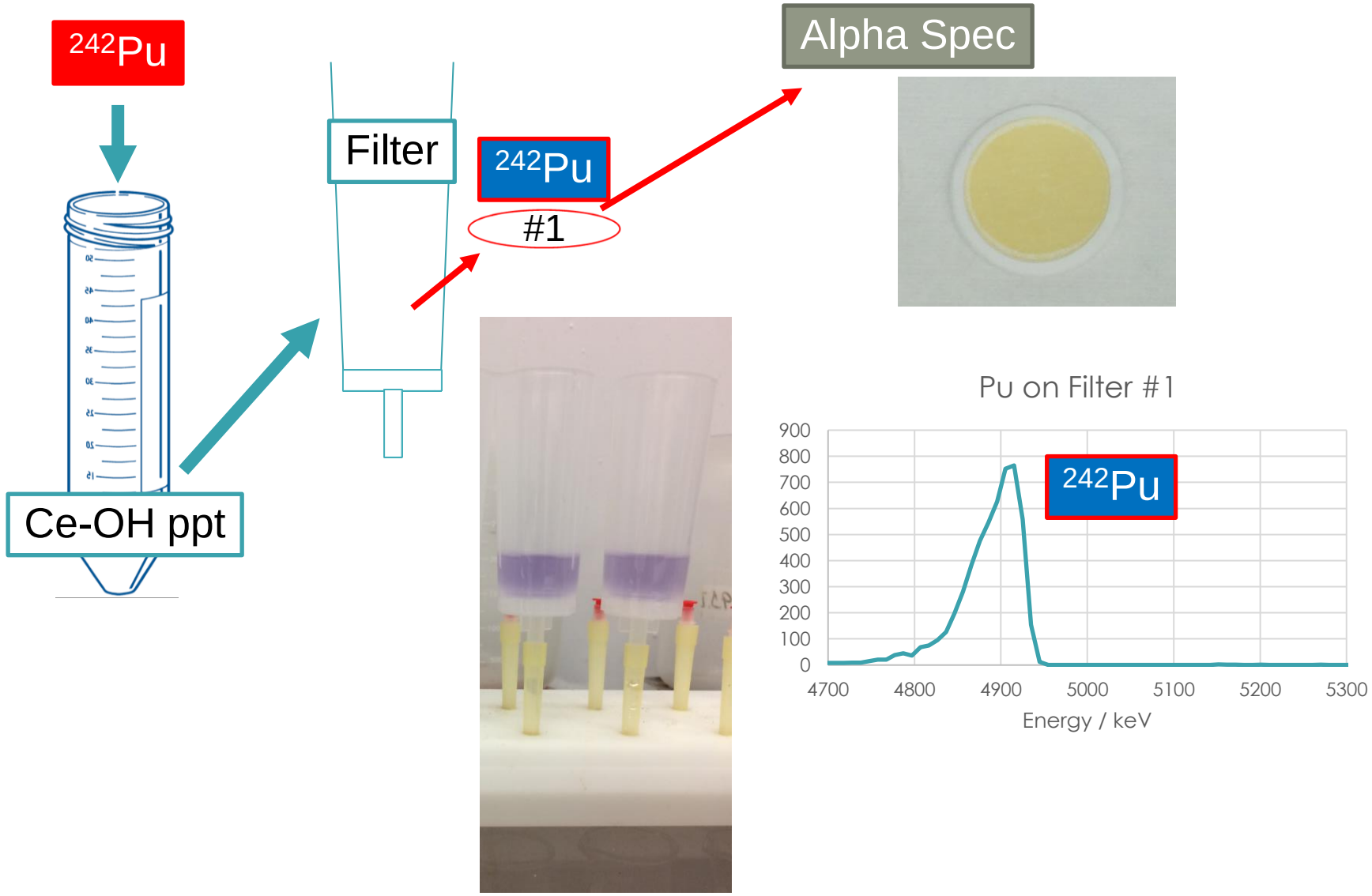


17 mm

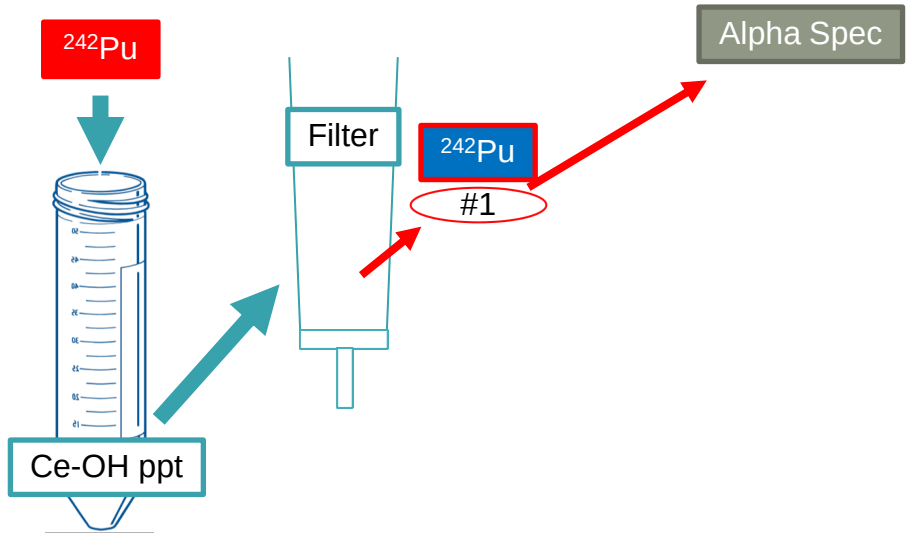


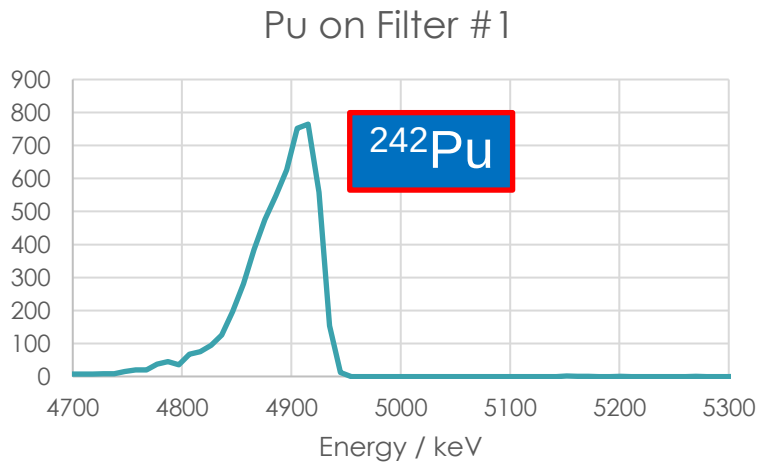
25 mm

Prepare Efficiency Standard by Micro-PPT

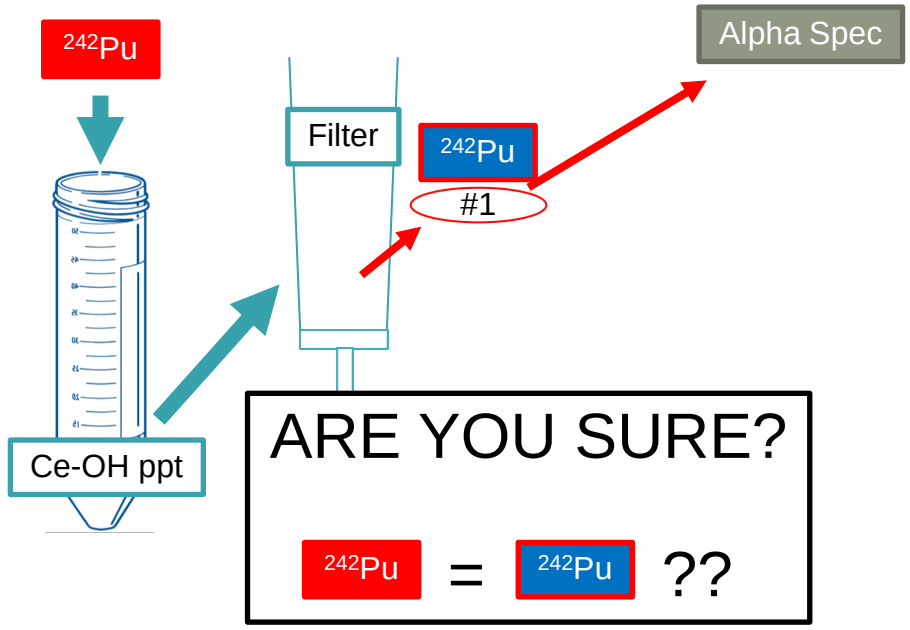


Added Activity	5.72 dpm
Micro-PPT Efficiency	23.1%
ED Efficiency	27.5%
