RRMC
Radiobioassay & Radiochemical Measurements Conference

The University of Iowa

Uranium Valence Control for analytical separations

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Issue

- Unexpected Behavior of U and/or Pu
- Low U yields
- U in Th fractions
- Incomplete reduction/oxidation of Pu
- Complex system:
  - $Al(NO_3)_3/HNO_3$
  - Sulfamic Acid
  - $TiCl_3$ Fe(II) Ascorbic Acid
  - $NaNO_2$ H_2O_2
  - Phosphate/Fluoride
  - Sample Matrix

Common Separation Schemes

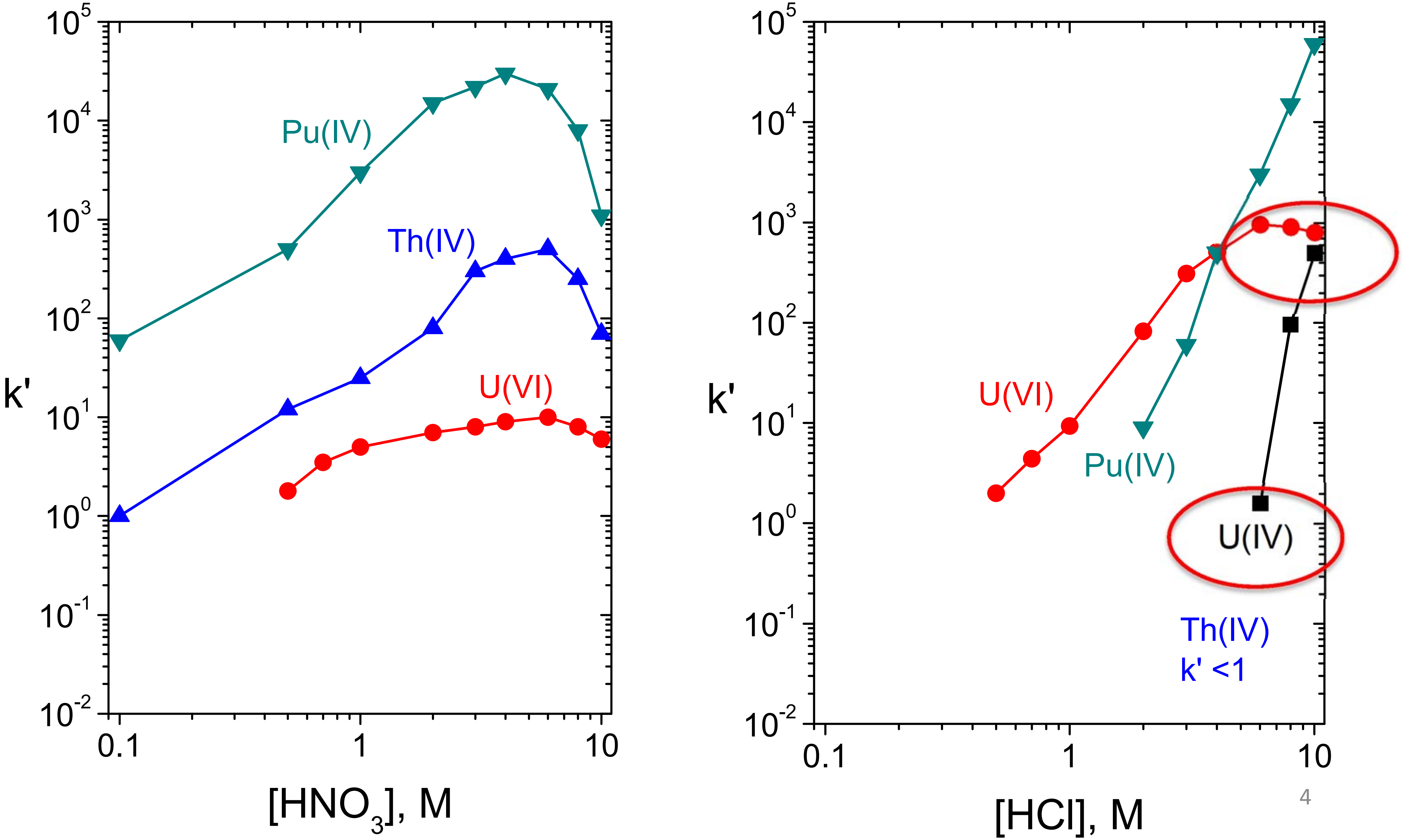
Test Factors that could:

