Development of a Sodium Bismuthate-Coated Polyacrylonitrile Resin for the Separation of Oxidized Americium from Curium

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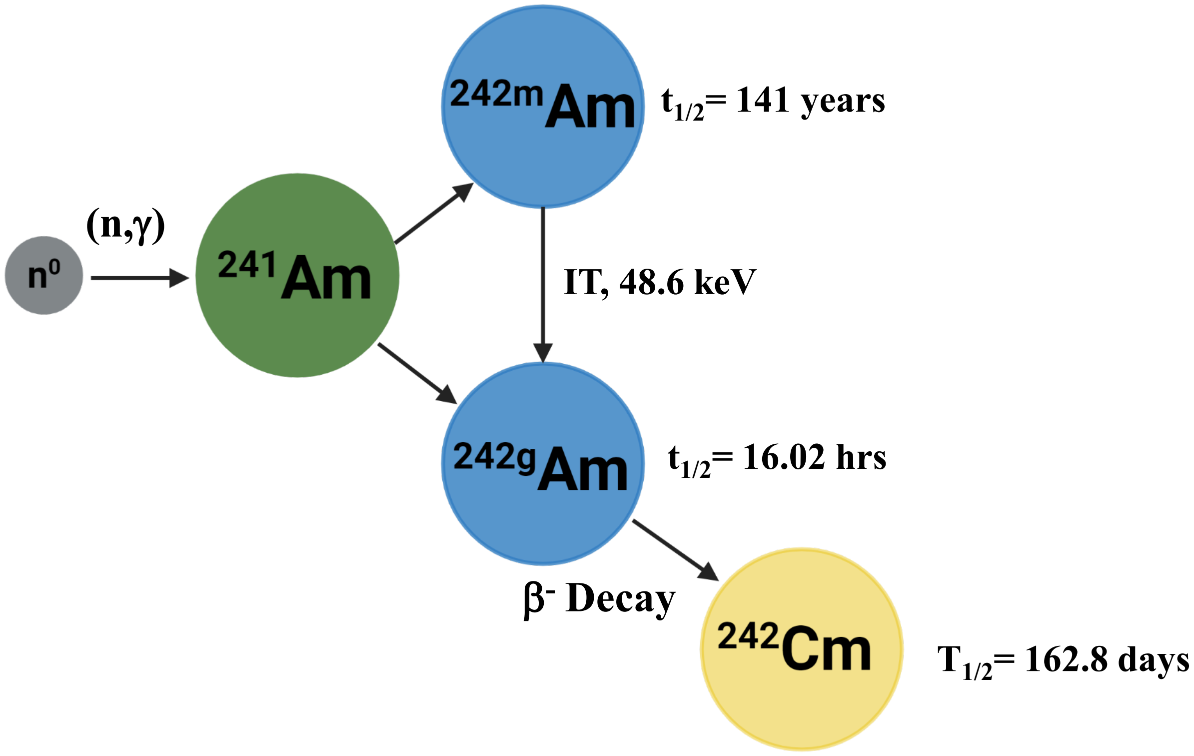
65th RRMC – TrisKem Workshop| November 3, 2022

Nuclear Data Needs for Stockpile Stewardship

- NNSA 2021 Stockpile Stewardship and Management Plan
  - Ensure safety and reliability of the stockpile without underground testing
- Nuclear Data Needs
  - Accurate cross section measurements
  - Am-242*m*/Am-242*g* Isomeric Ratio

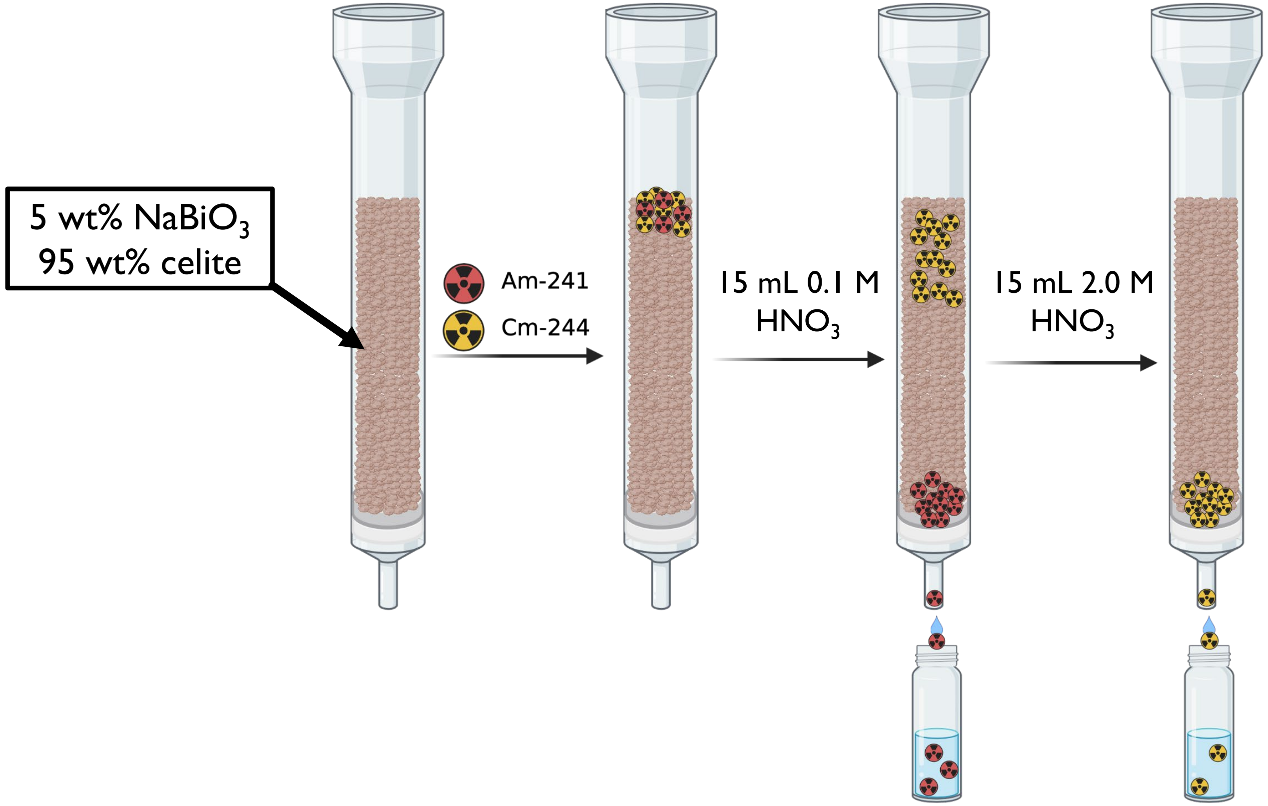


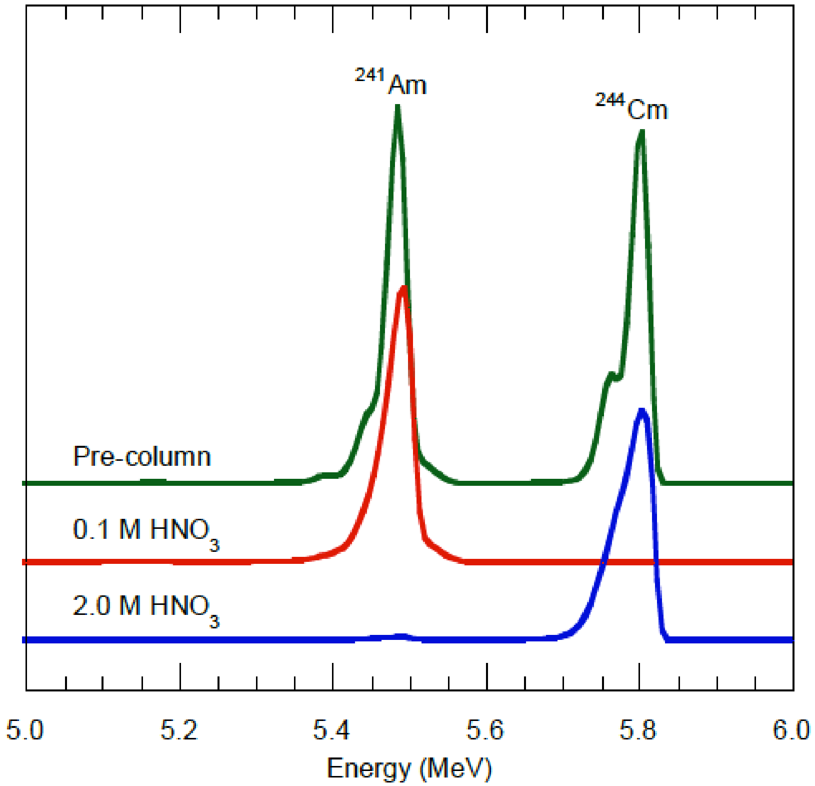
Measurement Strategy

Irradiate Am-241 targets at various neutron energies → Quantify Cm-242 at various times post-irradiation → Determine cross-section and Am-242g/m ratio as a function of neutron energy

Required: Complete separation and recovery of Am and Cm

Am/Cm SEPARATION USING 5% $NaBIO_3$ IN CELITE



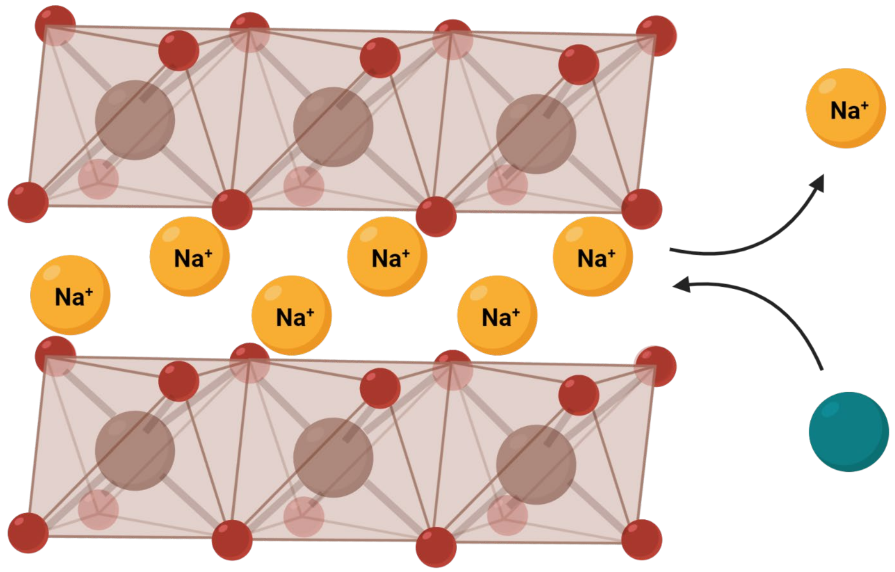


Richards, J. M.; Sudowe, R. *Anal. Chem.* **2016**, *88*, 4605-4608

$NaBIO_3$ OXIDIZING AGENT

Ilmenite Structure → Ion Exchange Properties

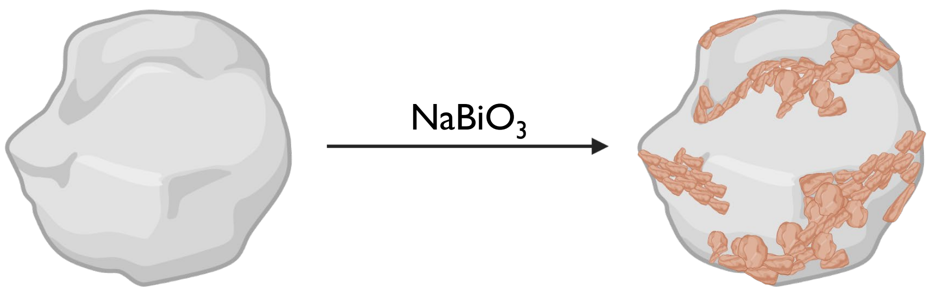
- Octahedral bismuth centers and sodium cations
- Literature shown for alkali, alkaline earth, and U(VI)



Kumada, N., *Solid State Ionics*, **1999**, *122*, 183-189
Einkauf, J. D., *Inorg. Chem.* **2018**, *57*, 15341-15349

$NaBiO_3$-PAN RESIN DEVELOPED BY TrisKem

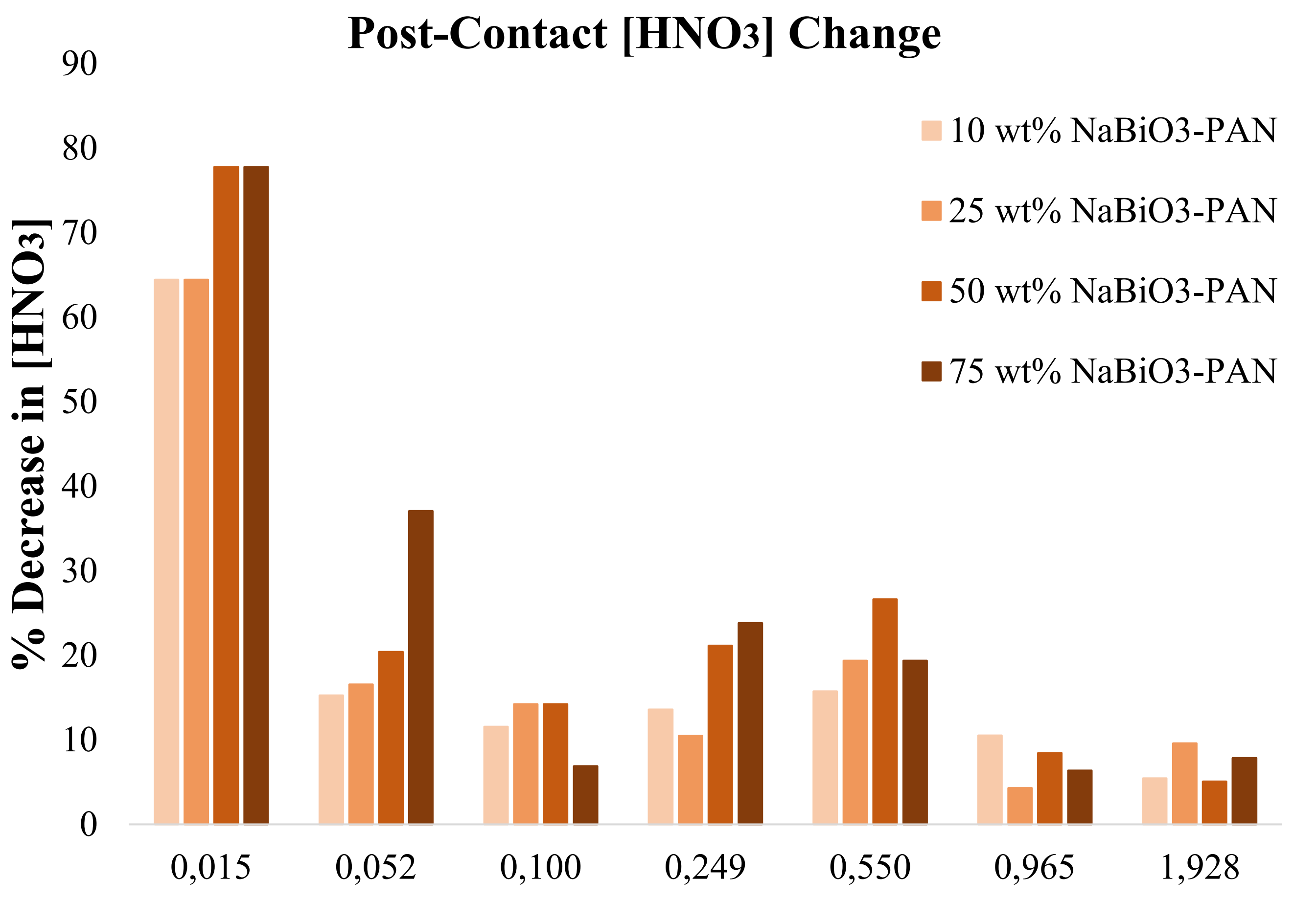
- Resin Preparation
  - $NaBiO_3$ not bound to resin
  - Not prepared with diluents like EXC resins