Difference	-16.0%

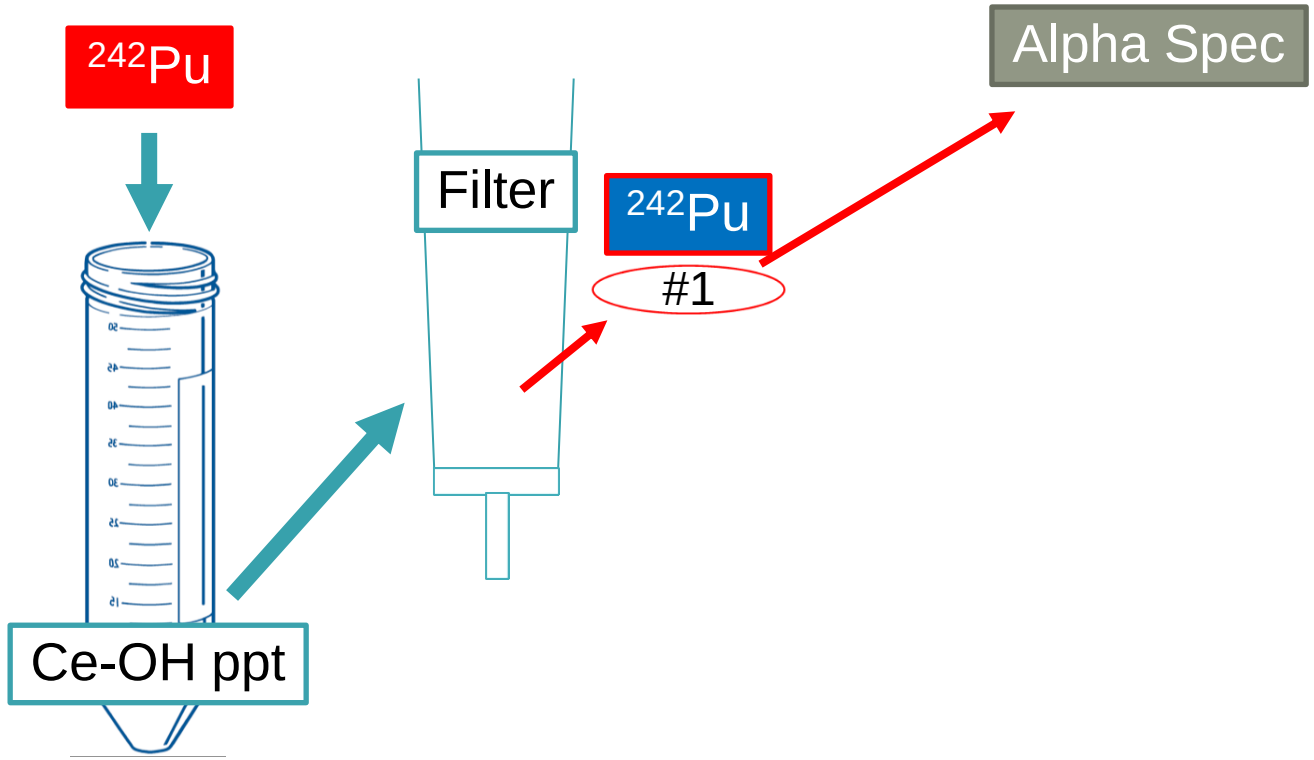




Added Activity	5.72 dpm
Micro-PPT Efficiency	23.1%
ED Efficiency	27.5%
Difference	-15.9%



How much ^{242}Pu is on the filter #1?



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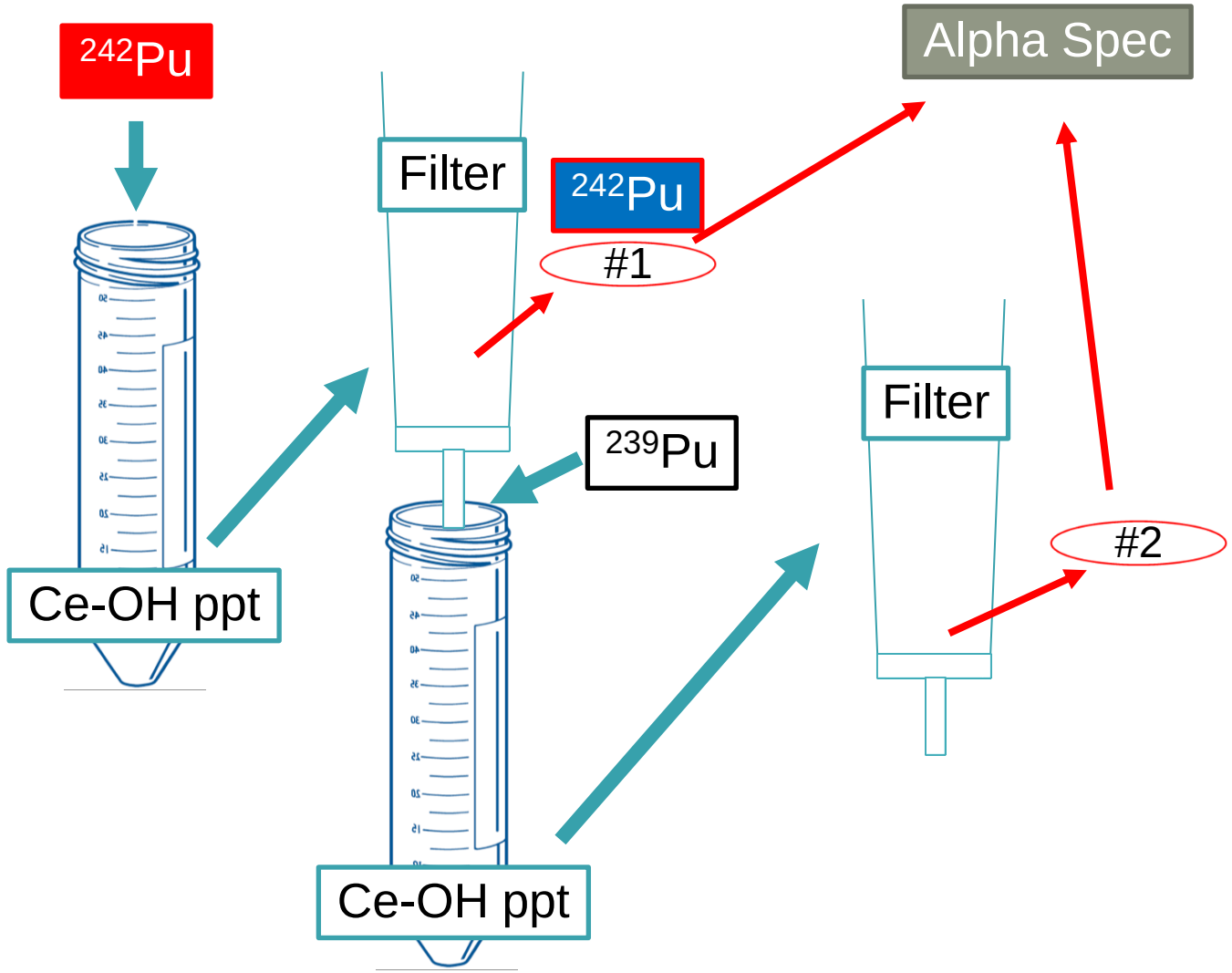