-Yield unexpected oxidation states

-Lead to poor recoveries

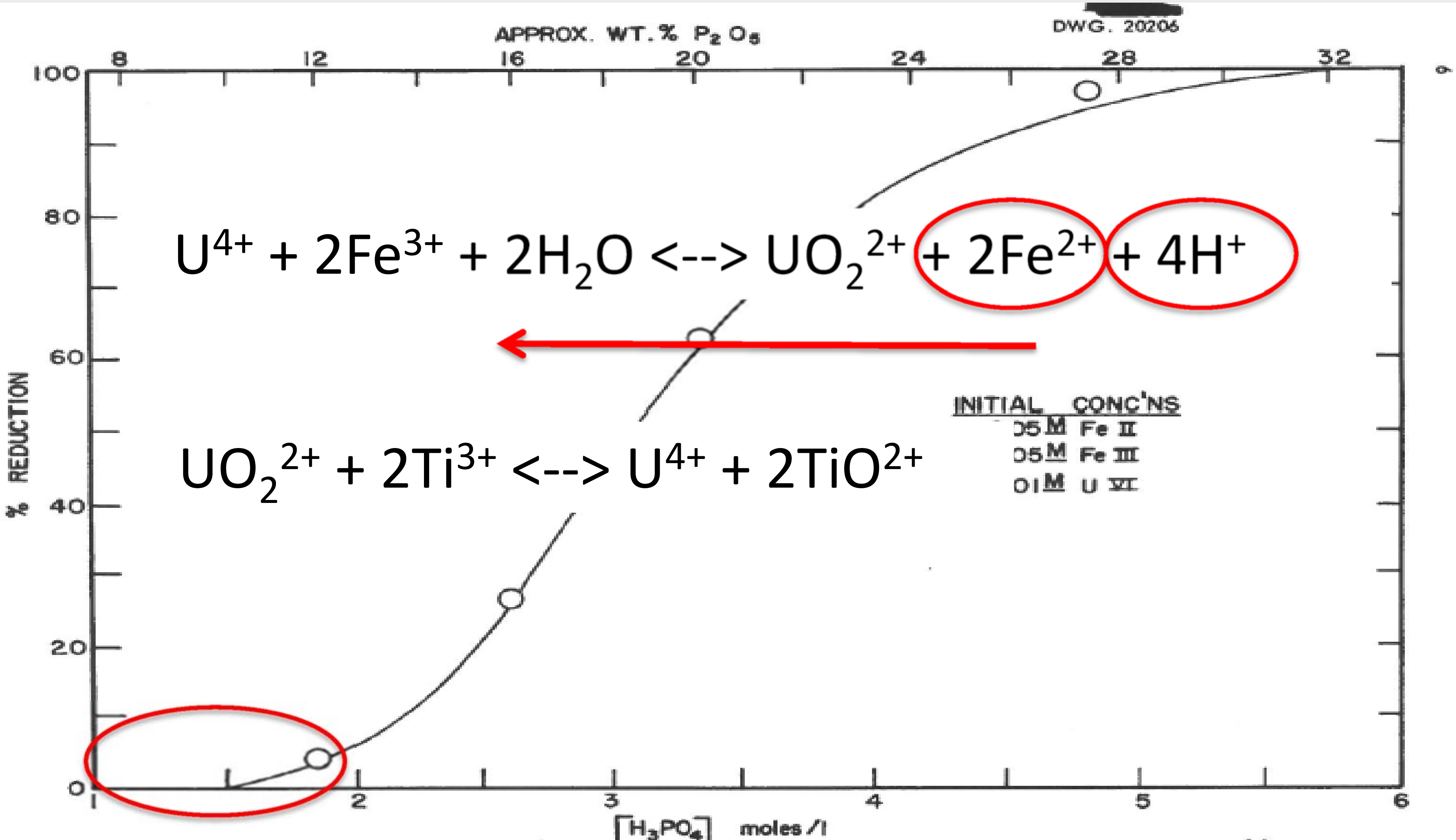
-Lead to poor separations

U on TEVA



Pu(IV)
Th(IV)
U(VI)
k'
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
0.1
1
10
$[HNO_3]$, M
U(VI)
Pu(IV)
U(IV)
Th(IV)
k' <1
k'
[HCl], M

Reduction of U(VI) to U(IV) by ferrous iron



$$U^{4+} + 2Fe^{3+} + 2H_2O \longleftrightarrow UO_2^{2+} + 2Fe^{2+} + 4H^{+}$$

$$UO_2^{2+} + 2Ti^{3+} \longleftrightarrow U^{4+} + 2TiO^{2+}$$

FIGURE 1. REDUCTION OF U(VI) TO U(IV) BY Fe(II) IN PHOSPHORIC ACID (0.36 M H_2SO_4) AT ROOM TEMPERATURE

C.F. Baes, Jr. “The reduction of Uranium(VI) by Ferrous Iron in Phosphoric Acid Solution: The formal electrode potential of the U(IV)/U(VI) couple,” Oak Ridge National Laboratory, ORNL 1581 (1953)

