NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

Experimental Characterization of Pu Separation by PUREX Process on a Low-Burnup, Pseudo-Fast-Neutron Irradiated DUO_2 for Product Decontamination Factors and Nuclear Forensics

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AIEN 304

TEES | TEXAS A&M ENGINEERING EXPERIMENT STATION

NUCLEAR SECURITY SCIENCE & POLICY INSTITUTE

Outline

Motivation

- Current Events
  - Joint Comprehensive Plan of Action
  - Non-safeguarded reactors
  - Islamic State of Iraq and Syria
- Past Events
  - Septemer 11, 2001
- Limited scope of IAEA safeguards
- "the awful arithmetic of the atomic bomb"
- Need for improved forensic capabilities

Example note

Background

Weapons
Types
Pu
Where it comes from

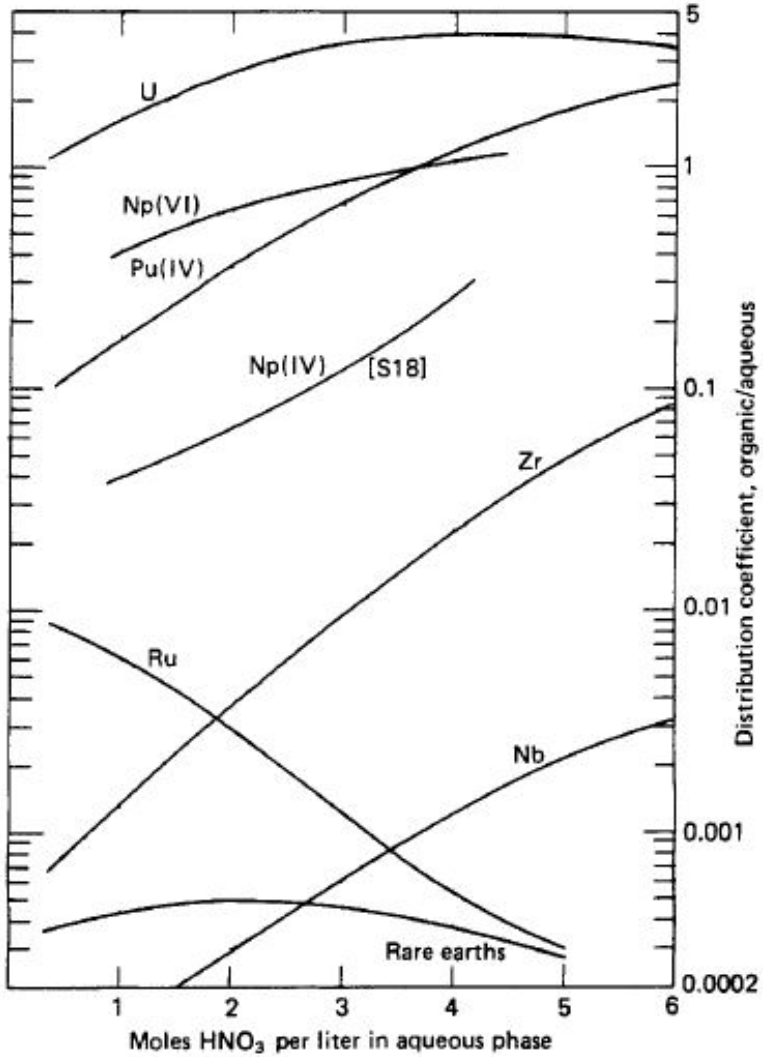
Motivation

- Weapons-grade Pu can be extracted from reactor discharged fuel with a burnup of about 1 (GWD/tU)
- Pu isotopes produced in irradiated fuel can vary
- Two examples of reactors which can intentionally discharge low burned fuel for extracting weapon-grade Pu are:
  - Fast Breeder Reactor
  - CANDU Reactor

1. Madras Atomic Power Station Kalpakkam, India
2. Expected criticality in Jan 2017
3. Cost from 450 million euros to 750 euros
4. Sodium-cooled reactor design - U238 for breeding
5. 100 GWd/t for core, 40 year life, 1750 tonnes of sodium about 75% of olympic sized swimming pool.
6. liquid sodium has a density a little less than water
7. MOX fuel (UO2 and PuO2) fuel
8. Fuel discharged at 100GWd/t, but I just mentioned that we are worried about 1GWd/t, mistake?

