INL/MIS-20-60173-Revision-0

Radiation Chemistry Research for Improved Nuclear Fuel Cycles

May 2020

Changing the World's Energy Future

Christopher A Zarzana, Gregory P Horne, Bruce J. Mincher, Cathy Rae, Gary S Groenewold

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517, DE-AC07-05ID14517, DE-AC07-05ID14517

Radiation Chemistry Research for Improved Nuclear Fuel Cycles

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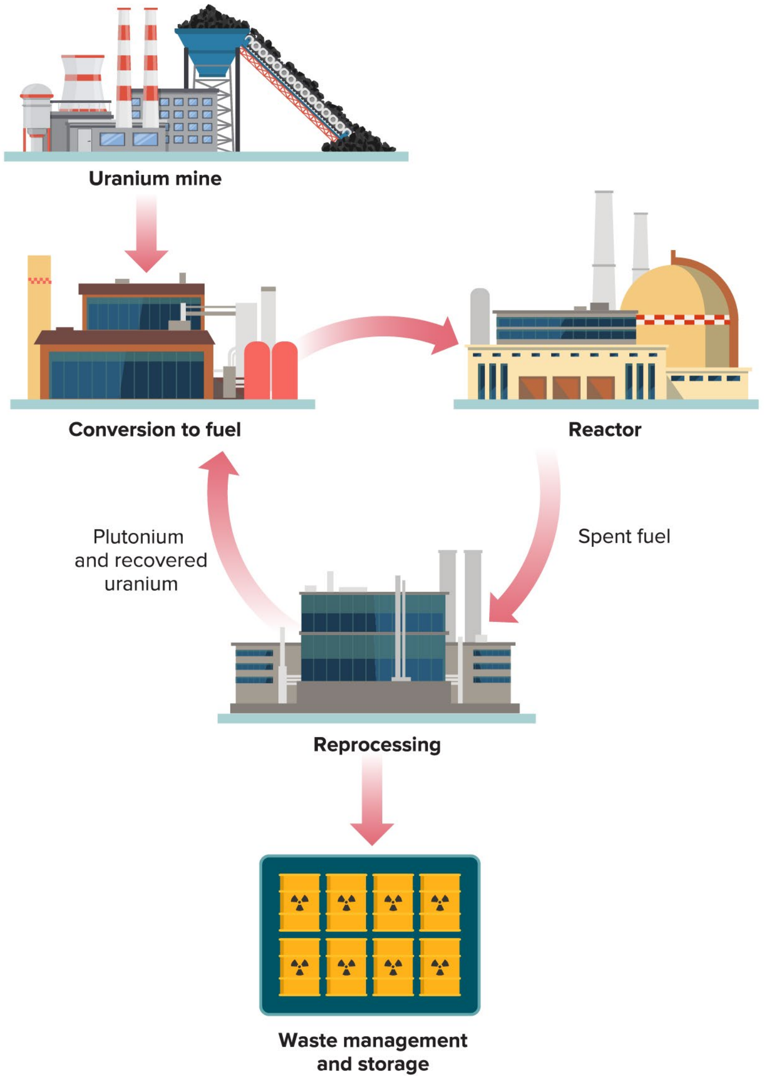
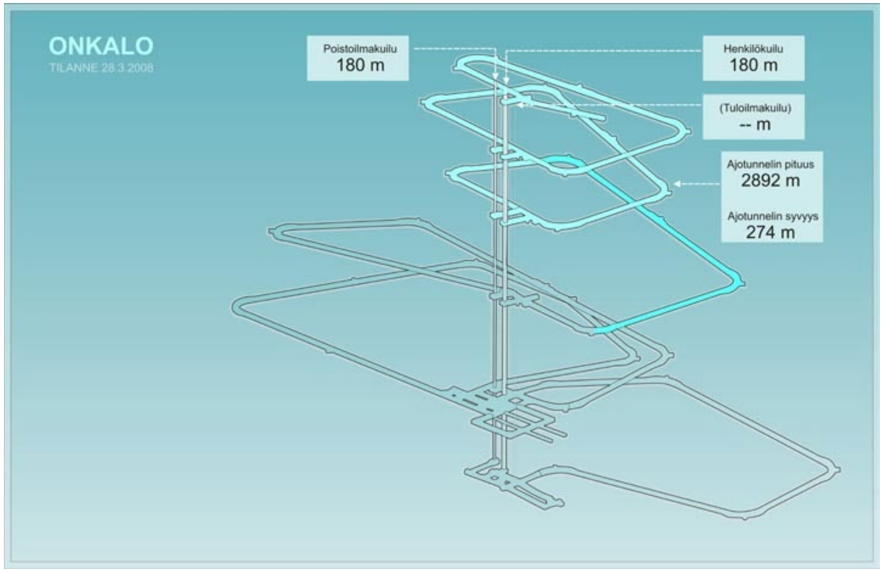
Nuclear Energy

- **Part of low-carbon energy portfolio**
- **Challenges related to disposal of used fuel**
- **Global inventory of near 250,000 tons of spent nuclear fuel**



Deep Geologic Storage

- **Often, there are political difficulties with siting repositories for spent fuel**
- **Question becomes: How do we most efficiently utilize nuclear repositories?**
  - Minimize volume that requires deep geologic storage
  - Reduction of the heat produced by the waste forms will allow more efficient utilization of the repository



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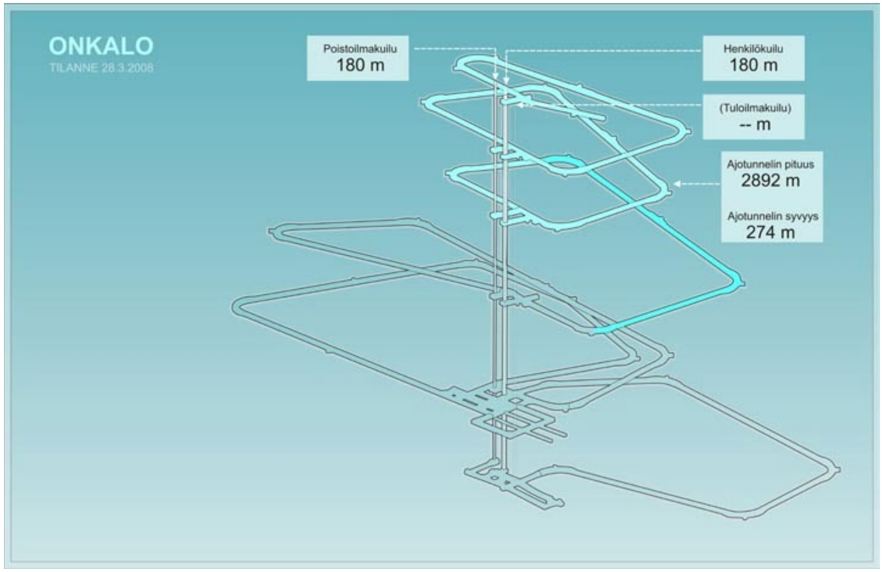
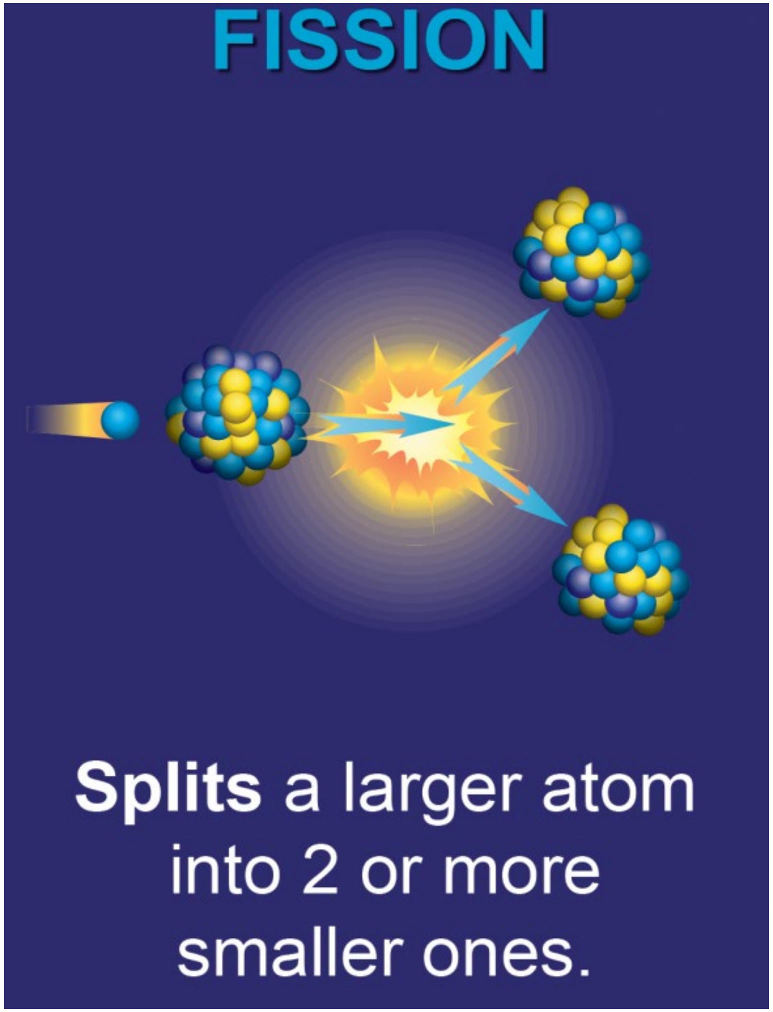
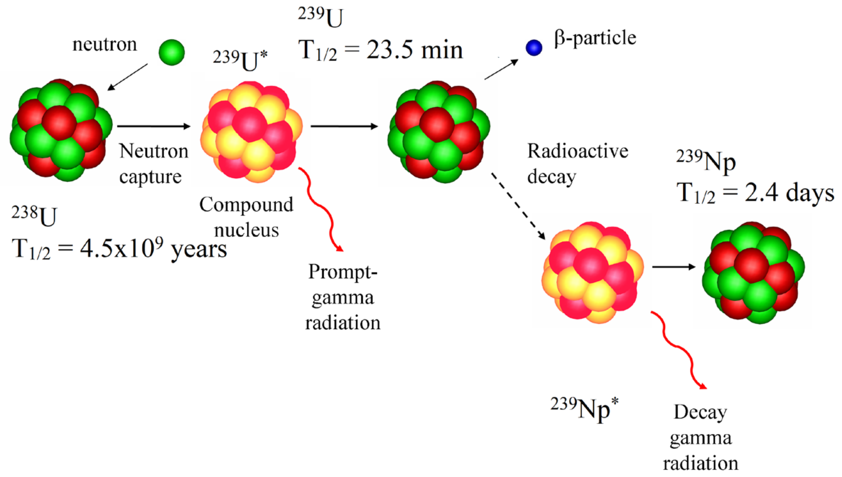


Processes in a nuclear reactor



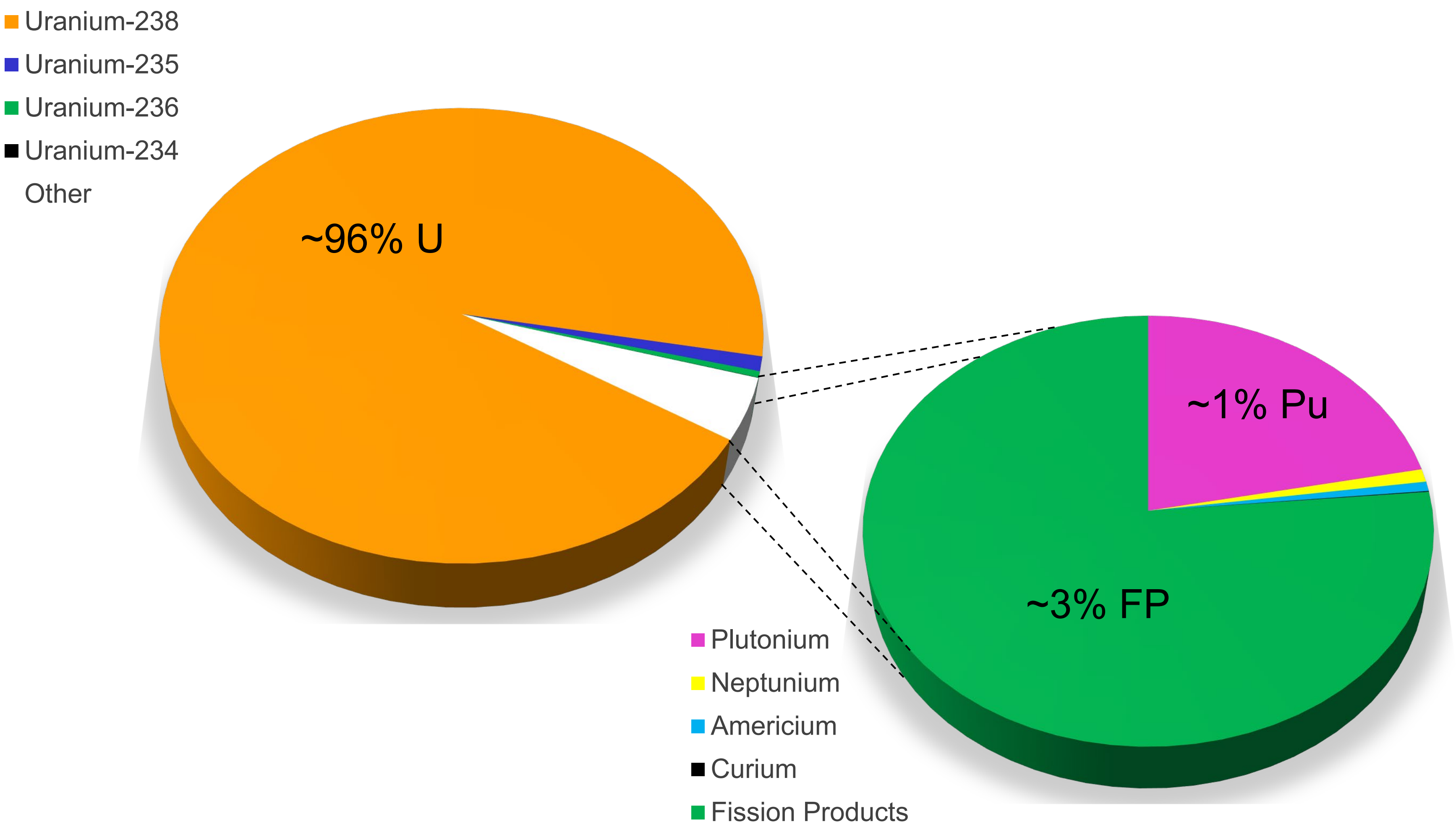
https://www.energy.gov/ne/downloads/infographic-fission-vs-fusion-whats-difference

Neutron Capture



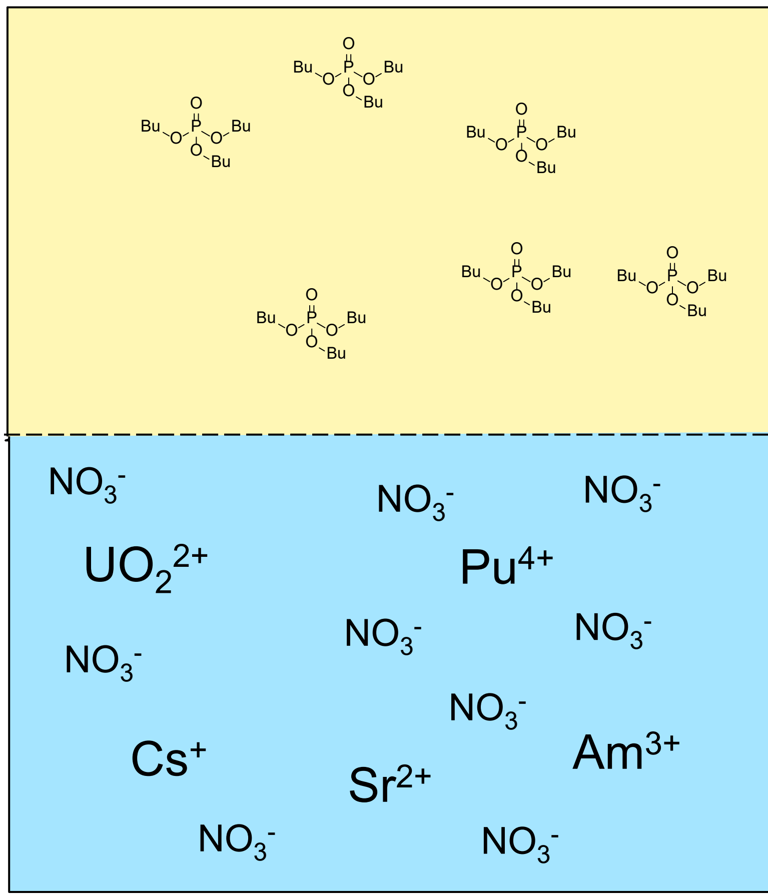
https://www.bnc.hu/?q=radiative_neutron_capture

Composition of Used Fuel

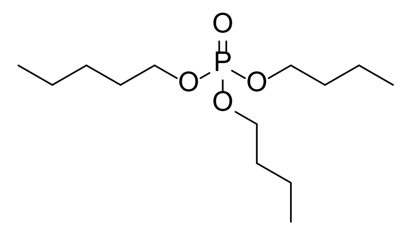


Plutonium Uranium Redox EXtraction (PUREX)