Worst Case Scenario

Ti^{3+}/Phosphate/Fluoride carryover from ppt

Reducing Chemistry in Load Solution

Strip Th with 6M HCl

No oxidation prior to source preparation

Low U yield + U in Th Fraction

Better Scenario

Ti3+/Phosphate/Fluoride carryover from ppt

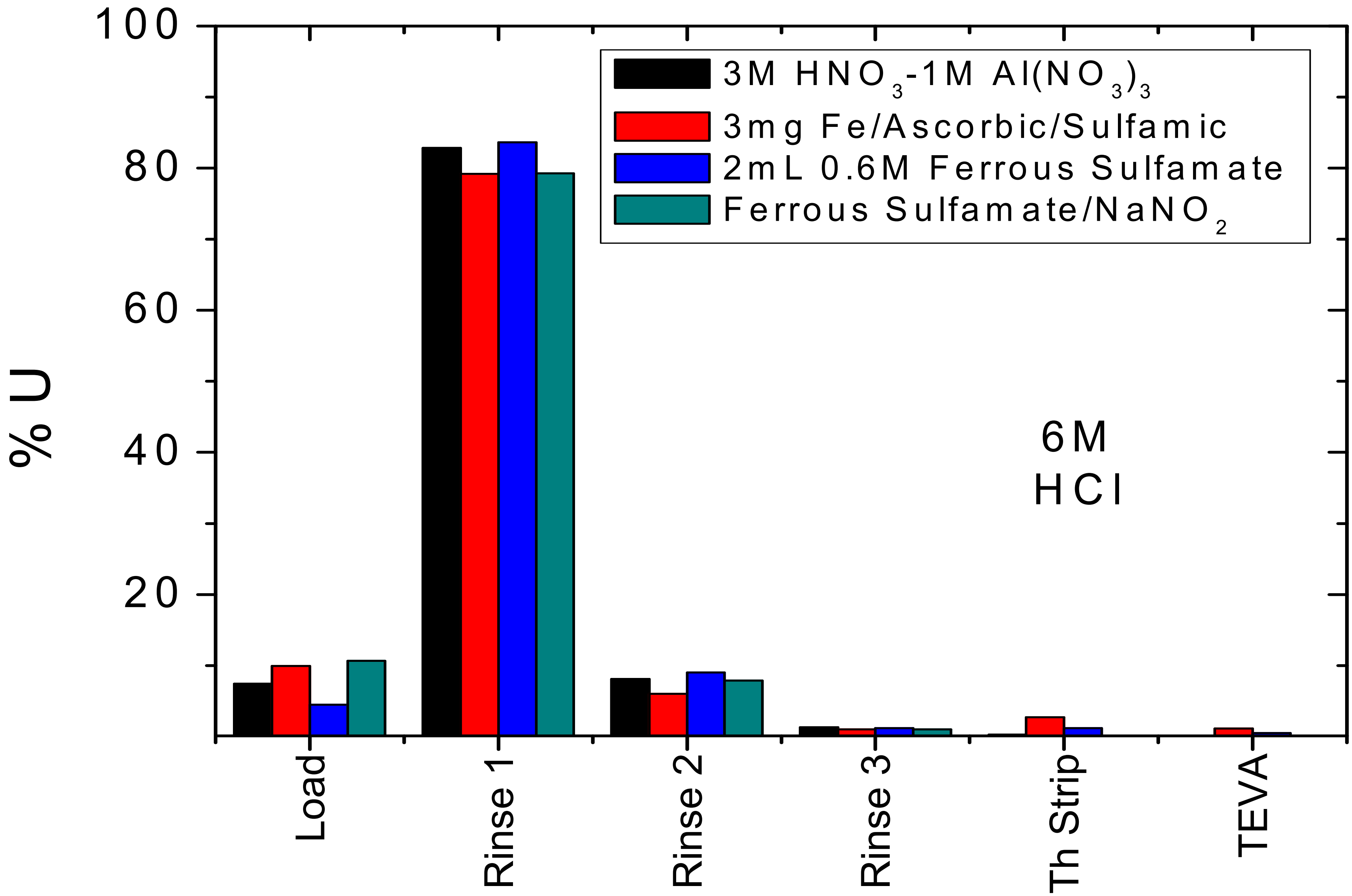
Oxidizing Chemistry in Load Solution

Strip Th with **9M** HCl