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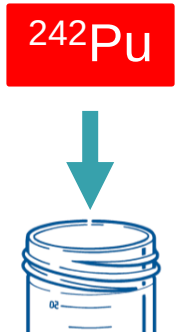

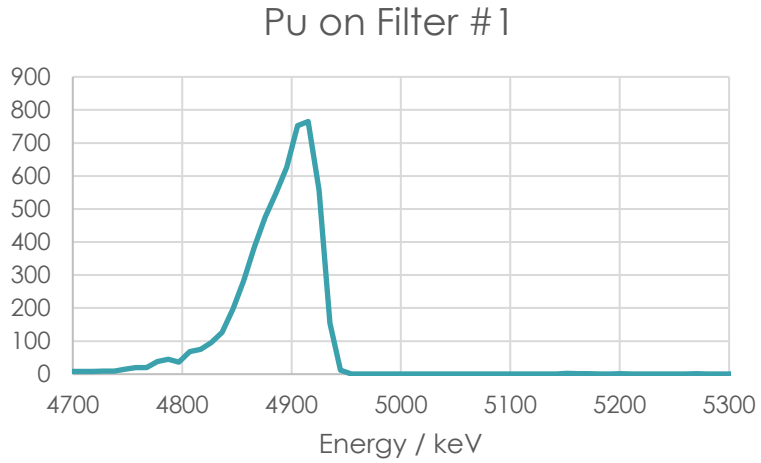

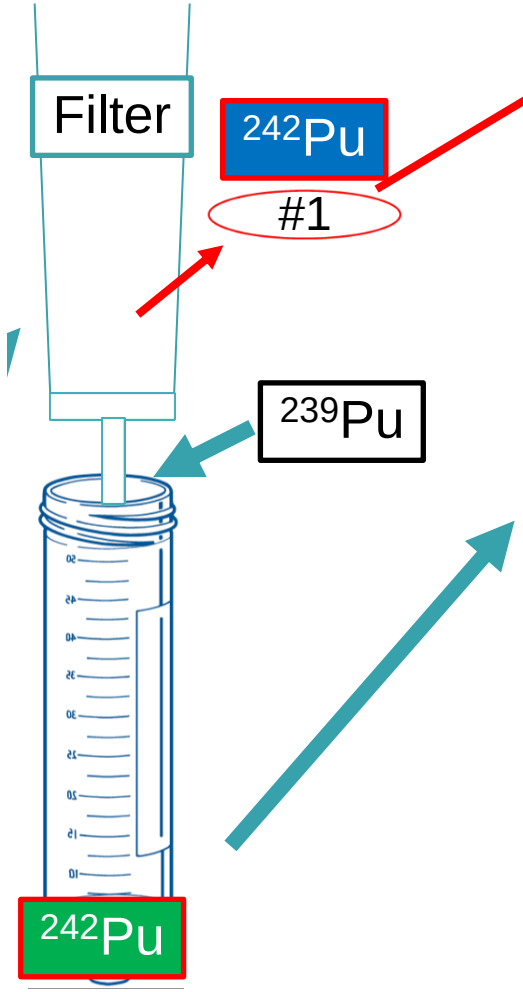

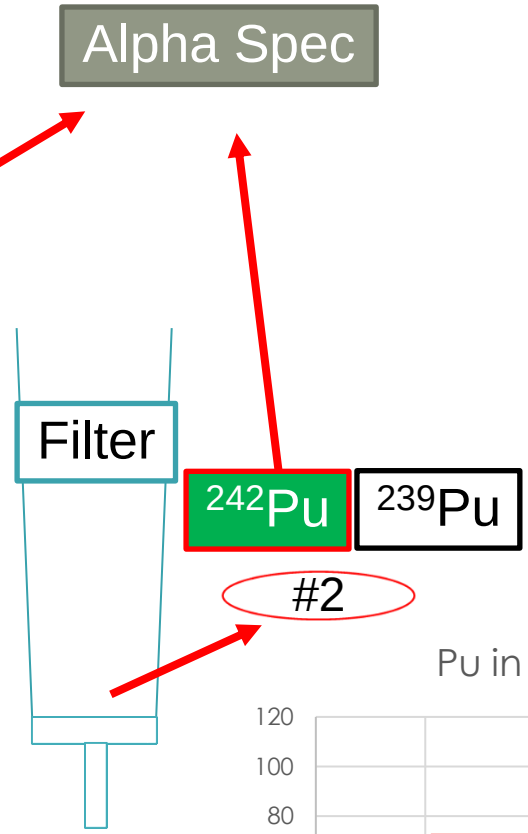

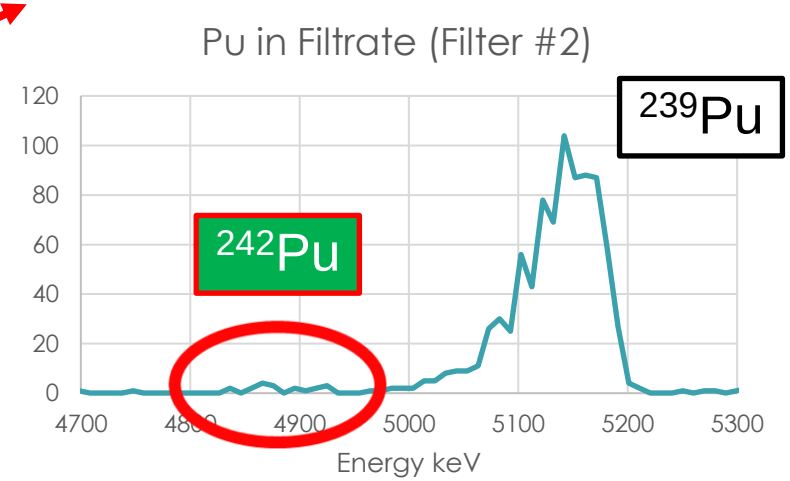

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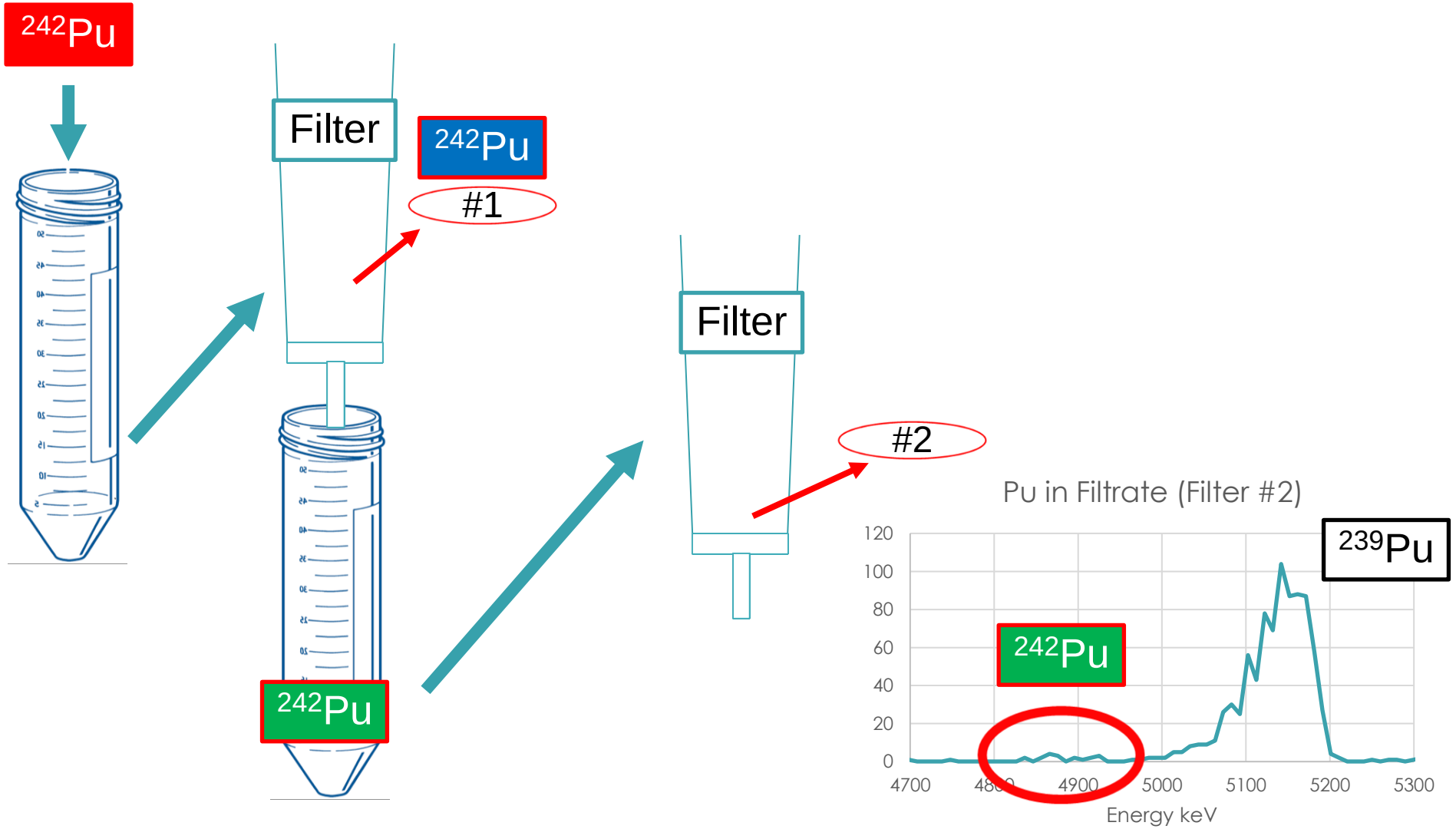
^{242}Pu on #1 = ^{242}Pu – ^{242}Pu calculated by #2