Organic Phase



Tributylphosphate
In kerosene



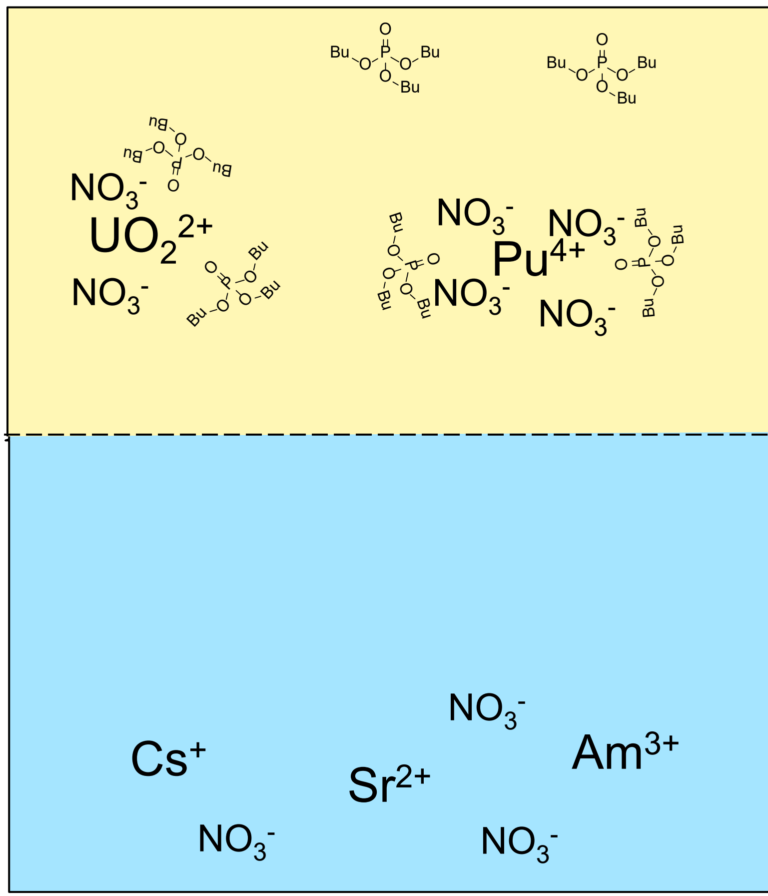
Aqueous Phase

Spent Nuclear Fuel (SNF)
dissolved in nitric acid

Plutonium Uranium Redox EXtraction (PUREX)

Organic Phase

Aqueous Phase



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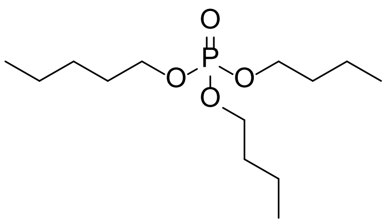
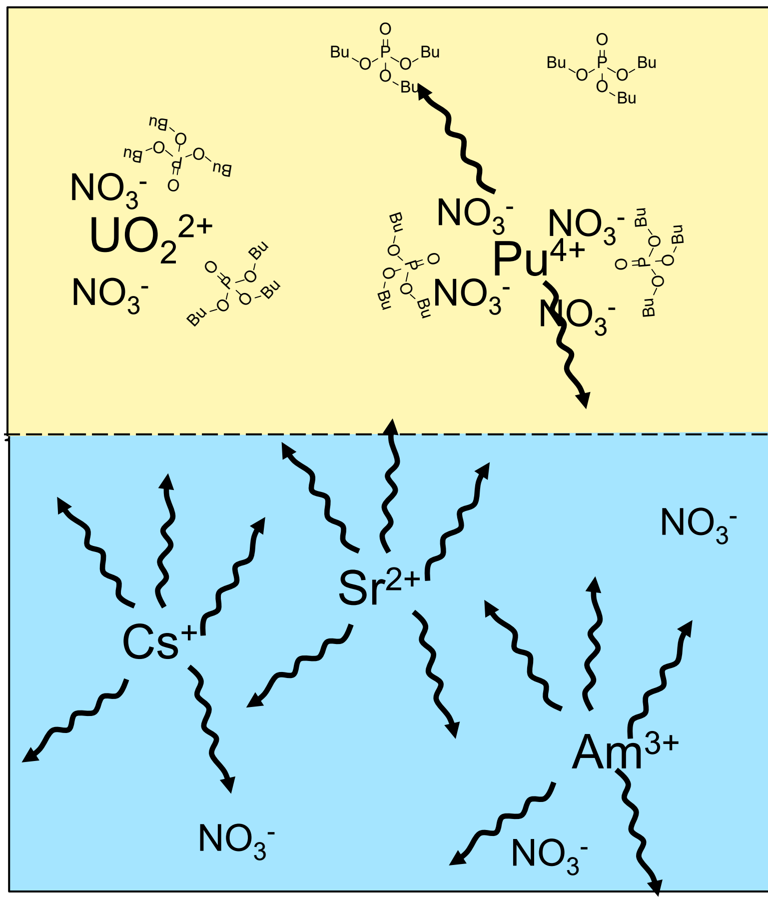


Spent Nuclear Fuel (SNF) dissolved in nitric acid

Problem: the fuel is highly radioactive!

Organic Phase

Aqueous Phase



Tributylphosphate
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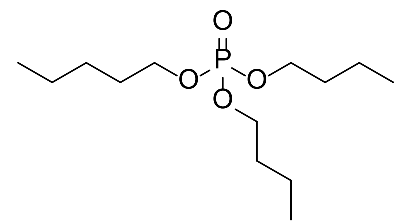
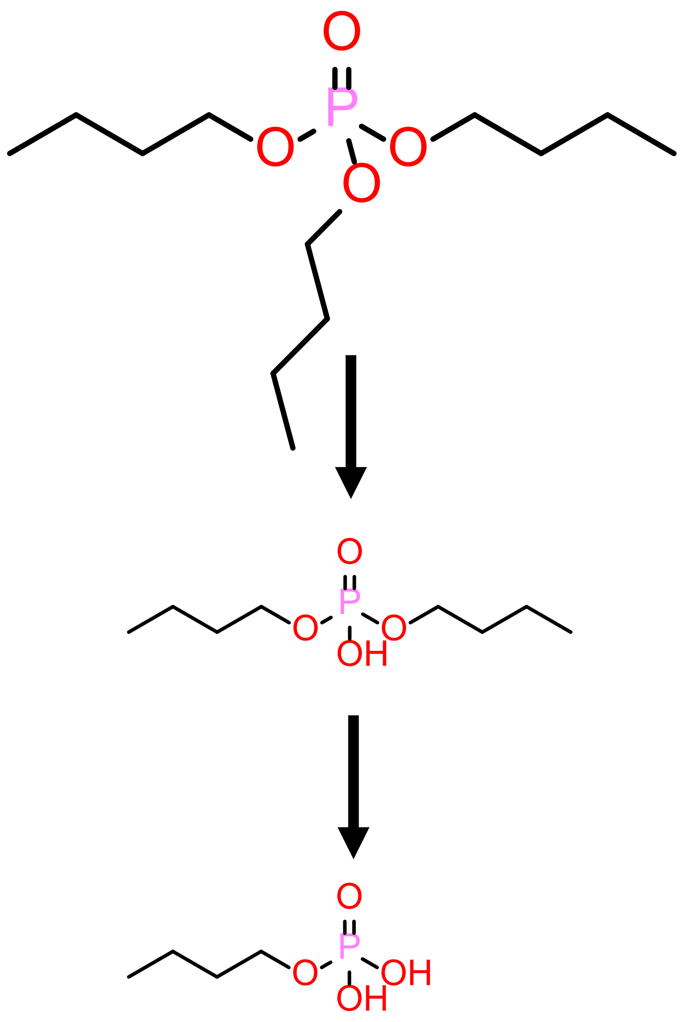


Spent Nuclear Fuel (SNF) dissolved in nitric acid

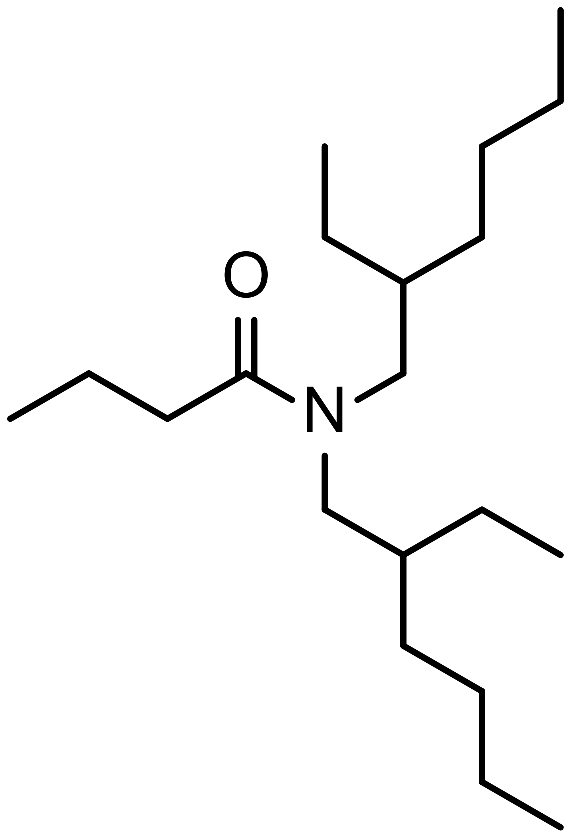
Radiation Degrades TBP, Reduces Process Efficiency

- **TBP breaks down into dibutylphosphate and monobutylphosphate**
- **TBP radiolysis results in loss of process efficiency**
  - Loss of TBP
  - Degradation products also reduce extraction efficiency
- **Research Goal: Understand fundamentals of organic-phase radiation chemistry**
  - Rates of degradation
  - Products of degradation
  - Leads to new, more radiation-resistant molecules and processes
  - Separation process models



Diethylhexyl butyramide (DEHBA) as TPB Replacements

- **Benefits over TBP[1]:**
  - Greater U selectivity
  - Consist only of Carbon Hydrogen Oxygen, and Nitrogen (CHON)
  - Uranium extraction processes based on monoamides exhibit higher radiolytic stability
    - Based on a comparison of extraction efficiencies as a function of absorbed radiation dose



1. Gasparini, G.M.; Grossi, G. Long chain disubstituted aliphatic amines as extracting agents in industrial applications of solvent extraction. Solvent Extr Ion Exch 4, 1233-1271, 1986.

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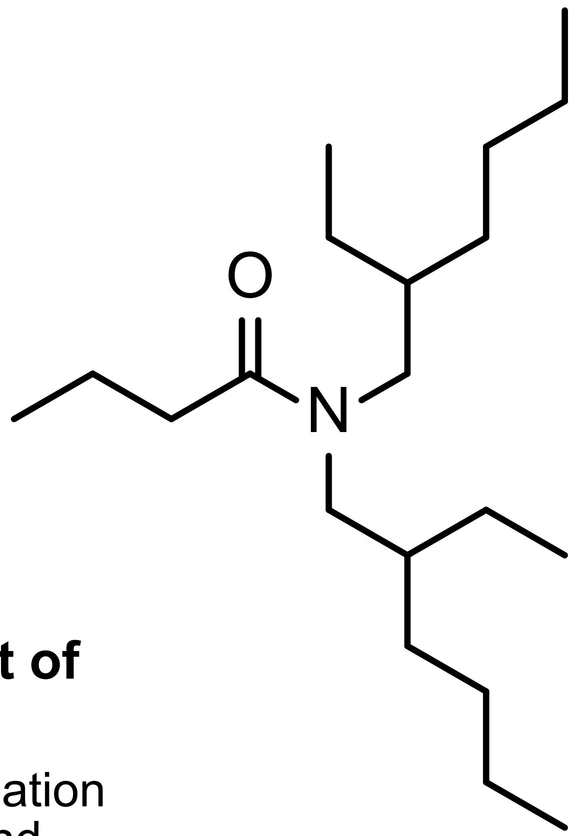
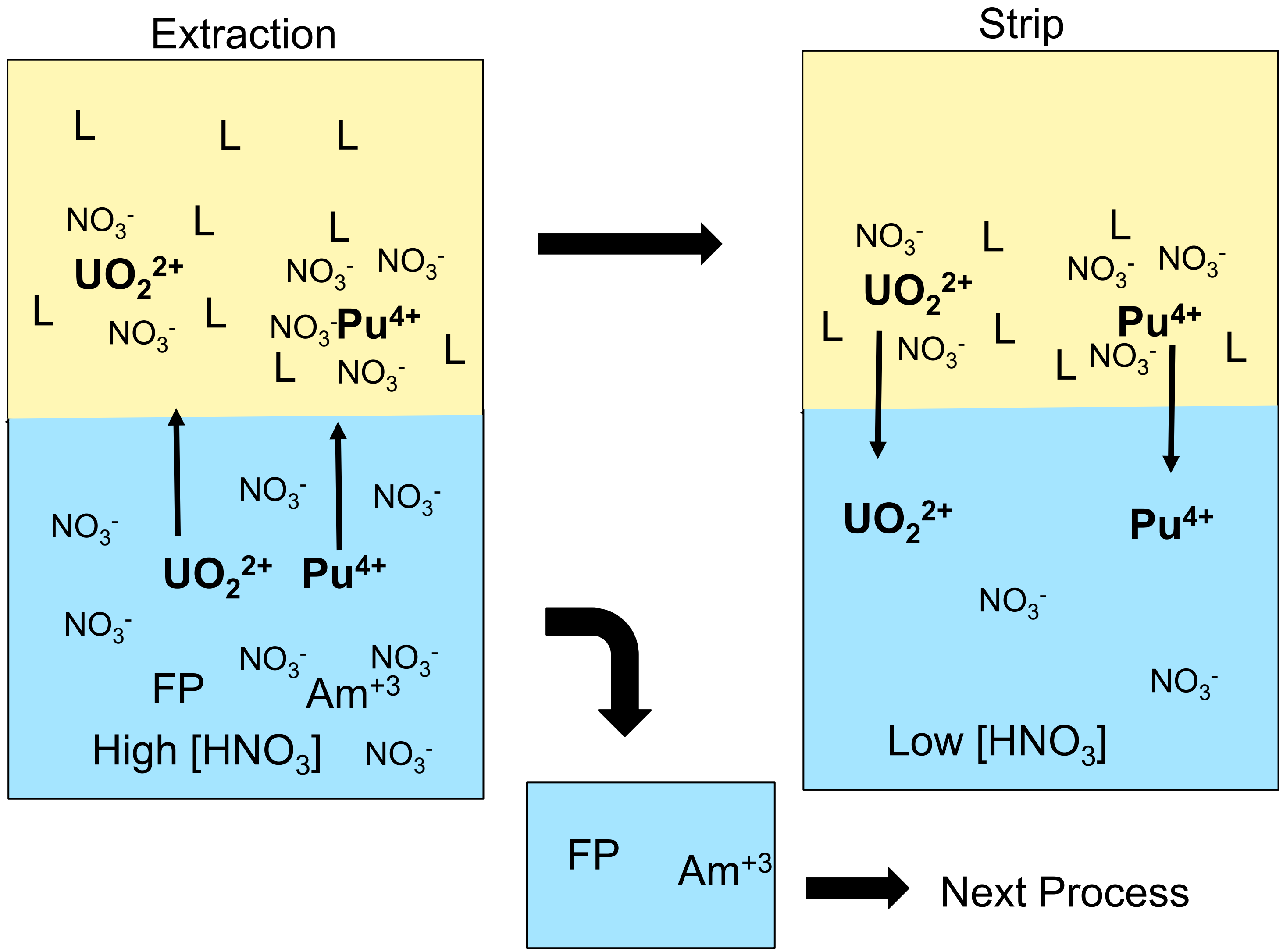
  - Uranium extraction processes based on monoamides exhibit higher radiolytic stability
    - Based on a comparison of extraction efficiencies as a function of absorbed radiation dose
- **We want to directly measure the effect of radiation on the ligand.**
  - Irradiate samples to various absorbed radiation doses and directly quantify amount of ligand remaining



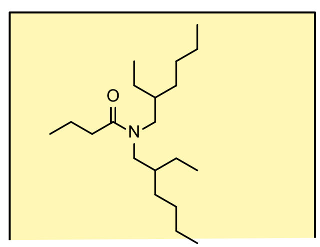
1. Gasparini, G.M.; Grossi, G. Long chain disubstituted aliphatic amines as extracting agents in industrial applications of solvent extraction. Solvent Extr Ion Exch 4, 1233-1271, 1986.