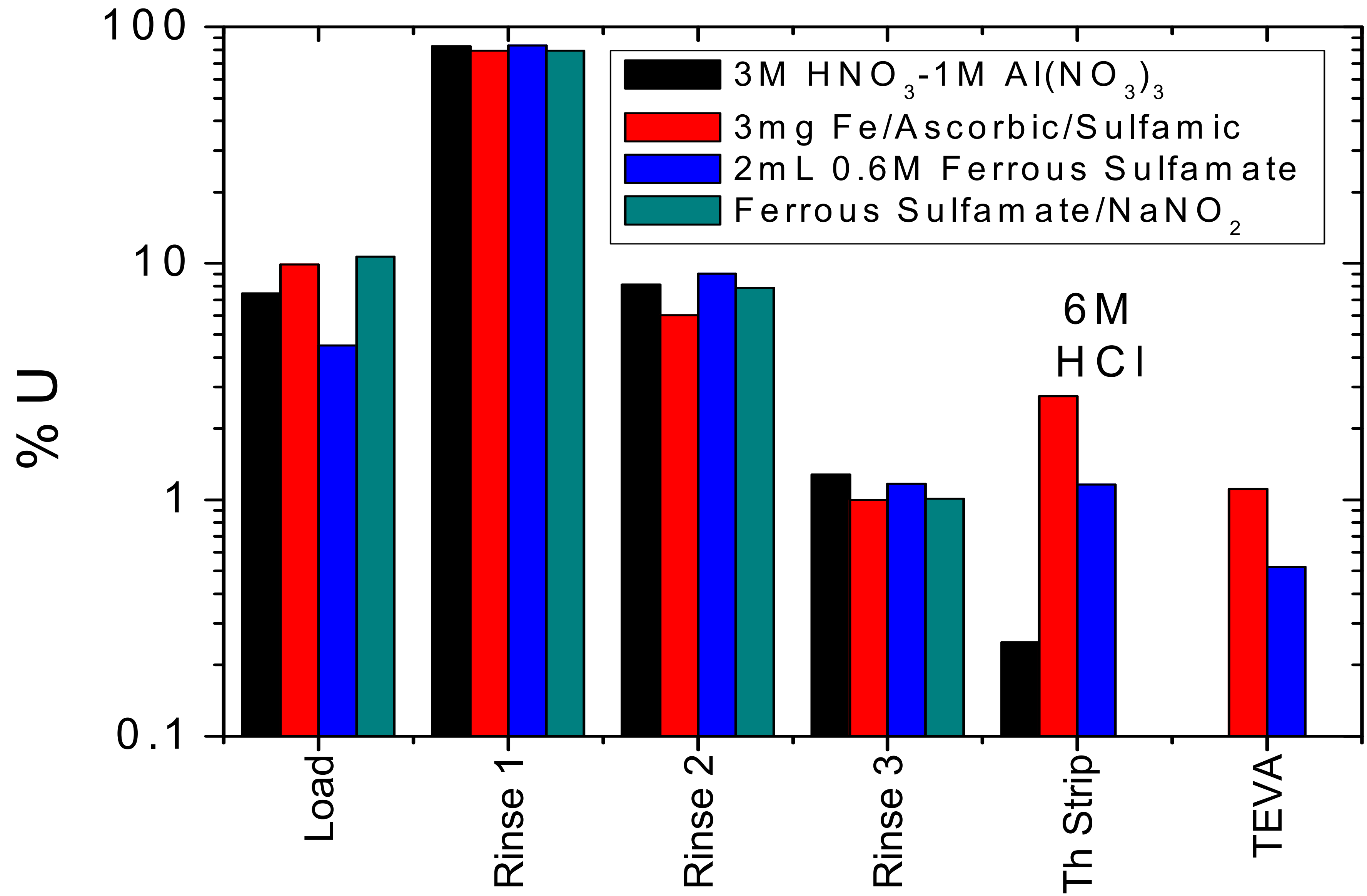
Oxidation prior to source preparation

High U yield + Clean Th Fraction

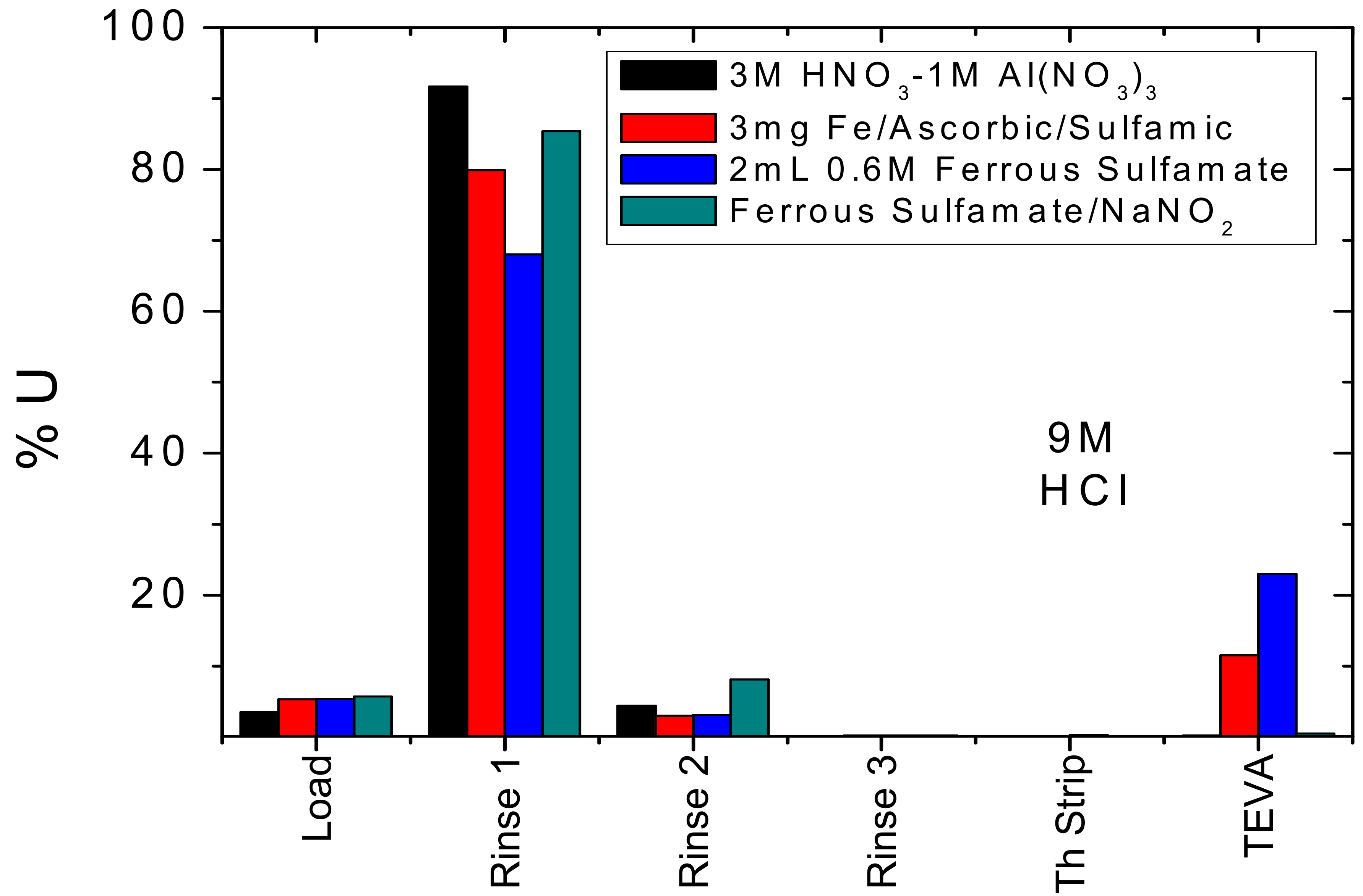
U on TEVA (6M HCl Th Strip)