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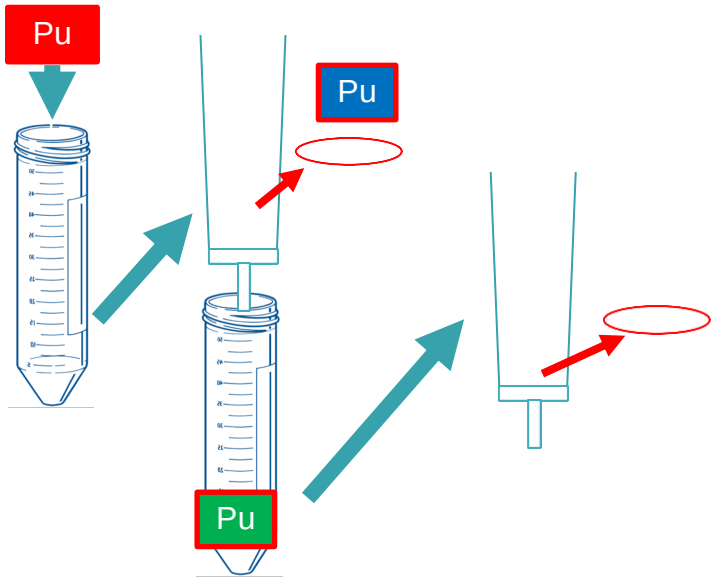
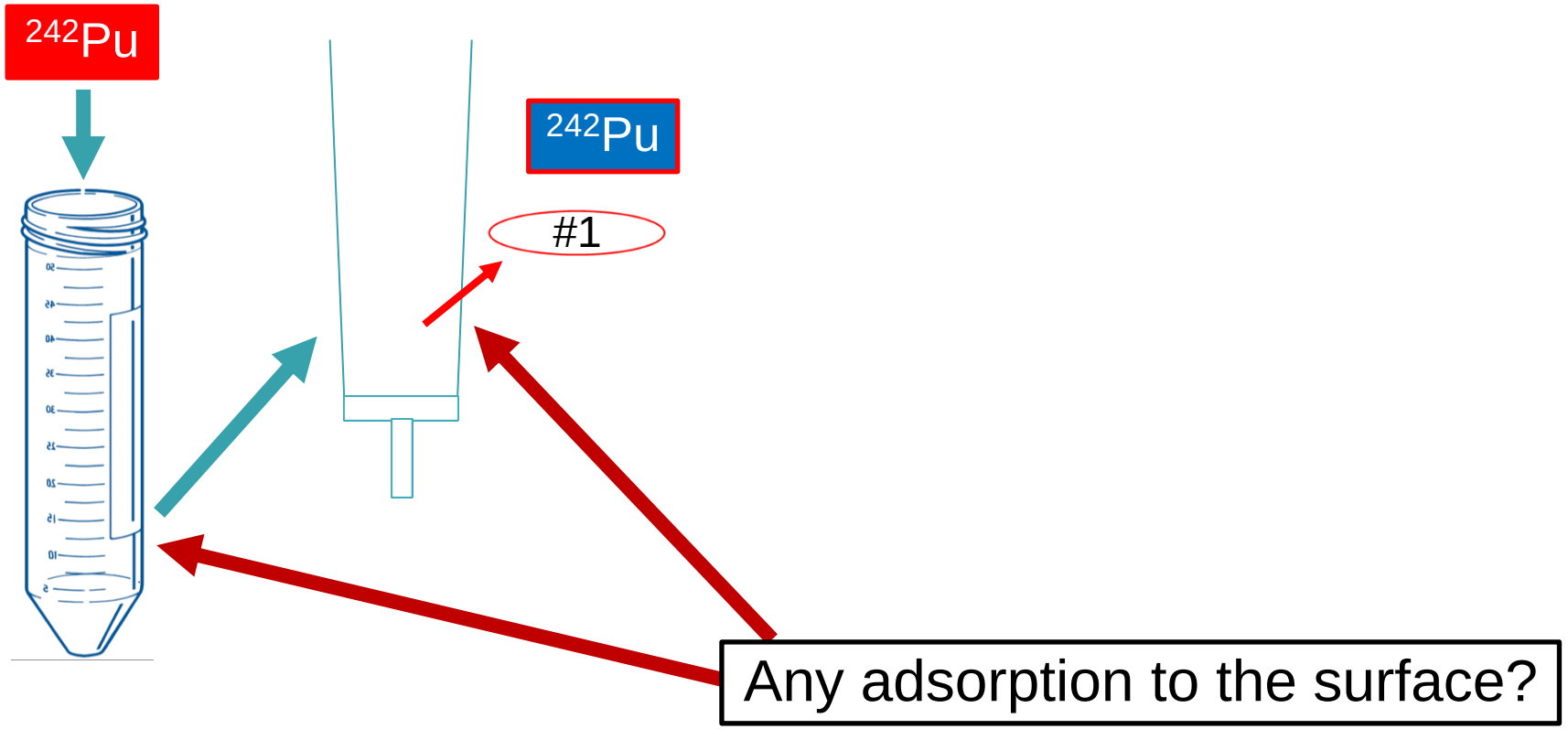
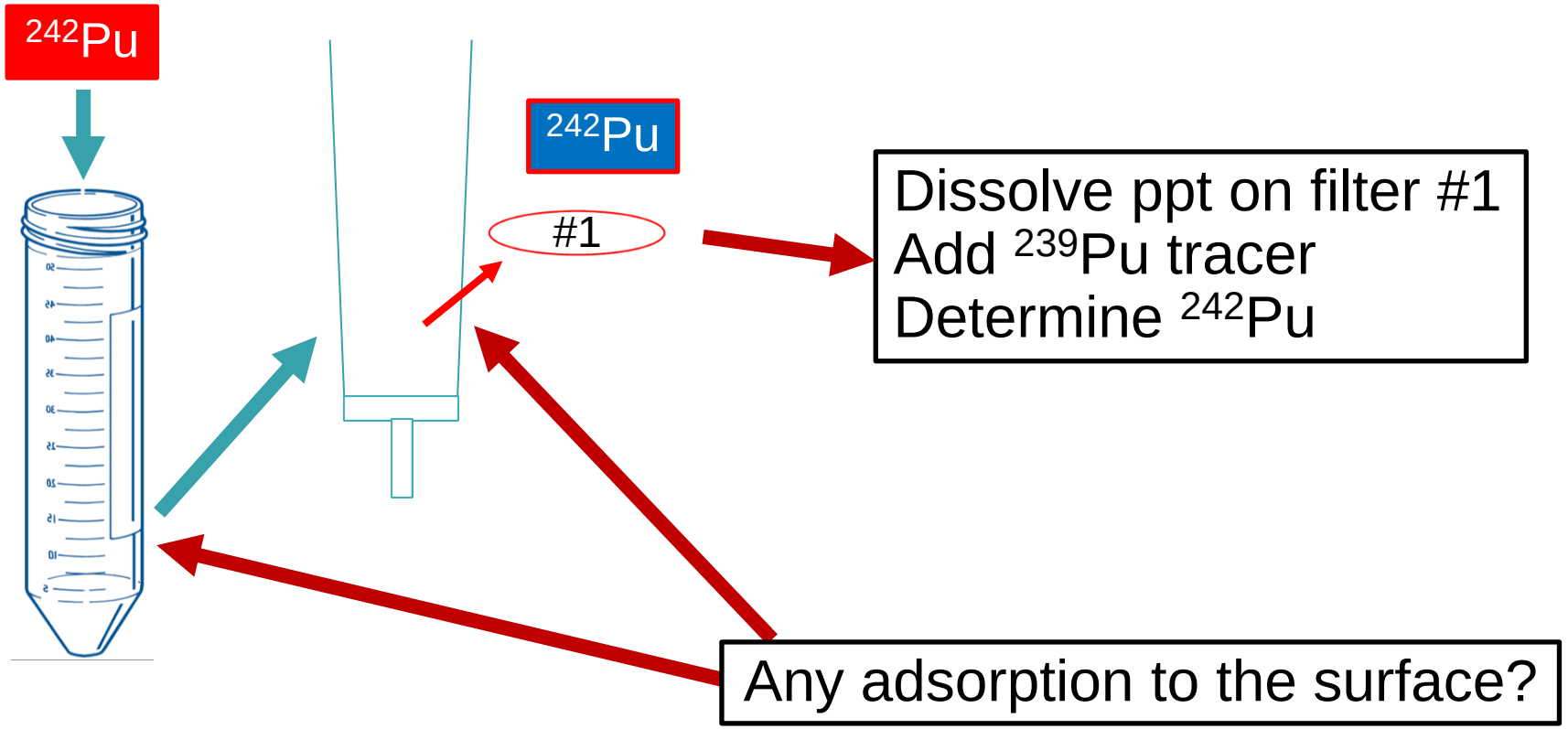
Added Activity	Pu	5.72 dpm
Activity in Filtrate	Pu	0.06 dpm
Activity on the Filter	Pu	5.66 dpm
Micro-PPT Efficiency		23.3% ← 23.1%
ED Efficiency		27.5%
Difference		-15.0% ← -16.0%



