INL/CON-23-75268-Revision-0

Impacts of Lanthanide Ion Complexation on the Radiation Robustness of Diglycolamide Extractants

November 2023

Changing the World's Energy Future

Michaela Renee Bronstetter, Gregory Peter Holmbeck, Alyssa Gaiser

Idaho National Laboratory

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Impacts of Lanthanide Ion Complexation on the Radiation Robustness of Diglycolamide Extractants

Michaela Bronstetter
November 16th, 2023

MICHIGAN STATE UNIVERSITY

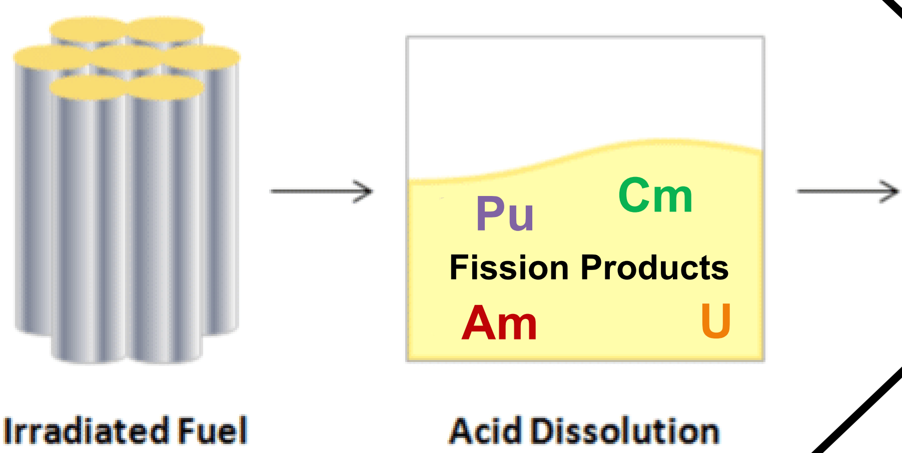
U.S. DEPARTMENT OF ENERGY | Office of Science

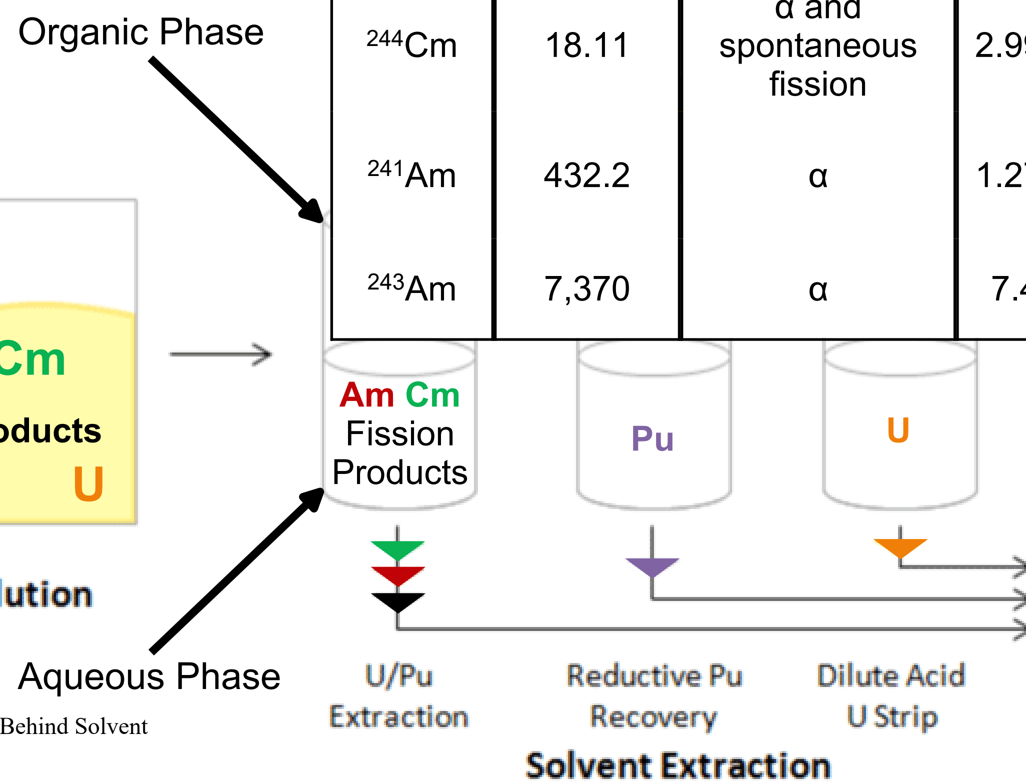
This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Nuclear Physics and used resources of the Facility for Rare Isotope Beams (FRIB), which is a DOE Office of Science User Facility, under Award Number DE-SC0000661.

