



U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Progress in high valent americium partitioning by solvent extraction

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Am partitioning from Ln's

- **Separation of trivalent actinides from trivalent lanthanides is problematic, even at the analytical scale.**

- **Two approaches:**
 - Soft-donor ligands favor the actinides: DTPA, BTBPs

 - Americium oxidation: Am(V) or Am(VI)
 - Oxo-cations in analogy with U, Np, Pu

 - Am⁴⁺ (not useful)
 - AmO₂⁺ (low charge density, poorly complexed)
 - AmO₂²⁺ (high charge density, well complexed)

What does it take to be successful?

■ 1. High yield for the oxidation.

- If the goal is to extract Am(VI), any produced Am(V) or residual Am(III) will lower the D_{Am} .
- If the goal is to leave Am(V) behind during a Ln(III) extraction, any produced Am(VI) or residual Am(III) will increase the D_{Am} .

■ 2. Reasonable stability for the high valence state.

- Am(V) and Am(VI) are easily reduced, even by their own radiolysis products.
- Am(V) ($t_{1/2}$ = weeks) is much more stable than Am(VI) ($t_{1/2}$ = hours) in nitric acid solution.
- Organic-phase contact times must be short.

Oxidation reagents, not very many choices:

■ Ammonium peroxydisulfate- the original americium oxidant:

- Asprey, L.B., S.E. Stephanou and R.A. Penneman. 1950. A new valence state of americium, Am(VI). J. Am. Chem. Soc. 72:1425-1426.



■ Depending on the concentration of $\text{S}_2\text{O}_8^{2-}$, either Am(V) or Am(VI) can be prepared.

- Mincher, B.J.; Schmitt, N.C.; Schuetz, B.K.; Shehee T.C.; Hobbs, D.T. 2015. Recent advances in *f*-element separations based on a new method for the production of pentavalent americium in acidic solution. *RSC Advances* 5:27205-27210.

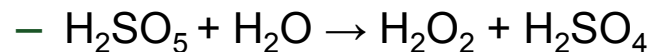
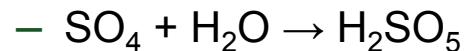
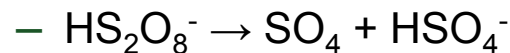
■ Quantitative preparation of Am(VI) assured with silver catalyzed peroxydisulfate and heat in dilute HNO_3 .

- Ward, M. and G.A. Welch. 1954. The oxidation of americium to the hexavalent state. J. Chem. Soc. 4038.



$S_2O_8^{2-}$ drawbacks:

- Doesn't work at acidity $> \sim 0.3$ M.
- In acidic solution produced H_2O_2 reduces Am(VI).
- Sulfate is undesirable in the waste-stream.
- Silver is also undesirable due to environmental regulations.



Other oxidizing agents in acid media?

- **Am(III) is not oxidized by ozone or Ce(IV) in acid.**

Katz, J.J., Seaborg, G.T., Morss, L.R. The chemistry of the actinide elements, Chapman and Hall, 1986, and our own attempts.

- **Am(III) has been oxidized using Ag-catalyzed Cesium Fluoroxysulfate in 1M HNO₃.**

Appelman, E.H., Diamond, H., Horwitz, E.P., Sullivan, J.C. 1991. Cesium fluoroxysulfate, CsSO₄F: A novel reagent for the rapid oxidation of americium at ambient temperature and its separation from curium. Radiochim Acta 55:61-64.

- **Am(III) has been oxidized using NaBiO₃.**

Hara M., and Suzuki, S. 1977. Oxidation of americium (III) with sodium bismuthate. J. Radioanal. Chem. 36:95-104.

Sodium bismuthate (NaBiO_3)

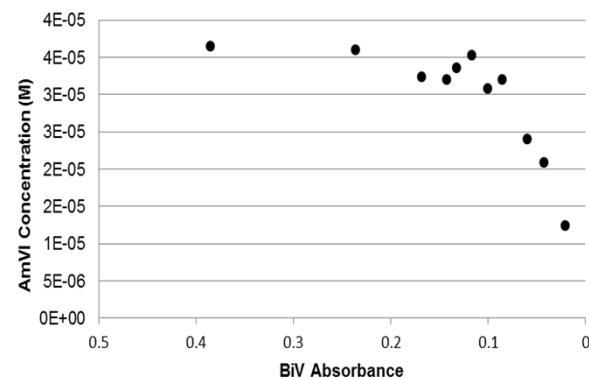
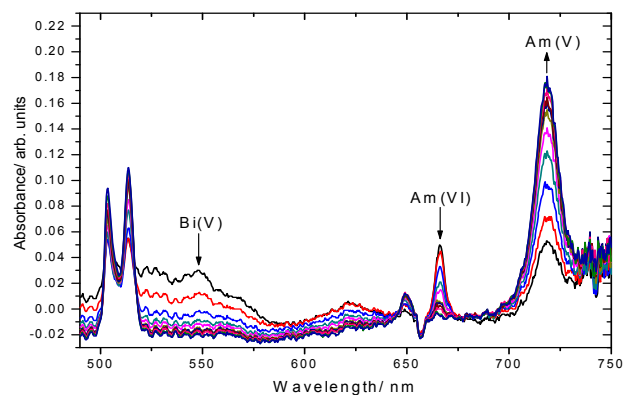
Hara M., and Suzuki, S. 1977. Oxidation of americium (III) with sodium bismuthate. J. Radioanal. Chem. 36:95-104.