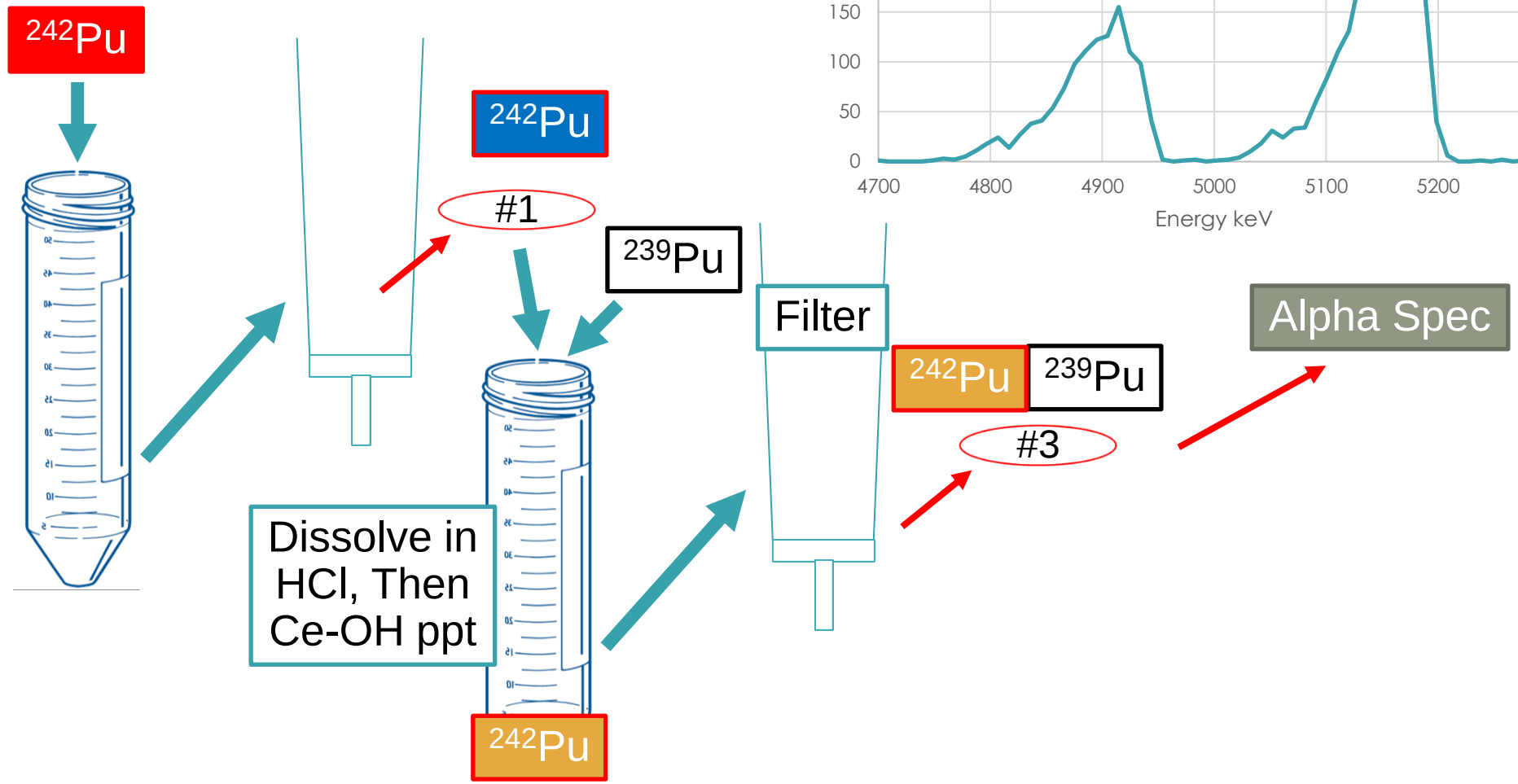
Is all the added ^{242}Pu accounted for?

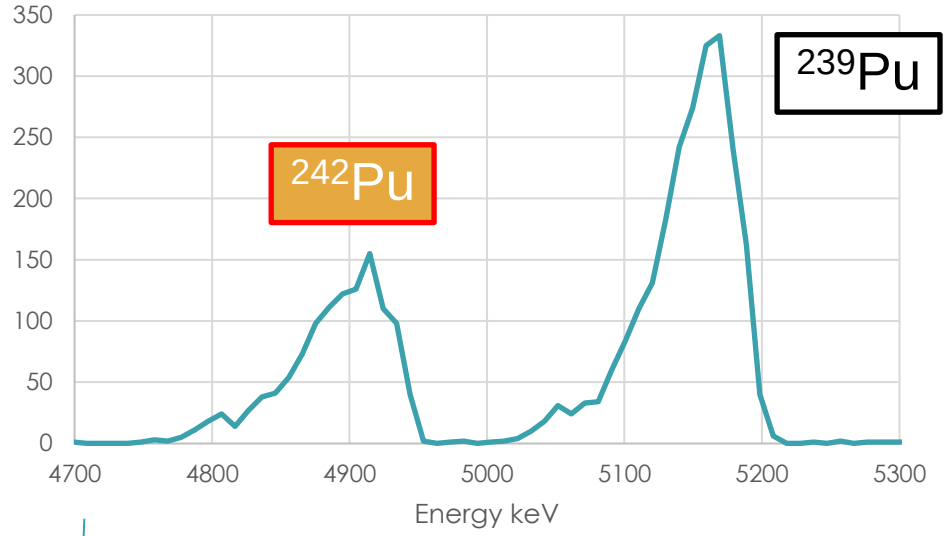


Is all the added ^{242}Pu accounted for?