Used Nuclear Fuel Separations

- Used Nuclear Fuel (UNF)
  - Contains High-Level Waste (HLW)
    - » Problematic Minor Actinides (MA)

Isotope	Half Life (years)	Decay Method	Activity (Bq/g)
^{244}Cm	18.11	α and spontaneous fission	2.99×10^{12}
^{241}Am	432.2	α	1.27×10^{11}
^{243}Am	7,370	α	7.4×10^{9}



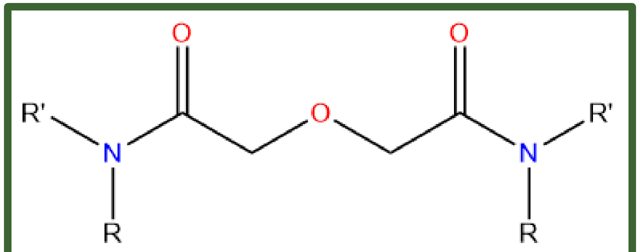


Clark, A.; Yang, P.; Shafer, J. Coordination of Actinides and the Chemistry Behind Solvent Extraction; 2018.

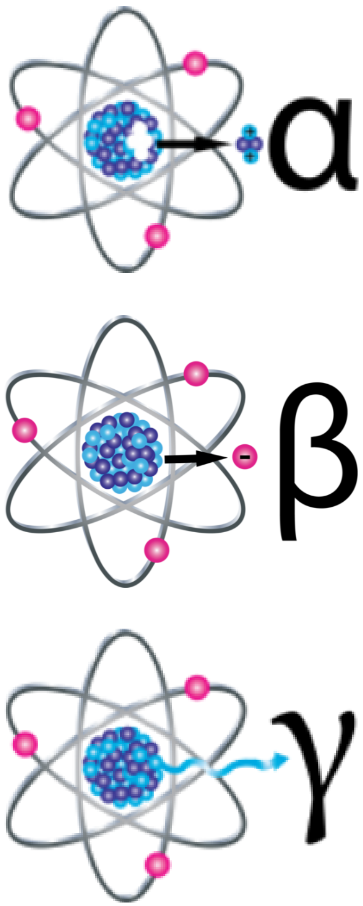
Radiation Units and Conversion Factors. Radiation Emergency Medical Management.

UNF Separation Challenges

- MA are difficult to separate from Ln(III)
  - Chemical behavior
    - » Oxidation state
    - » Size
- Radiation Fields
  - Alpha, Beta, & Gamma
    - » Extractant degradation
- Ideal extractant properties for UNF separation
  - Robust (against radiation fields)
  - Metal extracting properties
  - High acidity conditions



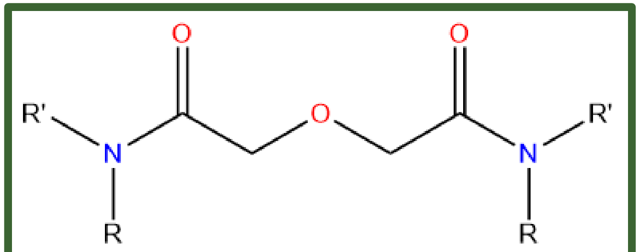
DGA
Diglycolamide



Alpha Beta and Gamma Radiation. Vaia.