Simplified Solvent Extraction Process

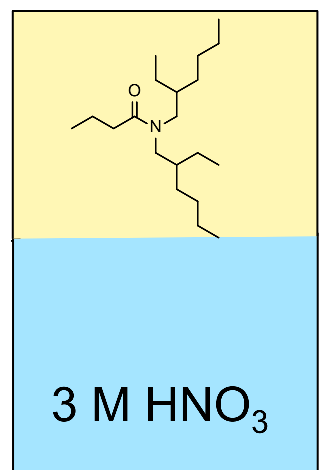


Gamma Irradiation Experiments

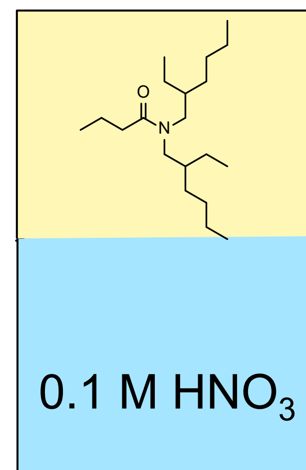
- **Irradiate samples**
  - ^{60}Co Gamma Cell source- 5.4 kGy h^{-1}
- **Typical Samples**
  - Ligand in dodecane
    - Organic only: control
  - Ligand in dodecane irradiated in contacted with 3 M HNO_3
    - Simulates extraction
  - Ligand in dodecane irradiated in contact with 0.1 M HNO_3
    - Simulates strip



Control



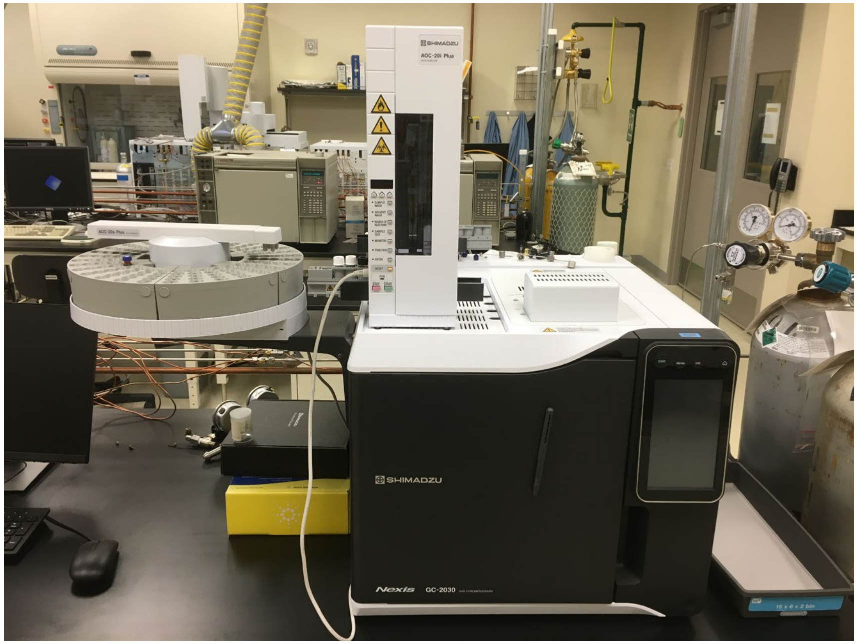
Extraction

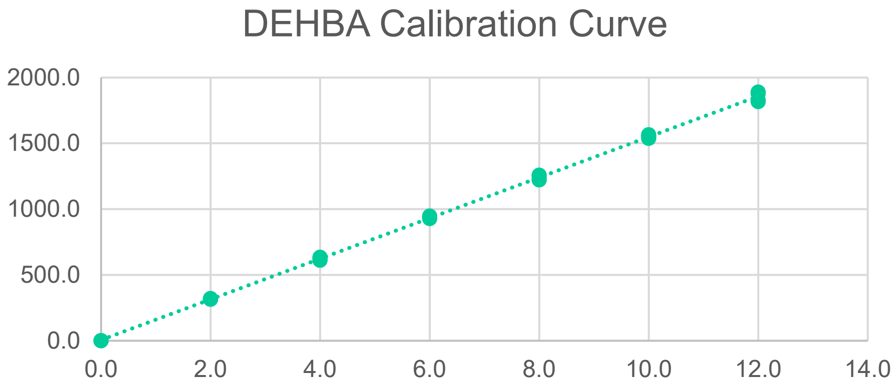


Strip

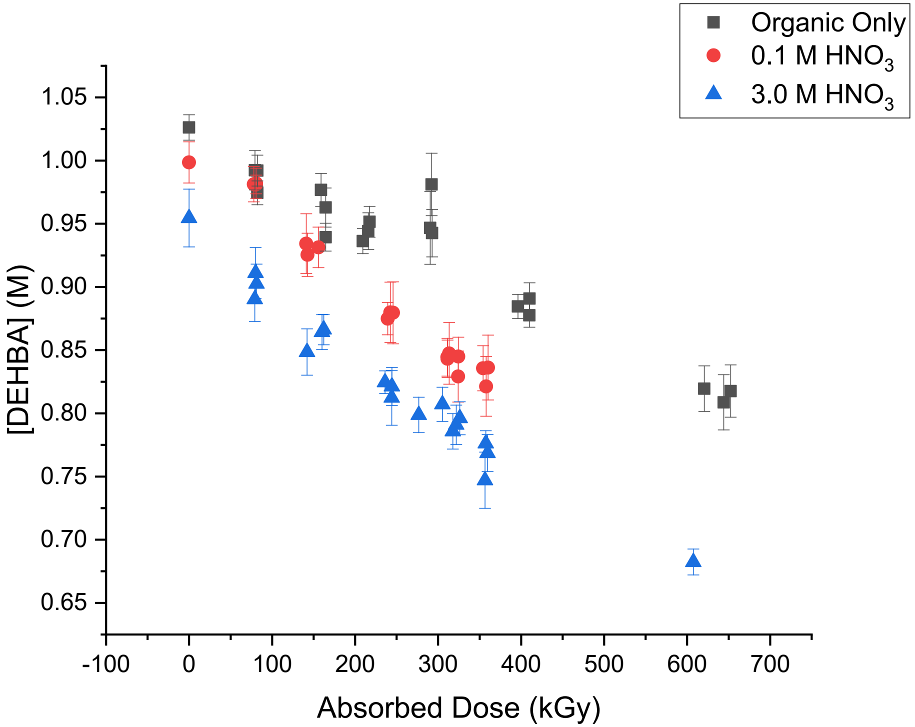
Sample Analysis: Quantification

- **Gas chromatography with flame ionization detection (GC-FID)**
  - Very stable detector: High precision
    - Usually < 2% relative standard deviation





Radiolytic Degradation of DEHBA



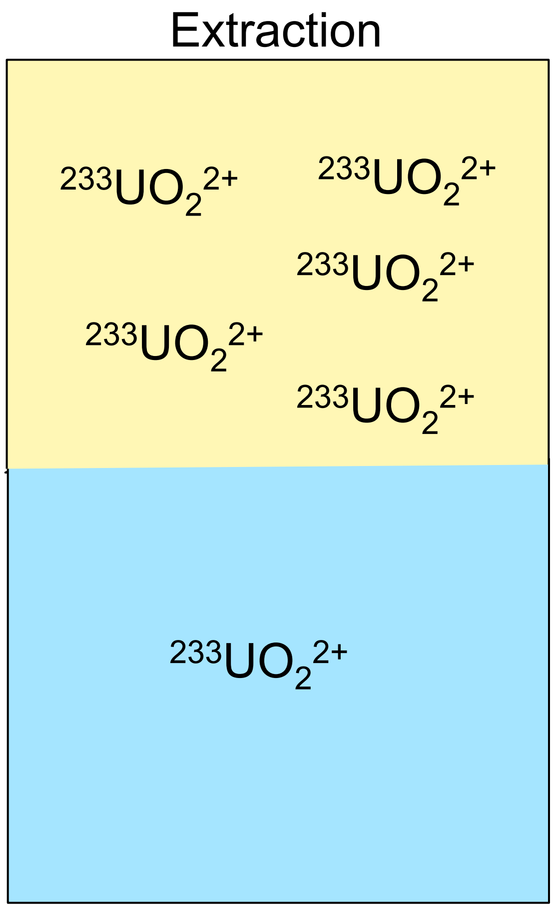
DEHBA Sample	G-value (μmol/J)
Organic Only	0.31 ±0.02
0.1 M HNO_3 contact	0.53 ±0.02
3.0 M HNO_3 contact	0.49 ±0.02
TBP in contact with acid	0.37 ±0.02

- **Pseudo-zeroth order degradation for all conditions**
  - Describe degradation with G-value: μmol of ligand destroyed per joule of absorbed radiation

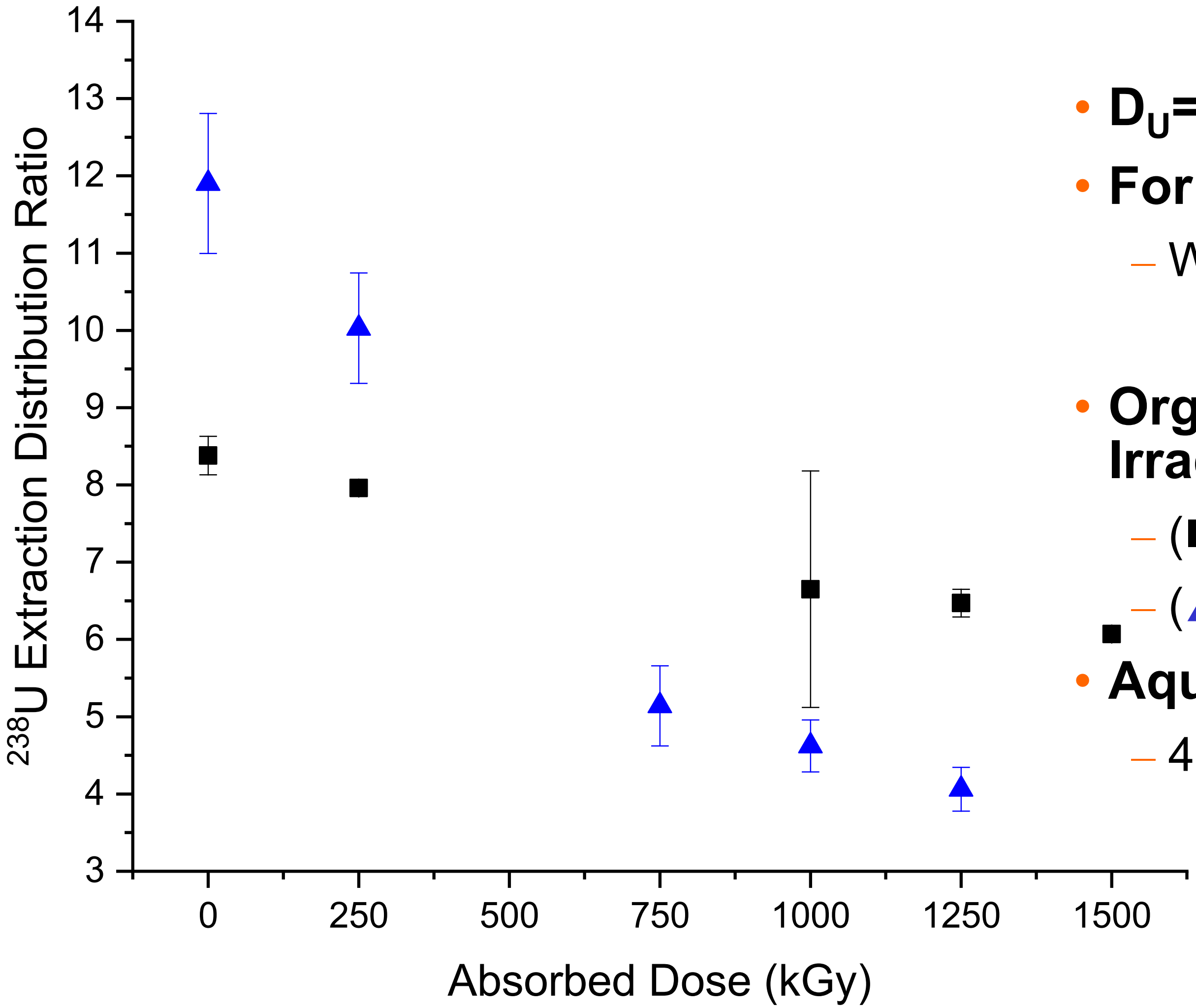
- **DEHBA is actually *less* radiolytically stable than TBP**
  - The difference in process performance is due to the degradation products

Measuring Separation Performance

- **Contact irradiated organic phase with tracer-loaded aqueous phase**
- **Use ^{233}U and ^{239}Pu as tracers**
- **Measure amount of tracer in both phases**
  - $D_U = [U]_{org}/[U]_{aqu}$

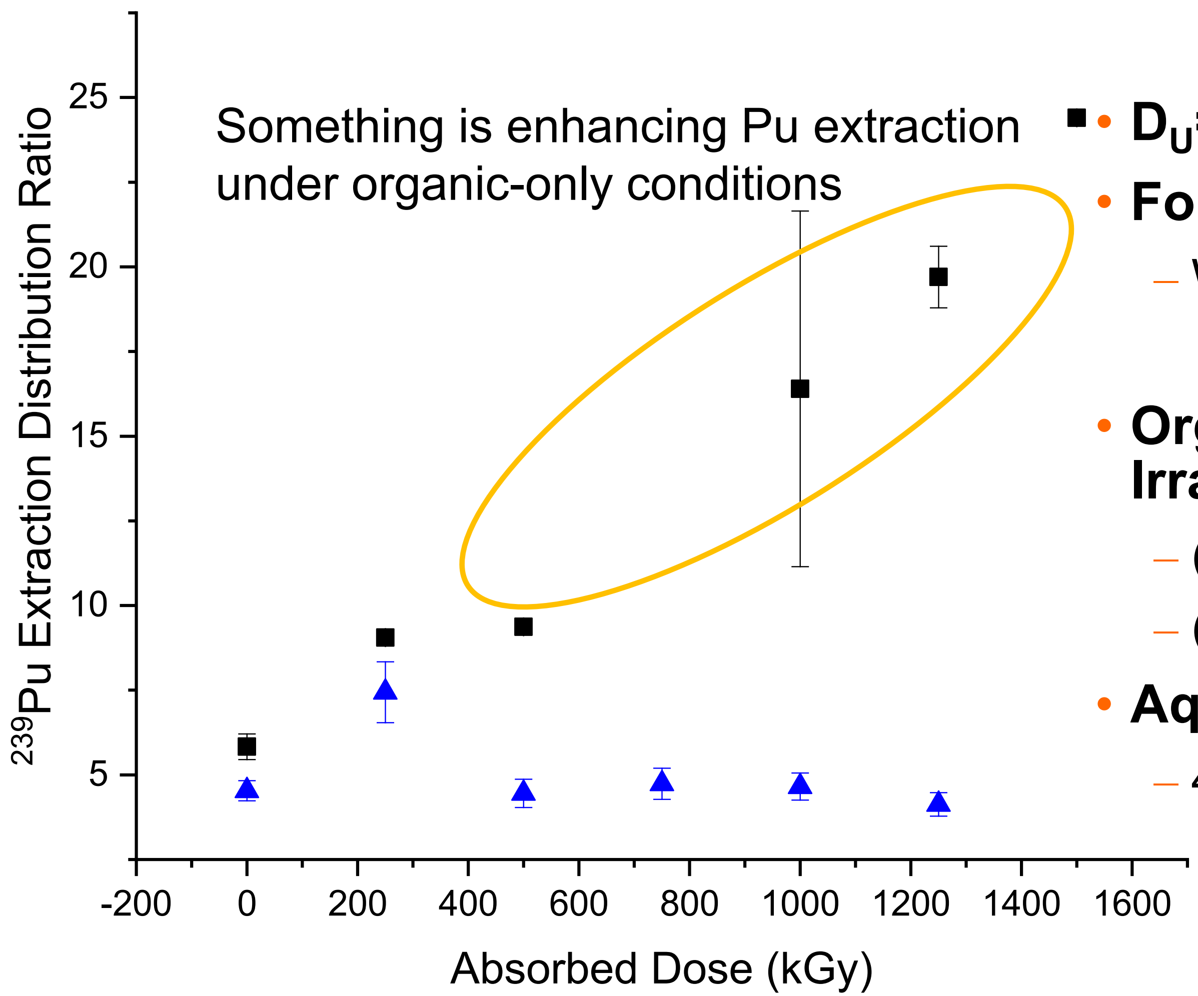


Uranium Extraction Behavior



- $D_U = [U]_{org}/[U]_{aqu}$
- **For extraction:**
  - Want $D_u > 1$
- **Organic Phase Irradiation Conditions**
  - (■) Organic Only
  - (▲) 3.0 M HNO_3 contact
- **Aqueous Phase:**
  - 4.0 M HNO_3

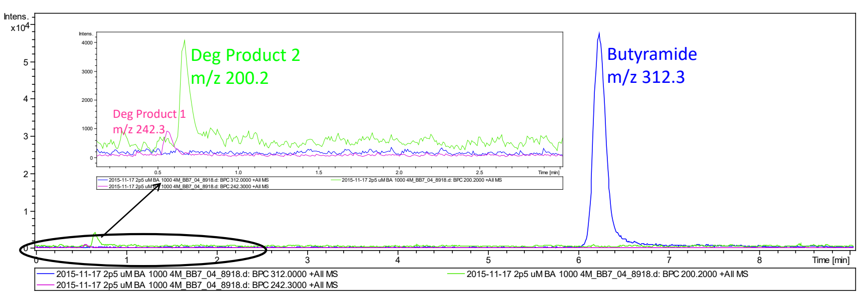
Plutonium Extraction Behavior



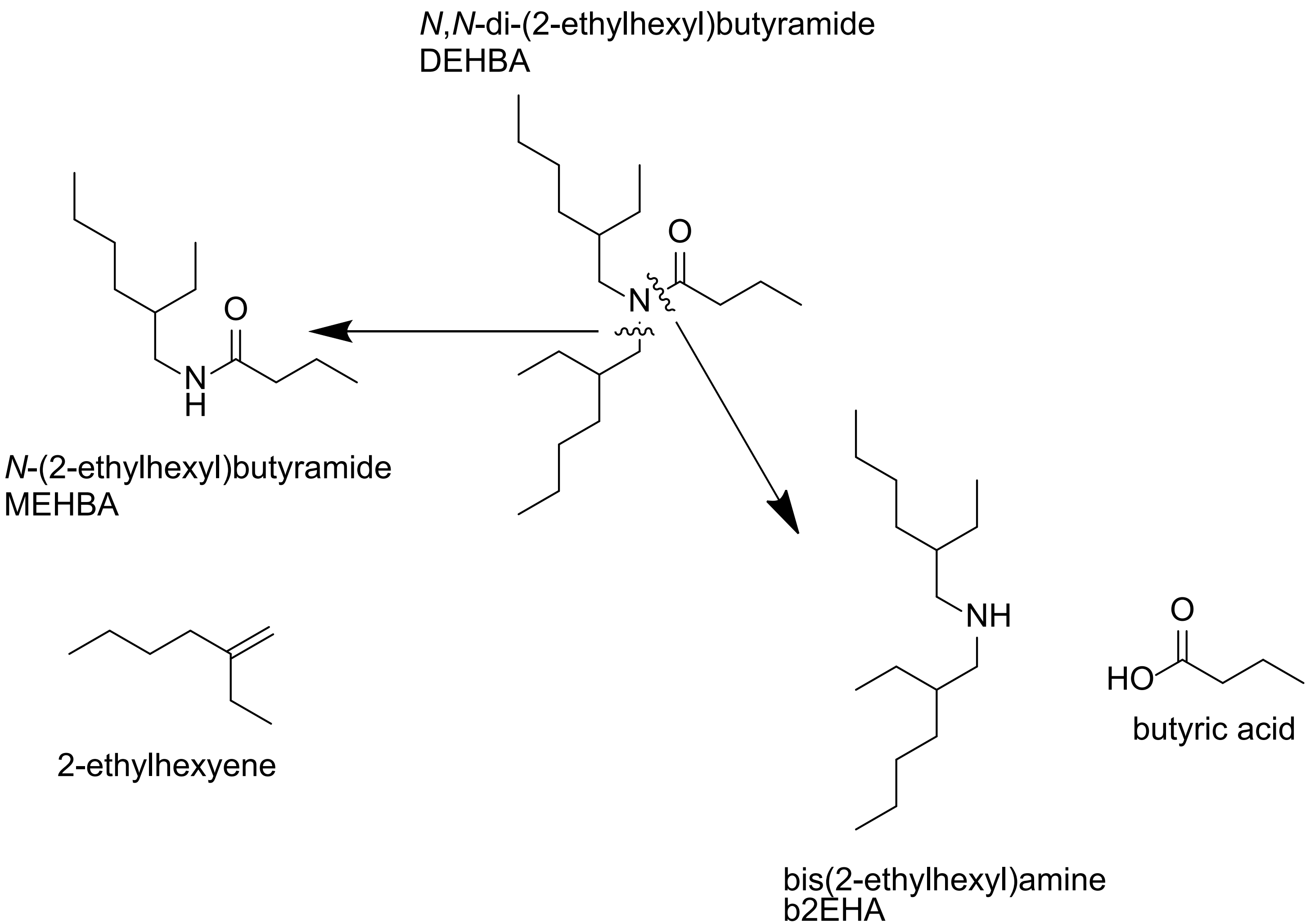
- D_U= $[Pu]_{org}/[Pu]_{aqu}$
- **For extraction:**
  – Want D_u>1
- **Organic Phase Irradiation Conditions**
  – (■) Organic Only
  – (▲) 3.0 M HNO_3 contact
- **Aqueous Phase:**
  – 4.0 M HNO_3