- Most developmental work at INL has employed this oxidant.

- Acts as its own holding oxidant.

■ Advantages:

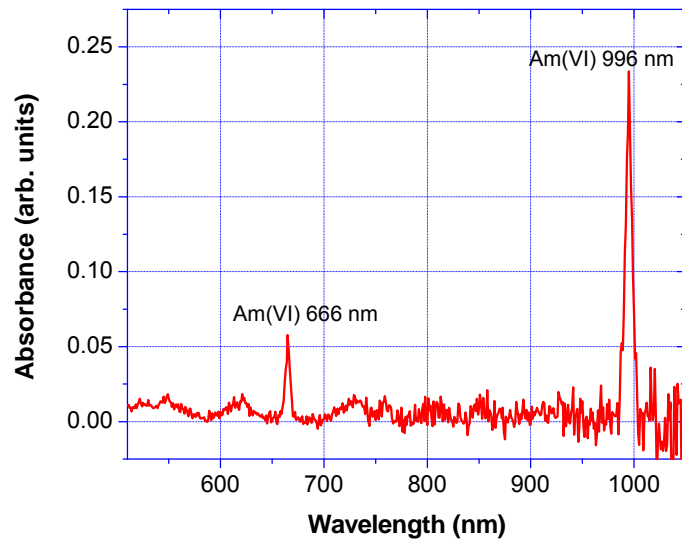
- An off-the-shelf reagent with long shelf-life.
- Americium can be oxidized to either Am(V) or Am(VI) in strong acid.
 - Room temperature oxidation – Am(VI)
 - Hot oxidation – Am(V)
- Sparingly soluble in nitric acid.



UV/Vis speciation of americium

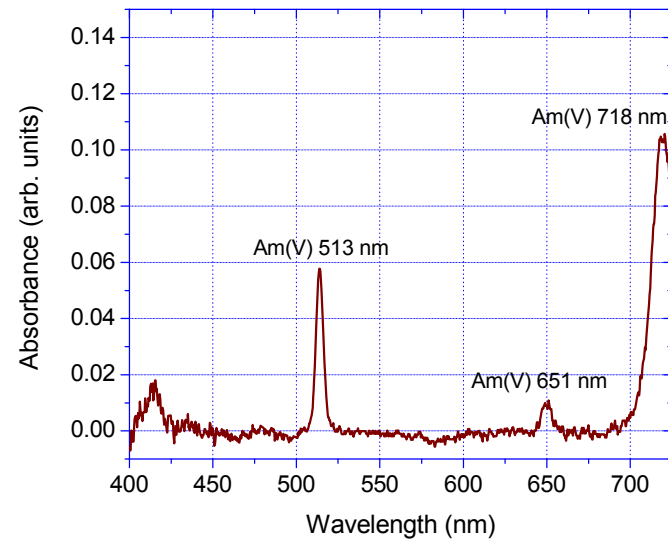
Compare with Am(III) $\epsilon_{503} \sim 387 \text{ M}^{-1}\text{cm}^{-1}$

$\epsilon_{666} = 27.9; \epsilon_{996} = \sim 83$



room-temp BiO_3^-

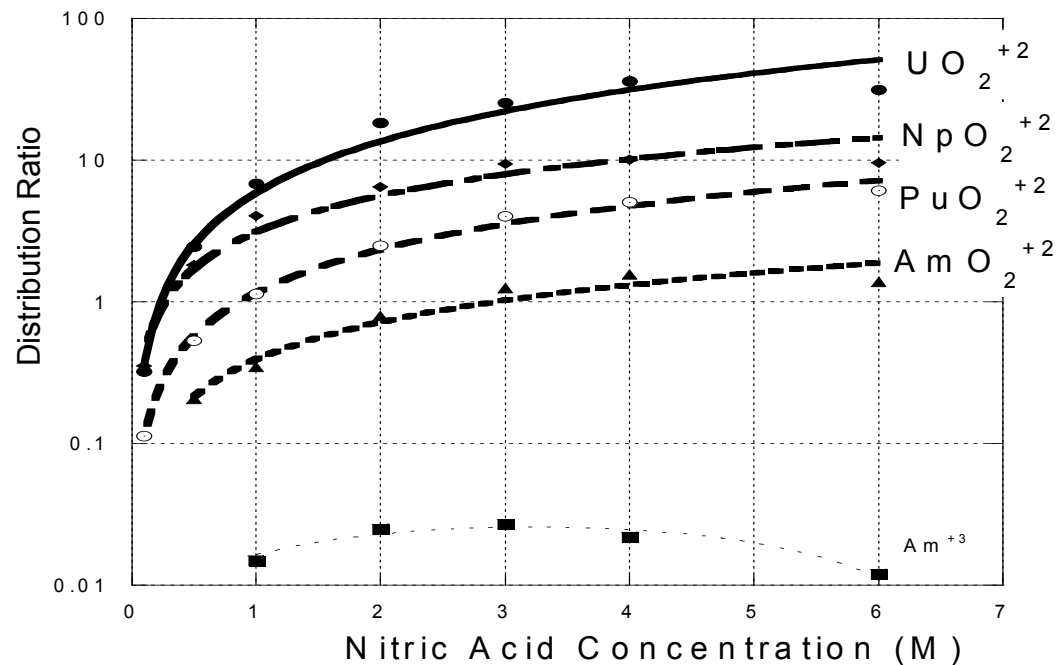
$\epsilon_{513} = \sim 45; \epsilon_{718} = 72.5$