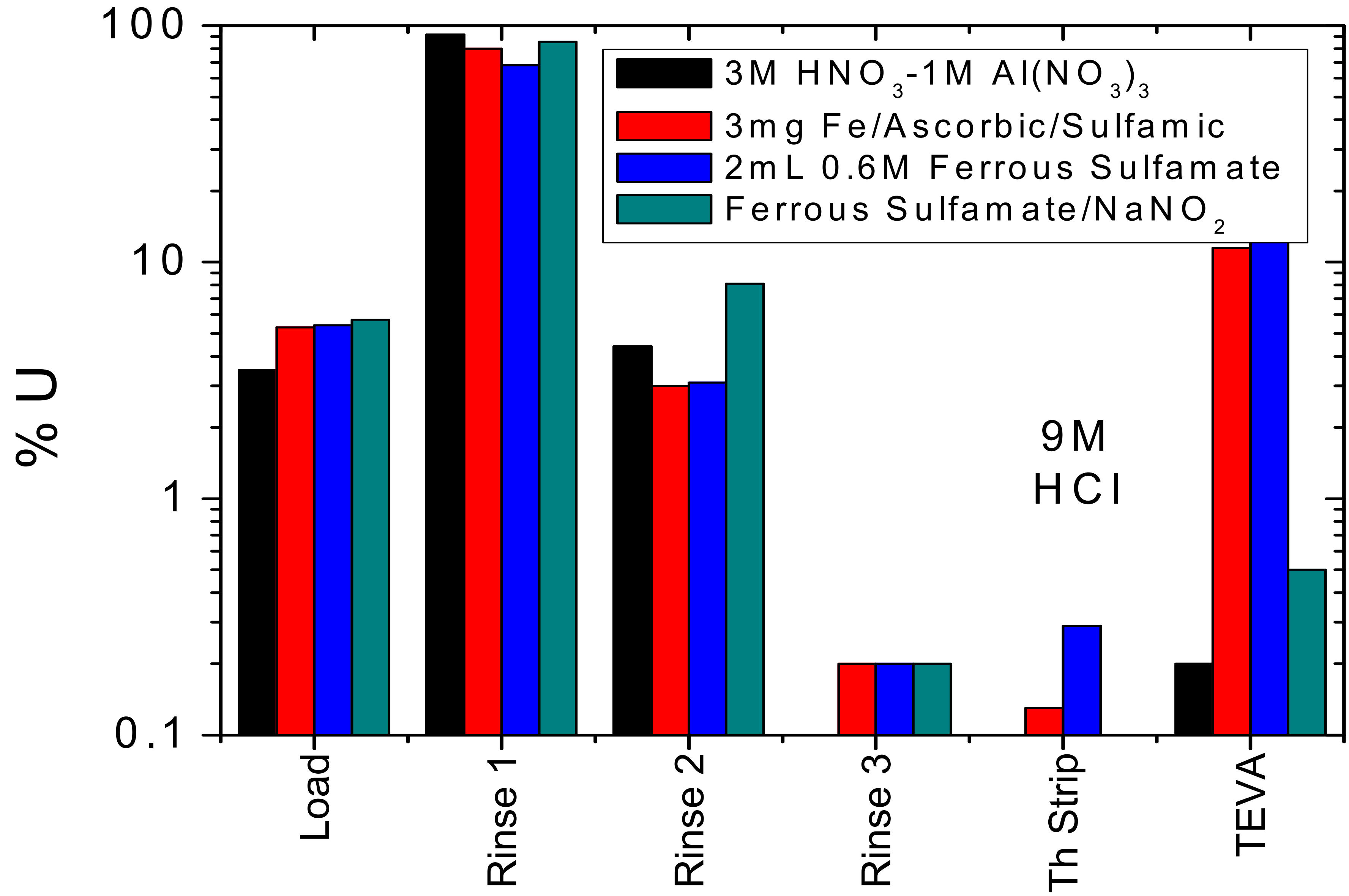
U on TEVA (6M HCl Th Strip)



U on TEVA (9M HCl Th Strip)