Sample Analysis: Identification

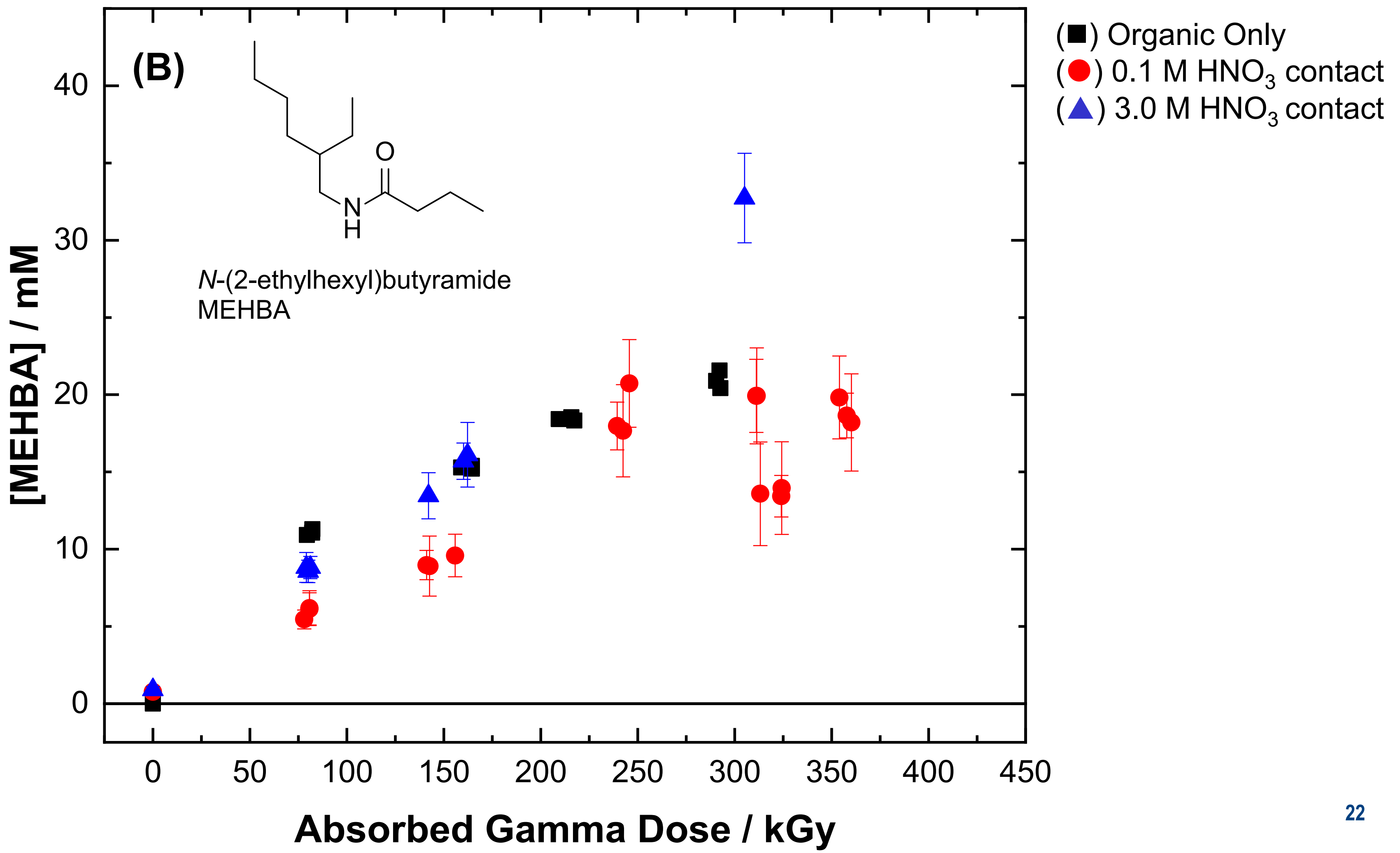
- **Ultra-high pressure liquid chromatography with electrospray ionization mass spectrometry (UHPLC-ESI-MS)**
  - Ligand systems are liquid making UHPLC a natural method
  - Common functional group ionizes efficiently
  - UHPLC-ESI-MS –identify nonvolatile compounds not detectable using GC-MS
  - Degradation products identified by exact mass and MS^2



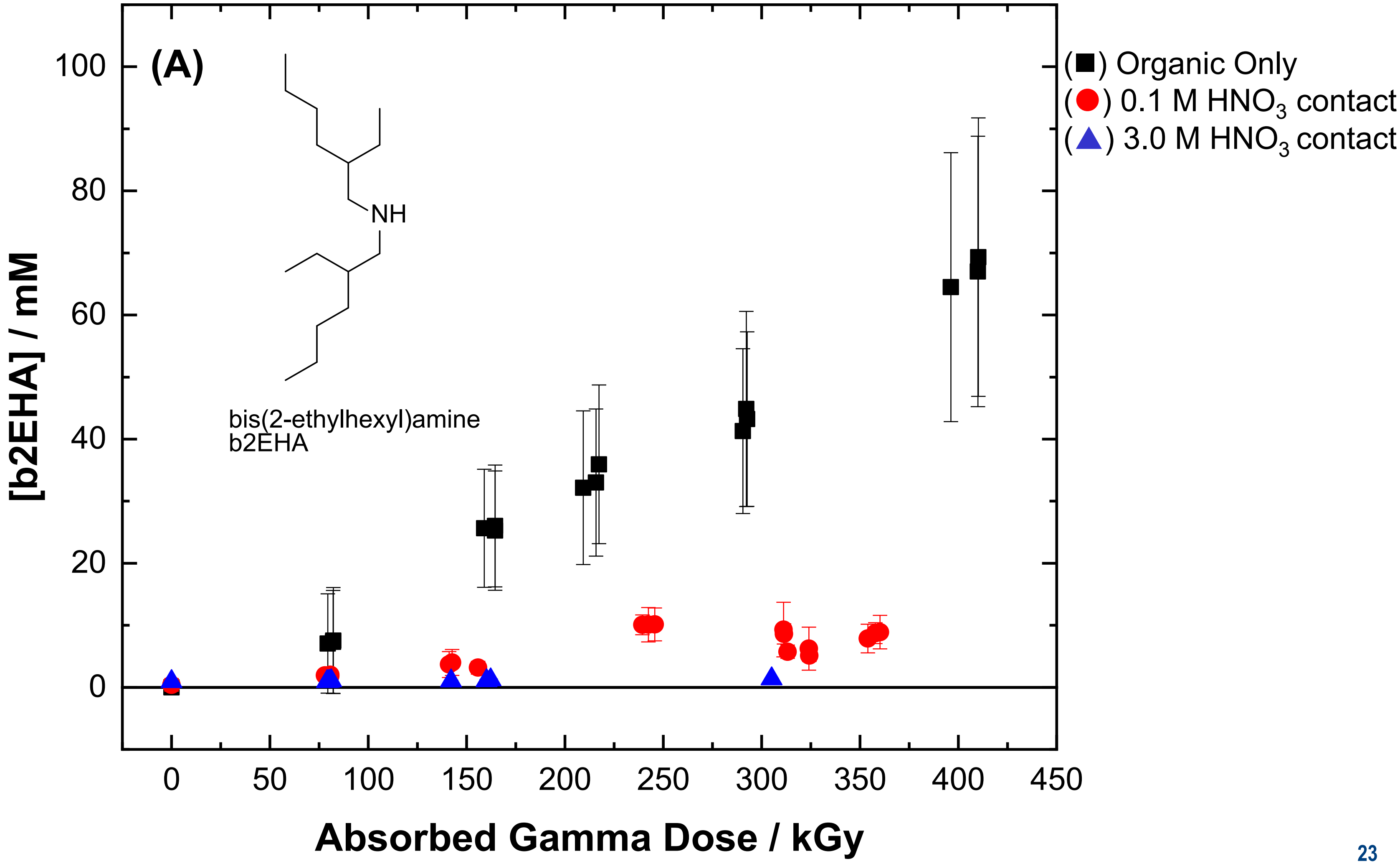
DEHBA Radiation Chemistry



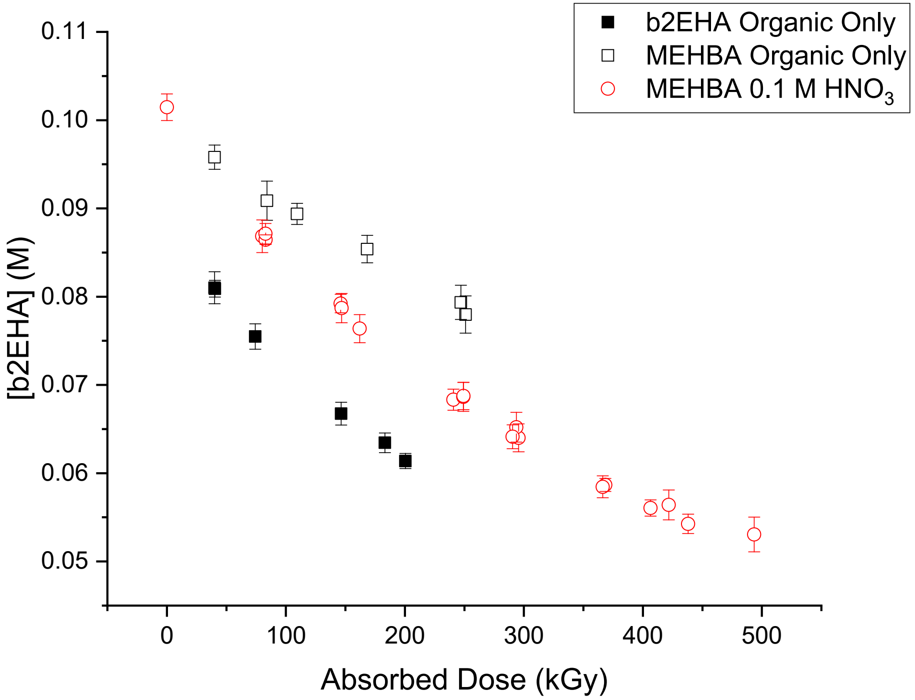
Quantification of MEHBA



Quantification of b2EHA



Radiolytic Degradation of DEHBA Degradation Products

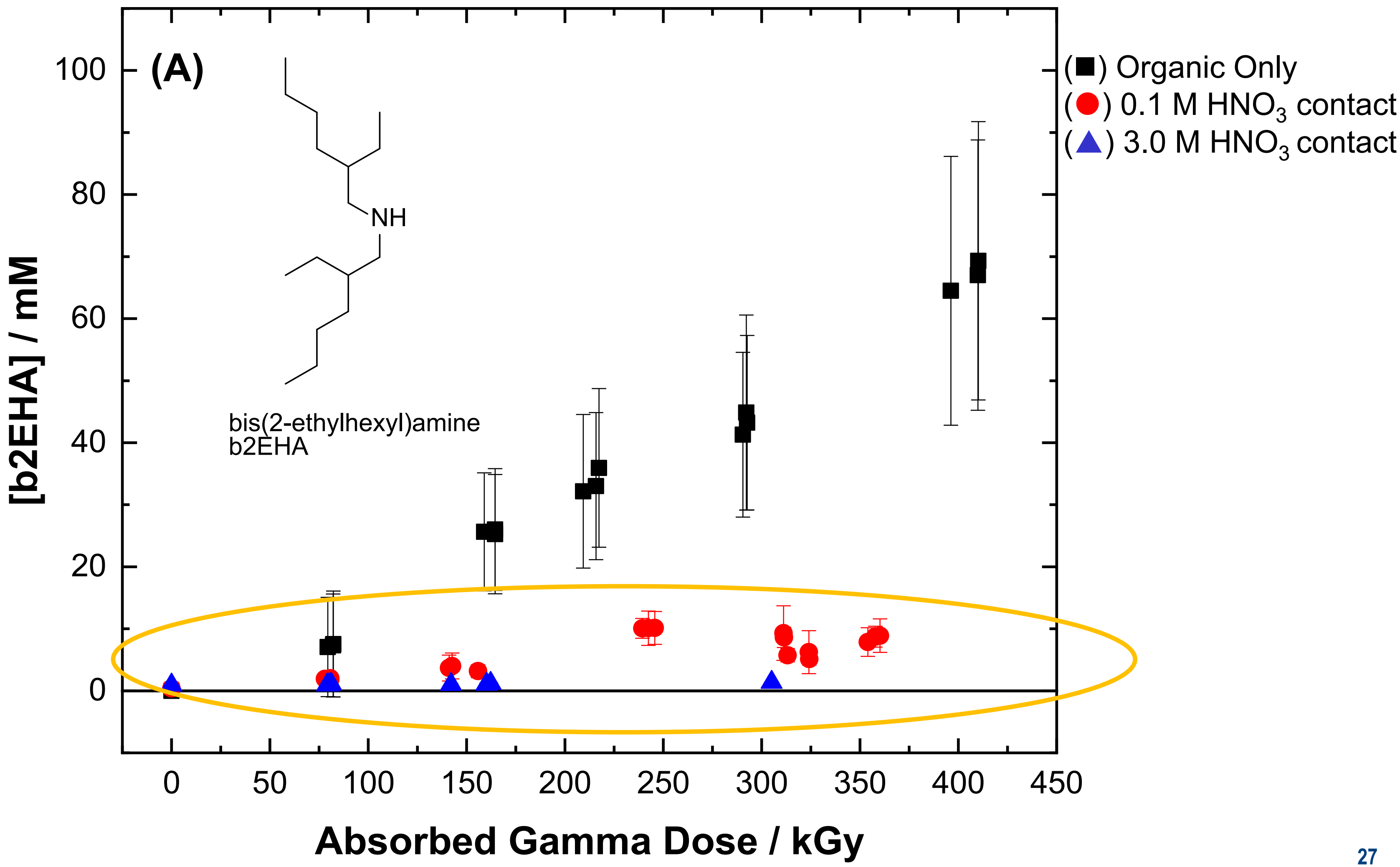


b2EHA Sample	G-value (μmol/J)
Organic Only	0.12 ±0.01
0.1 M HNO_3 contact	Hydrolysis
3.0 M HNO_3 contact	Hydrolysis
MEHBA Sample	**G-value (μmol/J)**
Organic Only	0.08 ±0.01
0.1 M HNO_3 contact	0.12 ±0.01
3.0 M HNO_3 contact	Hydrolysis