- Particle Size Analysis
  - Dried resin, broke up clumps, and separated with hand sieve
  - 125 - 500 micron range

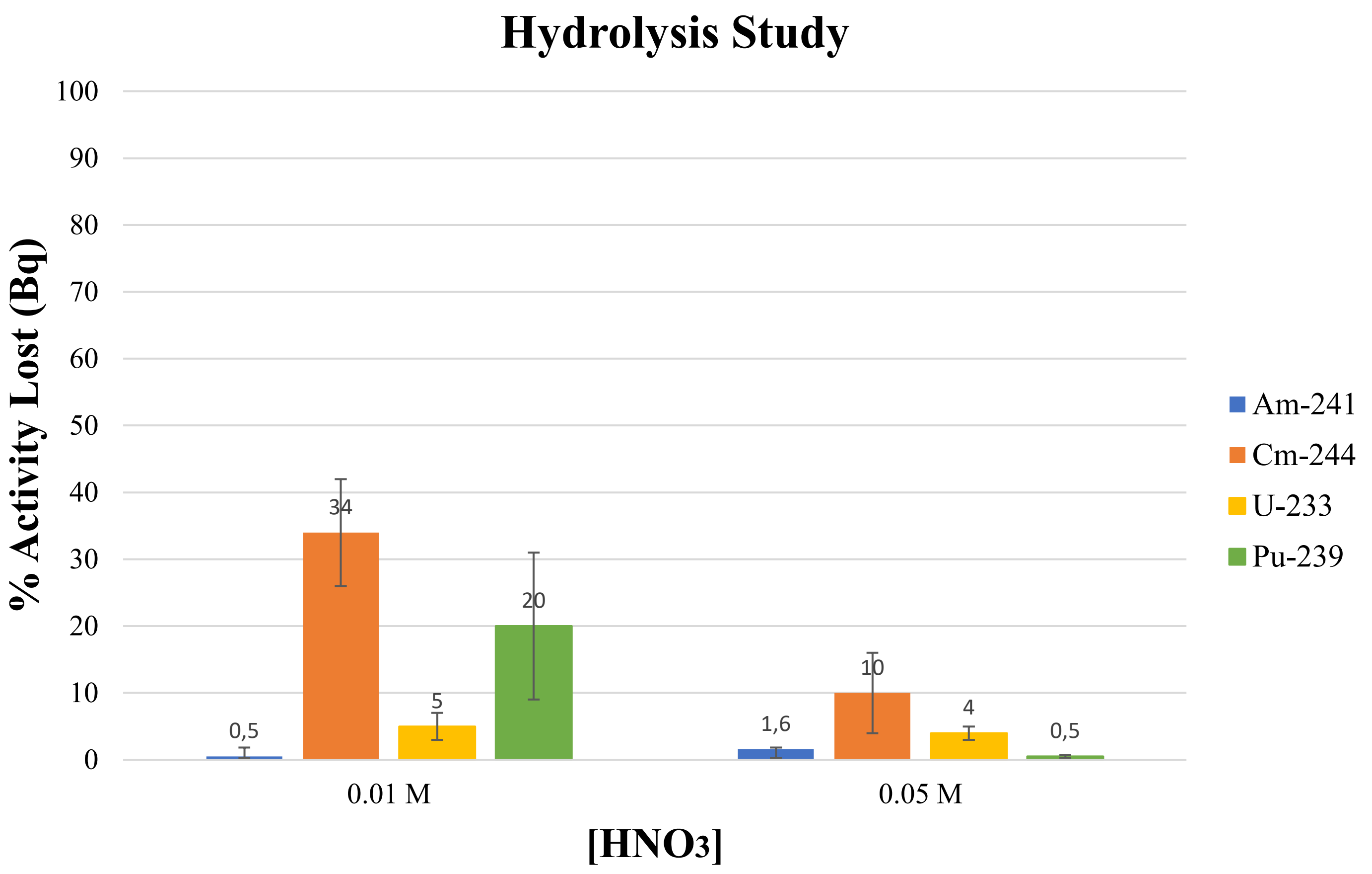
Effect on [HNO_3]

- Surface of sodium bismuthate is basic
- Change in Acid Concentration
  - HNO_3 solutions titrated prior to contact with resin
  - 1.5 mL of acid added to 50 mg of resin x2
  - Post-contact titrations
- Acidification of surface necessary

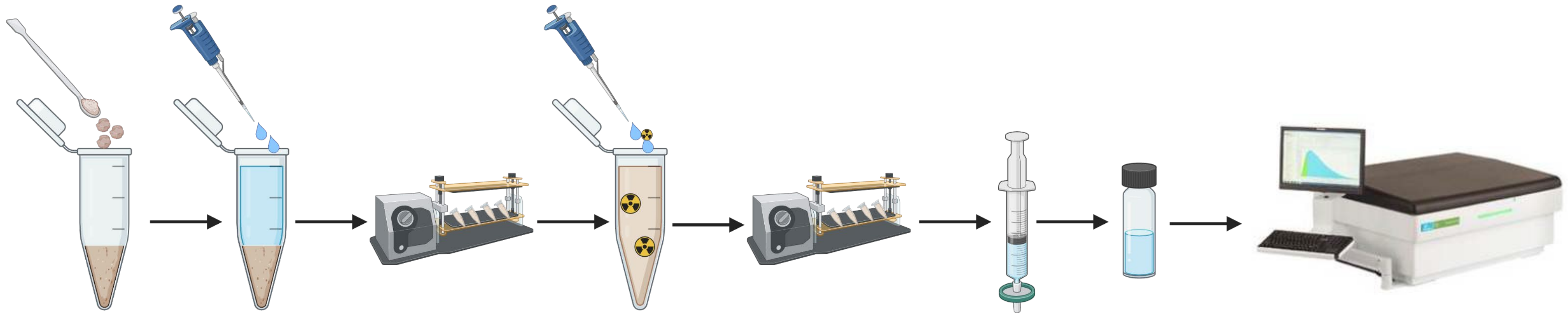


Hydrolysis Study

1. Contacted 1.5 mL of 0.01 and 0.05 M HNO_3 with 50 mg $NaBiO_3$ for 1 hour
2. Separated by centrifugation, transfer 1.45 mL supernatant to empty microcentrifuge tube
3. Spike with 50 µL radionuclide stock
4. Shake for 1 hour
5. Analyze 1 mL aliquot via LSC



METHOD: BATCH CONTACT STUDIES



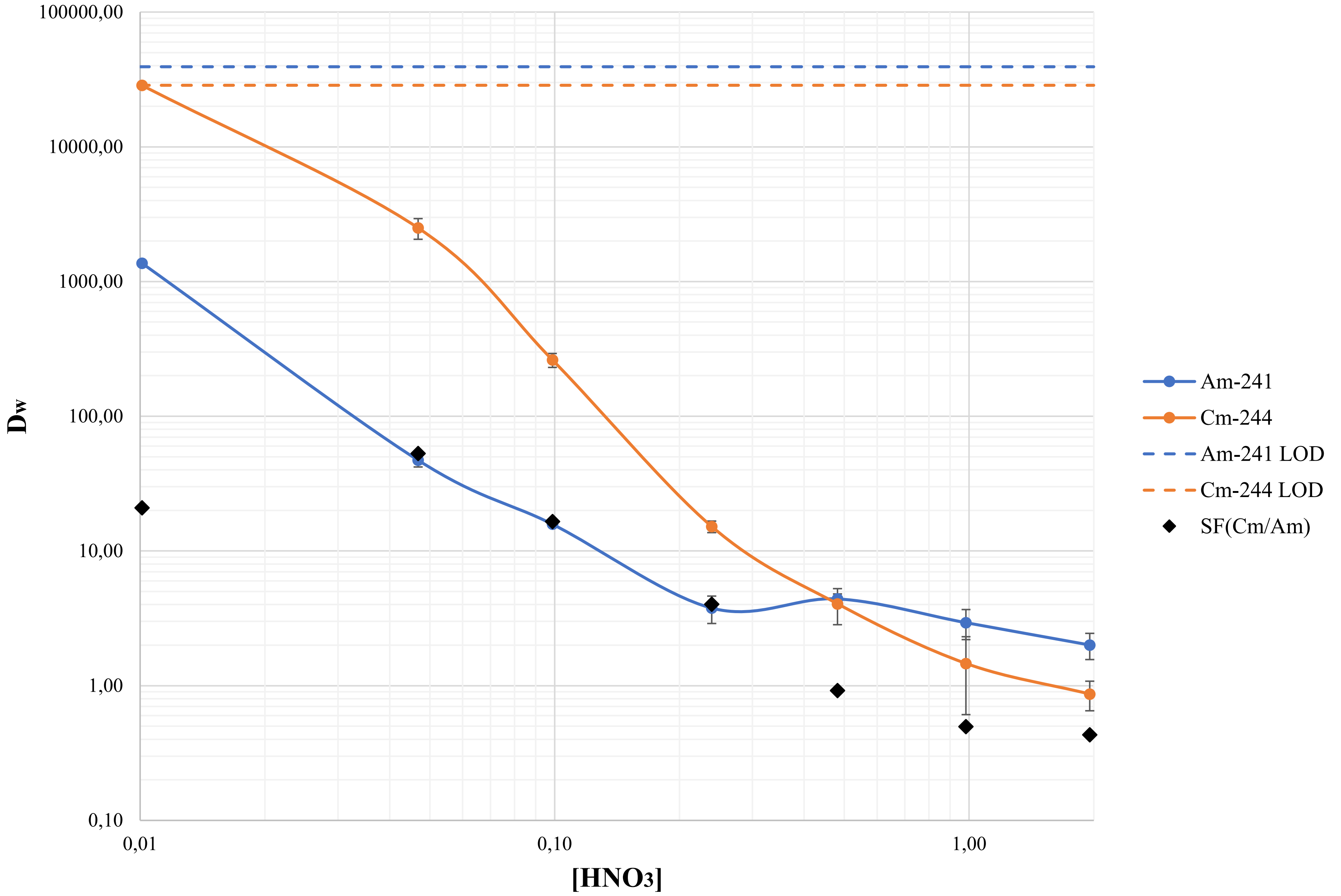
1a 1b 1c 2a 2b 3a 3b

1. **Preconditioning**
   a) 50 mg resin
   b) Desired acid concentration
   c) Agitate for 1 hour

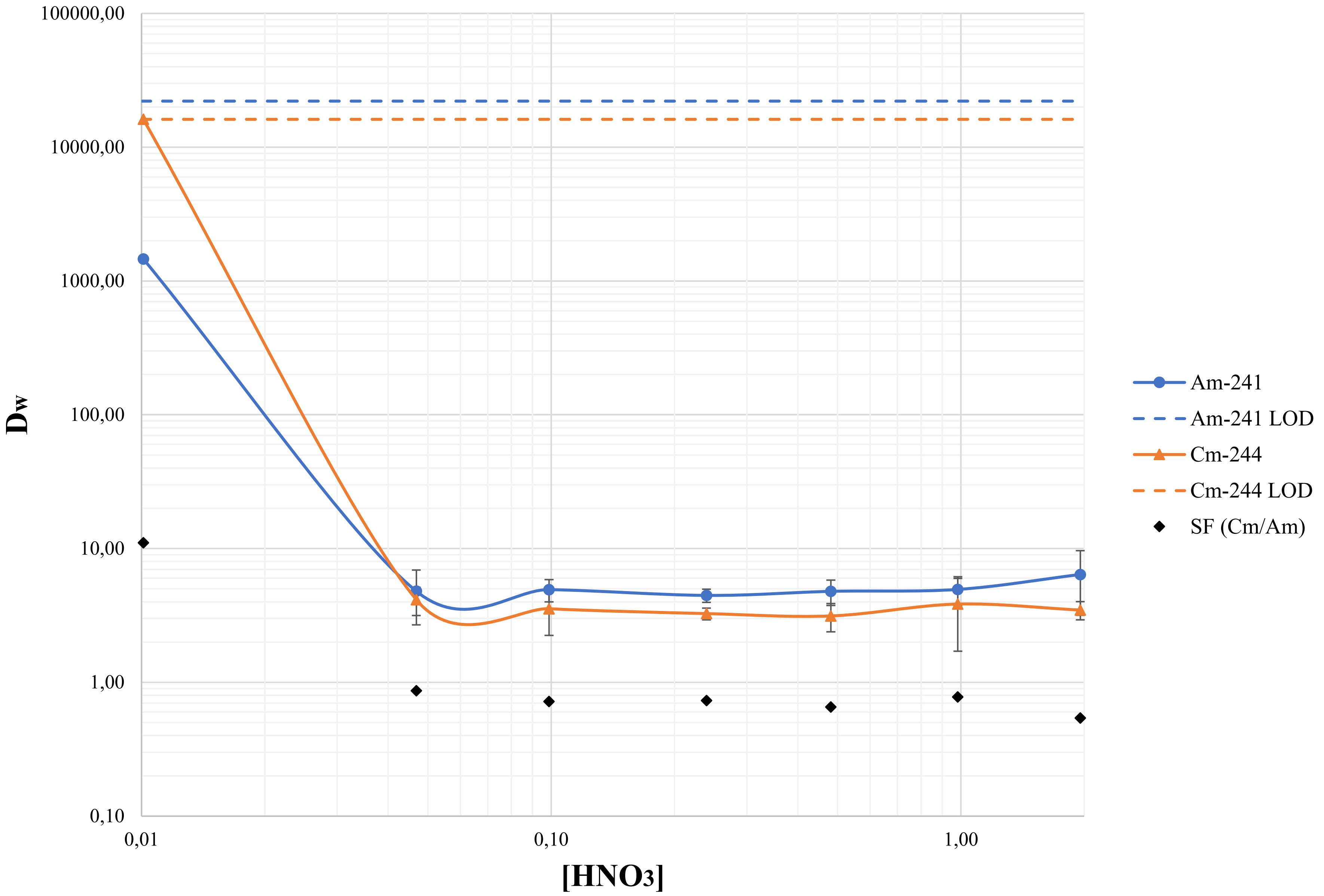
2. **Spiking**
   a) $^{241}Am/^{244}Cm$
   b) Agitate for 1 hour