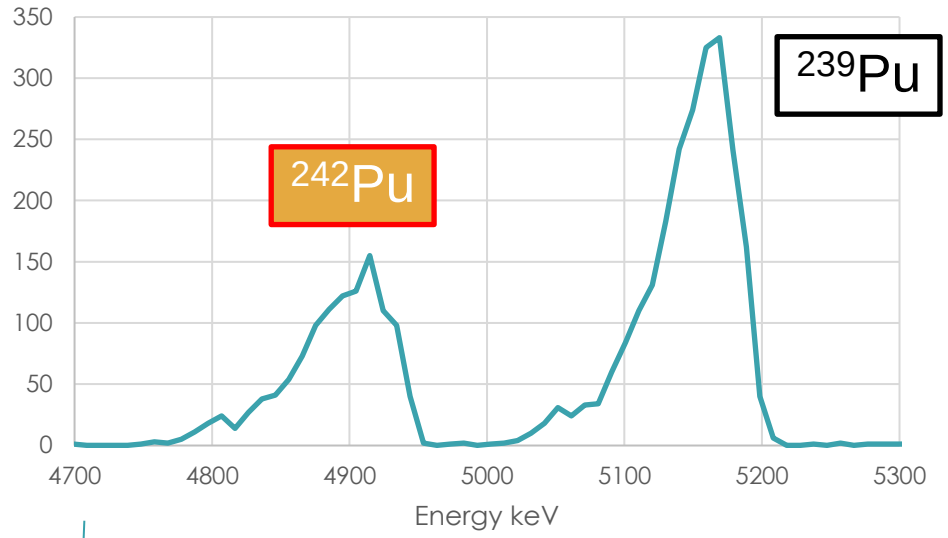


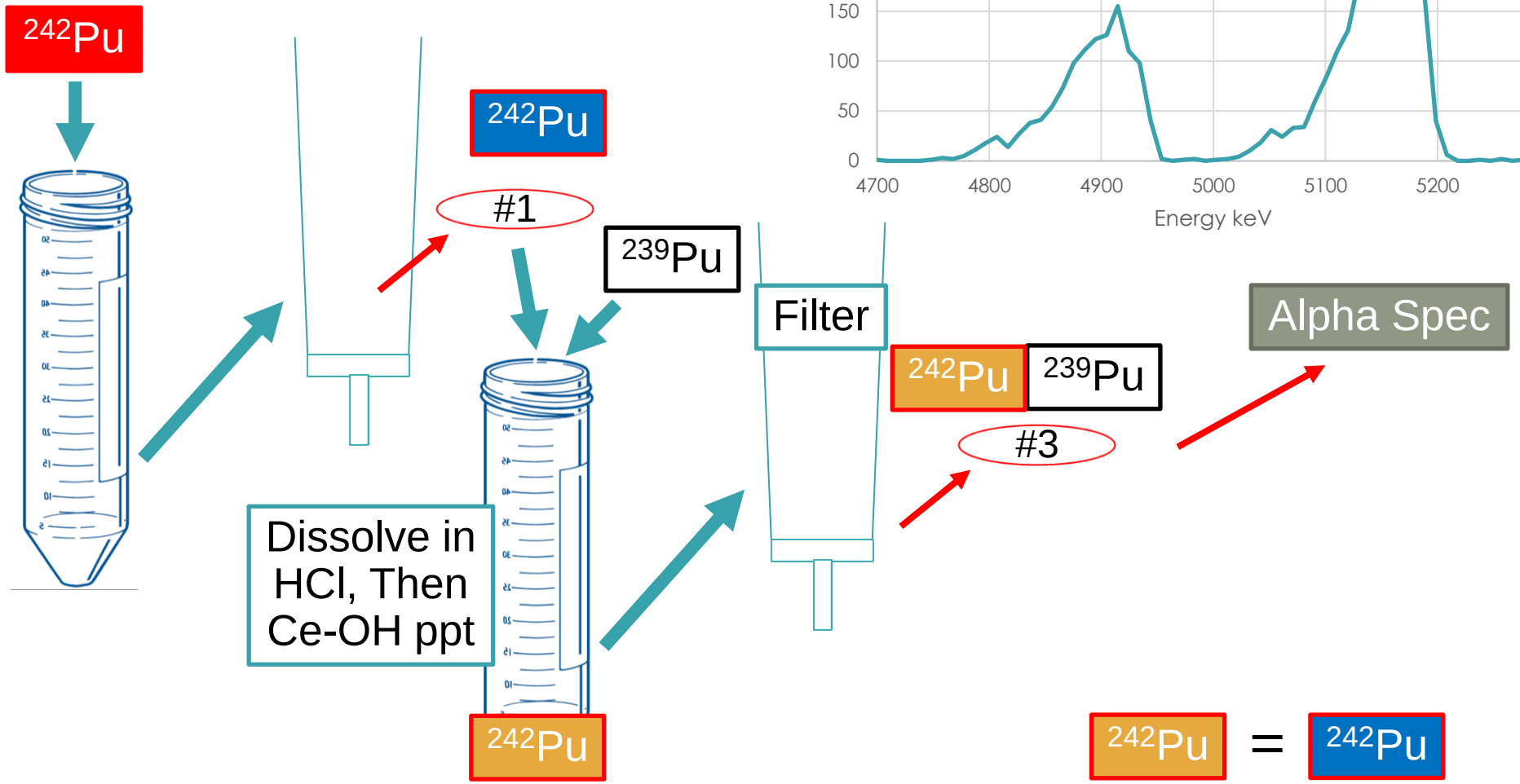
Did we cover all ^{242}Pu initially added?





Did we cover all ^{242}Pu initially added?





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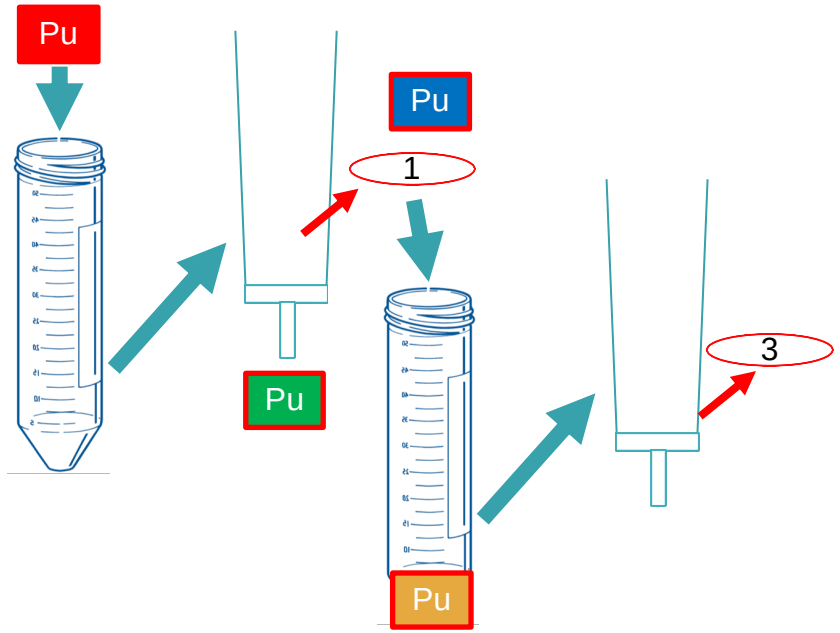
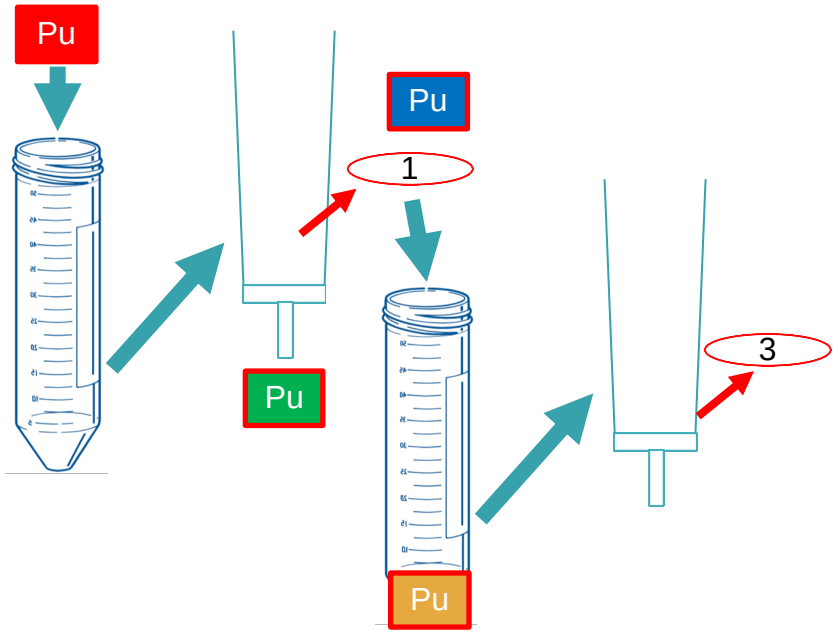
Added Activity Pu	5.72 dpm
Activity in Filtrate Pu	0.06 dpm
Activity on the Filter Pu	5.66 dpm
Activity Recovered from the Filter Pu	5.66 dpm