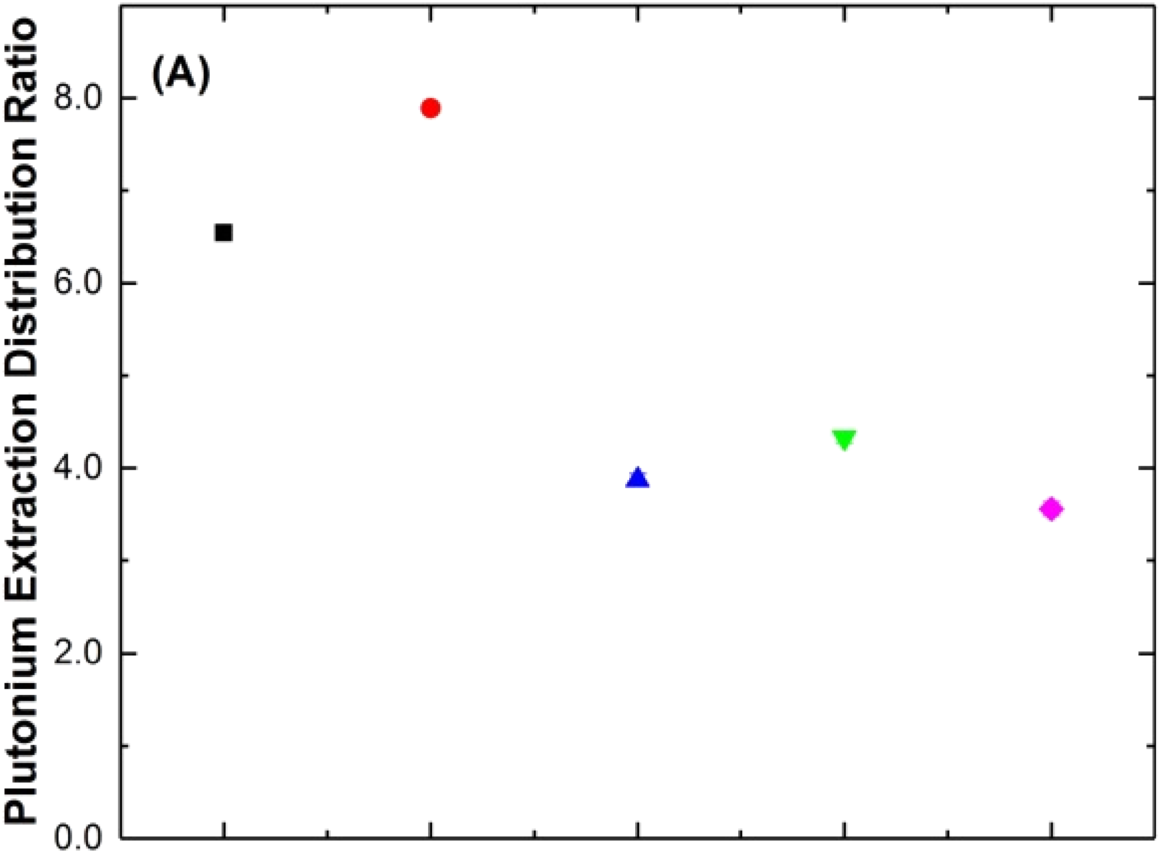
- **b2EHA much more stable to *radiolysis* than DEHAB**
- **Degrades rapidly when contacted with acid**

- **MEHBA much more stable to *radiolysis* than DEHAB**
- **Degrades rapidly when contacted with high concentrations acid**

Probably due to acid hydrolysis



b2EHA Enhances Pu Extraction

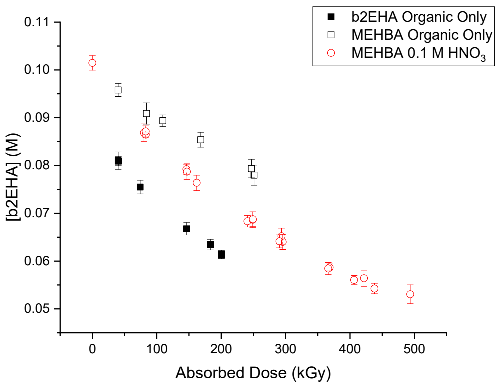


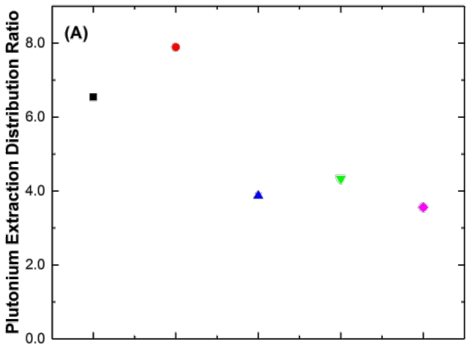
- (■) 1 M DEHBA
- (●) 0.8 M DEHBA + 80 mM b2EHA
- (▲) 0.8 M DEHBA + 80 mM butanoic acid
- (▼) 0.8 M DEHBA + 20 mM MEHBA
- (◆) 0.8 M DEHBA + 20 mM 2-ethylhexene

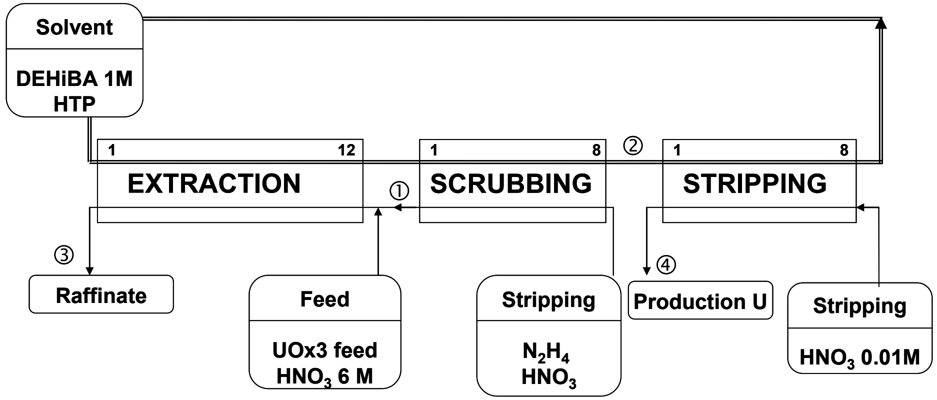
b2EHA is likely responsible for enhanced Pu extraction in organic-only conditions

What can we (eventually) do with this information?

- **Process modeling**
  - Extraction behavior
  - Radiolysis Rates
- **Solvent clean-up**







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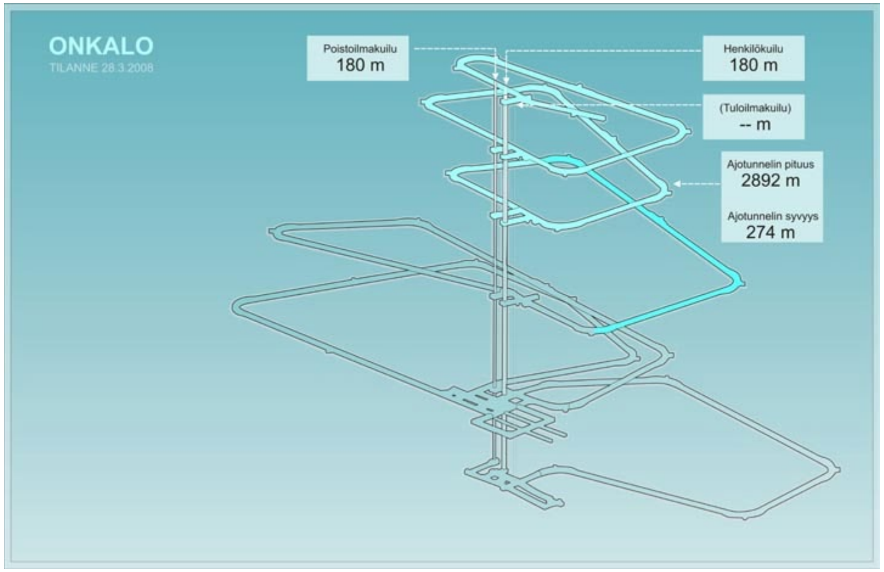
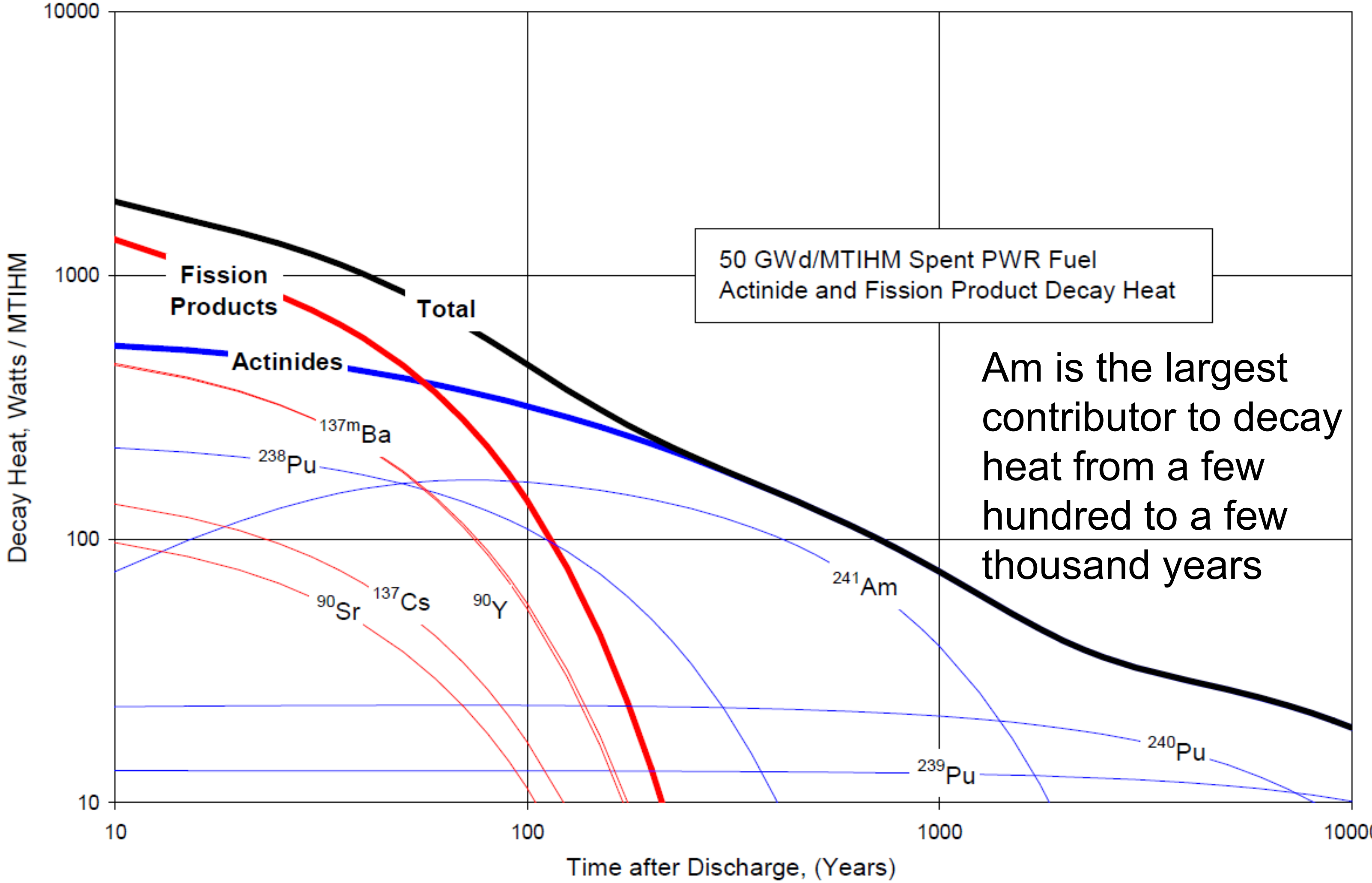


Heat Contributions of Used Fuel Components

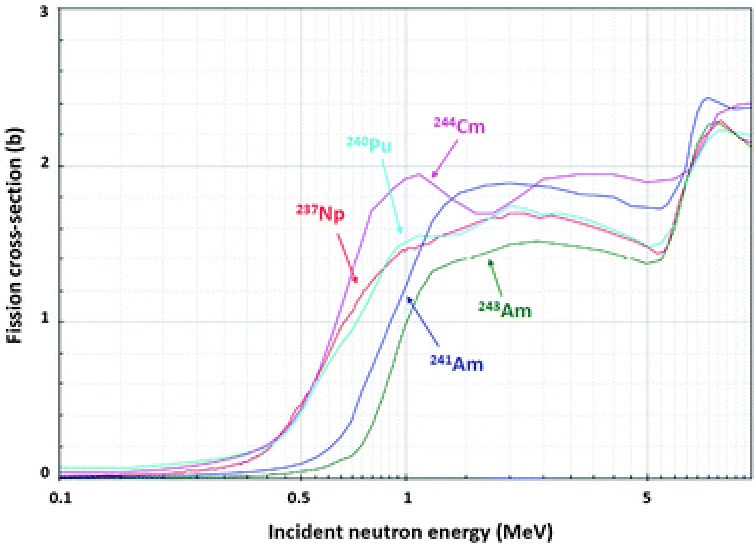


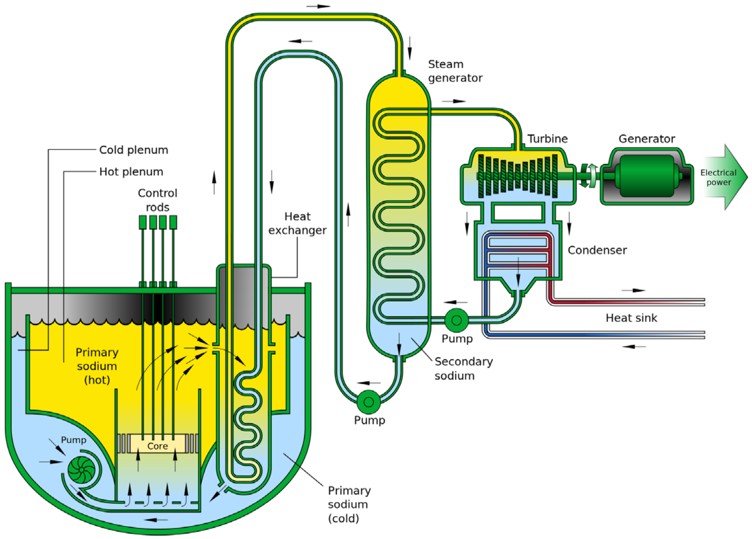
Am is the largest contributor to decay heat from a few hundred to a few thousand years

Wigeland, R. A.; Bauer, T. H.; Fanning, T. H.; Morris, E. E. Spent Nuclear Fuel Separations and Transmutation Criteria for Benefit to a Geologic Repository; Tucson, AZ, 2004.

Fast Neutron Reactors for Actinide Burning

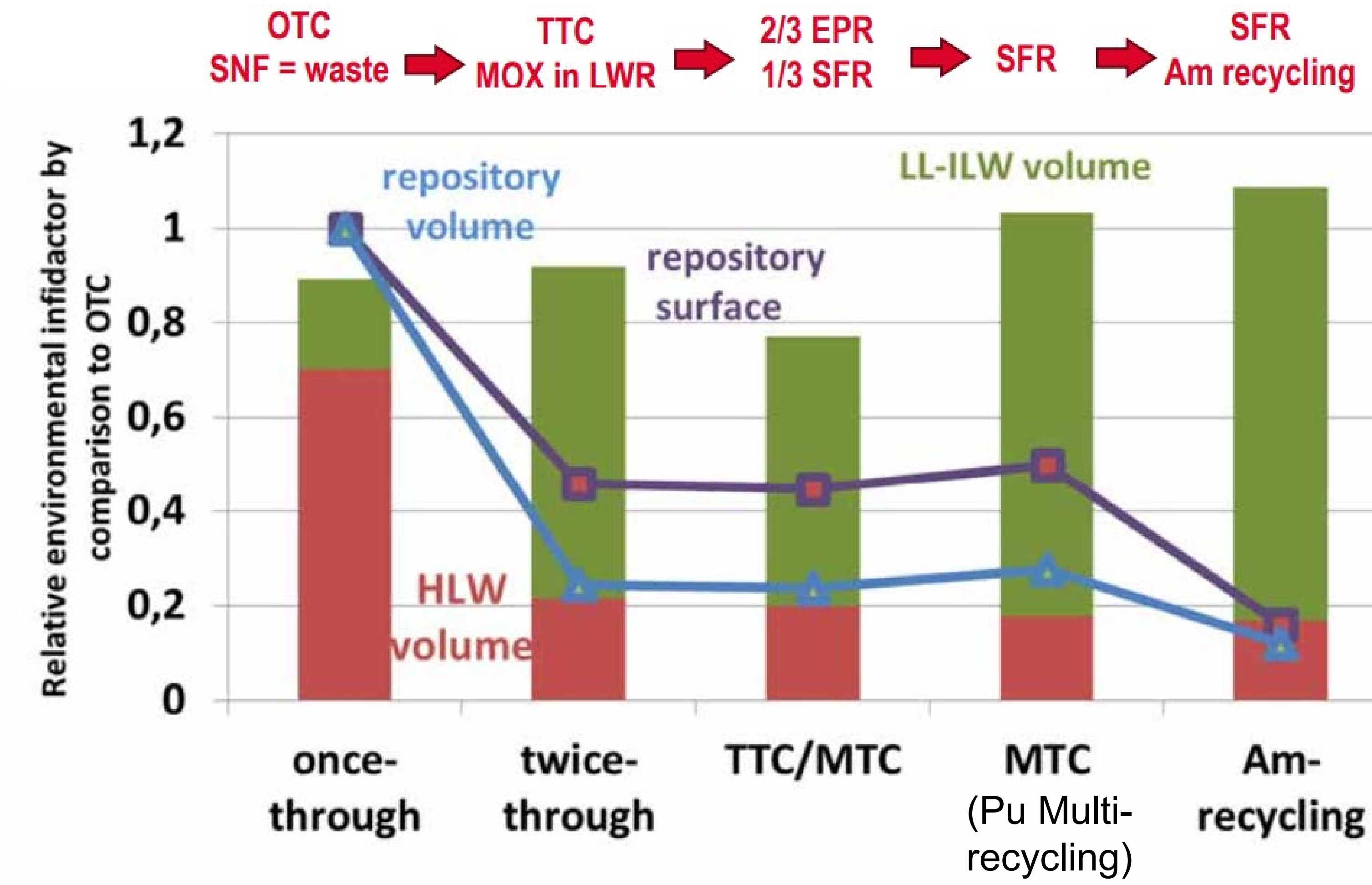
- **Use high-energy neutrons to fission the minor actinides**
  - Convert them to short-lived fission products
  - Reduce the size requirements for a deep geologic storage repository





(1) Colonna, N.; et al. Advanced Nuclear Energy Systems and the Need of Accurate Nuclear Data: The N_TOF Project at CERN. Energy Environ. Sci. 2010, 3 (12), 1910–1917, DOI: 10.1039/C0EE00108B.