3. **Analysis**
   a) Filter sample using PTFE syringe filter
   b) Transfer aliquot of the filtered eluent for analysis

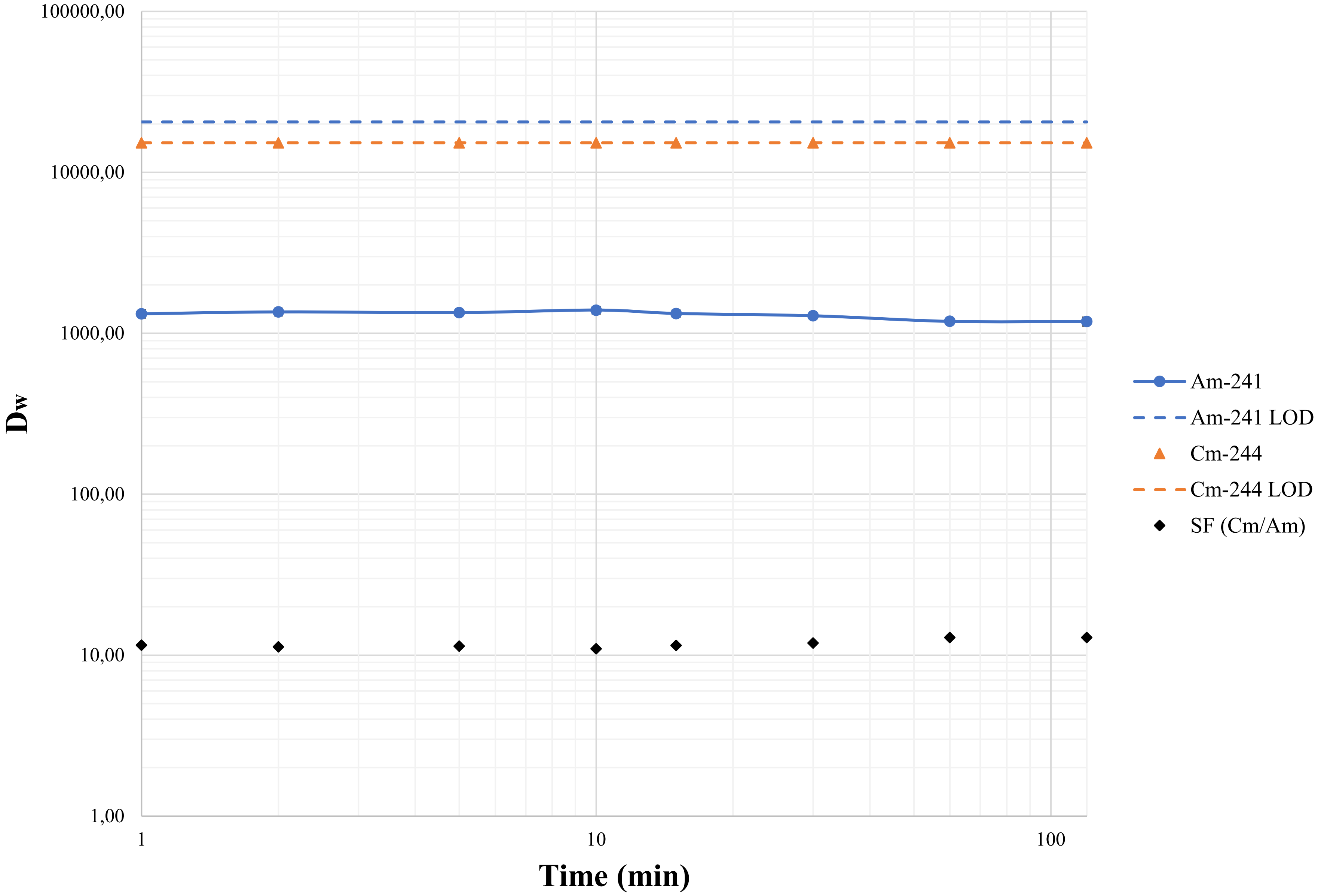
Am/Cm on $NaBiO_3$ Solid (Idaho National Lab)



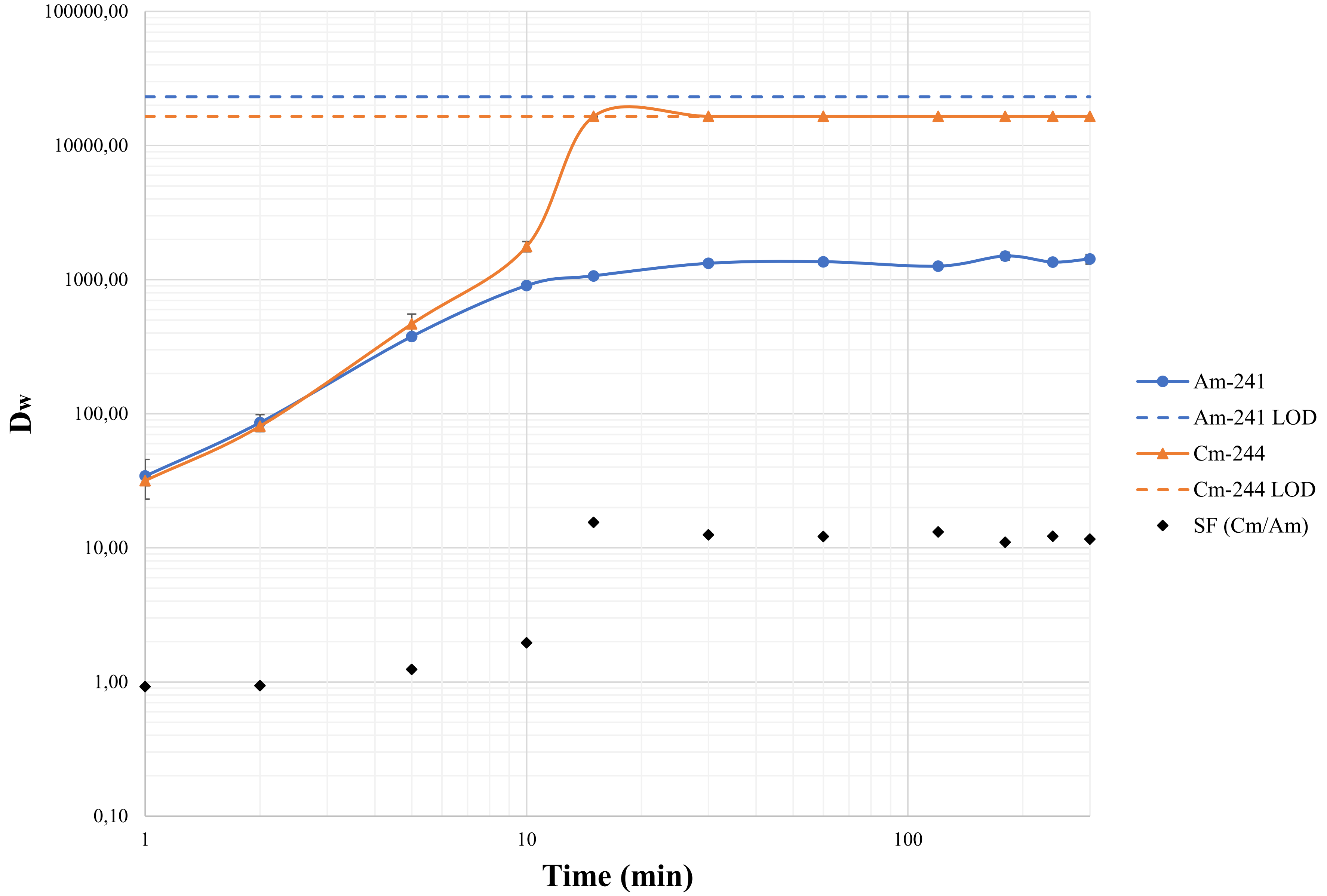
75 wt% $NaBiO_3$-PAN Concentration Dependency



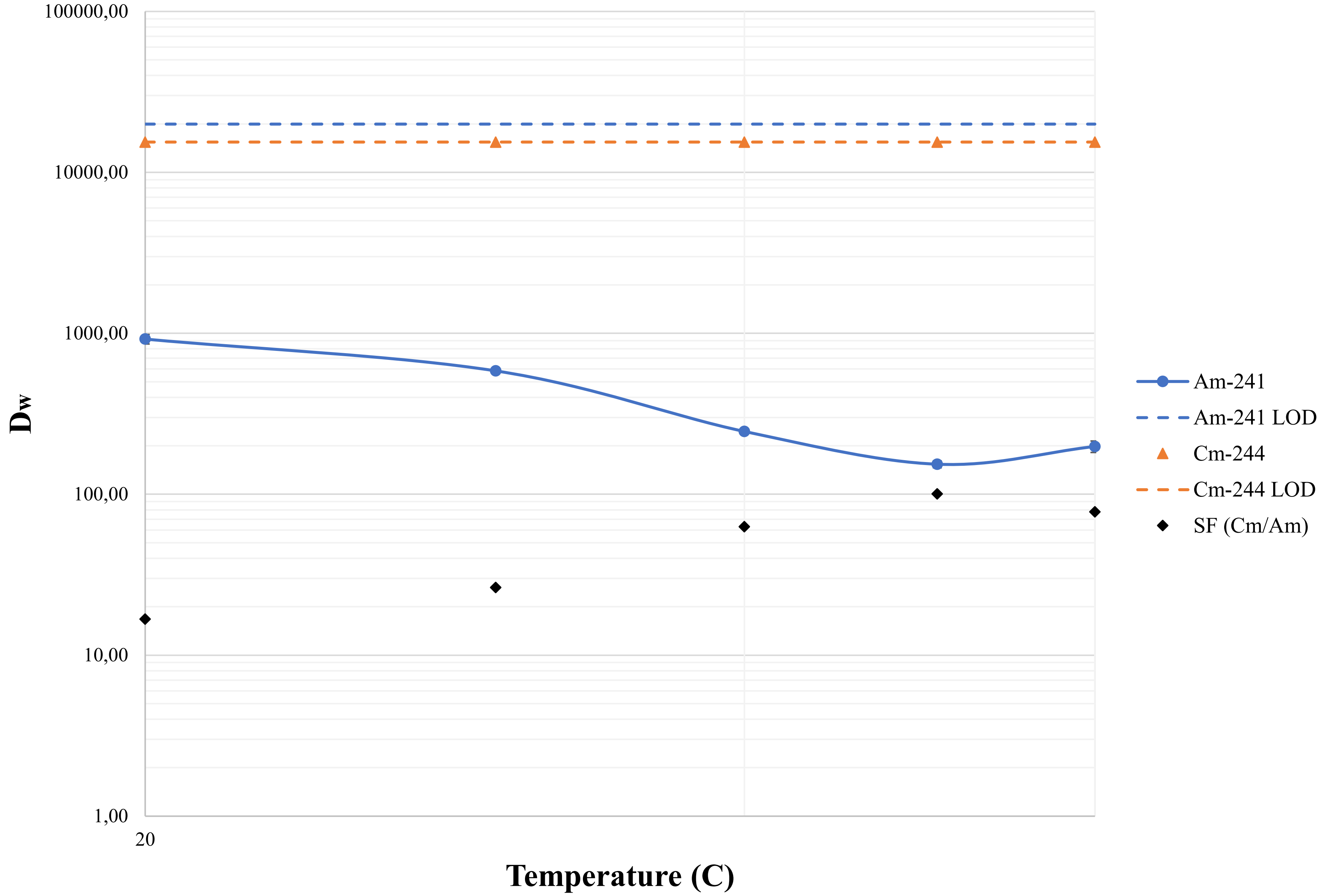
75 wt% $NaBiO_3$-PAN Precondition Time Dependency (0.01 M HNO_3)