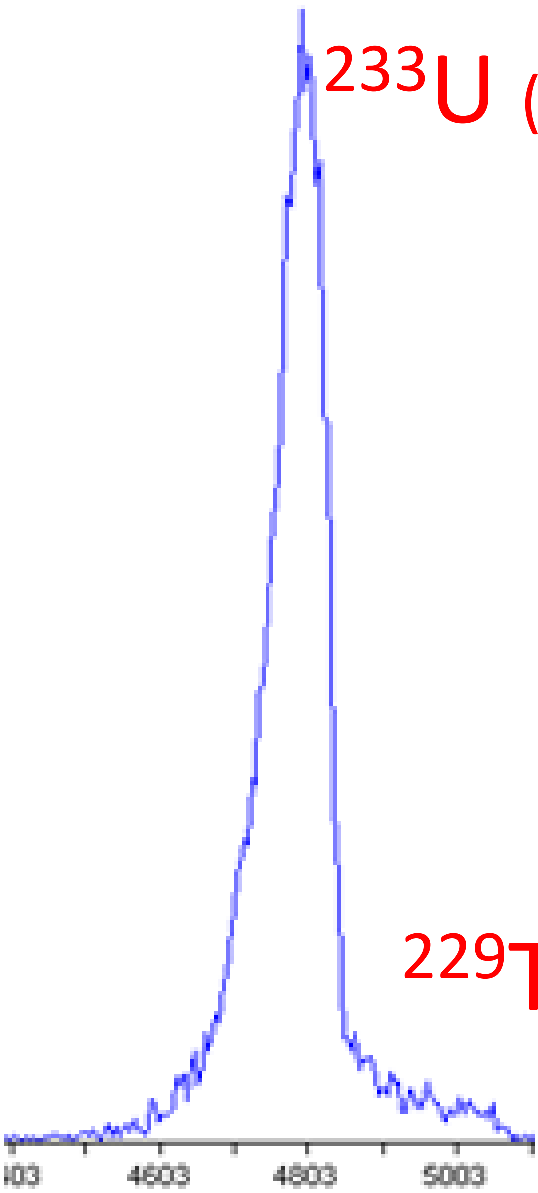


U on TEVA (9M HCl Th Strip)



Alpha Spectra (Th-229 + U-233, 6M HCl Th Strip)

50mg CeF_3 no H_2O_2

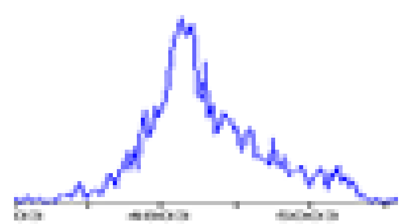


^{233}U (4.79-4.82 MeV)

^{229}Th (4.81-5.05 MeV)

Add H_2O_2!!!!!

50mg CeF_3 50uL H_2O_2



Other Factors (U in 6M HCl)

System	No $NaNO_2$	Add $NaNO_2$
Ferrous Sulfamate	1-8%	0.1-1.0%
1% $TiCl_3$	9-11%	0.2-0.3%
$LaF_3/TiCl_3$	2-3%	0.1-0.2%
Ca/PO_4^{3-}	2-3%	0.1-0.2%

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Summary

Many steps can be take to improve separations

Oxidizing Chemistry in Load Solution

Rinse to remove U(VI) – adding H_2O_2 may help

Strip Th with 9M HCl

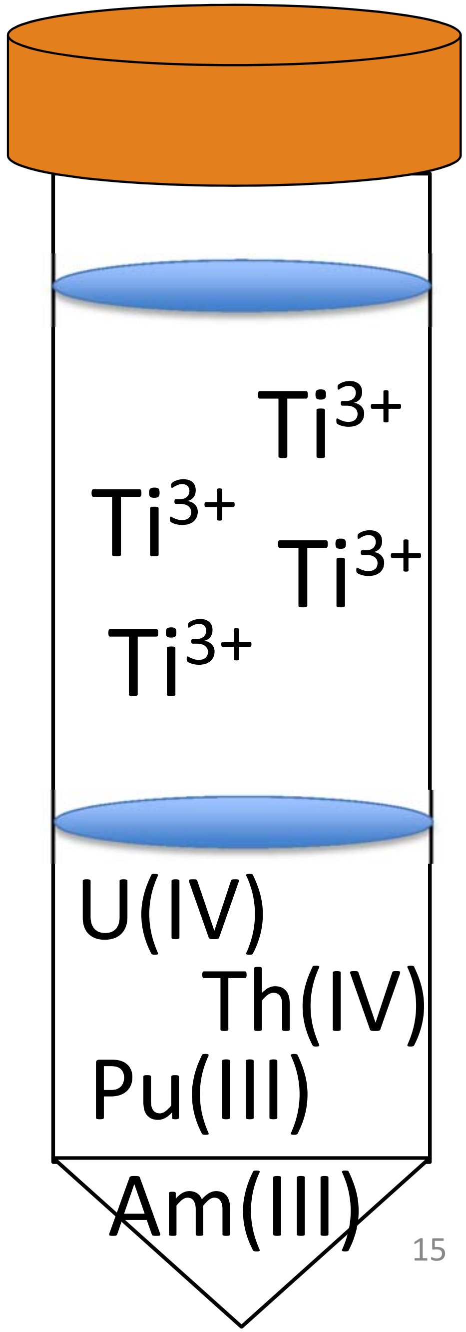
Add H_2O_2 prior to source preparation (except U)

Valence Adjustment Schemes ($TiCl_3$ Reduction/ppt)

$$Pu^{4+} + Ti^{3+} + H_2O <--> Pu^{3+} + TiO^{2+} + 2H^{+}$$

$$UO_2^{2+} + 2Ti^{3+} <--> U^{4+} + 2TiO^{2+}$$

Ti^{3+} PO_4^{3-} F^{-}



T.W. Newton "The Kinetics of the Oxidation-Reduction Reactions of U, Np, Pu, Am in Aqueous Solutions," *LANL TID-26506,* (1975)