Micro-PPT Efficiency	23.3% ← 23.3% ← 23.1%
ED Efficiency	27.5%
Difference	-15.0% ← -15.0% ← -15.9%



$^{242}Pu = {}^{242}Pu$

Sometimes things do not work as hoped for.

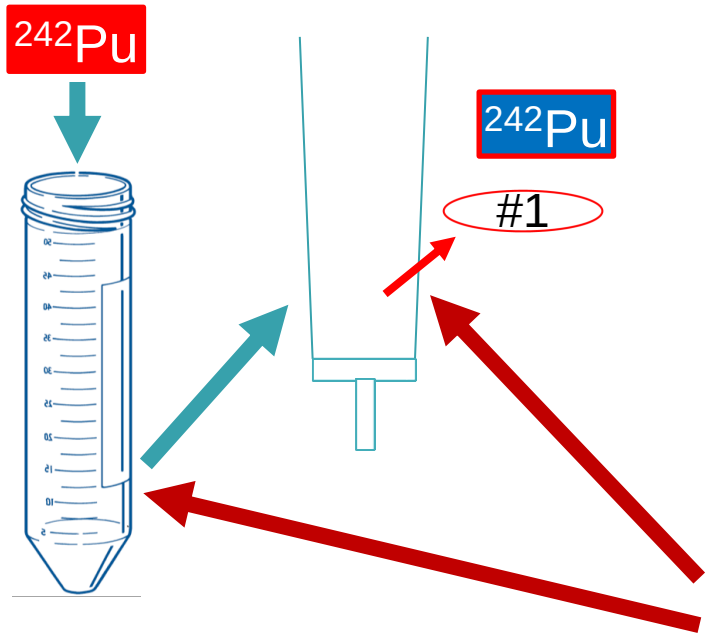
Added Activity Pu	5.75 dpm
Activity in Filtrate Pu	0.06 dpm
Activity on the Filter Pu	5.69 dpm → 23.4% efficiency
Activity Recovered from the Filter Pu	5.39 dpm → 24.7% efficiency
ED Efficiency	28.0%
Difference	-16.1% or -11.5%