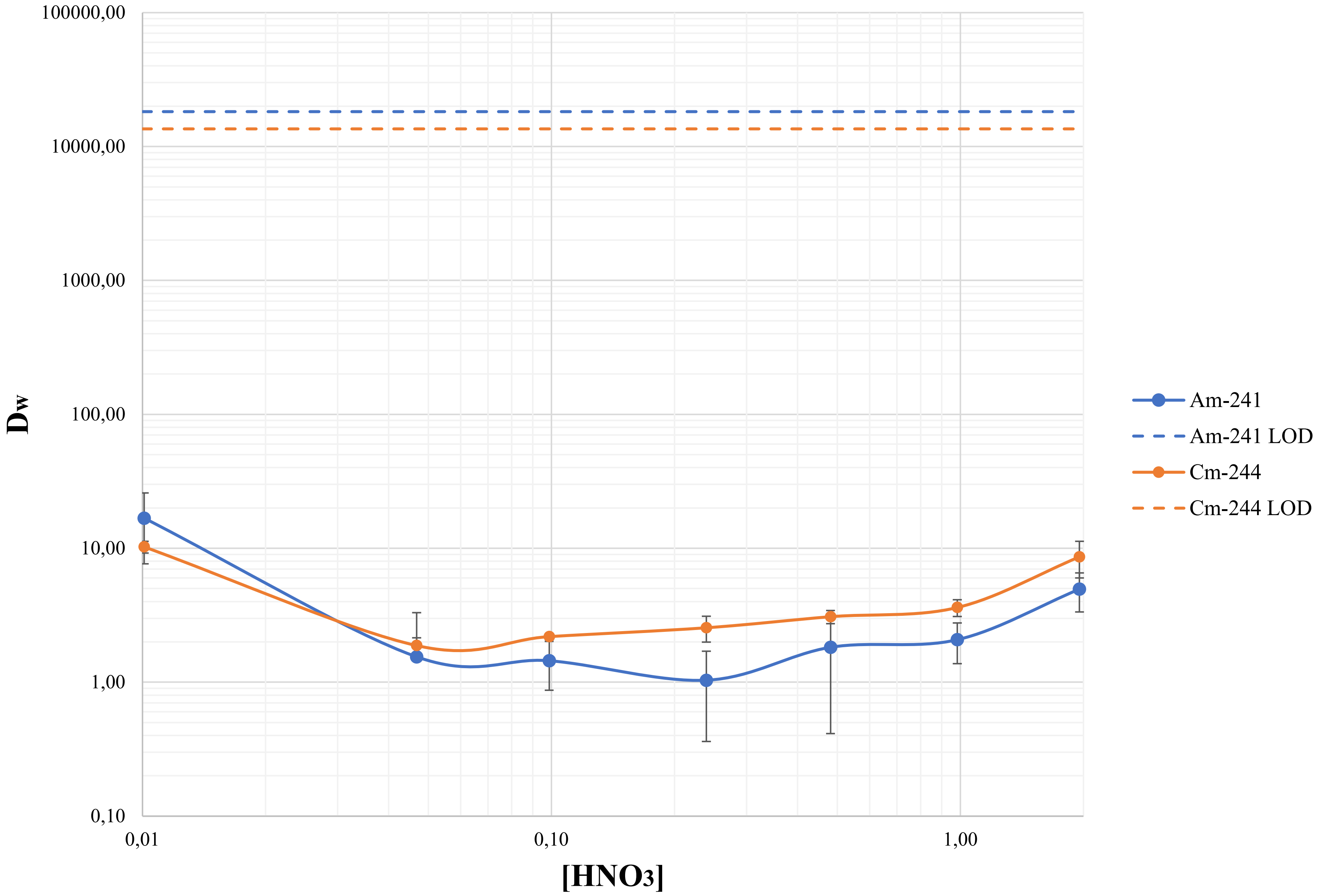
75 wt% $NaBiO_3$-PAN Contact Time Dependency (0.01 M HNO_3)



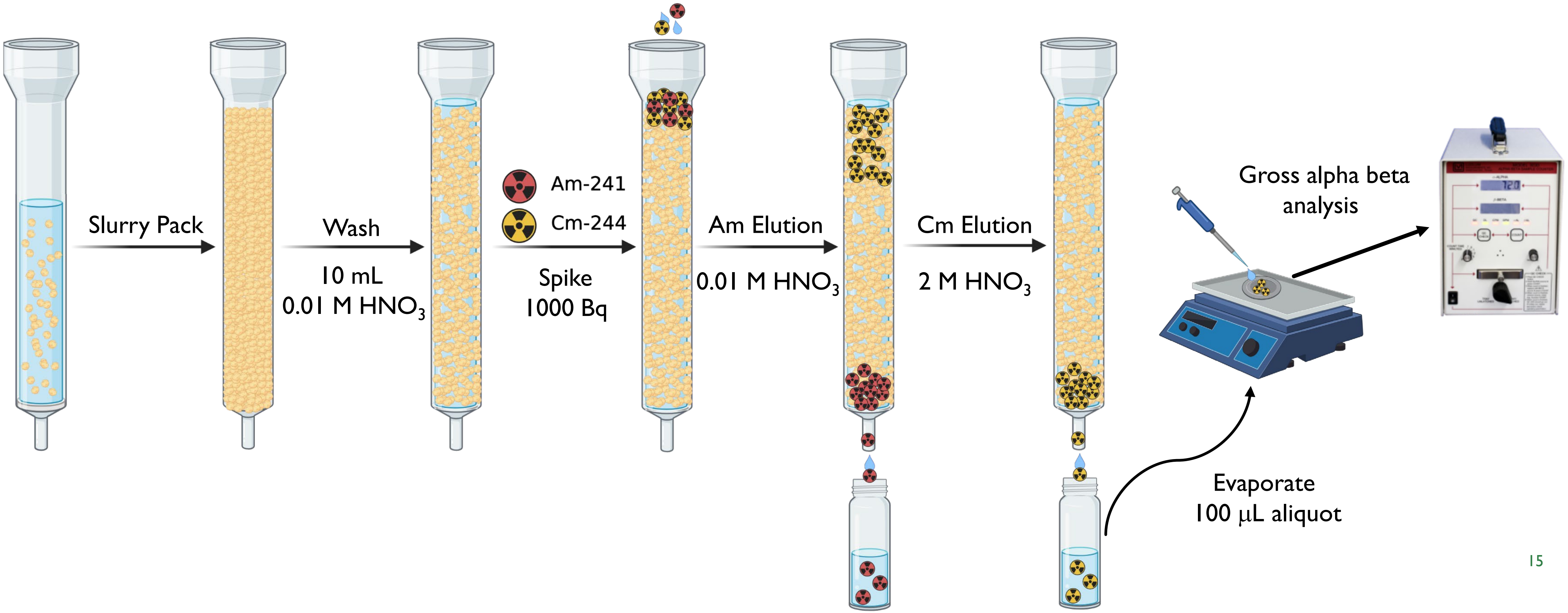
75 wt% $NaBiO_3$-PAN Temperature Dependency (0.01 M HNO_3)



Am/Cm on PAN Beads

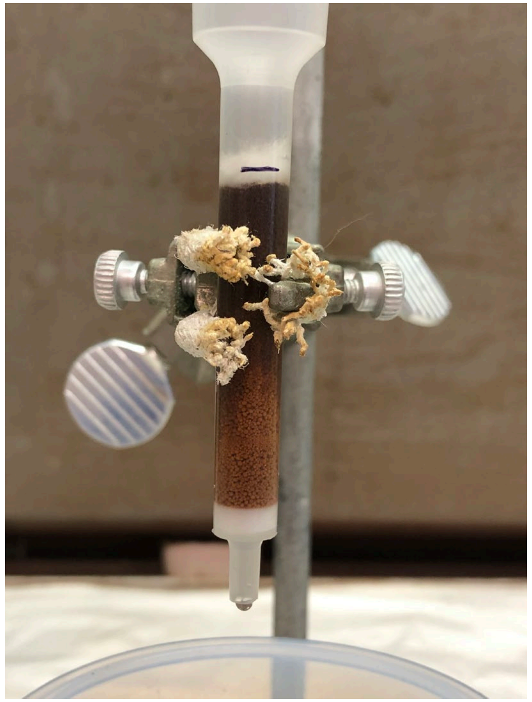


METHOD: CHROMATOGRAPHIC SEPARATIONS



COLUMN OBSERVATIONS

Small floaters had to be decanted when prepping slurry to prevent column clogging

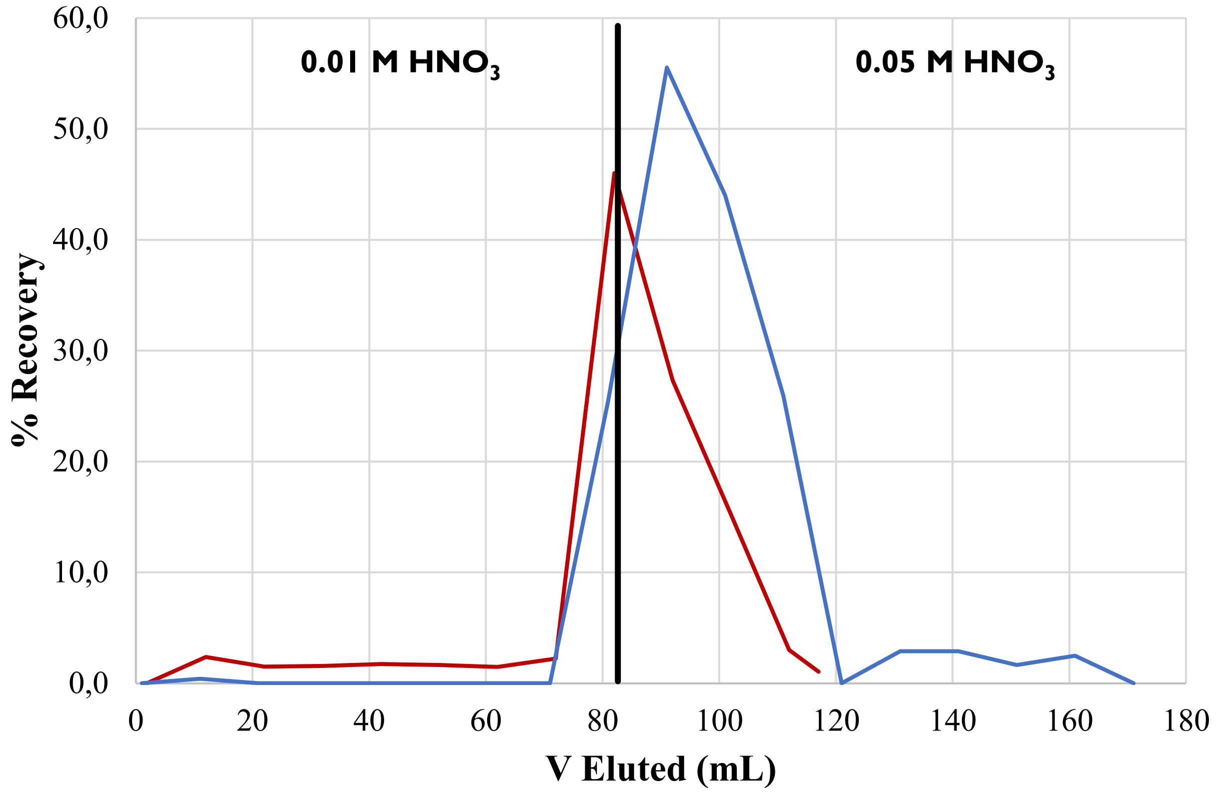


Resin turning black when acid introduced (Bi(V) → Bi(III)) Kozma, *et. al. Solid State Chem.* **2018**, *263*, 216-223)

Gas production restricting flow rate under gravity

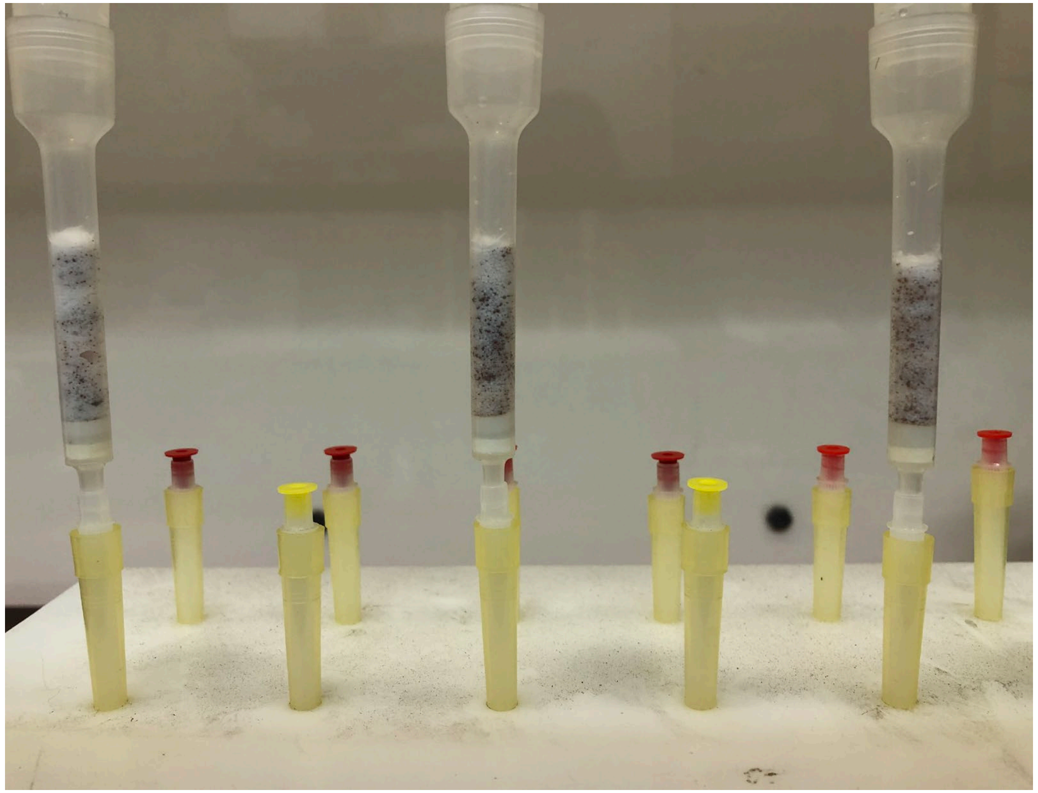
Color change 1 week post column

ATTEMPT #1: $NaBiO_3$-PAN COLUMN

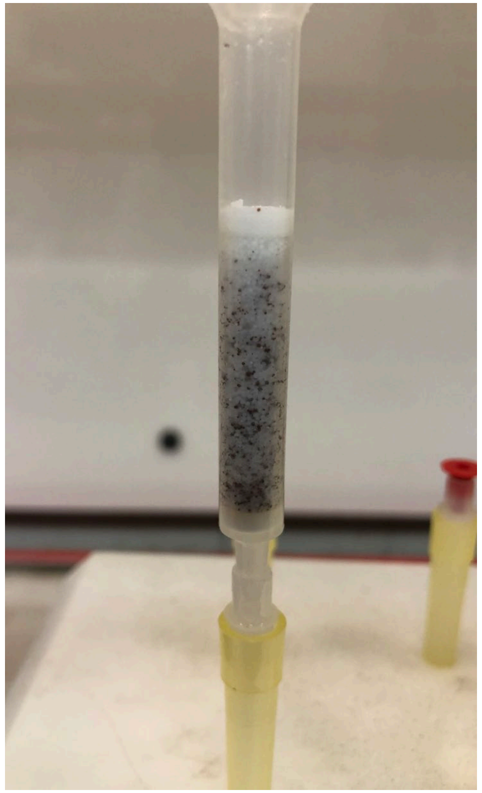


- 2% Am-241 recovery for every 10 mL of 0.01 M HNO_3 eluted
- 100% Am and Cm recovery in 0.05 M HNO_3
- Retention is **TOO HIGH** at 0.01 M HNO_3
- Very restricted flow under gravity, gas production