Effect on Repository Size of Different Fuel Cycles



Poinssot, C. Why Recycling the Actinides? A Sustainable Approach of Nuclear Fuel Cycles, 2015.

High-Level Partitioning and Transmutation Schemes

1. **Removal of uranium and/or plutonium**
2. **Separation of fission products (Cs and Sr)**
3. **Co-extraction of trivalent lanthanides and minor actinides**
4. **Separation of trivalent actinides from trivalent lanthanides**

U

Pu

^{90}Sr

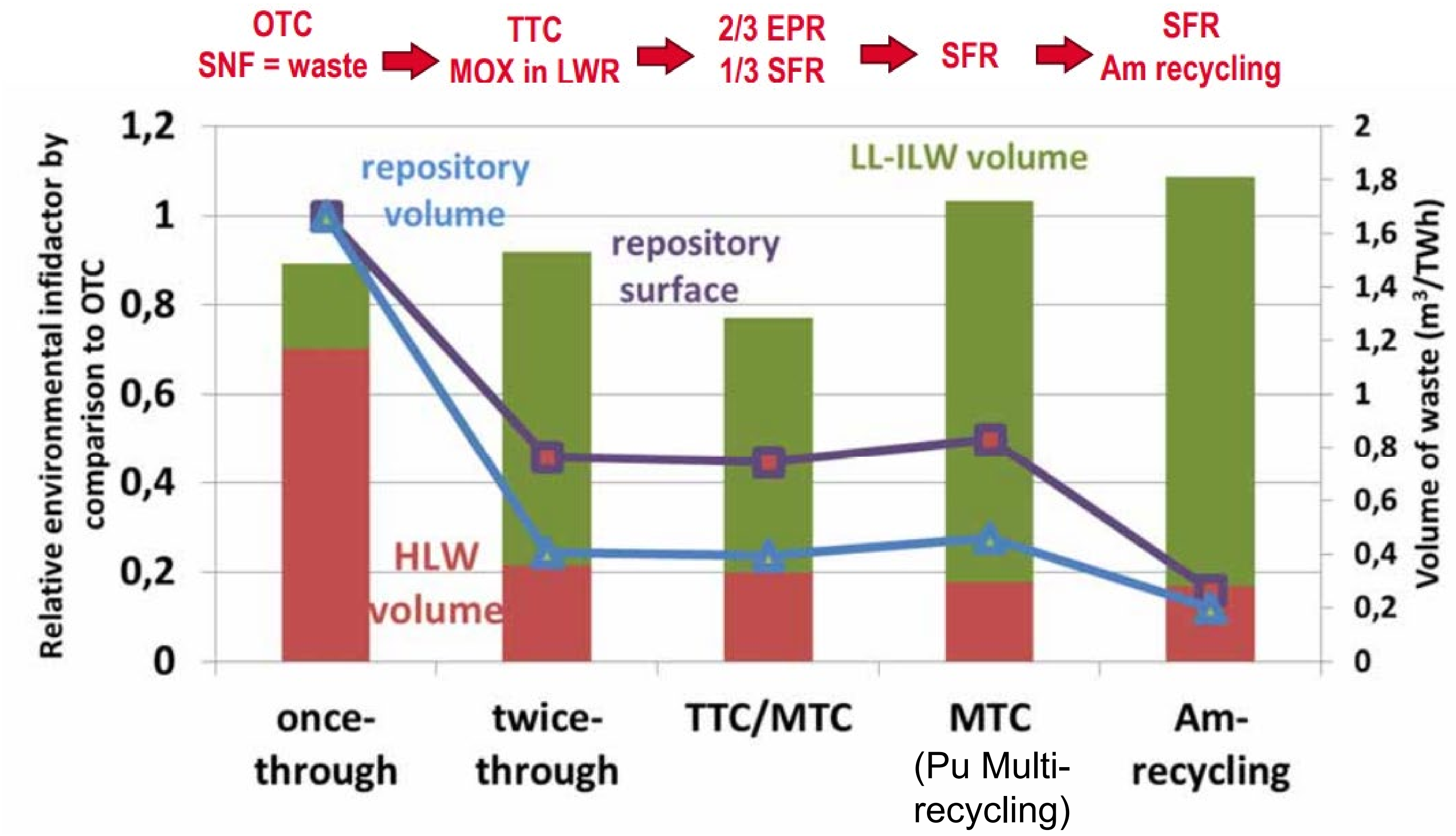
^{137}Cs

Cm

Ln

Am

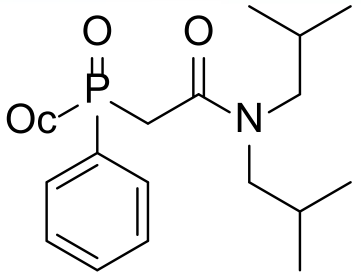
Am recycling reduced repository volume at the expense of more liquid waste

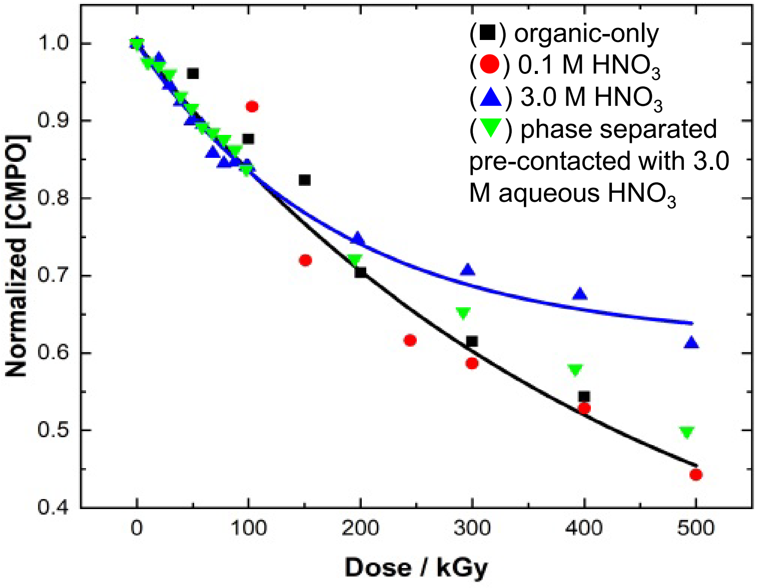


Poinssot, C. Why Recycling the Actinides? A Sustainable Approach of Nuclear Fuel Cycles, 2015.

CMPO

- **Originally designed to co-extract Pu, U, Am, and Cm**
- **Can also be used after PUREX-like process to co-extract An^{3+} and Ln^{3+}**
- **Radiation resistance increases in the presence of nitric acid**

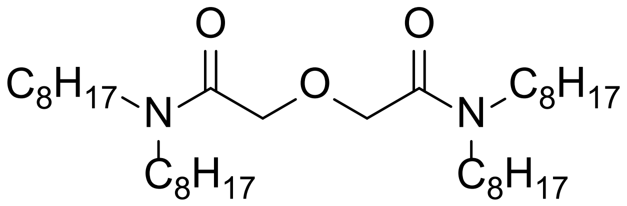




CMPO : octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide

Tetra-Octyl Diglycolamides: Another An/Ln Ligand

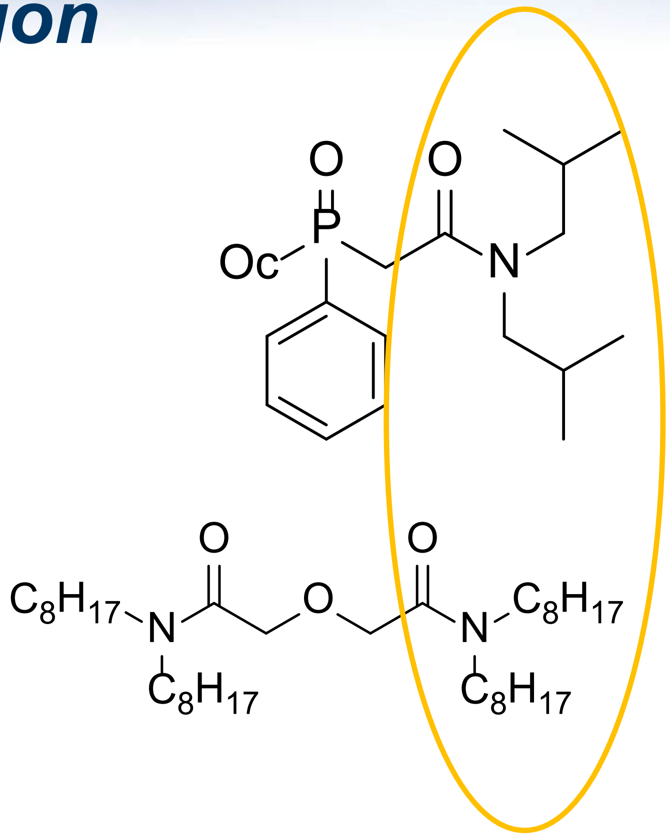
- High affinity for An(III)/Ln(III)
- High distribution ratios of An(III)/Ln(III) at process relevant nitric acid concentrations
- Easy/inexpensive synthesis with various possible modifications
- CHON
- Good hydrolytic/radiolytic stability



- Nitric acid has minimal influence on radiolytic stability.

Functional Group Responsible for Nitric-Enhanced Radiation Protection

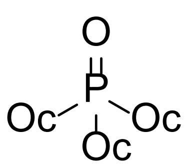
- **CMPO and the diglycolamides share amide functional groups**
- **Phenyl-phosphine oxide group is unique to CMPO**



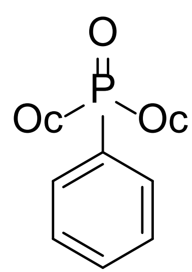
Functional Group Responsible for Nitric-Enhanced Radiation Protection

- **Hypothesis: Phenyl-phosphine oxide is responsible for nitric acid-enhanced radiation protection.**

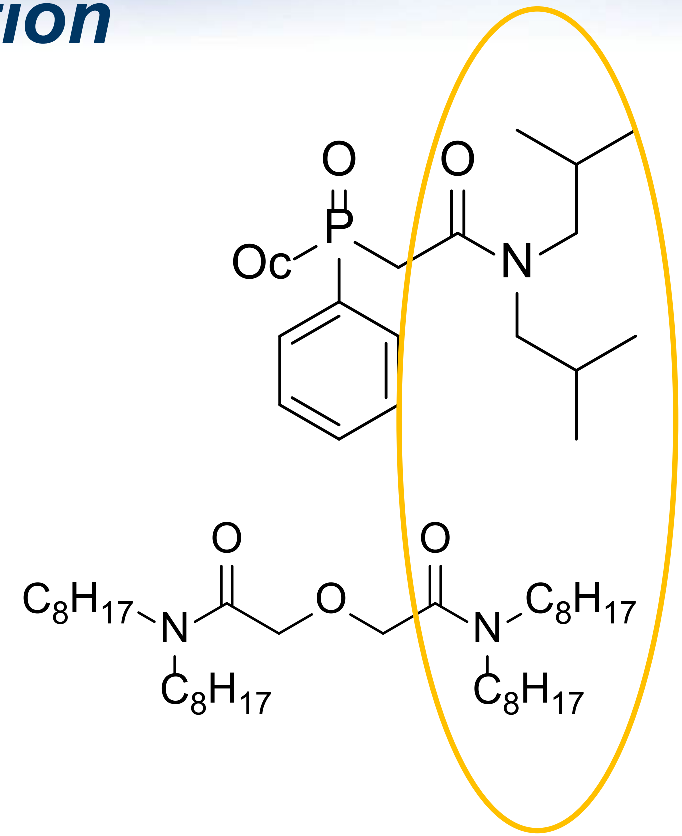
- **Test with model compounds:**



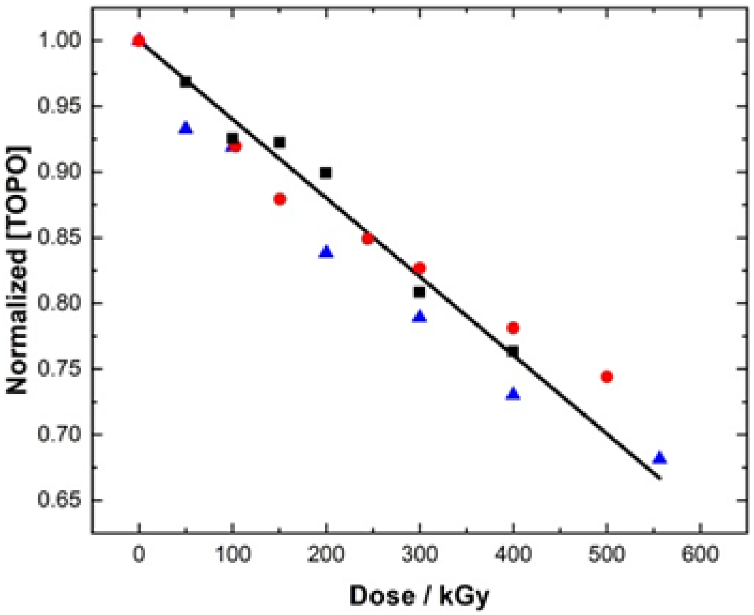
Trioctyl phosphine oxide (TOPO)

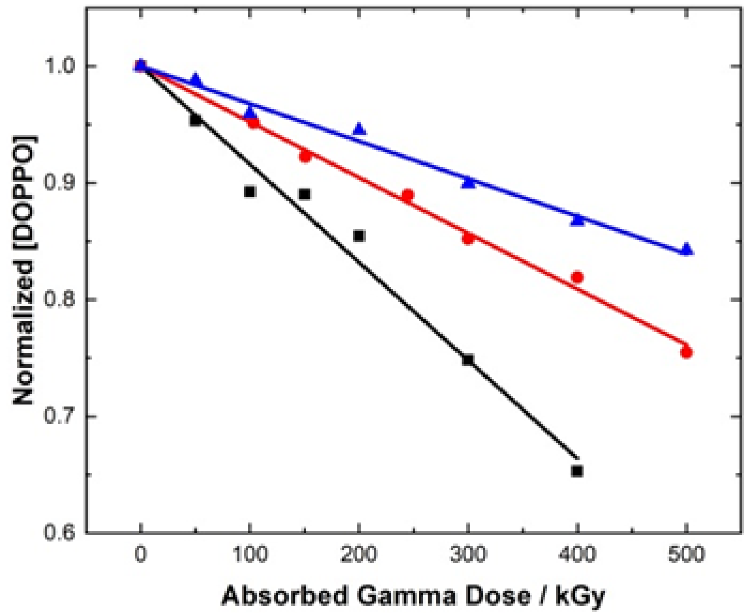


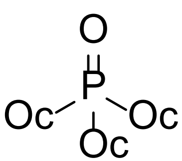
Dioctylphenyl phosphine oxide (DOPPO)



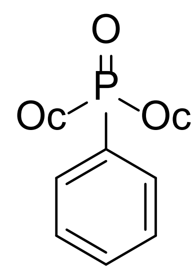
Model Compound Radiolysis







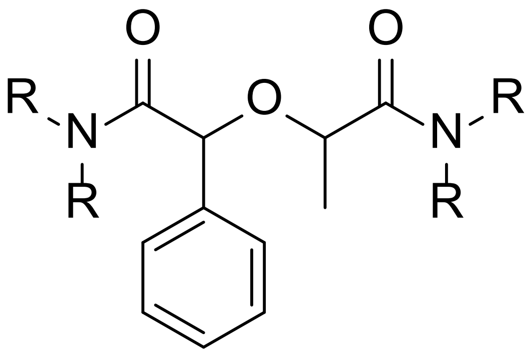
(■) Organic Only
(●) 0.1 M HNO_3 contact
(▲) 3.0 M HNO_3 contact



Phenyl-phosphine oxide group very likely responsible for nitric acid-enhanced radiation protection!

Can we improve the radiation resistance of DGAs?

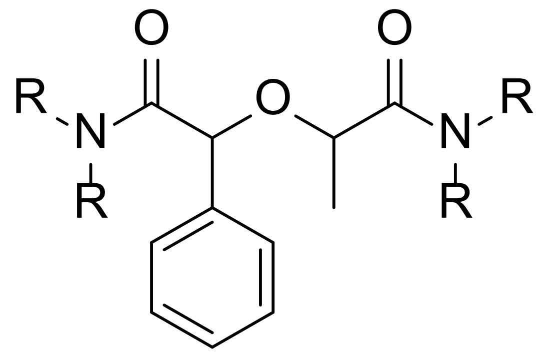
- **Phenylmethyl tetraoctyldiglycolamide**
  - PhMeTODGA
- **Synthesized by colaborators at the University of Twente, The Netherlands**



R = C_8H_{17}

Can we improve the radiation resistance of DGAs?

- **Does the phenyl group increase stability in the presence of nitric acid?**

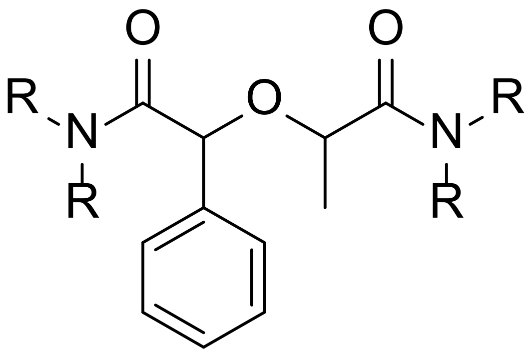


R = C_8H_{17}

Can we improve the radiation resistance of DGAs?