Smaller Picture

- Attribution for unpurified Pu has been previously studied [2, 6, 3]
- Interdicted Pu would likely have been processed
- Lack of literature on decontamination factors and distribution coefficients for useful forensic elements (Cs, Sb, Eu, Rb, Sr, Nd, Pm, and Sm)



Adapted from Stoller[7]

Background

What is PUREX - A type of laundry detergent?

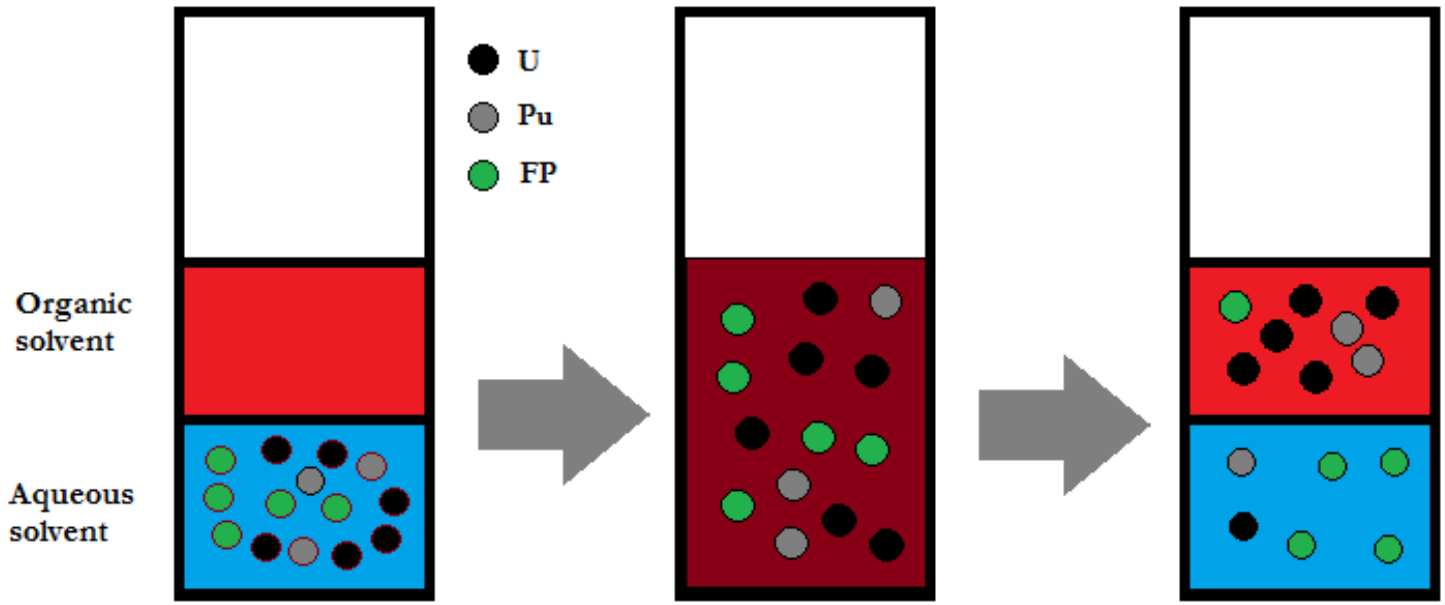
- Plutonium Uranium Redox EXtraction
  - Liquid-liquid solvent extraction
  - Many stages:
    1. Preparation for Dissolution
    2. Dissolution
    3. Preparation of Dissolved Feed
    4. Primary Decontamination - Extraction to organic*
    5. Scrubbing
    6. Plutonium Partition - Back-Extraction to aqueous*
    7. Plutonium Purification

* - Discussing Next

Extraction

$$UO_{2(aq)}^{2+} + 2NO_{3(aq)}^{-} + 2TBP_{(o)} \leftrightarrow UO_2(NO_3)_2 \cdot 2TBP_{(o)} \text{ [1]}$$