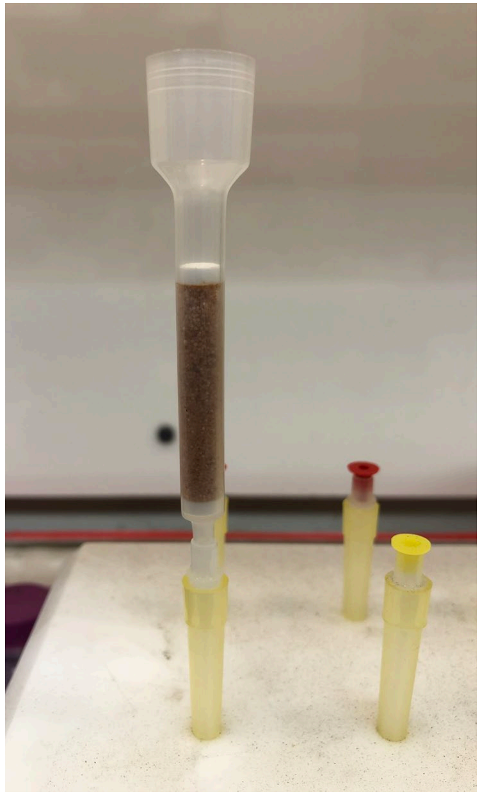
COLUMN OBSERVATIONS



Density differences and wide range of particle sizes affect flow dynamics and reproducibility

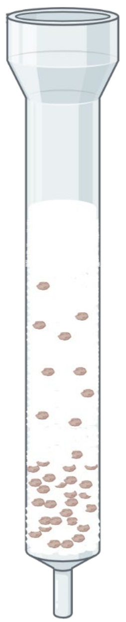


Better distribution with the 10 wt% $NaBiO_3$-PAN column. Involved a lot of mixing with pipette.

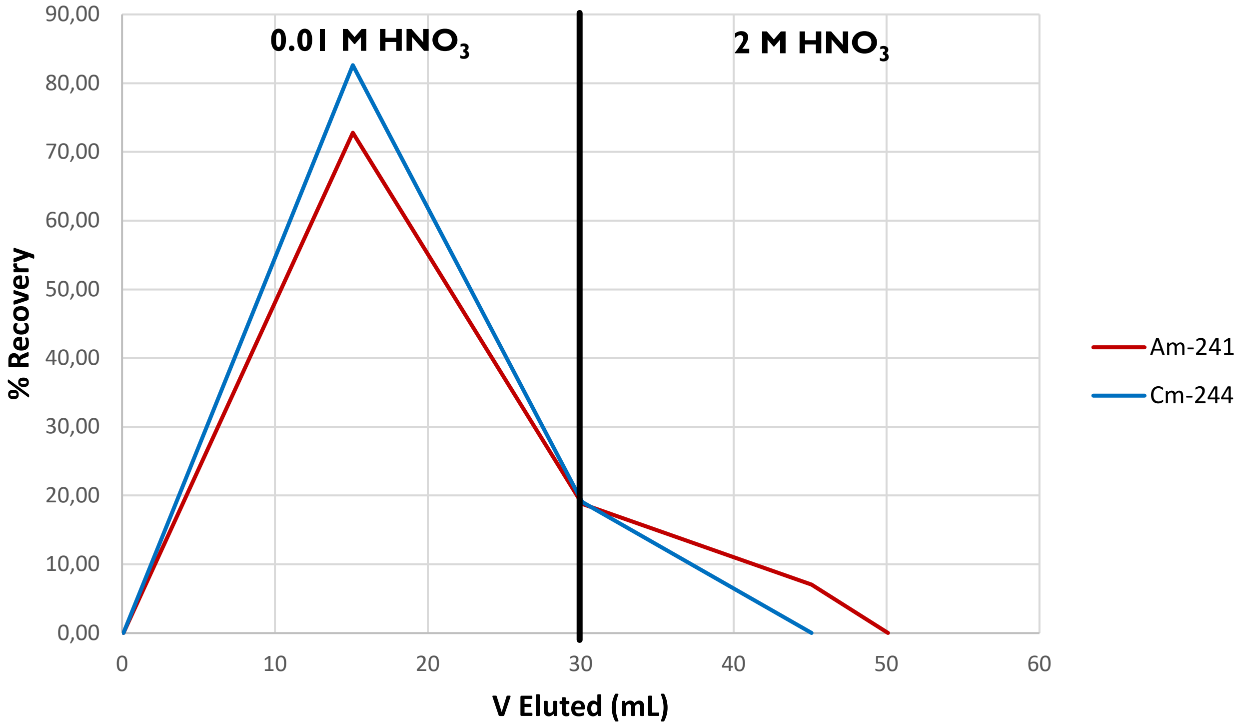


Dry packing shows more promising bed uniformity – tight packing released remaining solution in resin (pH ~11)

ATTEMPT #2: 5% $NaBiO_3$-PAN IN PAN-Normal

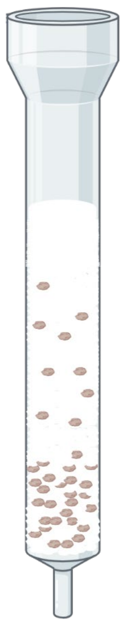


5 wt% $NaBiO_3$-PAN
95 wt% PAN-Normal

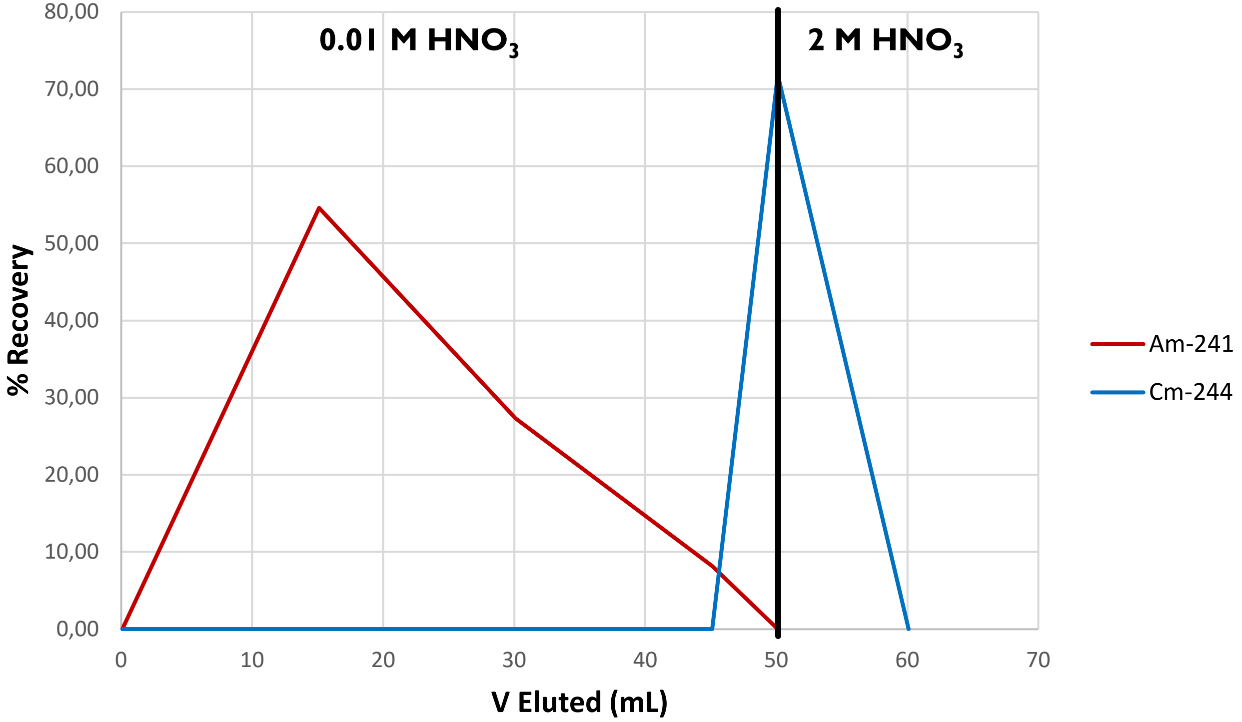


- Non-homogenous mixing of the two resins due to density
- Uneven bed packing
- 98% Am recovery, 100% Cm recovery
- Retention is **TOO LOW** at 0.01 M HNO_3

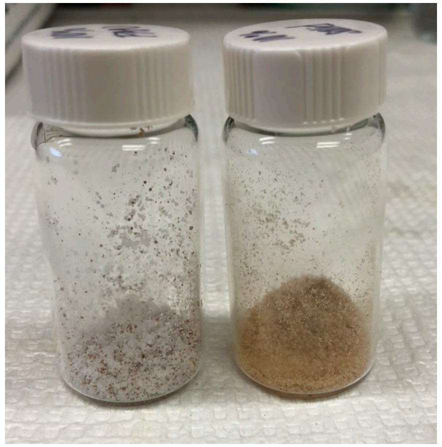
Attempt #3: 10% $NaBiO_3$-PAN with PAN Beads

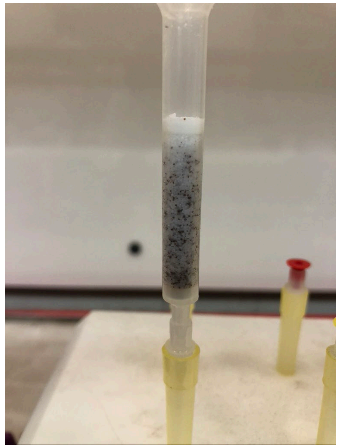


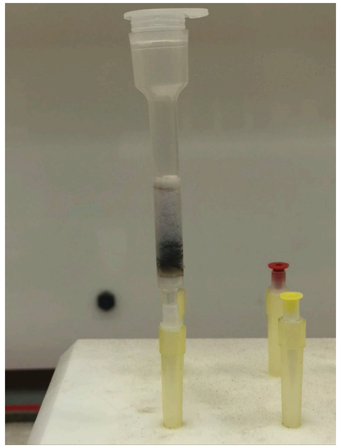
10 wt% $NaBiO_3$-PAN
90 wt% PAN-Normal



- 90% Am and 71% Cm recovery
- Separation! … with some Am breakthrough in the Cm fraction
- Starting to find the sweet $NaBiO_3$ concentration spot