80-90°C BiO_3^-

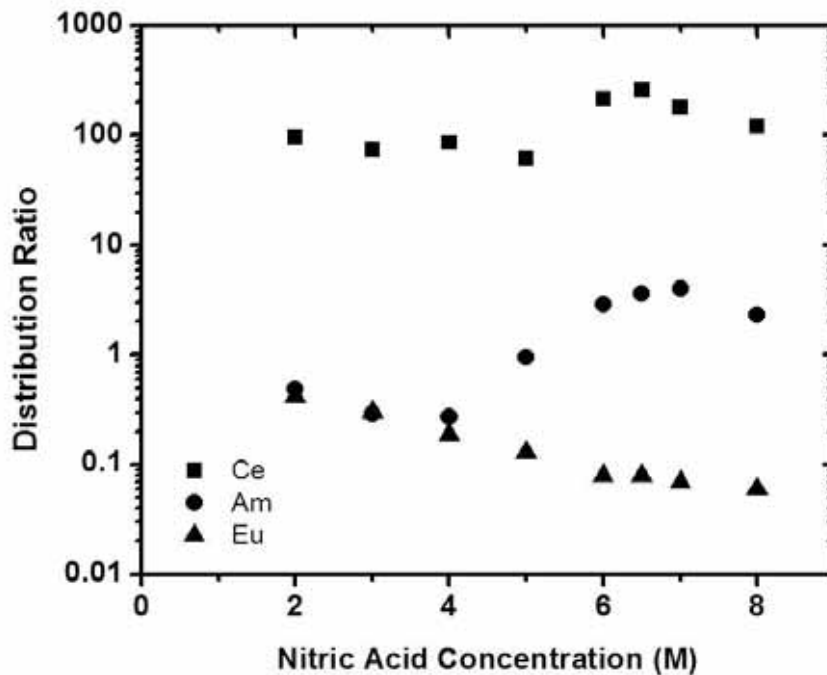
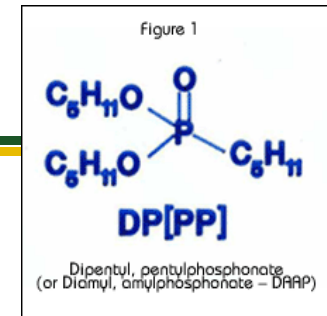
Americyl behaves predictably

Extraction of bismuthate-oxidized actinyl ions using 30% TBP/dodecane



Mincher, B.J.; Martin, L.R.; Schmitt, N.C. 2008. Tributyl phosphate extraction behavior of bismuthate-oxidized americium. *Inorg. Chem.* 47:6984-6989.

Am(VI) is readily extracted by DAAP; Ln(III) and Cm(III) are not.



Extraction at 6.5 M HNO₃
 Separation factors:

$$\alpha_{Am/Cm} = 80$$

$$\alpha_{Am/Eu} = 44$$

$$\alpha_{Am/Sm} = 56$$

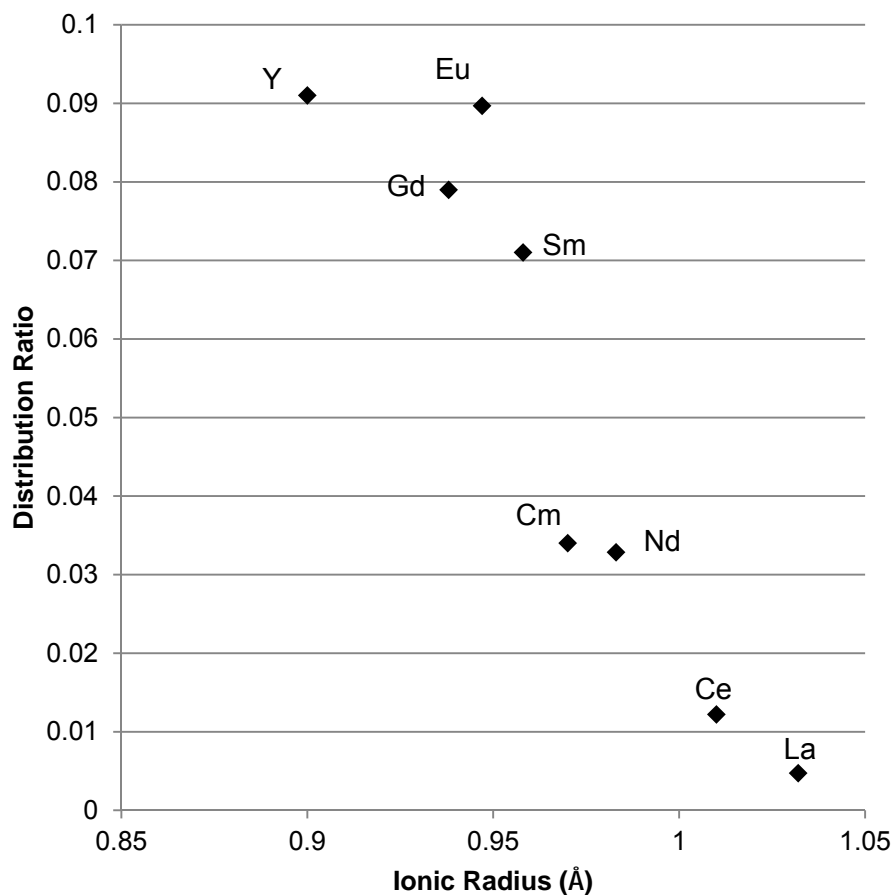
$$\alpha_{Am/La} = 800$$

$$\alpha_{Am/Gd} = 51$$

A lot of the interfering elements actually have their lowest D_M values at 6.5 M HNO₃.

Mincher, B.J.; Martin, L.R.; Schmitt, N.C. 2012. Diamylamylphosphonate solvent extraction of Am(VI) from nuclear fuel raffinate simulant. Solvent Extr. Ion Exch. 30:445-456.

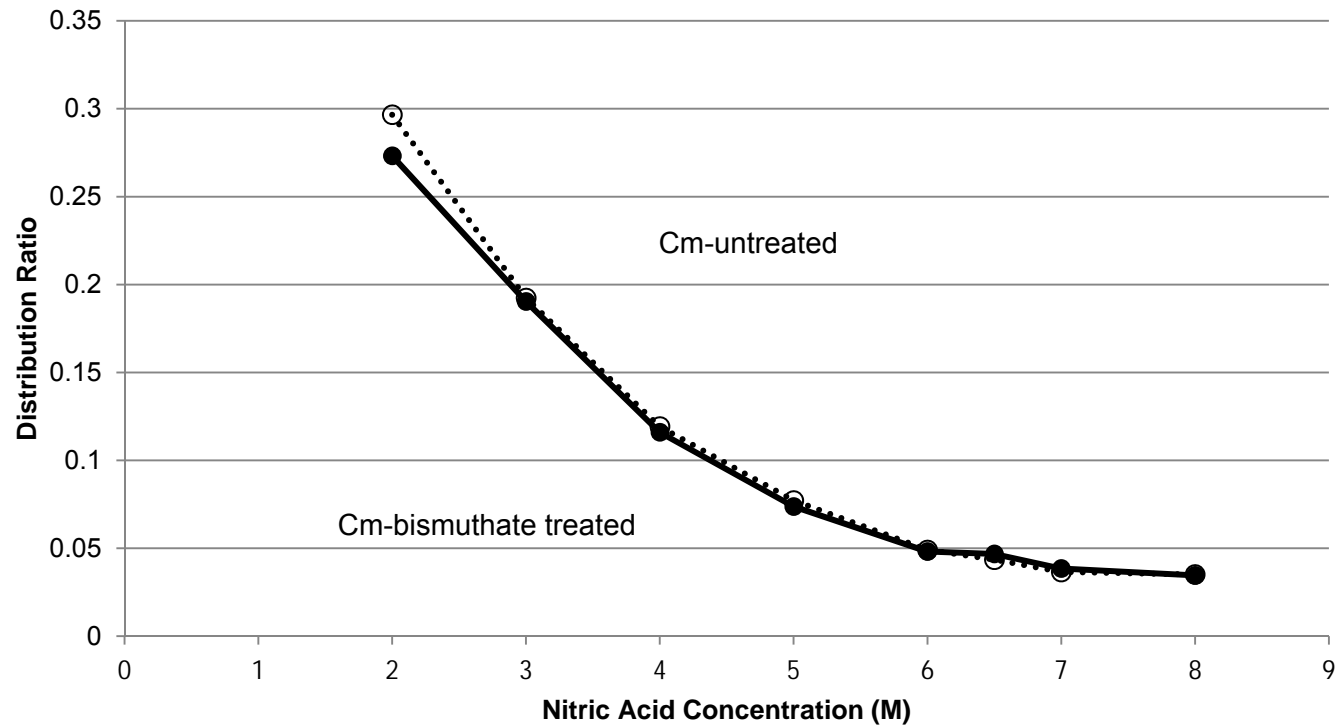
Behavior of lanthanide fission products extracted from simulant adjusted to 6.5 M HNO₃