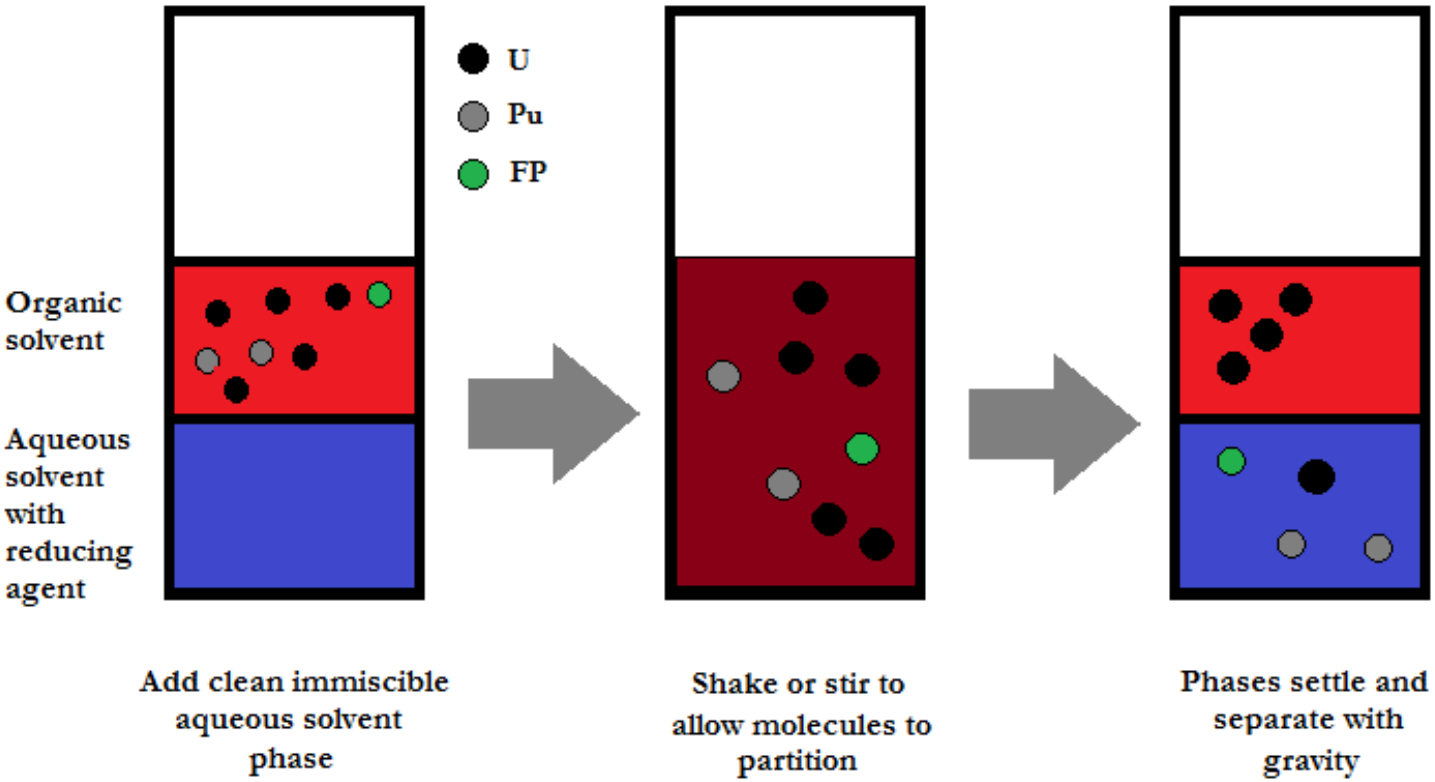
$$Pu_{(aq)}^{4+} + 4NO_{3(aq)}^{-} + 2TBP_{(o)} \leftrightarrow Pu(NO_3)_4 \cdot 2TBP_{(o)}$$



1. Most of the fission products are left in the aqueous solution at valence III and V states[4]

Back-Extraction

$$Pu(NO_3)_4(TBP)_{2(o)} + Fe^{2+}_{(aq)} \leftrightarrow Pu^{3+}_{(aq)} + 4NO^{-}_{3(aq)} + 2TBP_{(o)}$$ [5]



1. The fission products that contribute mostly to the radioactive contamination of product in PUREX are zirconium, niobium, and ruthenium - with multiple oxidation states.