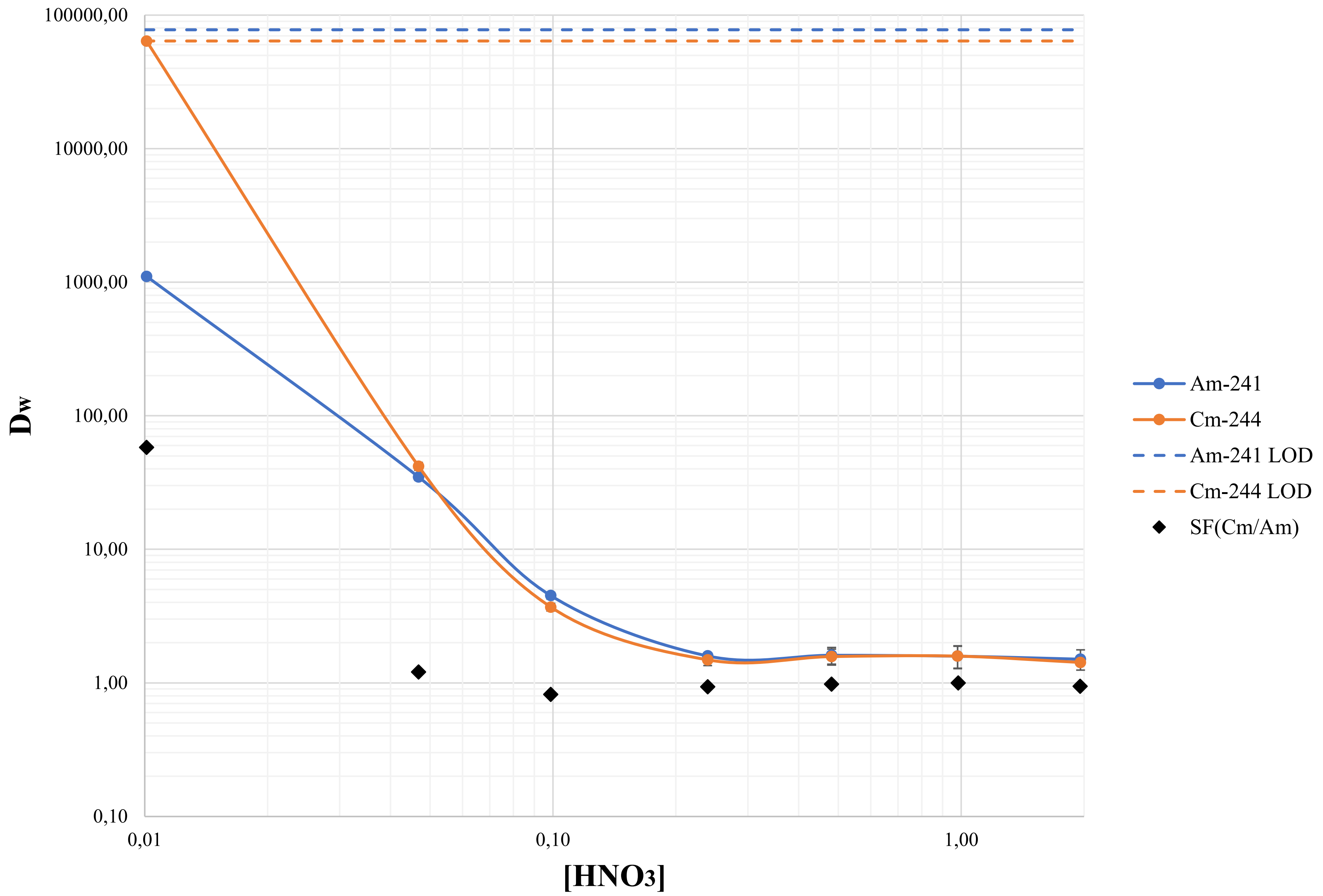




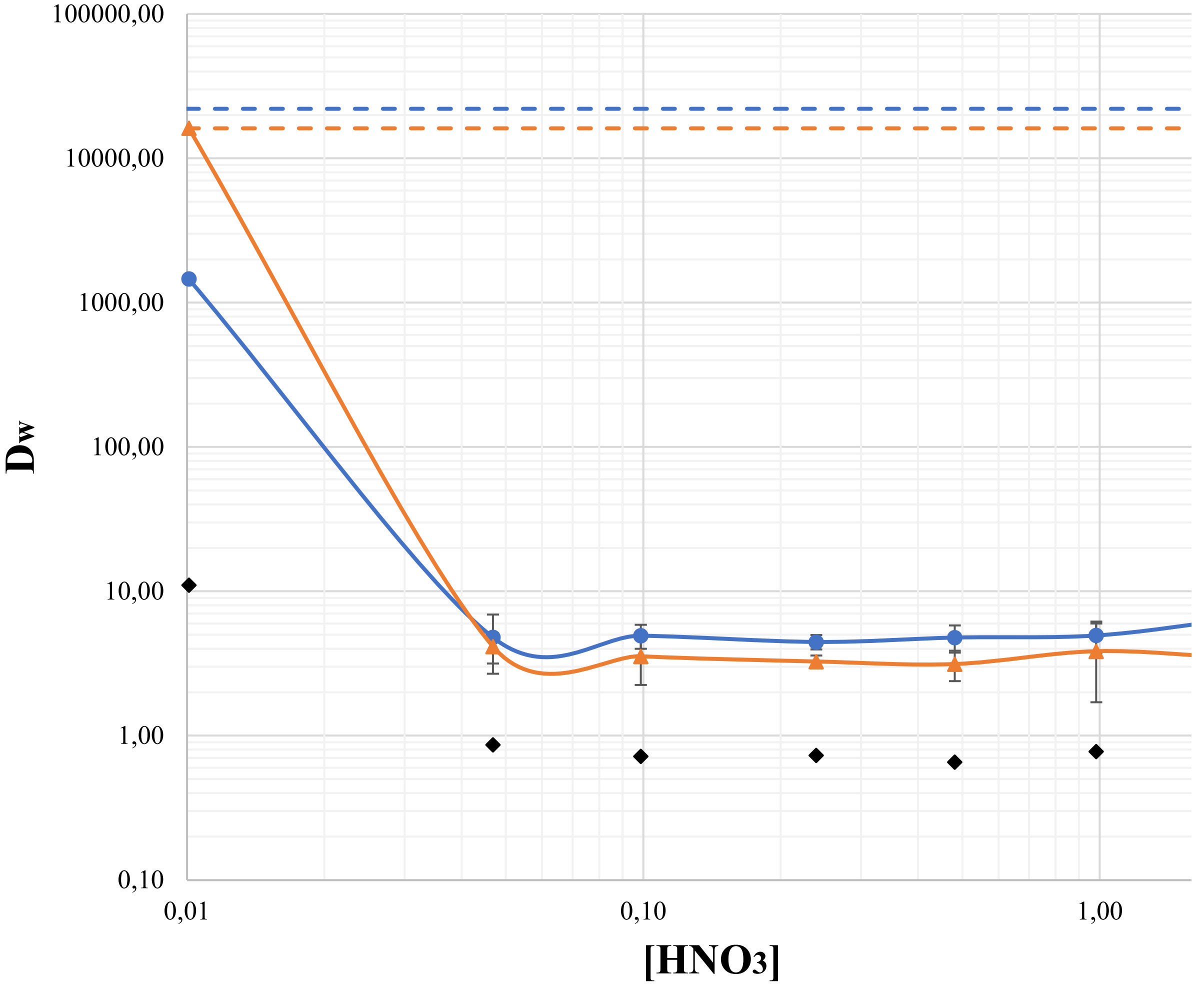
Next… Improving the resin

- At high amounts of $NaBiO_3$ coating, both radionuclides are strongly retained
  - Vary $NaBiO_3$ loading on resin
  - 10%, 25%, 50%, 75%
- Exploring PES beads as backbone
- Comparing $NaBiO_3$ sources & purity

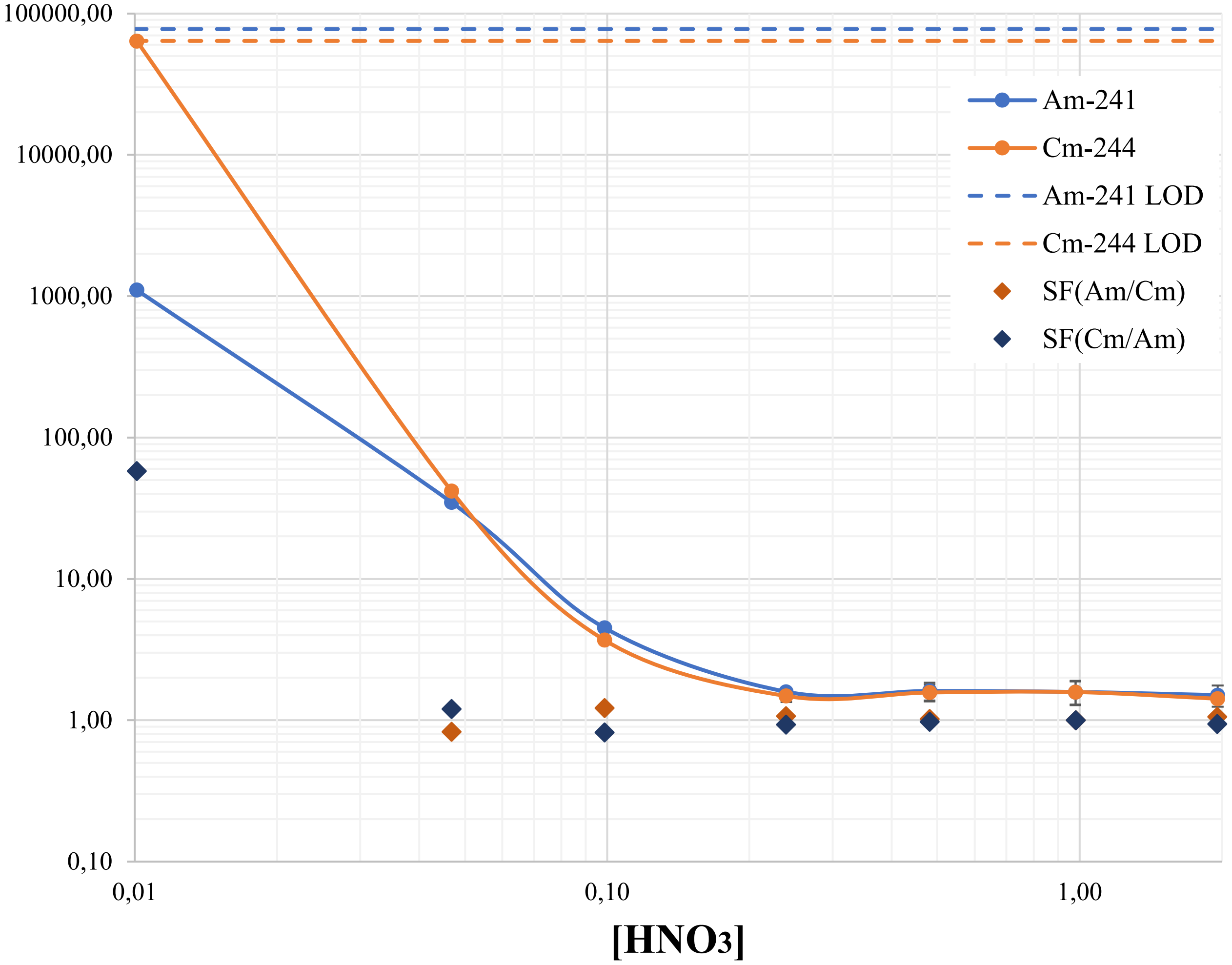
Am/Cm on 75% $NaBiO_3$-PAN (New Lot)

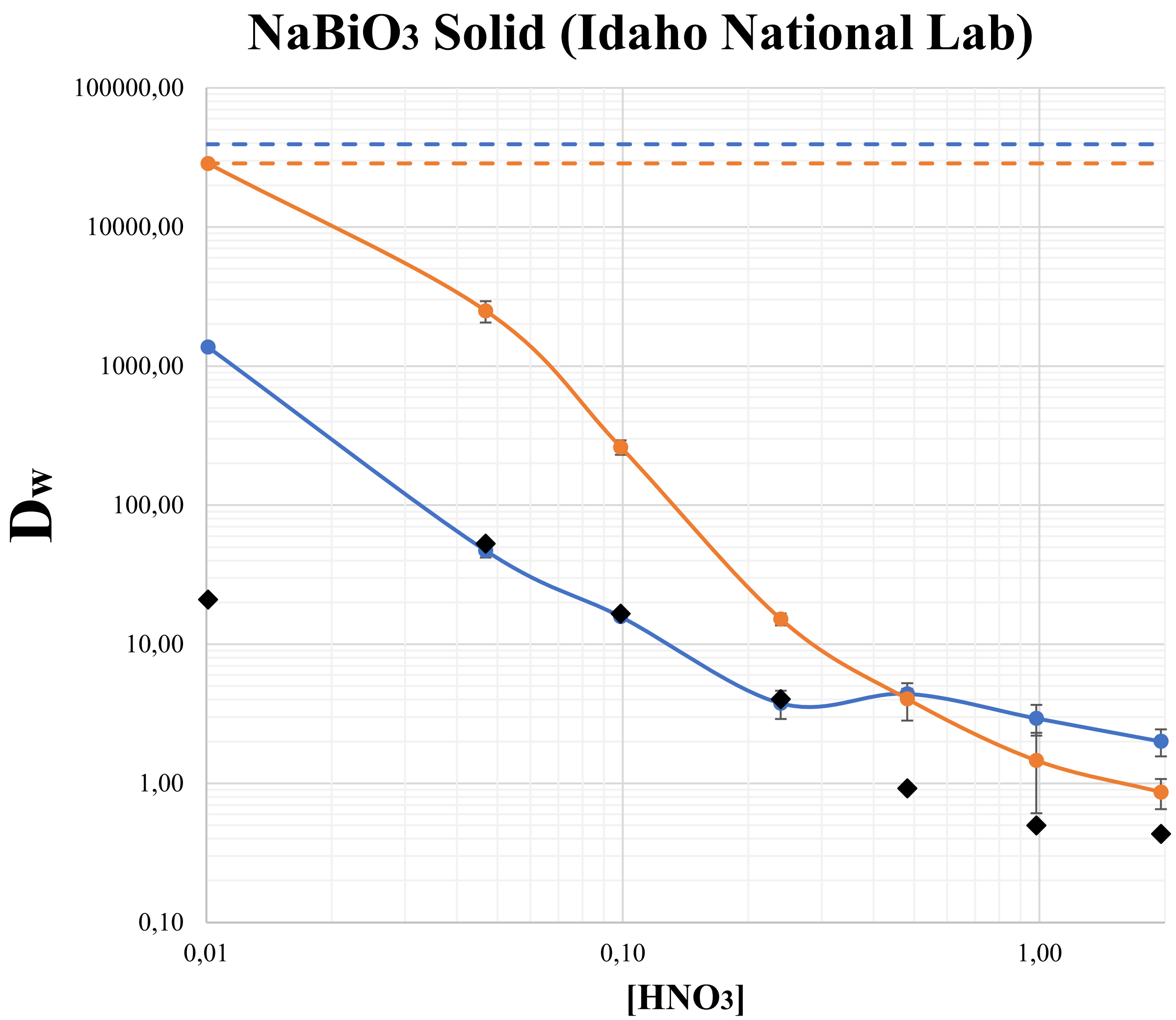


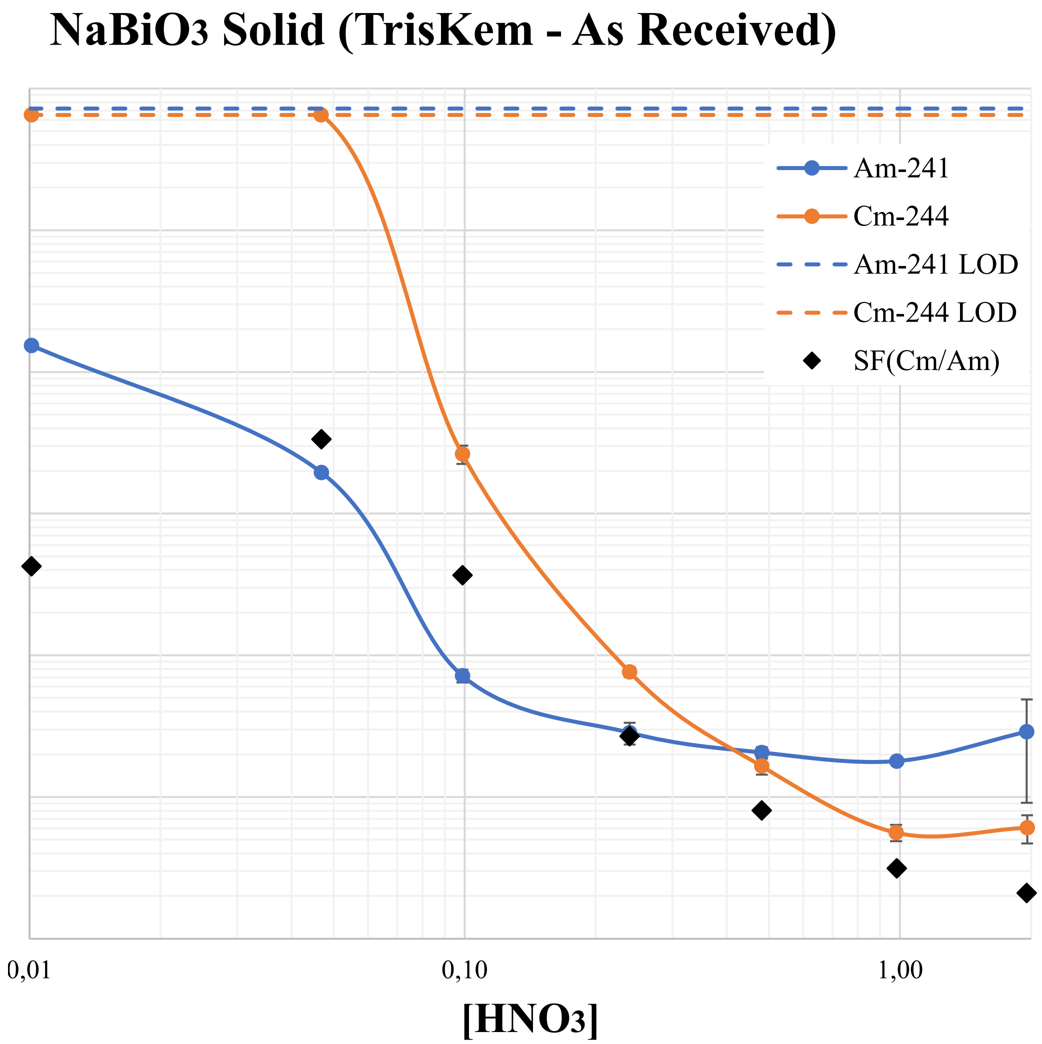
Am/Cm 75 wt% $NaBiO_3$-PAN (Old Lot)