Valence Adjustment Schemes (HNO_3 Dissolution)

Actinide	($TiCl_3$) Precipitation
Th(IV)	Th(IV)
U(IV/VI)	U(IV)
Np(IV/V/VI)	Np(IV)
Pu(III/IV/VI)	Pu(III)
Am/Cm(III)	Am/Cm(III)

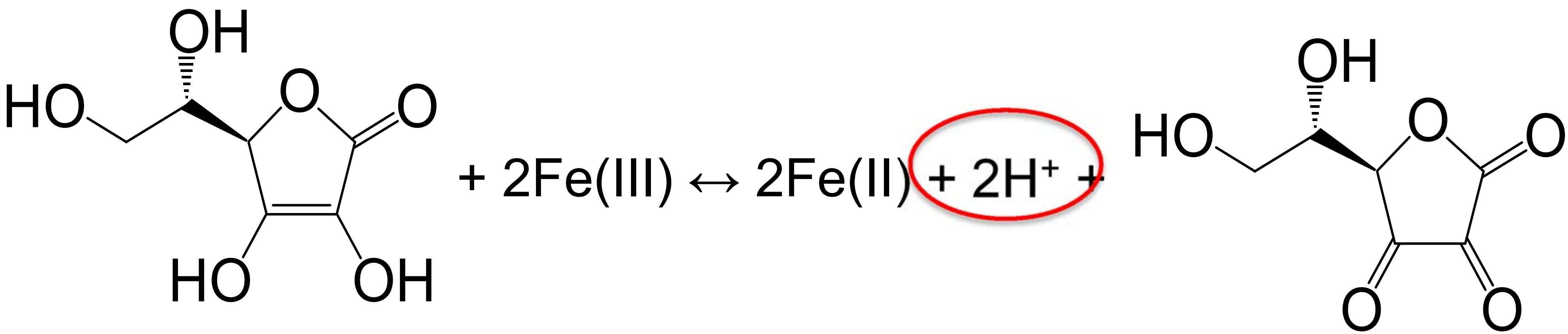
$$NO_3^- + 3H^+ <--> HNO_2 + H_2O$$

$$NO_3^- + H_2O + 2e^-$$
$$<--> NO_2^- + 2\,^-OH$$

Morse, Edelstein, Fuger, "The Chemistry of the Actinide and Transactinide Elements," 3rd Edition, Vols 3 and 4, Springer (2006).

Valence Adjustment Schemes (Ferrous/Sulfamate/Ascorbic acid)

$$HNO_2 + H_3NSO_3 \rightarrow H_2SO_4 + N_2 + H_2O$$



I.L. Jenkins "Factors Governing the Choice of a ^{237}Np/^{238}Pu Separation Process," *Actinides Reviews*, 1, 187 (1969).

Valence Adjustment Schemes (Ferrous/Sulfamate/Ascorbic acid)

$$PuO_2^{2+} + Fe^{2+} \longleftrightarrow PuO_2^{+} + Fe^{3+}$$

$$PuO_2^{+} + Fe^{2+} + 4H^{+} \longleftrightarrow Pu^{4+} + Fe^{3+} + 2H_2O$$

Np(IV)

$$Pu^{4+} + Fe^{2+} \longleftrightarrow Pu^{3+} + Fe^{3+}$$

$$U^{4+} + 2Fe^{3+} + 2H_2O \longleftrightarrow UO_2^{2+} + 2Fe^{2+} + 4H^{+}$$

T.W. Newton"The Kinetics of the Oxidation-Reduction Reactions of U, Np, Pu, Am in Aqueous Solutions," *LANL TID-26506,* (1975)

Valence Adjustment Schemes ($NaNO_2$)

$$HNO_2 \text{<-->} NO_2 + NO + H_2O$$

$$HNO_2 + H_3NSO_3 \rightarrow H_2SO_4 + N_2 + H_2O$$

$$\text{Ascorbic acid} + 2NO_2 \text{<-->} 2H^+ + 2NO_2^- + \text{Dehydroascorbic acid}$$

$$Fe^{2+} + NO_2 \text{<-->} Fe^{3+} + NO_2^-$$

$$Pu^{3+} + NO_2 \text{<-->} Pu^{4+} + NO_2^-$$

$$H^+ + NO_2^- \text{<-->} HNO_2 \qquad H^+ + \underline{HNO_2} + NO_3^- \text{<-->} \underline{2NO_2} + H_2O$$

A. Brunstad, "Oxidation of Plutonium(III) by Sodium Nitrite, Hanford Atomic Products Operation, Richland, Washington, HP-51655 (1957)