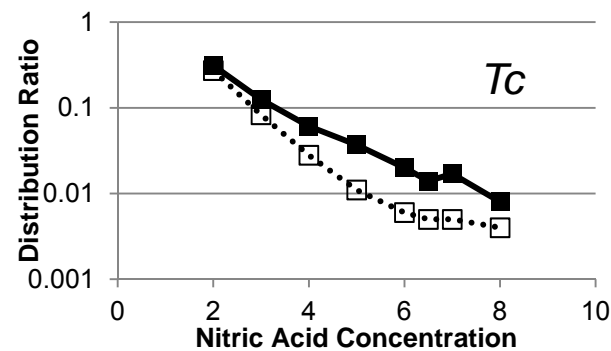
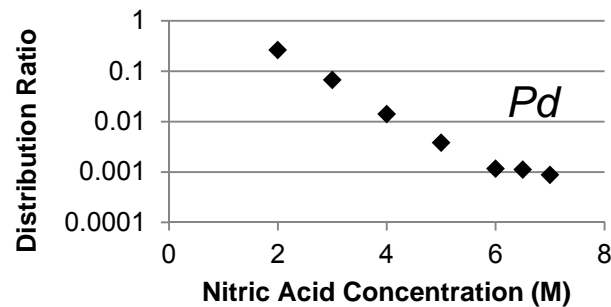
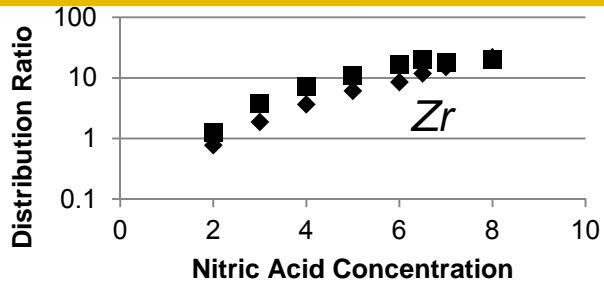
Ln	D_{Ln}	$D_{Ln(Bi)}$
Y	0.091	0.095
La	0.005	0.006
Ce	0.012	884
Nd	0.033	0.037
Sm	0.071	0.081
Eu	0.090	0.094
Gd	0.079	0.179

Mincher, B.J.; Schmitt, N.C.; Tillotson, R.D.; Elias, G.; White, B.M.; Law, J.D. 2013. Characterizing diamylamylphosphonate (DAAP) as an americium ligand for nuclear fuel cycle applications. Solvent Extr. Ion Exch. 2014. 33:153-166.

Curium extraction from simulant adjusted to 6.5 M HNO₃.



Non-lanthanide constituents



M	D_M	$D_{M(Bi)}$
Zr	11.9	20.7
Tc	0.005	0.014
Ru	0.002	5.42
Mo	0.092	0.102
Cs	<0.001	<0.001
Sr	<0.005	<0.005
Ba	<0.005	<0.005
Rh	<0.001	<0.001
Cd	<0.001	nm
Pd	0.001	nm
Ag	<0.001	nm

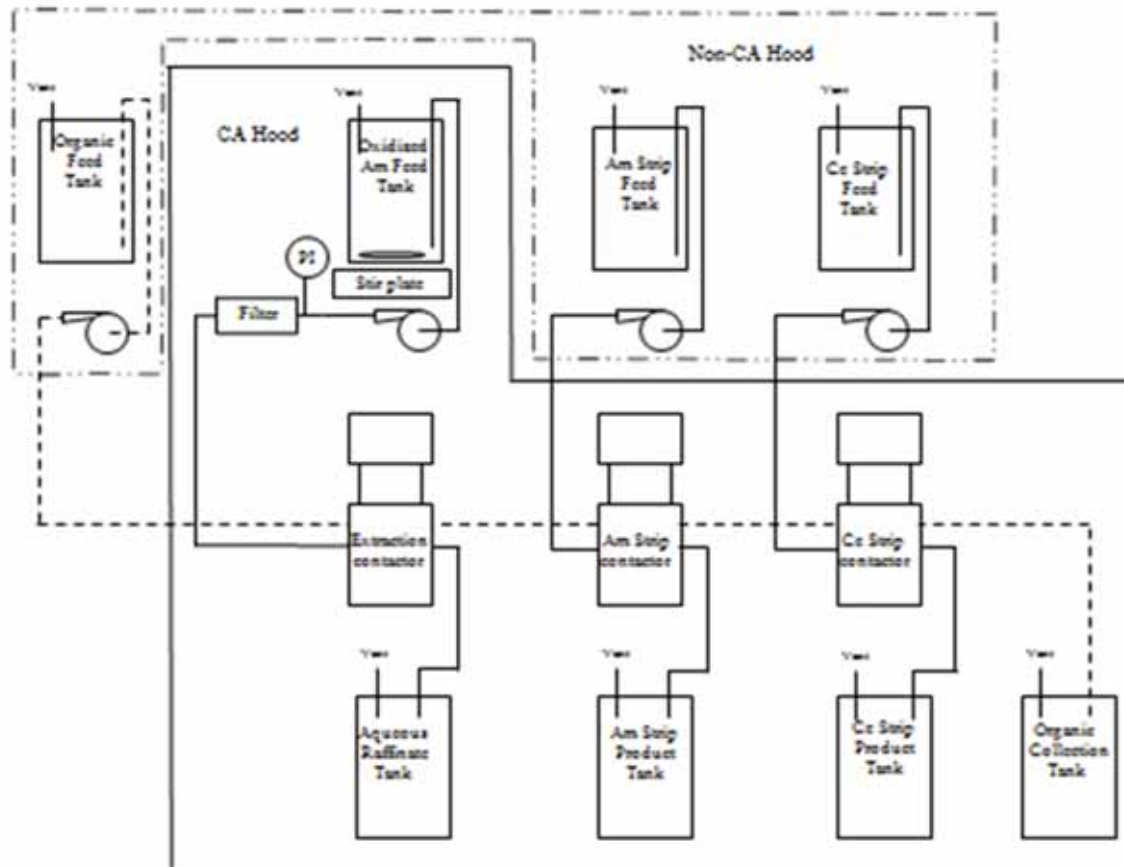


Hot test preparation

- Feasibility was first demonstrated in 2013 using Ce oxidation, bismuthate-filtration, DAAP extraction and Ce peroxide stripping using 5-cm contactors.
- Some Ce(IV) losses due to oxidation of the stainless steel- especially in high-surface area cross-flow (CUF) filter.
- This and batch tests convinced us that no wetted surfaces in the hot test could be stainless, or plastics.
- Custom-built contactor for extraction stage with wetted surfaces tantalum lined or of PVDF; bismuthate filter was teflon.
- Unfortunately, batch tests with all the same reagents to be used in the hot test showed lower than expected D_{Am} , ~1.8 instead of 4-5.