Am/Cm 75 wt% $NaBiO_3$-PAN (New Lot)

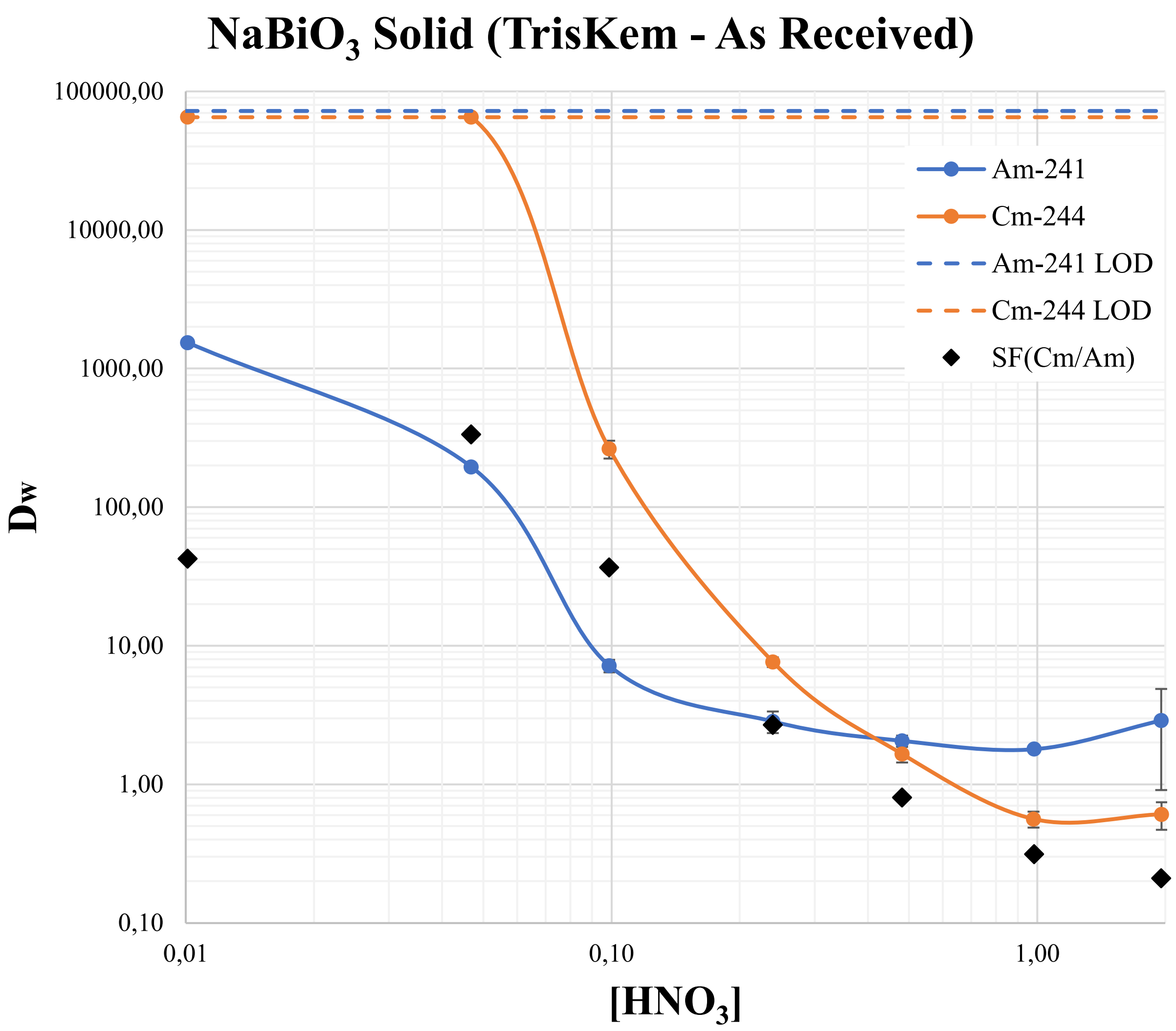


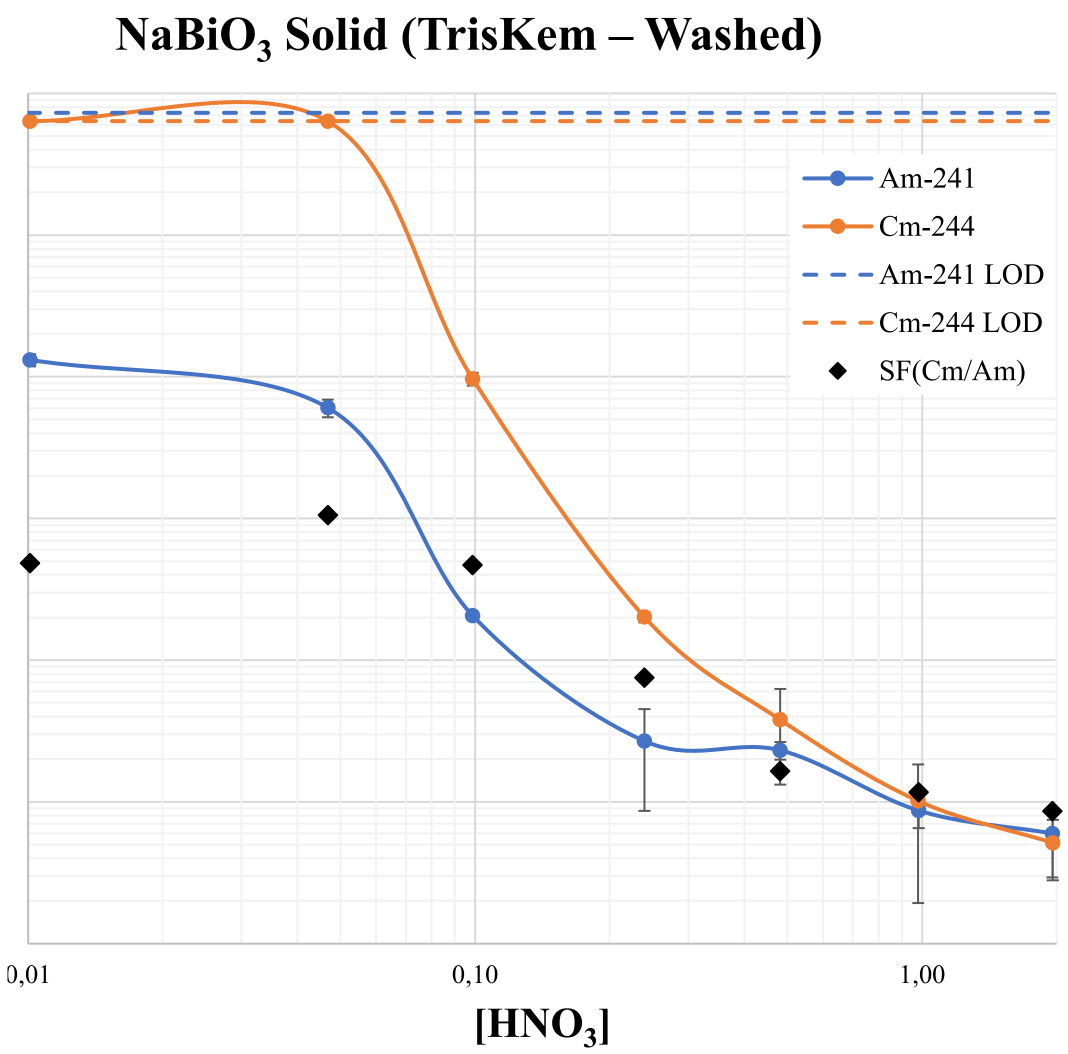

NaBiO3 Solid (Idaho National Lab)
Dw
100000,00
10000,00
1000,00
100,00
10,00
1,00
0,10
0,01
0,10
1,00
[HNO3]


NaBiO3 Solid (TrisKem - As Received)
Am-241
Cm-244
Am-241 LOD
Cm-244 LOD
SF(Cm/Am)
0,01
0,10
1,00
[HNO3]

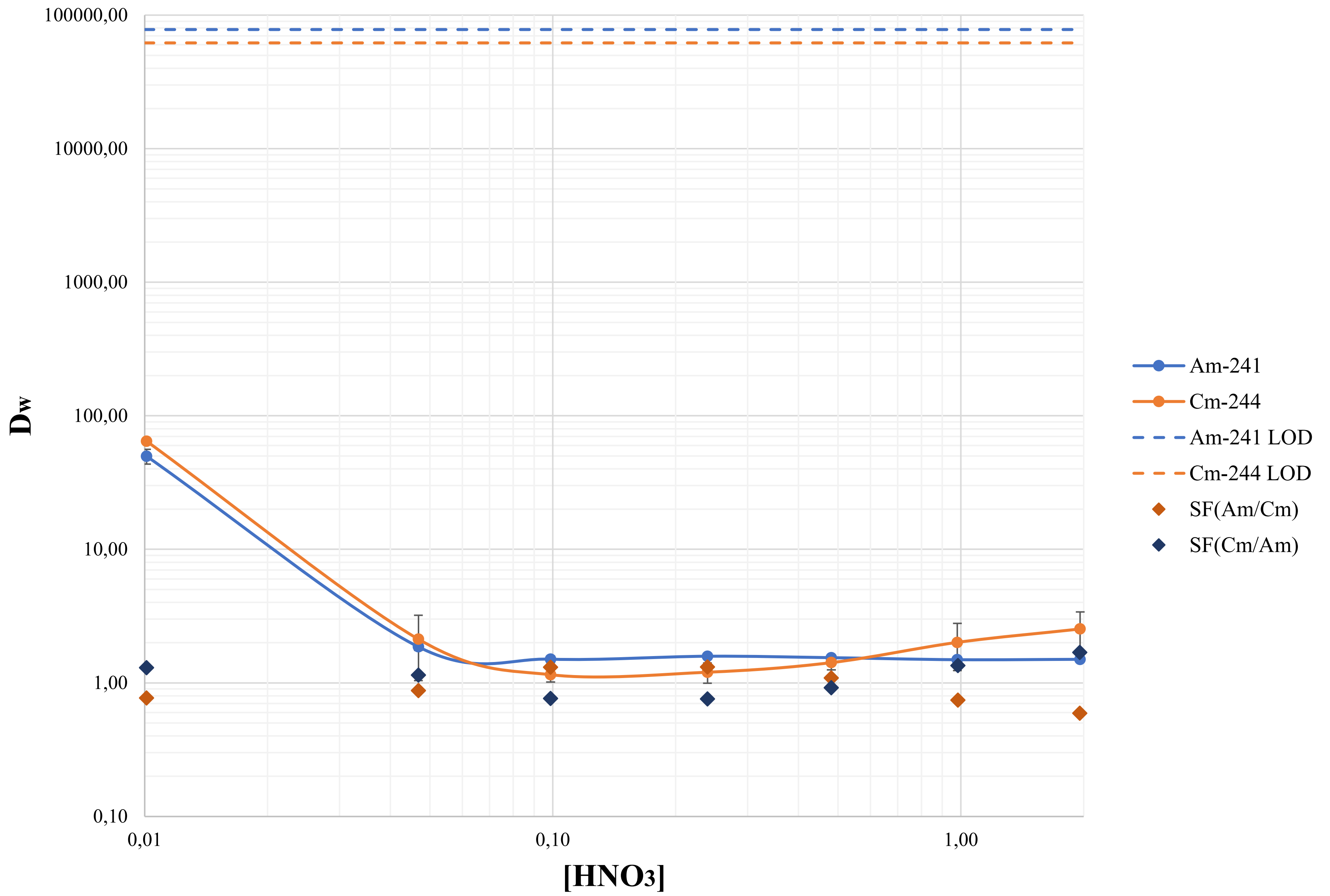
$NaBiO_3$ Source Purity - Peroxides

- $NaBiO_3$ Synthesis
- Peroxide contaminants → incomplete or non-oxidation of Am
  - Am(III) → Am(VI) → Am(V) + Am(III)
  - Am(III) → Am(V)
- Remove through repeated washes with DI-H_2O (?)