Distribution Coefficients - The Missing link

- Distribution Coefficient (D): The ratio between the organic and aqueous phases (aka: D-values)

$$D = \frac{c_o}{c_{aq}}$$

- Specific element to element
- Vary widely with:[7]
  - Composition of phases
  - Solution saturation
  - Temperature of the solvent
- The fraction of mass, f_o deposited in the organic phase, assuming a volume ratio between the aqueous and organic phases, V_R, is:

$$f_o = (1 + D^{-1} V_R^{-1})^{-1}$$

1. Distribution coefficients can be reported in terms of volume basis (weight per unit volume), or a mass basis (mass of solute per unit mass of solute free solvent)- usually reported on volume basis
2. Note not a function of density, even though the two solutions have different densities, when solving for this value it cancels out
3. Solved this way to show, volume matters, and to give me a more intuitive sense of where things are going

Decontamination Factors - The Pot of gold

- After several cycles of Pu extraction/scrubbing/back-extraction are completed, the effectiveness of a PUREX cycle is described by the decontamination factor (DF):

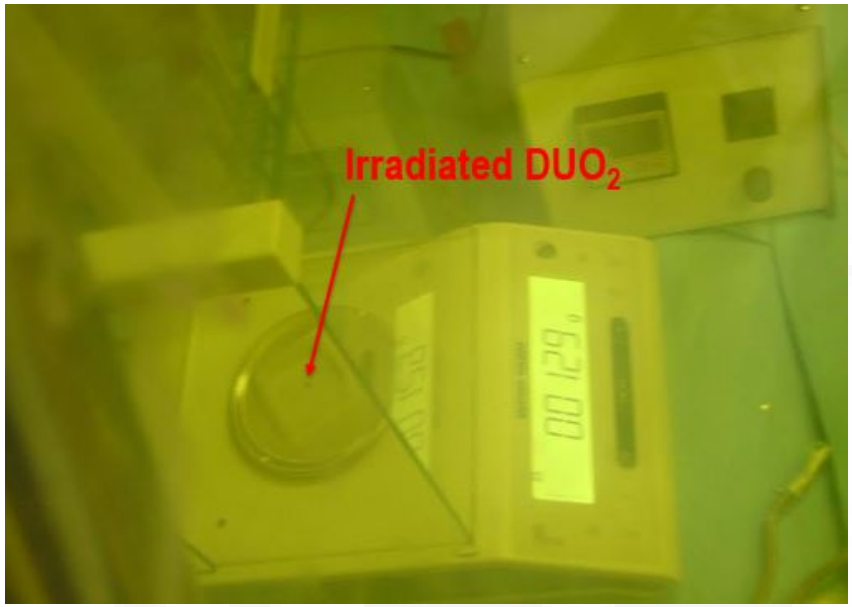
$$DF_j = \frac{\left|\frac{c_j}{c_{Pu}}\right|_{initial}}{\left|\frac{c_j}{c_{Pu}}\right|_{final}}$$

- DFs are characteristic of different process cycles
- Larger values (10^7) for industrial scale PUREX (compared to benchtop)[7, 1]