- **Yes!**

PhMeTODGA Sample	Dose Constant (kGy^{-1})
Organic Only	$(5.0 \pm 0.5) \times 10^{-3}$
0.1 M HNO_3 contact	$(5.4 \pm 0.4) \times 10^{-3}$
3.0 M HNO_3 contact	$(4.4 \pm 0.5) \times 10^{-3}$

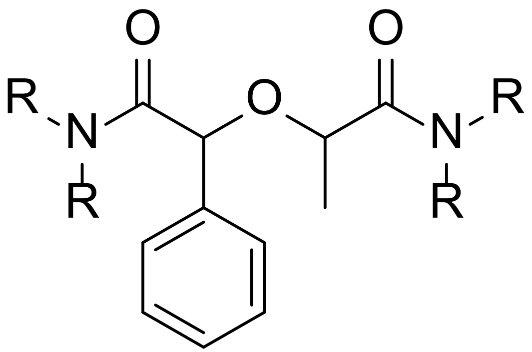


R = C_8H_{17}

Can we improve the radiation resistance of DGAs?

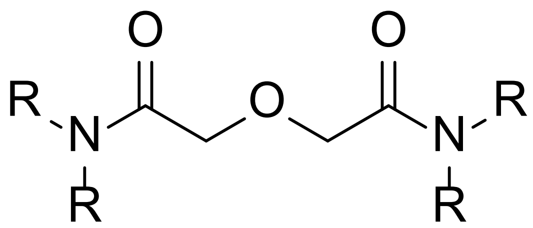
- **Yes! but…..**

PhMeTODGA Sample	**Dose Constant (kGy^{-1})**
Organic Only	$(5.0 \pm 0.5) \times 10^{-3}$
0.1 M HNO_3 contact	$(5.4 \pm 0.4) \times 10^{-3}$
3.0 M HNO_3 contact	$(4.4 \pm 0.5) \times 10^{-3}$



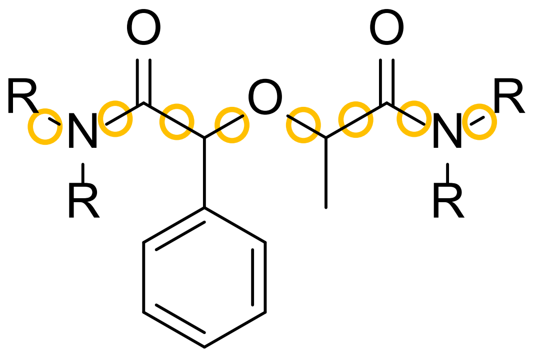
R = C_8H_{17}

TODGA Sample	**Dose Constant (kGy^{-1})**
Organic Only	$(4.1 \pm 0.3) \times 10^{-3}$
0.1 M HNO_3 contact	$(4.5 \pm 0.2) \times 10^{-3}$
3.0 M HNO_3 contact	$(3.8 \pm 0.3) \times 10^{-3}$



PhMeTODGA Degradation Product Analysis

- **Quantification of degradation products gave us information about degradation pathways for DEHBA**
- **What about PhMeTODGA?**



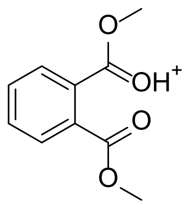
R = C_8H_{17}

Characterization of Irradiated Organics

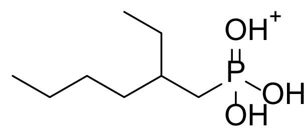
- **High Resolution High Mass Accuracy Mass Spectrometry**
  - Bruker micrOTOF-Q II:
    - quadrupole time-of-flight
    - Mass range: 3000 *m/z*
    - Resolution: ~15,000 (full-width half-max)
    - Mass Accuracy: ~±0.002 Da
    - ESI, APCI, APPI ion sources
    - Waters Acquity H-Class Plus UPLC front-end

- **Unambiguous molecular formula**
- **Some structural information from tandem MS**
- **Decent quantification accuracy (typically better than 10%), but narrow dynamic range (~2 orders of magnitude)**

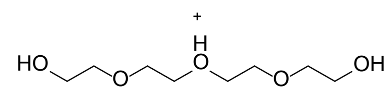
High Mass Accuracy Yields Molecular Formula



Dimethyl phthalate
$C_{10}H_{11}O_4^+$
m/z: 195.0652
Δm: -0.0493
-253 ppm

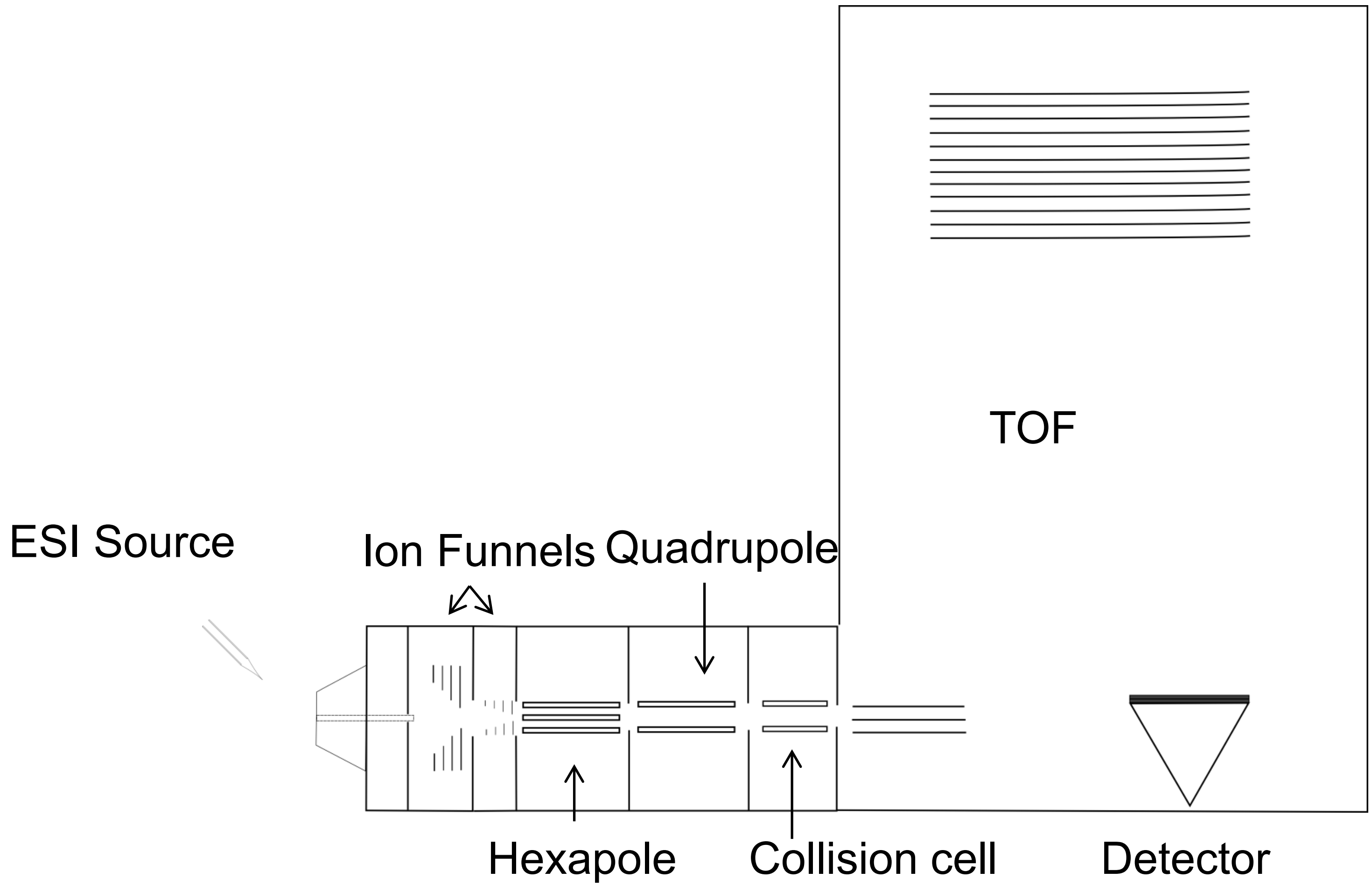


2-ethylhexyl phosphonic acid
$C_8H_{20}O_3P^+$
m/z: 195.1145

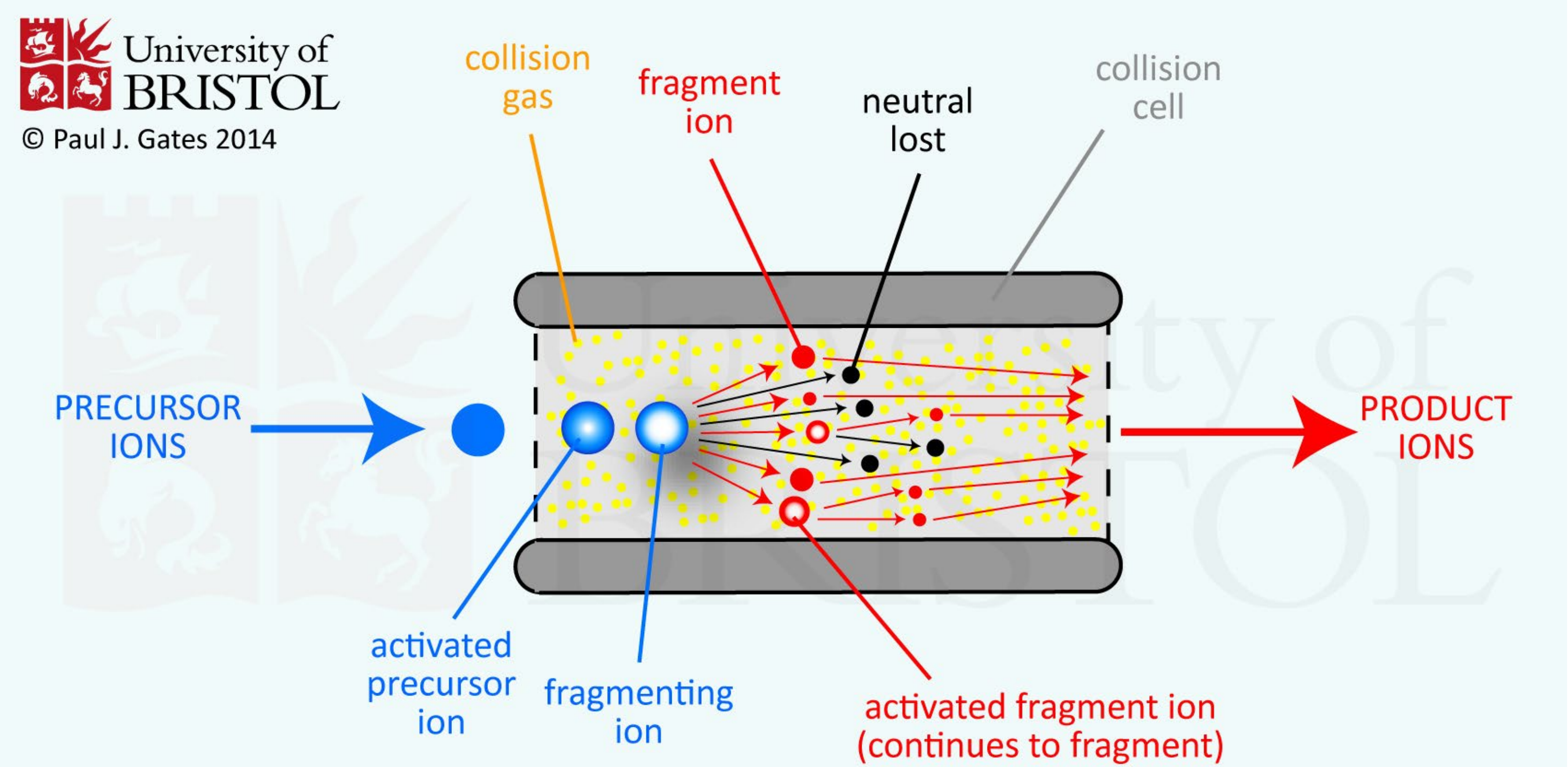


Polyethylene glycol (n=4)
$C_8H_{19}O_5^+$
m/z: 195.1227
Δm: +0.0082
+42 ppm

Orthogonal Quadrupole Time-of-Flight MS

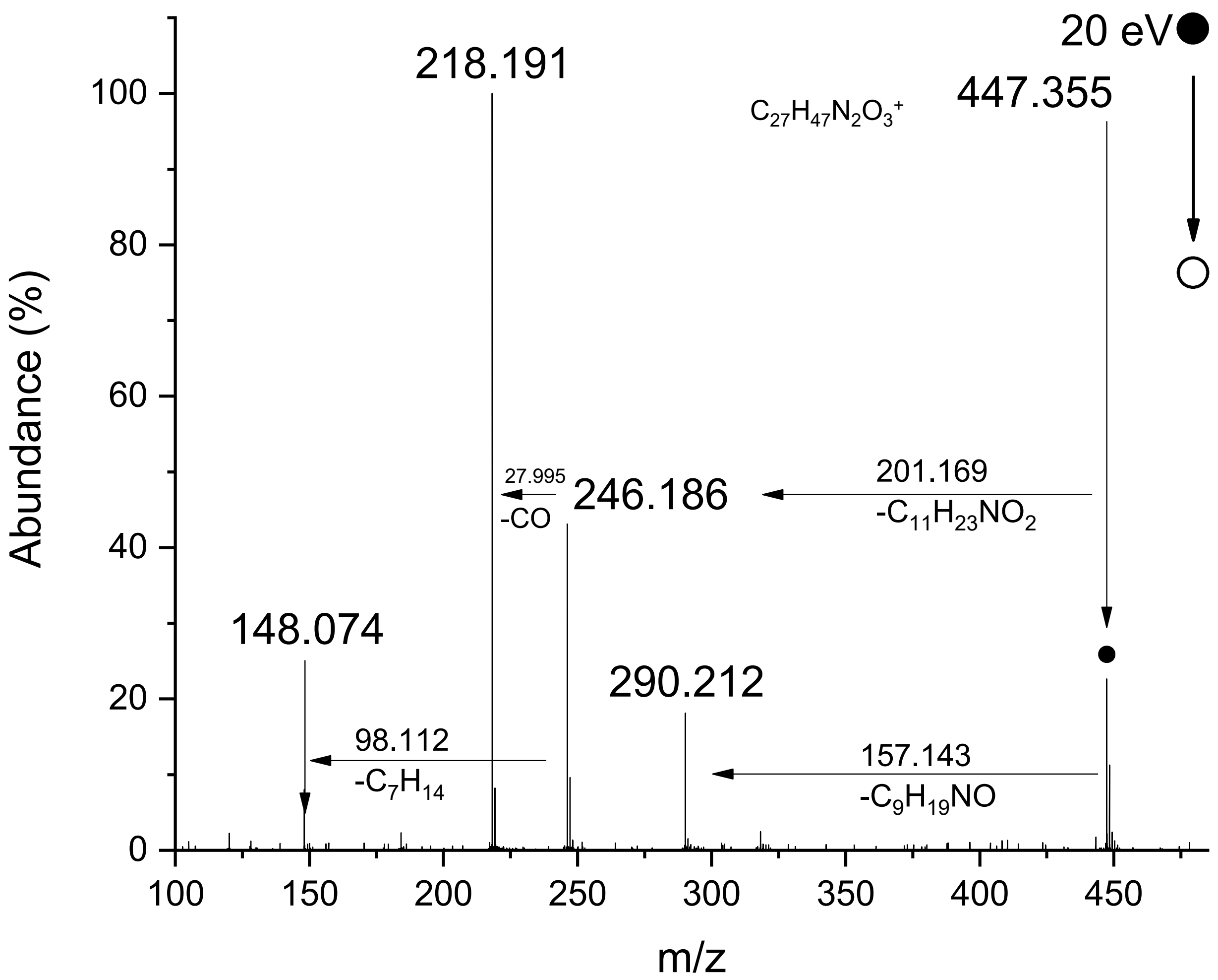


Collision-induced Dissociation (CID)