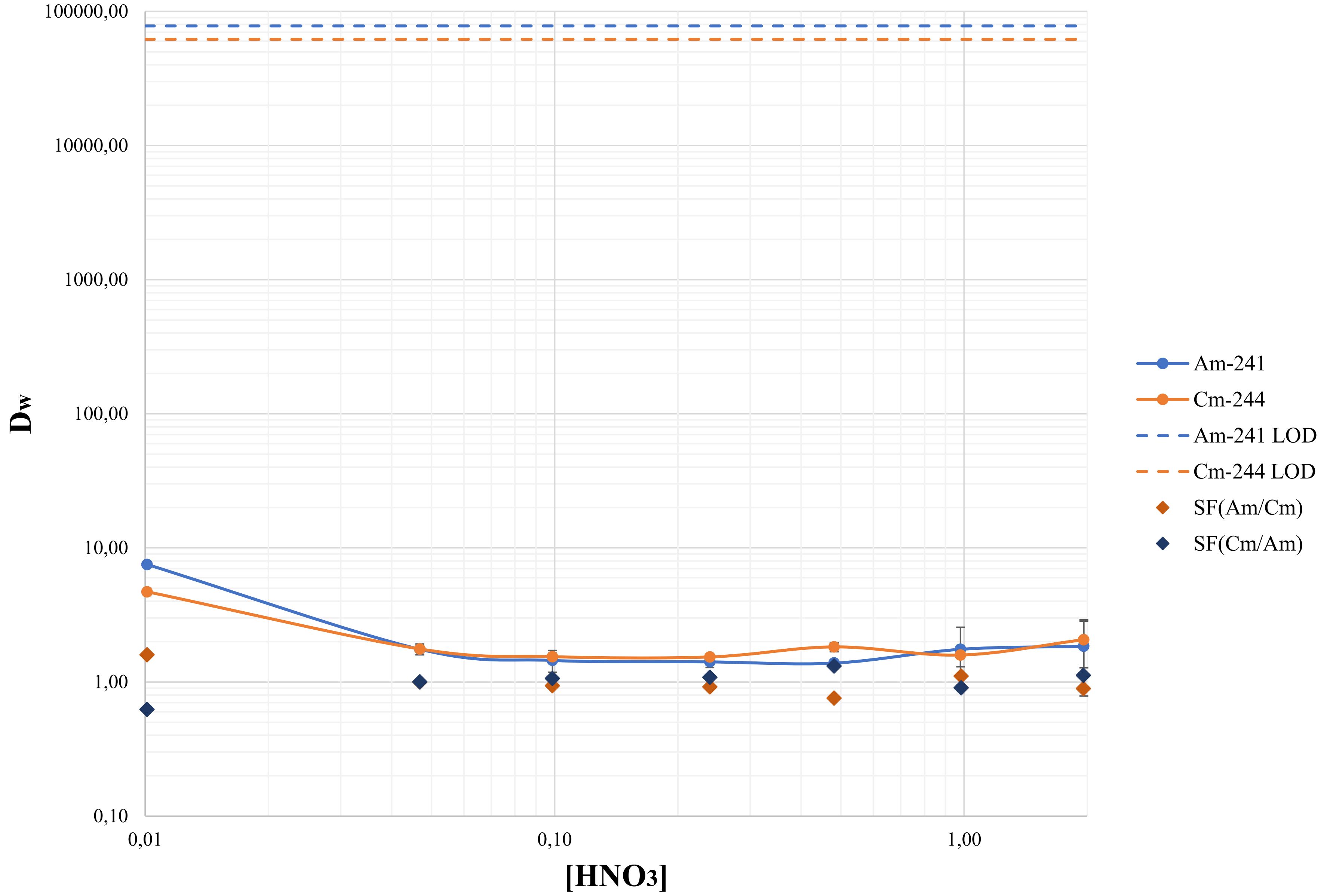

NaBiO$_3$ Solid (TrisKem - As Received)
100000,00
10000,00
1000,00
100,00
10,00
1,00
0,10
Dw
0,01
0,10
1,00
[HNO$_3$]
Am-241
Cm-244
Am-241 LOD
Cm-244 LOD
SF(Cm/Am)


NaBiO$_3$ Solid (TrisKem – Washed)
0,01
0,10
1,00
[HNO$_3$]
Am-241
Cm-244
Am-241 LOD
Cm-244 LOD
SF(Cm/Am)

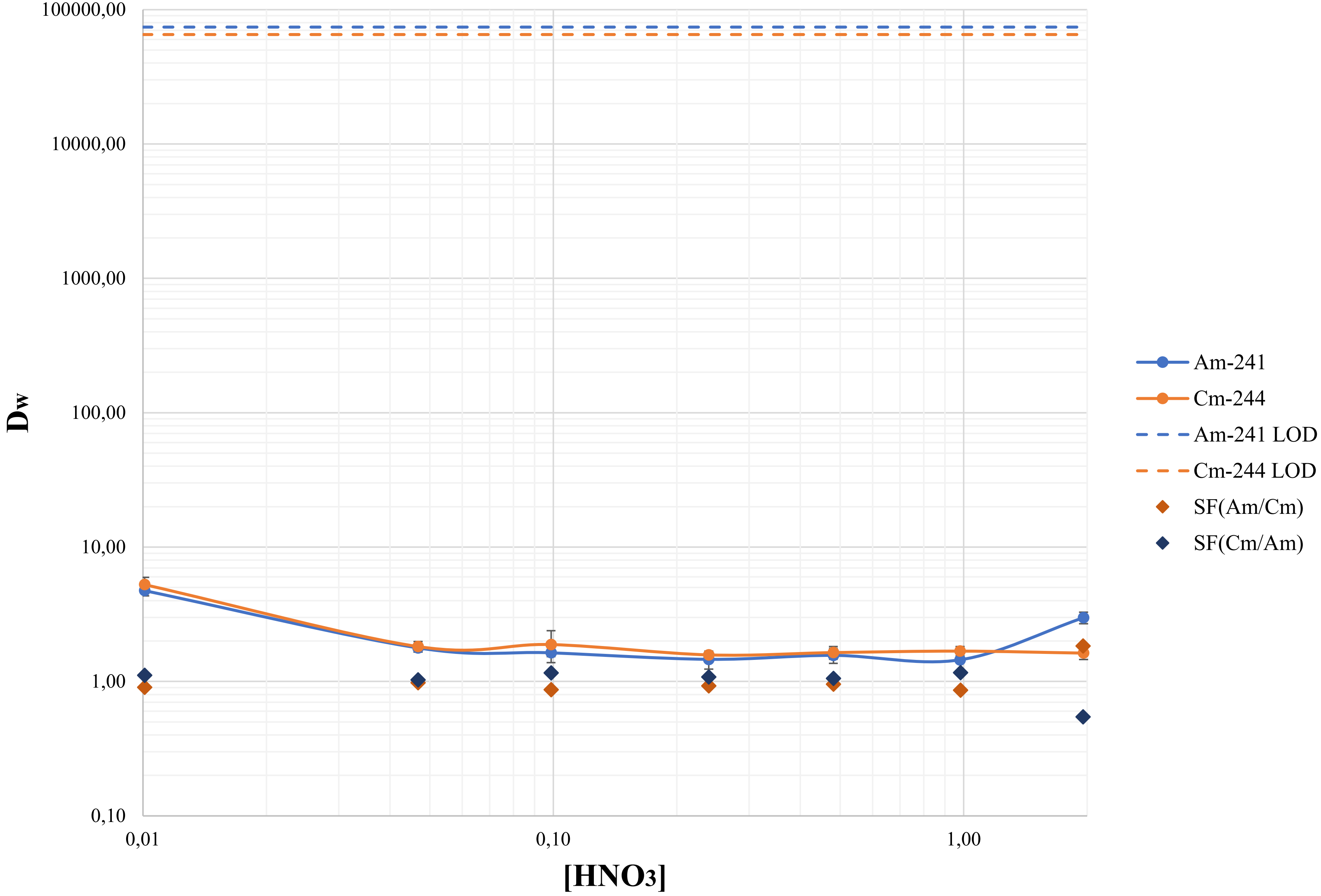
Am/Cm on 50 wt% NaBiO3-PAN



Am/Cm on 25 wt% $NaBiO_3$-PAN



Am/Cm on 10 wt% $NaBiO_3$-PAN

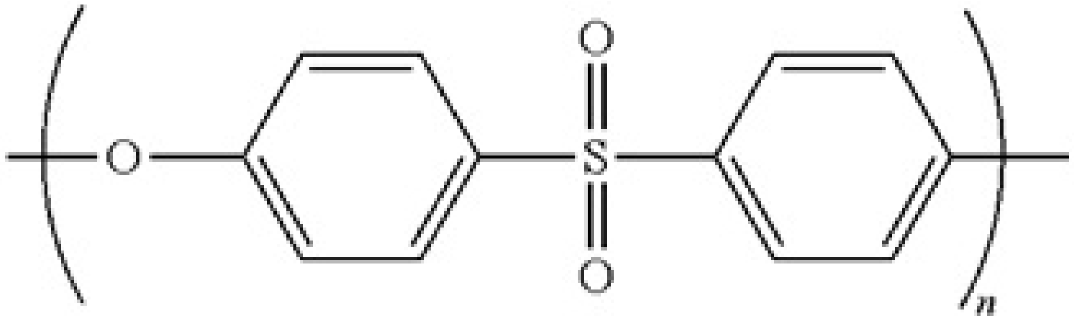


Polyacrylonitrile Support

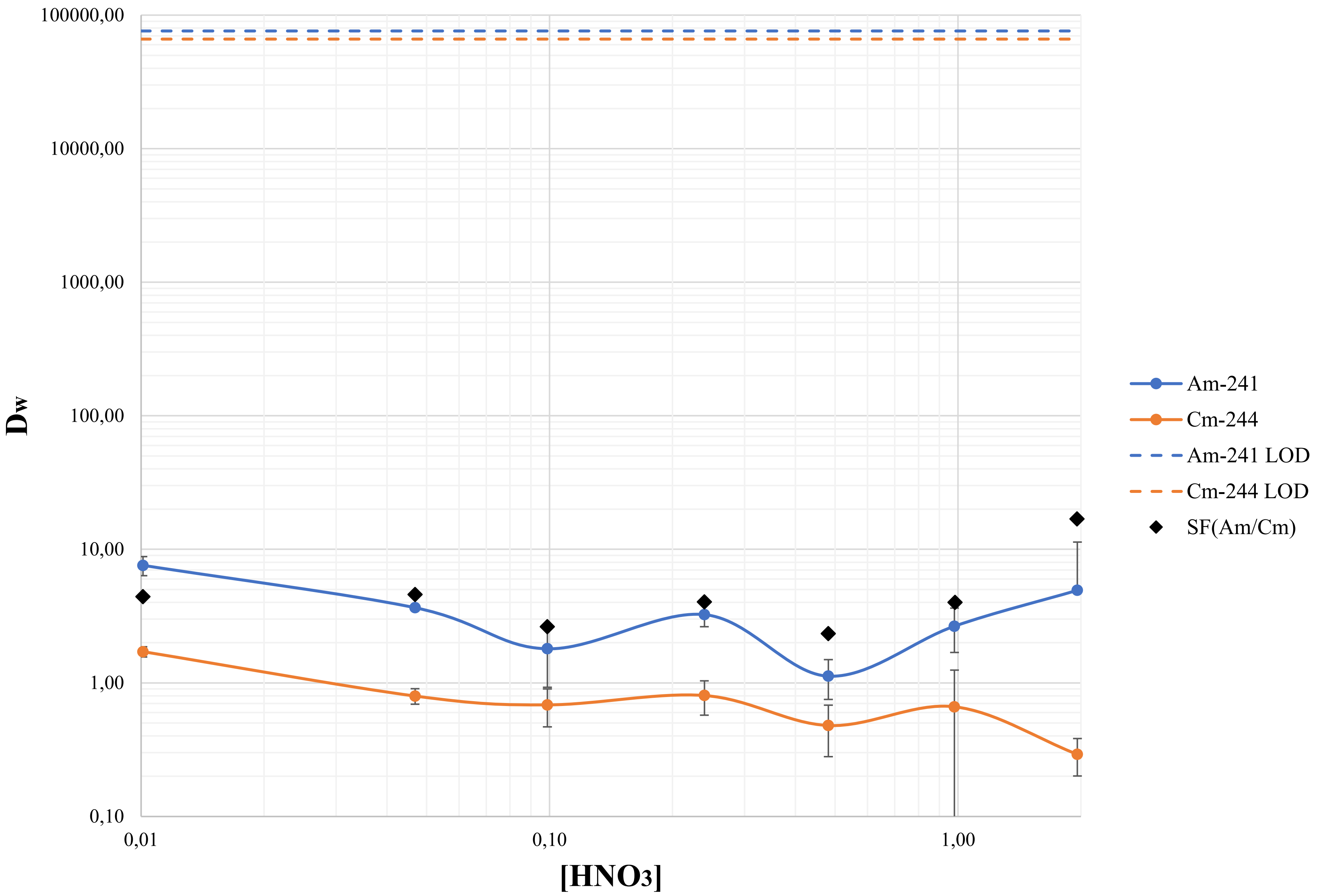
- No evidence of oxidation
  - Identical Am/Cm behavior → trivalent speciation
  - Organic PAN reducing Am(V)/Am(VI)?
- No evidence of ion exchange
  - No Cm(III) adsorption → exchange site access
  - $NaBiO_3$ on surface or in pores?
  - PAN incorporation into solid structure?
    - Zirconium Phosphate

Polyethersulfone (PES) Support

- 10 wt% $NaBiO_3$ coating
- Greater stability in acid than PAN
- Potential benefit of additional electrostatic interactions



Am/Cm on 10% $NaBiO_3$-PES Fresh



Alternative Chromatographic Systems

- Inorganic Supports/Filter Aids
  - Silica Gel/Powder → Mixed Bed or Coated
  - Alumina
- Pre-treatment with $NaBiO_3$ → Cation Exchange
  - Zirconium Phosphate
  - Zirconium Oxide

$NaBiO_3$ Dissolution/Degradation

- What is the concentration of total Bi (Bi(V) + Bi(III)) in solution as a function of:
  - [HNO3]
  - Time
  - Radionuclide concentration, size, charge
- ICP-OES: Total [Bi]
- UV-Vis-NIR: Bi(V):Bi(III)
- **Bi(III) Interference: How is Cm(III) adsorption affected?**

Beyond Resin Development

- Oxidation & Speciation
  - UV-Vis analysis in the presence of $NaBiO_3$ to determine speciation and oxidation kinetics
  - Function of time, [$NaBiO_3$]
  - Compare speciation determination methods – fluoride precipitation vs. UV-Vis
- Ion Exchange
  - What is the ion exchange mechanism for Am and Cm with Na^+?
  - Potential complexation vs ion exchange??
    - EXAFS / XANES Studies

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MOUNTAIN & PLAINS ERC

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