Hot test in rad fume hood



A series of three, 5-cm CINC Model V02 centrifugal contactors was used to extract oxidized americium from simulant (stage 1), nominal americium stripping (stage 2) and nominal Ce stripping (stage 3).

Stage 1 custom built using inert materials.



Hot test results

- Oxidation of feed 6.5 M HNO₃-simulant containing tracer ²⁴³Am and ¹³⁹Ce with 60 mg/mL sodium bismuthate with stirring for 2 h.
- **Stage 1** was extraction: 1 M DAAP/dodecane. Am removal was 62%- (compare to 65% in batch contacts). Ce was 95%.
- **Stage 2** was nominal Am strip: dilute acidic H₂O₂: $D_{Am} \sim 3.5$ vs. 0.4 expected. (~15 % of Am back extracted- Ce behaved as expected with $D_{Ce} \sim 33$).
- **Stage 3** was nominal Ce strip: more H₂O₂: $D_{Am} \sim 2.5$; $D_{Ce} \sim 2.9$

Hot Test Conclusions

- **Americium extraction by contactors was same as in batch tests. We can oxidize and extract Am(VI) using process equipment.**
- **Stripping was harder than we thought; perhaps due to short contact times. This is fortuitous. We can now introduce multiple extraction and scrub stages, thought to be impossible before.**
- **Stripping should still be possible, given longer residence time with the aqueous phase, or higher reductant concentrations.**

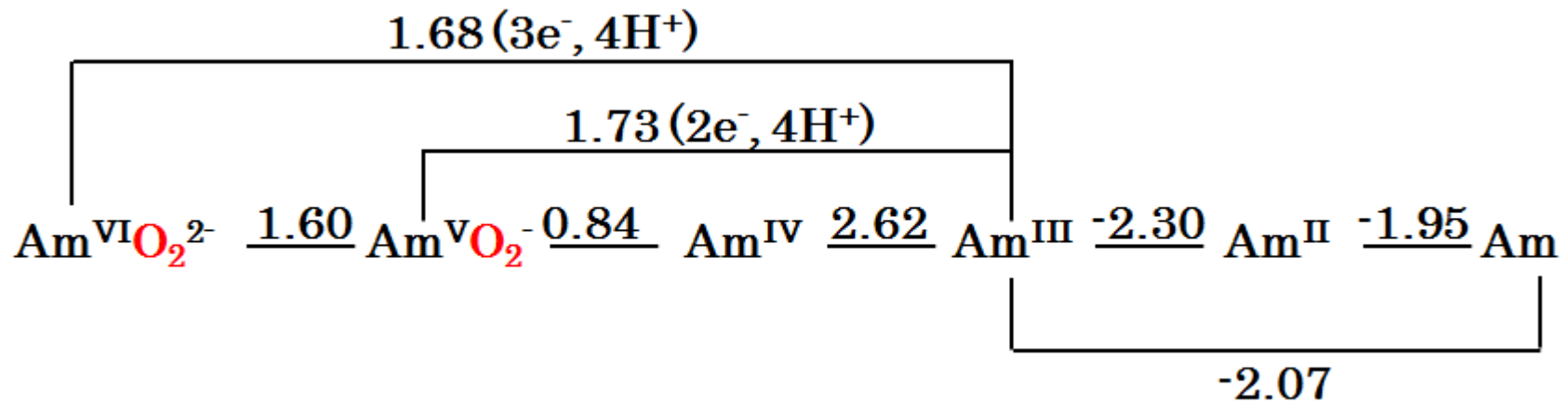
Bismuthate has some disadvantages

- Sparingly soluble in nitric acid, thus large amounts of undissolved solids.
- Oxidation is slow; 1-2 h
- Reduction product is Bi(III), which interferes with Ln(III) extraction when extracting them away from Am(V). Interfered with attempts at TRUEX.
 - Mincher, B.J.; Schmitt, N.C.; Case, M.E. 2011. A TRUEX-based separation of americium from the lanthanides. *Solvent Extr. Ion Exch.* 29: 247-259.
- Bi(III) does not affect Am(VI) extraction, but does ppt as the carbonate upon caustic scrub.
- Am(VI) yield isn't always predictable.