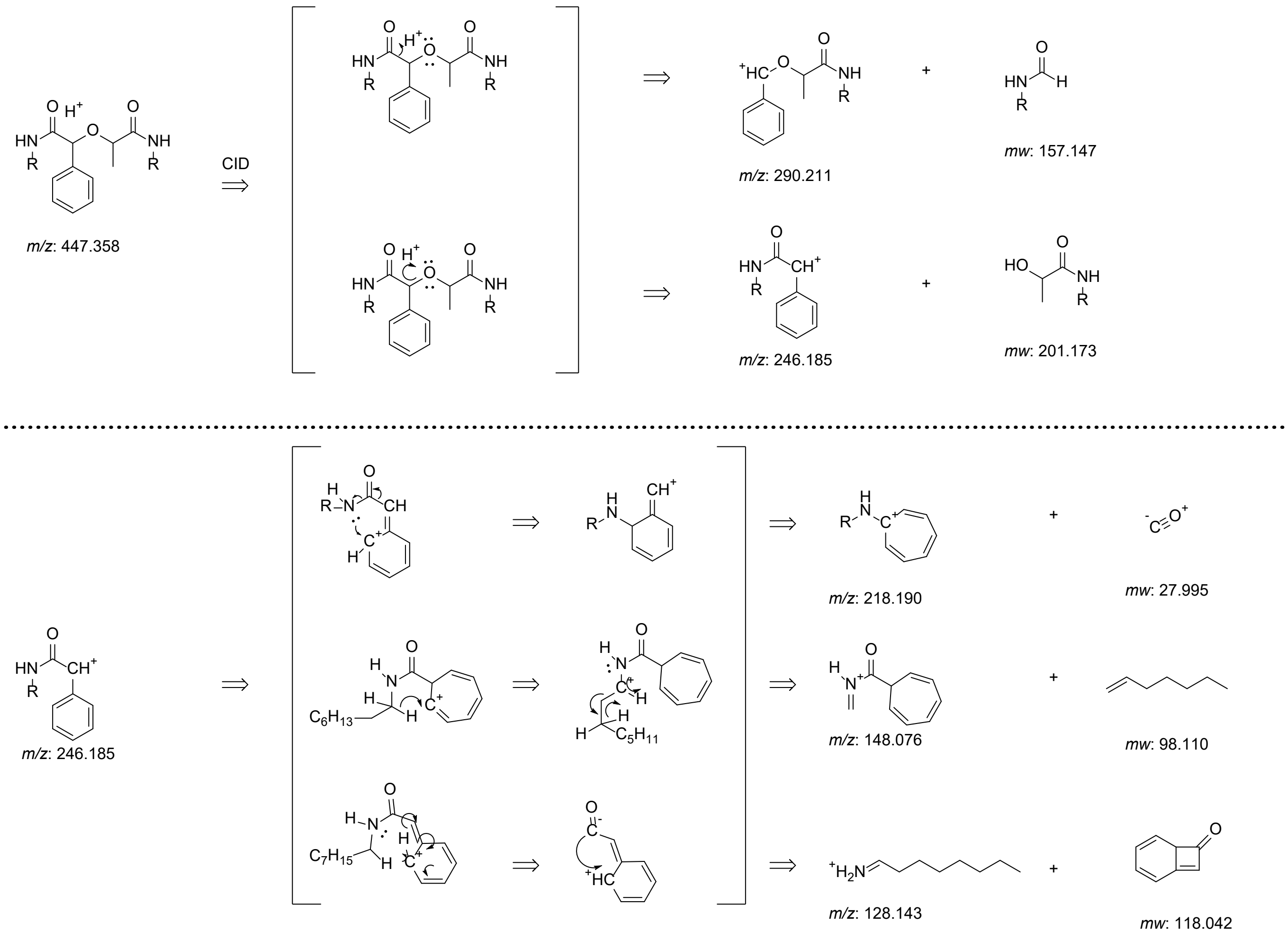


http://www.chm.bris.ac.uk/ms/cid.xhtml

Example for PhMeTODGA Cmpd 6

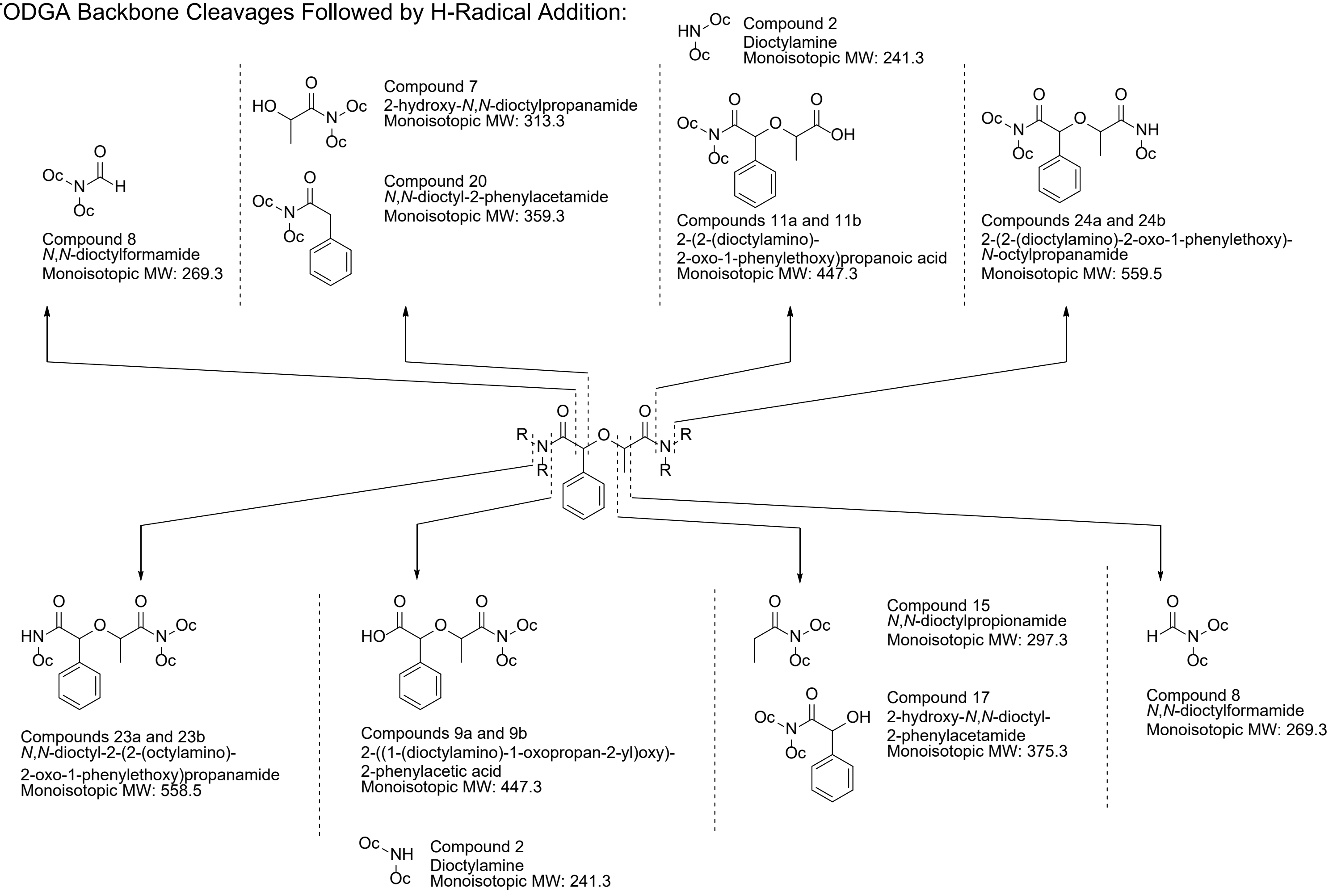


Proposed Gas-Phase Fragmentation Mechanisms



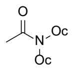
PhMeTODGA Degradation Product Analysis

PhMeTODGA Backbone Cleavages Followed by H-Radical Addition:

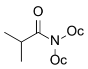


But wait, there's more……

PhMeTODGA Backbone Bond Cleavage Followed by CH_3-Radical Addition:

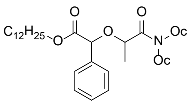


Compound 10
N,*N*-dioctylacetamide
Monoisotopic MW: 283.3

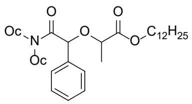


Compound 18
N,*N*-dioctylisobutyramide
Monoisotopic MW: 311.3

Dodecanol Esterification:

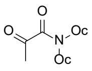


Compound 25
dodecyl 2-((1-(dioctylamino)-1-oxopropan-2-yl)oxy)-2-phenylacetate
Monoisotopic MW: 615.5

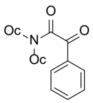


Compound 26
dodecyl 2-(2-(dioctylamino)-2-oxo-1-phenylethoxy)propanoate
Monoisotopic MW: 615.5

Oxidation of Primary PhMeTODGA Radiolysis Products:

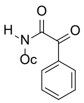


Compound 12
N,*N*-dioctyl-2-oxopropanamide
Monoisotopic MW: 311.3



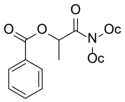
Compound 19
N,*N*-dioctyl-2-oxo-2-phenylacetamide
Monoisotopic MW: 373.3

Oxidation of Secondary PhMeTODGA Radiolysis Products:



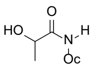
Compound 4
N-octyl-2-oxo-2-phenylacetamide
Monoisotopic MW: 261.2

Oxidation of OH-Radical Addition:

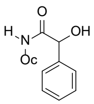


Compound 22
1-(dioctylamino)-1-oxopropan-2-yl benzoate
Monoisotopic MW: 417.3

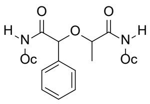
Primary PhMeTODGA Radiolysis Product Bond Cleavages Followed by H-Radical Additions:



Compound 1
2-hydroxy-*N*-octylpropanamide
Monoisotopic MW: 201.2

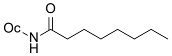


Compound 3
2-hydroxy-N-octyl-2-phenylacetamide
Monoisotopic MW: 263.2



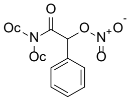
Compounds 6a and 6b
N-octyl-2-(2-(octylamino)-2-oxo-1-phenylethoxy)propanamide
Monoisotopic MW: 446.4

Unknown Formation Mechanism:

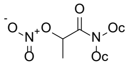


Compound 5
N-octyloctanamide
Monoisotopic MW: 255.3

Nitrate-Radical Additions:

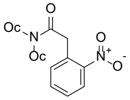


Compound 21
2-(dioctylamino)-2-oxo-1-phenylethyl nitrate
Monoisotopic MW: 420.3



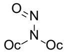
Compound 14
2-(dioctylamino)-2-oxo-1-phenylethyl nitrate
Monoisotopic MW: 358.3

Aromatic Nitration:



Compound 16
2-(4-nitrophenyl)-*N*,*N*-dioctylacetamide
Monoisotopic MW: 404.3

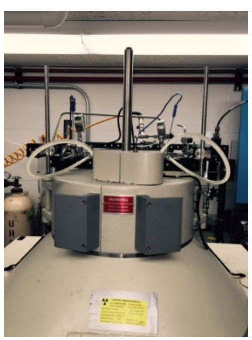
Nitrosamine Formation:

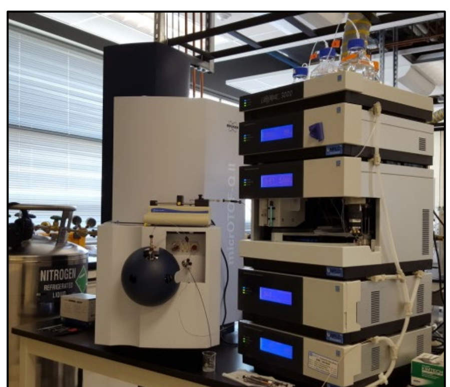


Compound 13
N,*N*-dioctylnitrous amide
Monoisotopic MW: 270.3

Future Directions

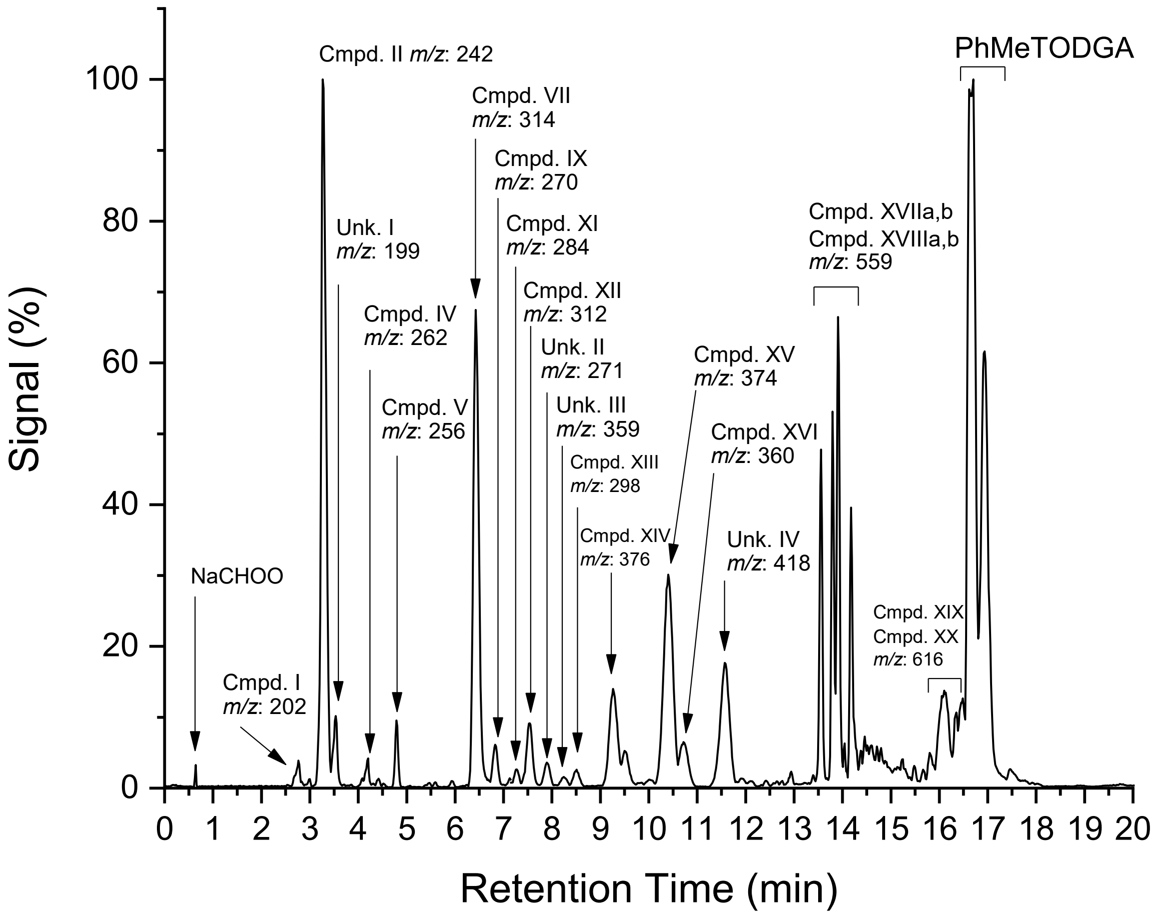
- **Prepare degradation products by irradiating high concentrations of ligand to high doses**
- **Separate and purify degradation products using preparative-scale high-performance liquid chromatography (HPLC)**
  - Produce amounts for structure conformation with NMR, quantification standards
    - Improve identification
  - Eventually enough for solvent extraction experiments
    - Enable modeling





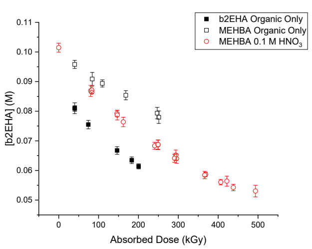
Future Directions, cont.....

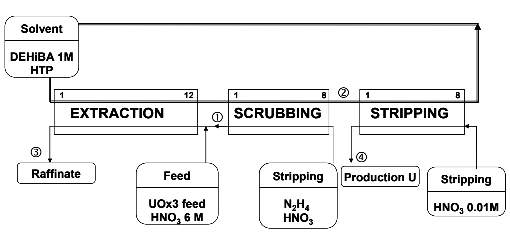
- **New methods to statistically reveal which chromatographic peaks are degradation products**

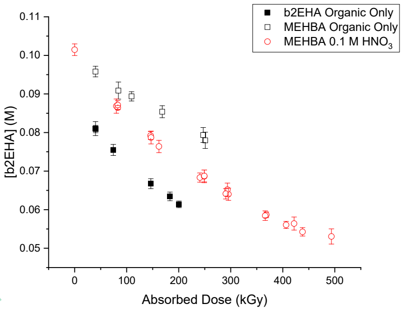


Conclusions

- **Radiation chemistry studies can provide:**
  - Detailed information about the performance of processes for separating used nuclear fuel
  - Identify problematic degradation products
  - Develop process models to predict and control industrial separation
  - Fundamental radiation chemistry can help with ligand design
- **Standards greatly enhances obtainable information**







Center for Radiation Chemistry Research

- **The CR2 mission is to:**
  - Address radiation chemistry challenges throughout the nuclear fuel cycle and beyond.
  - Advance our fundamental and applied knowledge of ionizing radiation phenomena.
  - Train the next generation of radiation chemists, to preserve the world's expertise for future generations.
- **https://cr2.inl.gov/**

Gregory Horne

Dean Peterman

Peter Zalupski

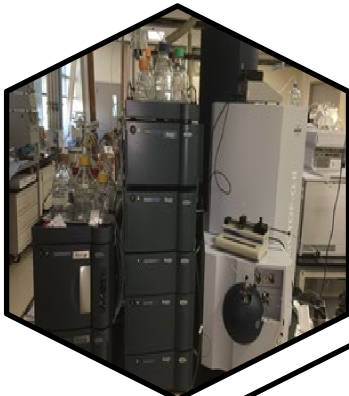
Travis Grimes

Elizabeth Parker-Quaife

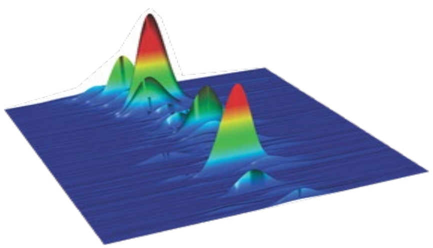
Corey Pilgrim

David Meeker

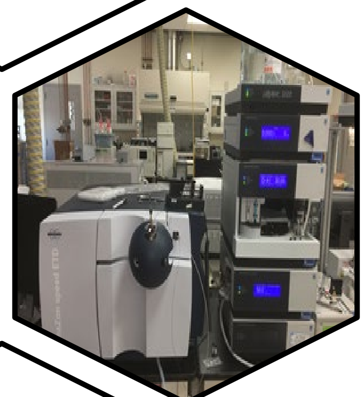
Molecular Chromatography and Mass Spectrometry Group



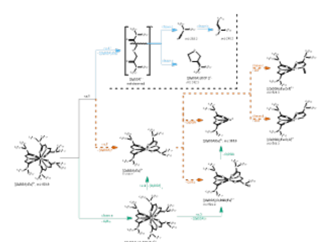
Molecular Identification and Quantification



Complex Mixture Analysis



Intrinsic Complex Coordination



- **Personnel**
  - Gary Groenewold
    - Gary.Groenewold@inl.gov
  - Brittany Hodges
    - Brittany.Hodges@inl.gov
  - Chris Zarzana
    - Christopher.Zarzana@inl.gov
  - Cathy Rae
  - Dayna Daubaras

Acknowledgements

- Work funded by the US-DOE Assistant Secartary for NE, under the FCR&D Radiation Chemistry program; DOE-Idaho Operations Office Contract DE-AC07-05ID14517 and Nuclear Energy Universities Program (NEUP) DE-NE0008406 grant.

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Landscape of Separations Processes