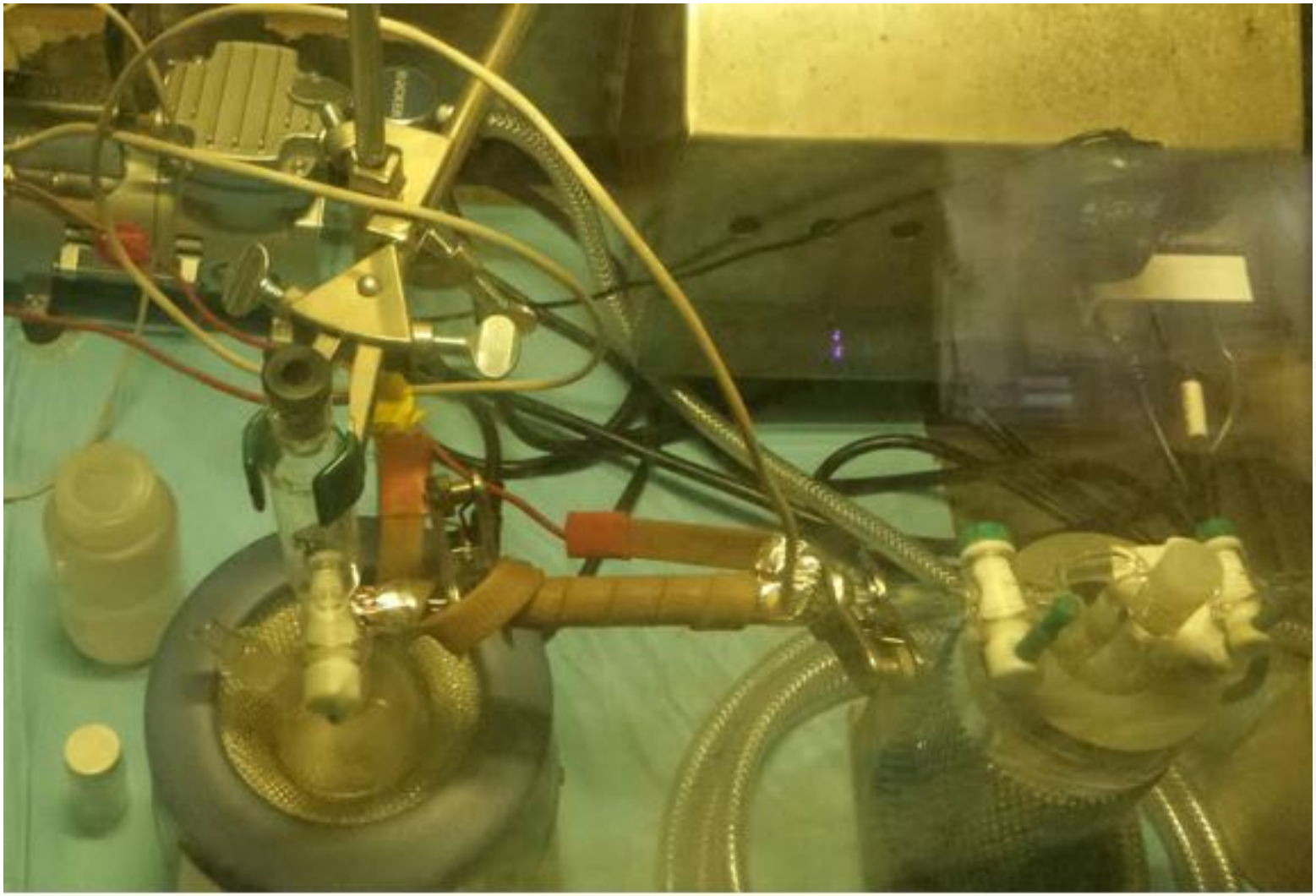
Previous Work

Irradiation

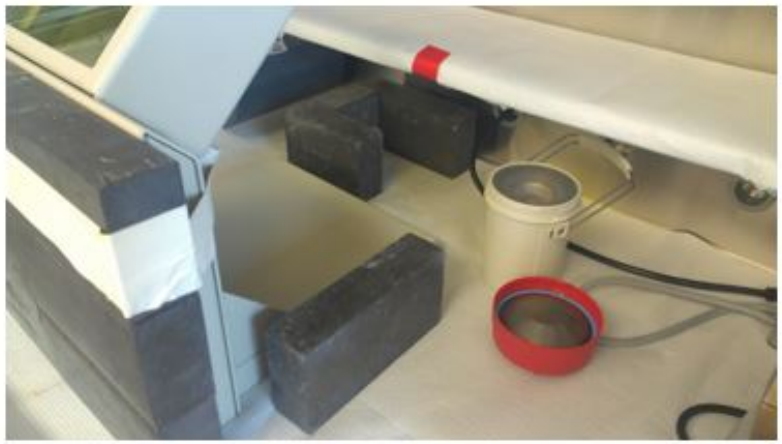
- 12.9 $\pm$ 0.1 mg of DUO_2 was irradiated
  - High Flux Isotope Reactor at Oak Ridge National Laboratory
- Burnup was 4.43 $\pm$ 0.31 GWd/tHM[8]
- 0.196 $\pm$ mg of total Pu was produced as measured by ICP-MS