DGAs – Promising Extractants

- DGA
  - Pros:
    - » Partitioning of An(III)
      - High distribution ratio
    - » Highly stable
      - Irradiations
    - » Low [DGA] needed
    - » Can be used in both polar and non-polar solvents (applications)
  - Cons:
    - » Understudied (irradiations, metal loading)
    - » Metal loading effectiveness is dependent on:
      - [HA]
      - [DGA]
      - [M^{3+}]



DGA
Diglycolamide

Ansari et al. *Chem Rev* **2012**, *112* (3), 1751–1772.

Previous DGA Irradiation Studies

- Kimberlin et al.
- Holmbeck et al.

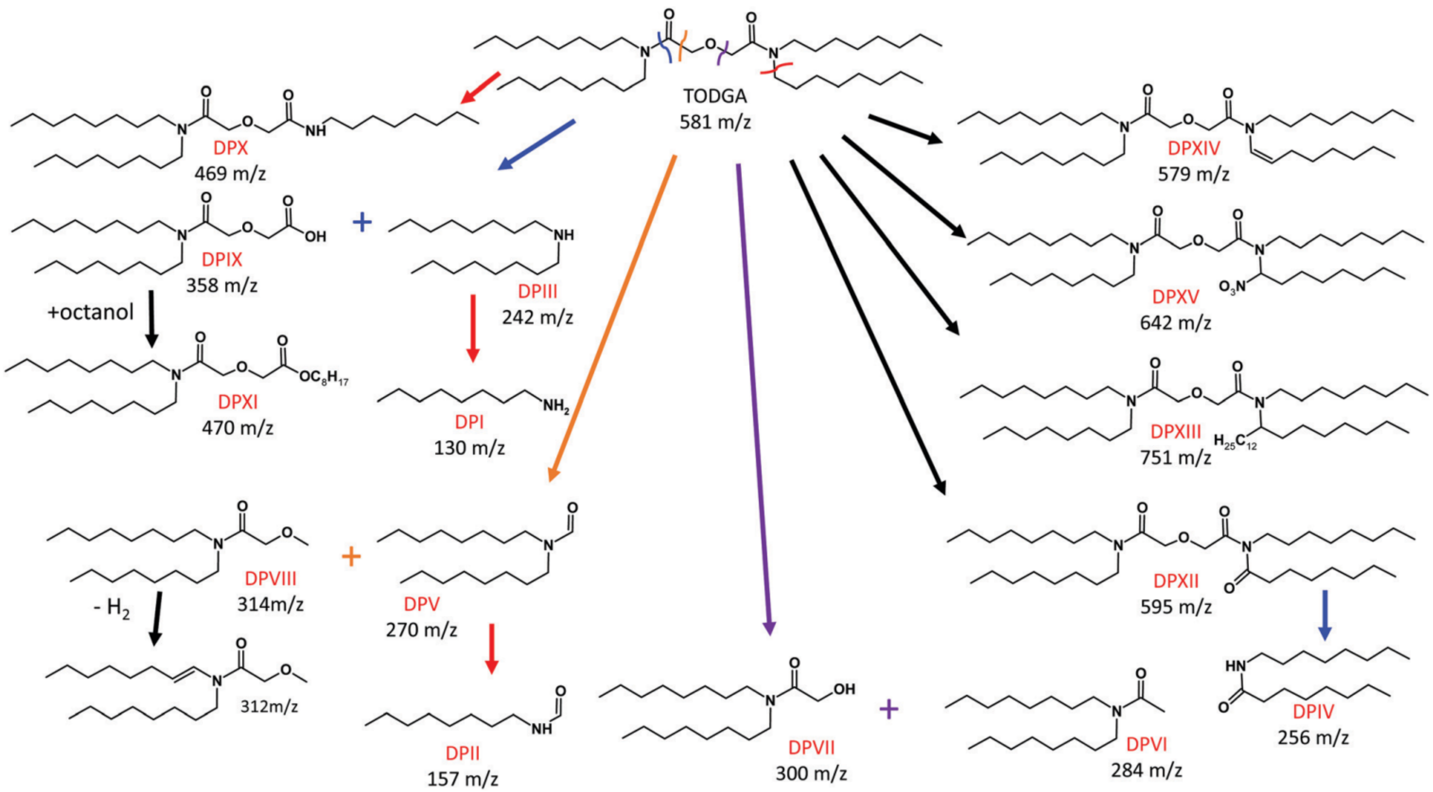
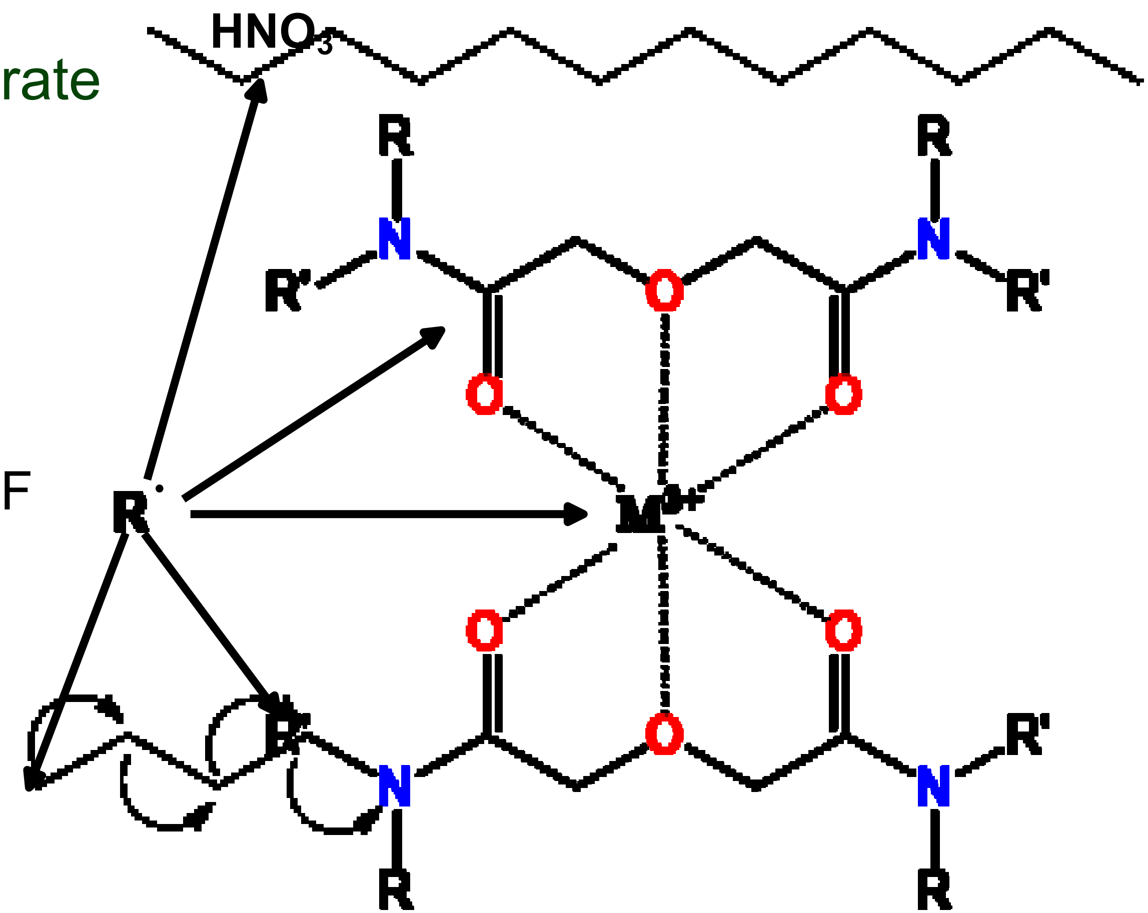