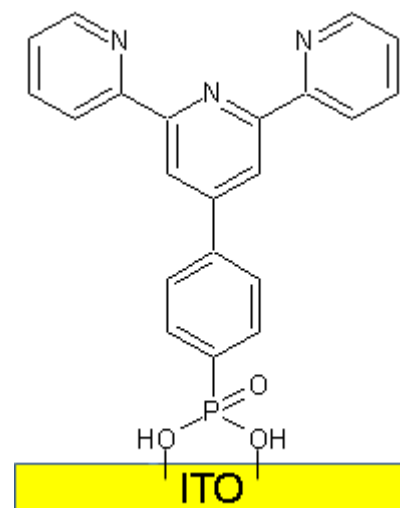
An alternative is Electrochemistry



Functionalized electrodes

University of North Carolina Chapel Hill (Chris Dares and Tom Meier.)

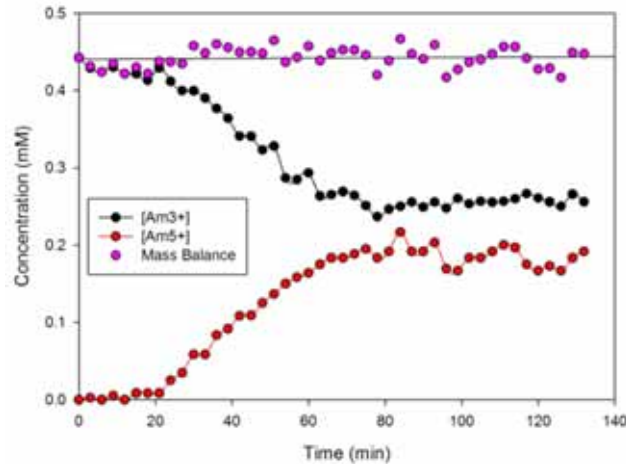
- Indium Tin Oxide substrate.
- Nano-particles for high surface area.
- Surface derivatized with terpyridine ligand.
- Phosphonate linkage binds ligand to metal oxide surface.
- Holding the Am on the surface appears to facilitate multiple electron transfer.



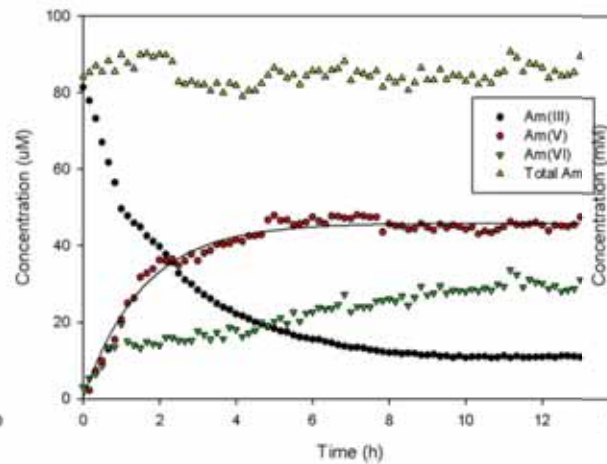
Bypassing Am(IV) to electrolytically make Am(V) and Am(VI)

Working electrode- terpy-functionalized n-ITO/ aux electrode Pt foil
0.1 M HNO₃/0.95 M NaNO₃

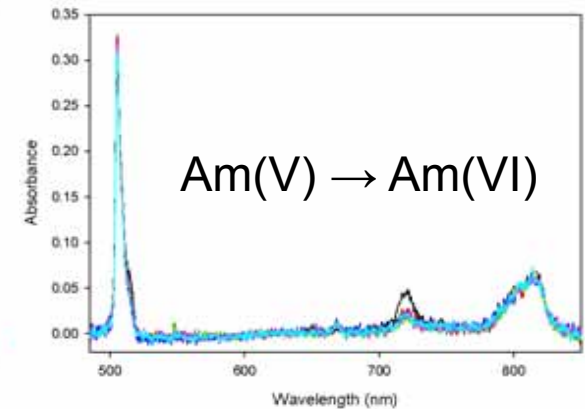
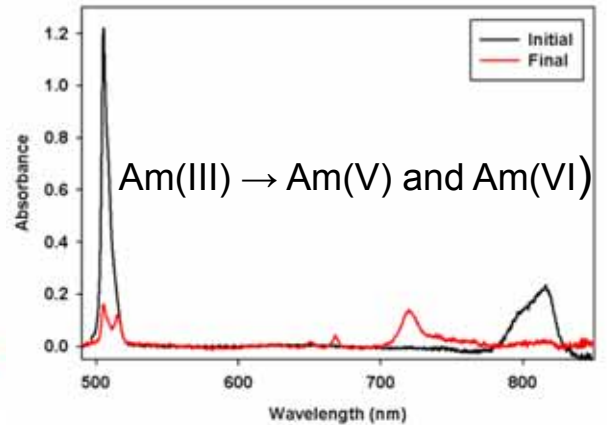
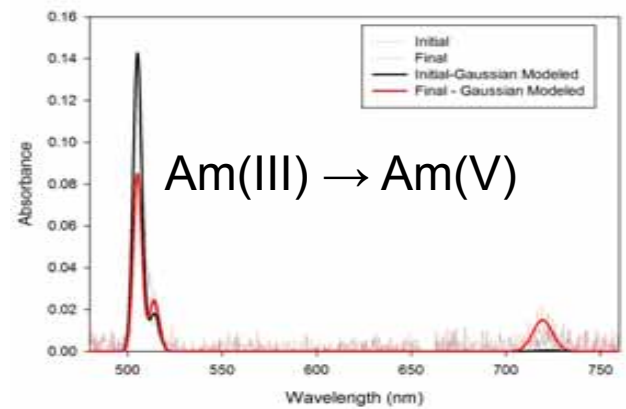
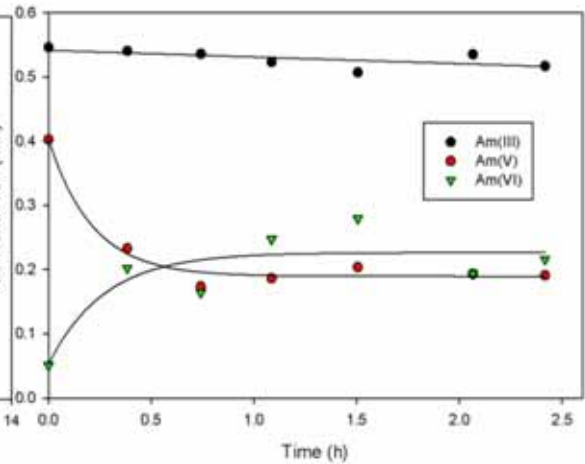
1.8V vs Ag/AgCl