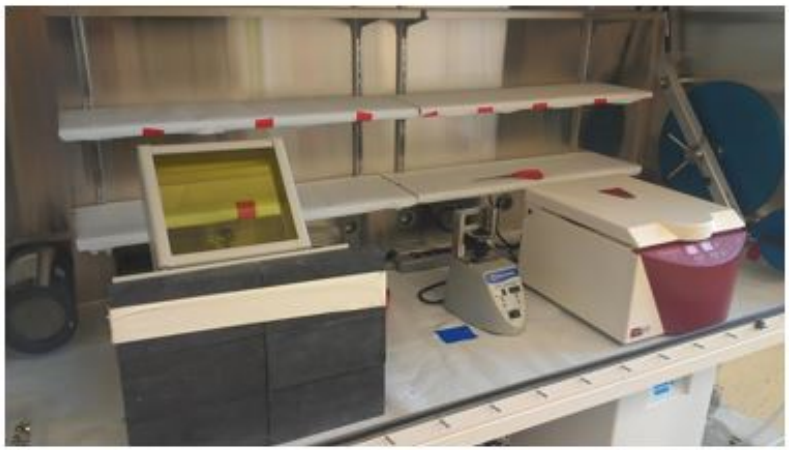


Dissolution of the spent fuel pellet



Glovebox





Experiments

- Single stage extraction and back-extraction
  - Purpose: quantify product recovery, D-values and DF values for single stage extraction and back extraction
  - Conditions:

Starting Solution	Extraction Solution	Back extraction solution
4 M nitric acid	30% vol.% TBP, 70 vol.% kerosene	0.024 M ferrous sulfamate in 0.75 M nitric acid

- Multi-contact extraction and back-extraction
  - Purpose: Maximize recovery of Pu with 4 extractions, 3 back extractions
  - Conditions:

Starting Solution	Extraction Solution	Back extraction solution
4 M nitric acid	30% vol.% TBP, 70 vol.% kerosene	0.024 M ferrous sulfamate in 4 M nitric acid

Previous Experiment Results

Recoveries of U and Pu

	Pu Recovery	U Recovery
Single stage	(83.4±9.5)%	(11.2±1.3)%
Multi-contact Cycle 1	(99.7±4.2)%	(6.8±0.3)%
Multi-contact Cycle 2	(93.0±4.6)%	(6.6±0.3)%
Overall Experiment 2	(92.7±6.0)%	(0.45±0.03)%

Previous Experiment Results

Decontamination Factors

Element (Z)	SS	Error	MC Cycle 1	Error	Isotopes Used
Rb(37)	39.0	5.9	11.8	0.8	^{85}Rb
Sr(38)	283	43	84.6	5.9	^{90}Sr
Mo(42)	5.7	0.8	1.9	0.2	^{97,98,100}Mo
Ru(44)	59.2	6.4	16.6	2.5	^{101,102,104}Ru
Pd(46)	65	14	8.9	1.2	^{110}Pd
Cd(48)	74	17	22.1	2.5	^{112}Cd
Cs(55)	177	28	52.9	3.9	^{133}Cs
Ce(58)	43	16	11.5	4.9	^{140,142}Ce
Nd(60)	19.2	2.1	5.9	0.4	^{143}Nd
Pm(61)	12.8	1.9	3.9	0.3	^{147}Pm
Sm(62)	11.5	1.5	3.6	0.3	^{151}Sm
Eu(63)	10.0	1.4	3.6	0.3	^{154}Eu
U(92)	7.4	1.2	14.7	0.9	^{238}U

Conclusions

- Two PUREX experiments were conducted
  - Single stage: Determined DC values for Pu, U and several FP
  - Multi-contact: Utilized Experiment 1 to recover over 92% of Pu while leaving less than 1% of the U
- DF values were measured for 12 FP elements
- DF values were lower than those typically found in industrial scale PUREX plants due to multiple extraction and back-extraction steps without an intermittent scrubbing step.
- This work provide DF data that will be built upon for nuclear forensic investigations of interdicted Pu.