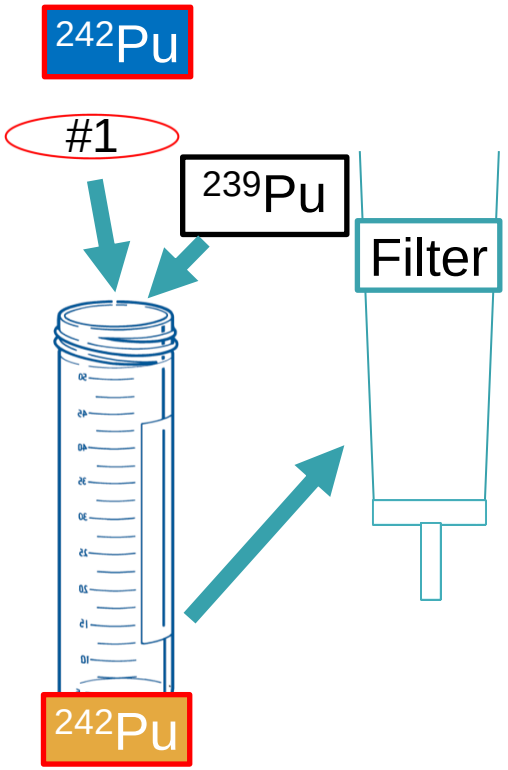


$^{242}Pu \neq {}^{242}Pu$

Where did 0.30 dpm of ^{242}Pu go?

- Lost Pu on the surface of plasticware by adsorption?
- Pu did not re-dissolve in HCl?





Why do we care about the detector efficiency?

$$Recovery = \frac{Tracer\ Counts}{Count\ Time \times Efficiency \times Tracer\ Activity}$$

$$Activity = \frac{Analyte\ Counts}{Tracer\ Counts} \times Tracer\ Activity$$

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Why do we care about the detector efficiency?

$$Recovery = \frac{Tracer\ Counts}{Count\ Time \times Efficiency \times Tracer\ Activity}$$

For Alpha Tracer

$$Activity = \frac{Analyte\ Counts}{Tracer\ Counts} \times Tracer\ Activity$$

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Why do we care about the detector efficiency?

$$Recovery = \frac{Tracer\ Counts}{Count\ Time \times Efficiency \times Tracer\ Activity}$$

For Alpha Tracer

$$Activity = \frac{Analyte\ Counts}{Tracer\ Counts} \times Tracer\ Activity$$

For Beta Tracer

$$Activity = \frac{Analyte\ Counts}{Count\ Time \times Efficiency \times Recovery}$$

From Beta Counting

Why do we care about the detector efficiency?

$$Recovery = \frac{Tracer\ Counts}{Count\ Time \times Efficiency \times Tracer\ Activity}$$

For Alpha Tracer

$$Activity = \frac{Analyte\ Counts}{Tracer\ Counts} \times Tracer\ Activity$$

For Beta Tracer

$$Activity = \frac{Analyte\ Counts}{Count\ Time \times Efficiency \times Recovery}$$

Correct efficiency is required when beta tracers are used.

Summary

- Electrodeposition
  - Sharp Resolution, Longer Procedure, Labor Intensive
- Fluoride Micro-Precipitation
  - Simpler Procedure, Hazardous HF
- Hydroxide Micro-Precipitation
  - Simpler / Safer Procedure, Non-Selective Precipitation

- Efficiency needs to be established for micro-precipitation.

Acknowledgements

- April Tucker — Lab Manager
- Jaimie Daum — Radiochemist
- Joe Conner — Counting Room Technical Lead
- Susan Lambert — Counting Room Technician
- Rob Jones — Group Leader
- Govind Rao — Ex Group Leader
- Rebecca Mueller — Summer Student
- Joey Michaud — Summer Student

KI **Kenneth Inn** 午前 5:45

宛先 あなた

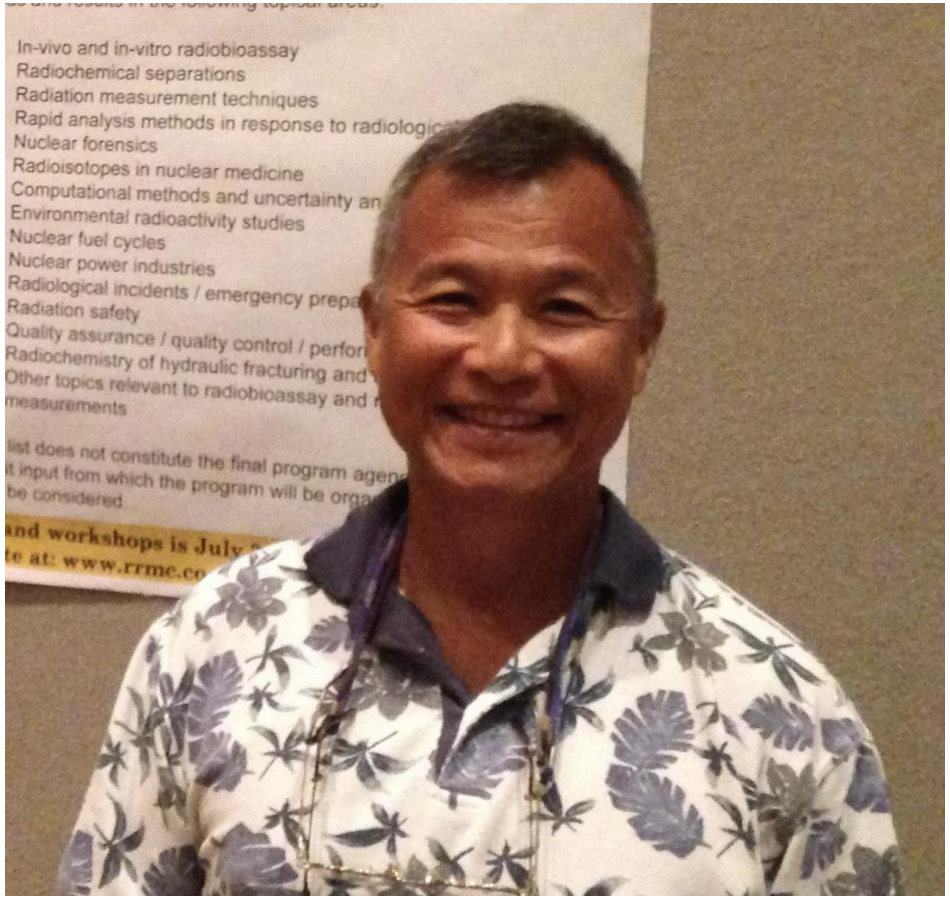
Hiromu,

I saw your title for the CIRMS meeting. It looked interesting. Would you share it with me?

Please pass my best wishes to all for me.

Best wishes to you and your family,

Ken



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Thank you.

Hiromu Kurosaki

hzk@ornl.gov

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