2.25V



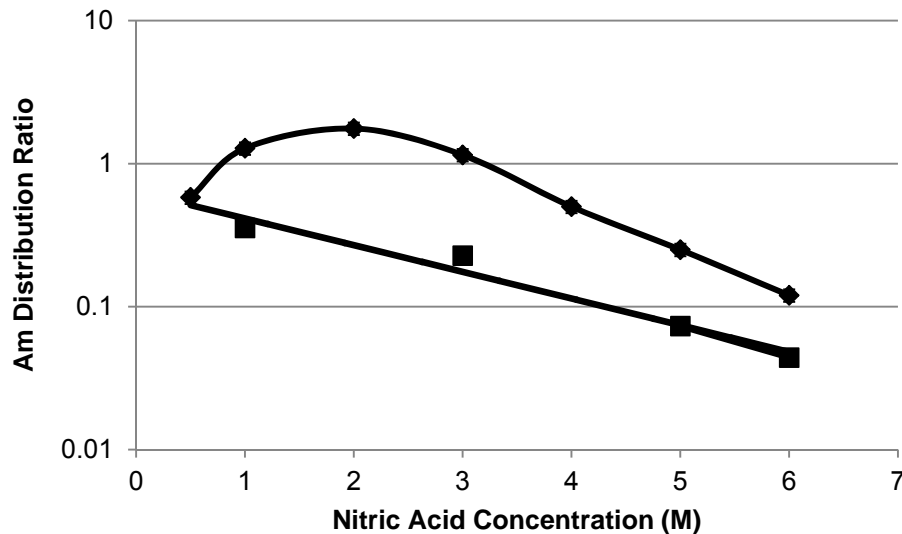
1.8V



Other chemical oxidizing agents are under investigation.

■ PNNL (Gregg Lumetta et al.):

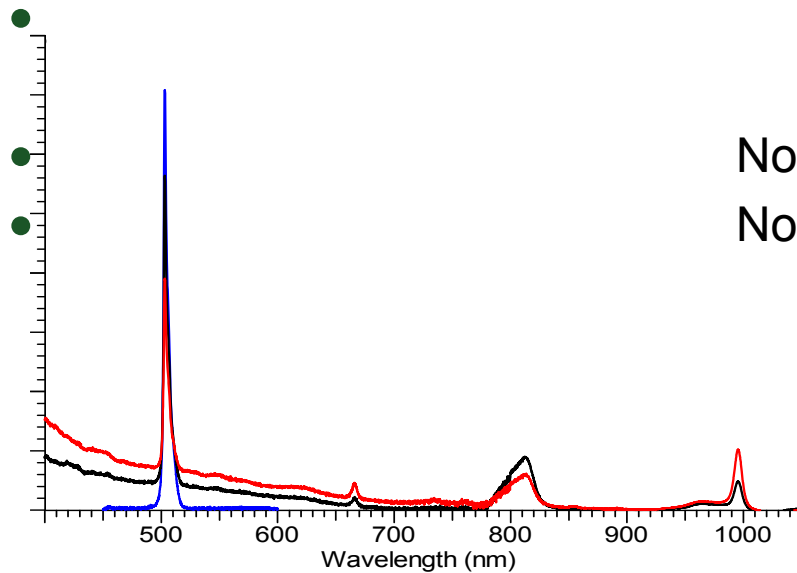
- Copper (III) periodate: $M_5[Cu^{III}(HIO_6)_2] \cdot nH_2O$, where $M = K^+$ or Na^+
- In acidic medium, the Cu^{3+}/Cu^{2+} potential is $\sim +2.4$ V
- $\sim 99\%$ yield for AmVI in up to 3.5 M HNO_3 .



Other chemical oxidizing agents are under investigation.

■ LANL (George Goff et al.):

- Ozone alone is not sufficient to oxidize Am(III) in HNO₃ solutions, however, Ag acts as a catalyst for ozone oxidation.
- Have obtained quantitative Am(VI) in 3 M HNO₃, and partial oxidation in up to 8 M HNO₃.



No evidence of Am(IV) or Am(V)
No solvent extraction data yet.