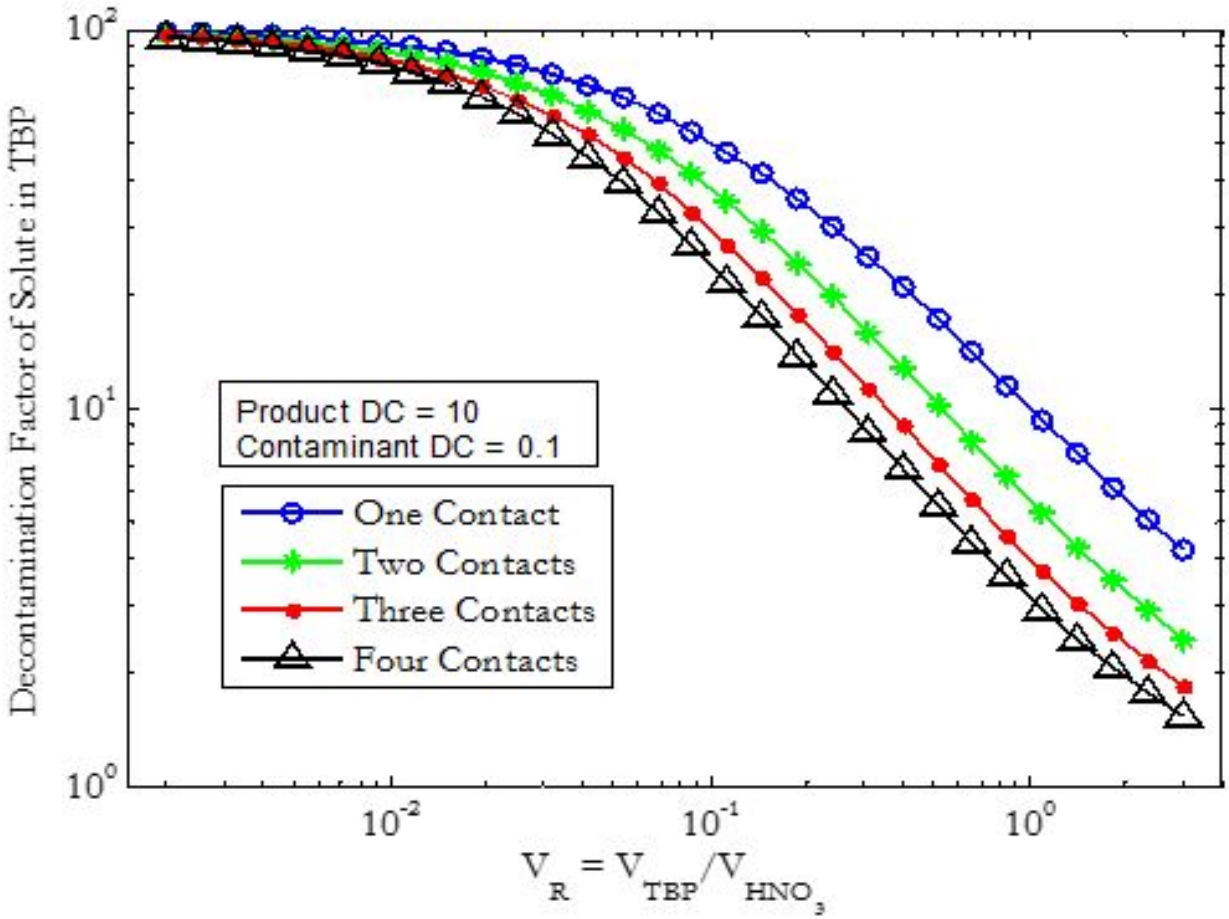
Future Work

Future Work

- Modify Multi-contact extraction, to recover a larger fraction of Pu
- Investigation of how D-values for (Cs, Sb, Eu, Rb, Sr, Nd, Pm, and Sm) change as a function of nitric acid concentration
- Determine statistical uncertainty of D and DF values.
  - Repeat above experiments 3-5 times
- Connect D-values with process information to DF values

Questions?

Previous Experiment Results



Decontamination Factors for multi-contact extraction.

References I

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[2] Sunil S Chirayath, Jeremy M Osborn, and Taylor M Coles. Trace fission product ratios for nuclear forensics attribution of weapons-grade plutonium from fast and thermal reactors. *Science & Global Security*, 23(1):48–67, 2015.

[3] Alexander Glaser. Isotopic signatures of weapon-grade plutonium from dedicated natural uranium-fueled production reactors and their relevance for nuclear forensic analysis. *Nuclear Science and Engineering*, 163(1):26–33, 2009.

[4] Kenneth D Kok. *Nuclear engineering handbook*, volume 60. CRC Press, 2009.

[5] RJM Konings, LR Morss, J Fuger, LR Morss, NM Edelstein, and J Fuger. The chemistry of the actinide and transactinide elements. *Springer, Dordrecht*, 4:2113–224, 2006.

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[7] Sidney M Stoller, Walter Henry Zinn, Stuart MacLain, and Atomic Energy Commission USA. *Reactor handbook. 2. Fuel reprocessing*. Interscience Publ., 1961.

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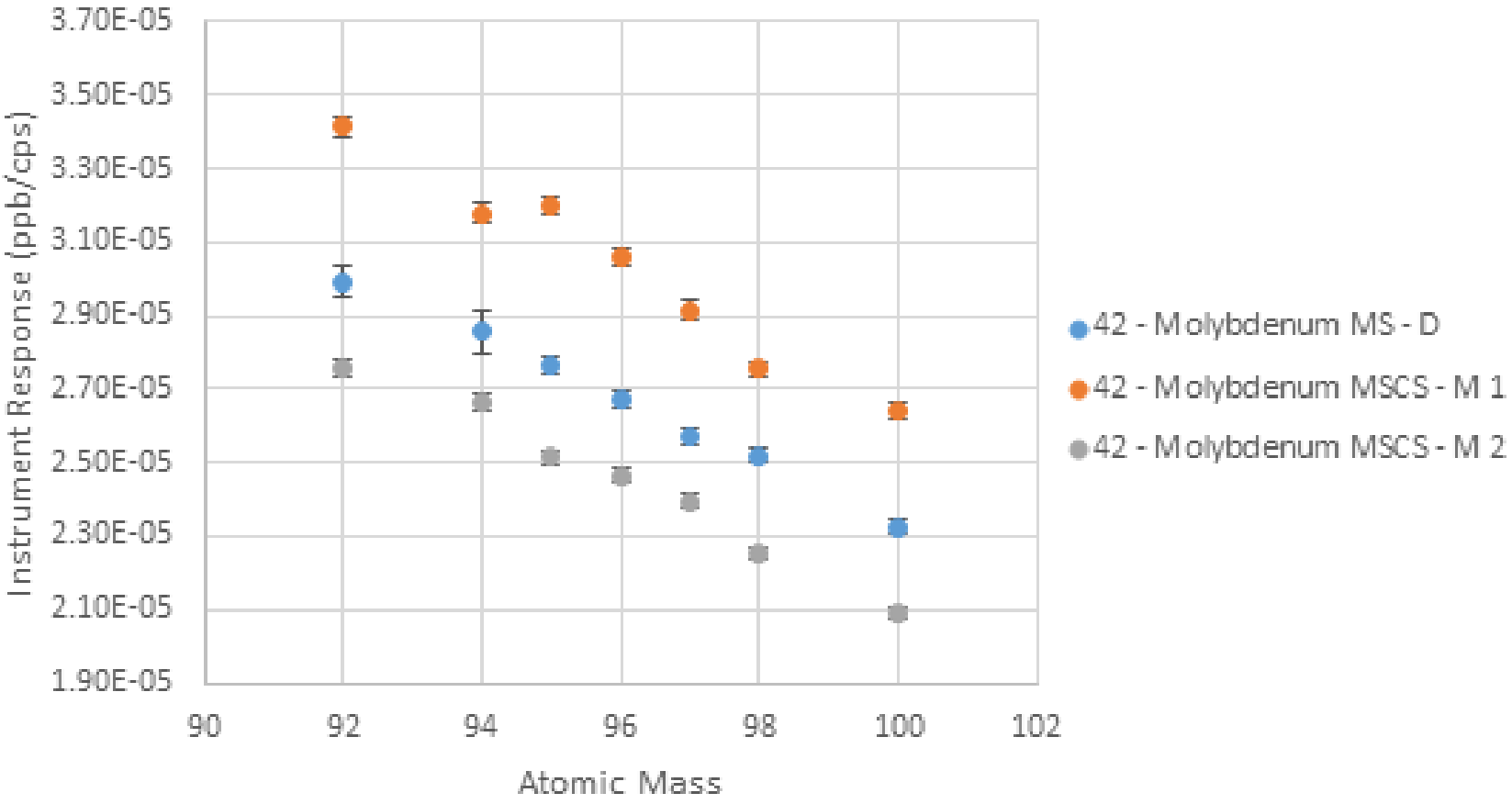
[8] Mathew Wayne Swinney. *Experimental and Computational Assessment of Trace Nuclide Ratios in Weapons Grade Plutonium for Nuclear Forensics Analysis*. PhD thesis, 2015.

Mass Spec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Instrument Response (ppb/cps)
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100
102
Atomic Mass
42 - Molybdenum MS - D
42 - Molybdenum MSCS - M 1
42 - Molybdenum MSCS - M 2