Fig. 4 Degradation schema proposed for the formation of the main degradation product of TODGA and *m/z* of the protonated species.

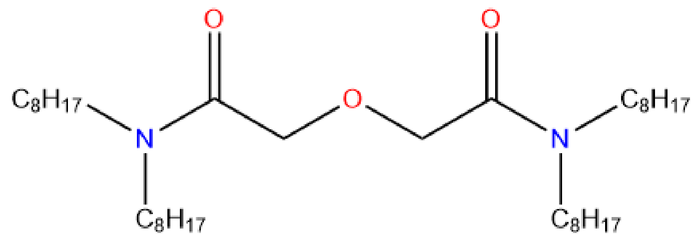
Kimberlin et al. *Phys. Chem. Chem. Phys.* **2022**, *24* (16), 9213–9228.

Hypothesis

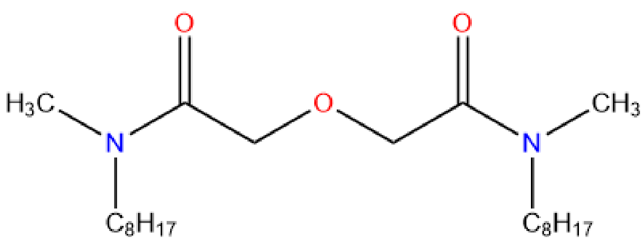
- Metal ion complexation will accelerate the degradation rate of a DGA
  - Metal
  - DGA structure
  - Solvent
- Goals
  - Various DGA analysis in UNF conditions
    - » Degradation
    - » Radicals
    - » Metal loading
- Impacts
  - f-block exploration
  - Future NFC implementation



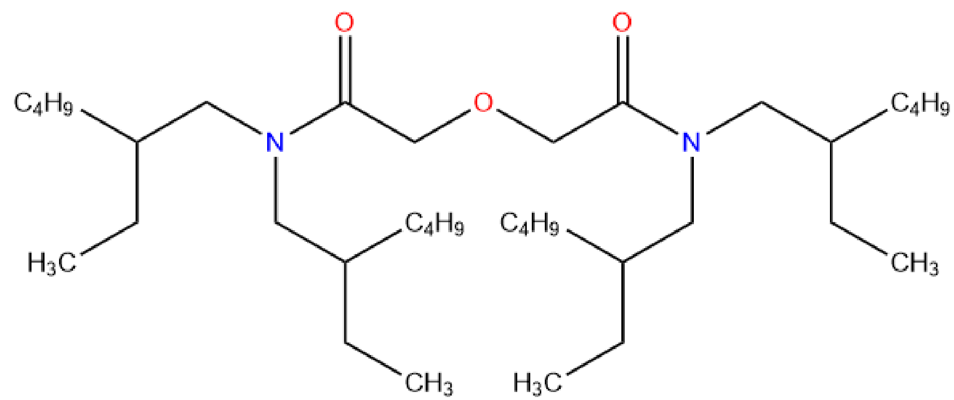
DGAs of Interest



TODGA
N,N,N′,N′-tetraoctyldiglycolamide



DMDODGA
N,N,-dimethyl-*N′,N′*-dioctyldiglycolamide

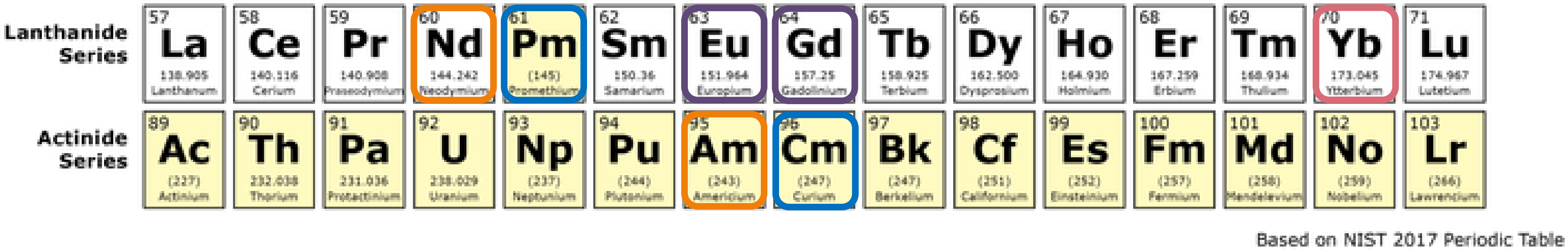


T2EHDGA
N,N,N′,N′-tetra(2-ethylhexyl)diglycolamide

DGA Metal Loading

- Chemical behavior □ An(III) and Ln(III) in UNF
  - Oxidation state
  - Size

+3 +3 +3 +3 +3 +3 +3 +3 +3 +3 +3 +3 +3 +3 +3

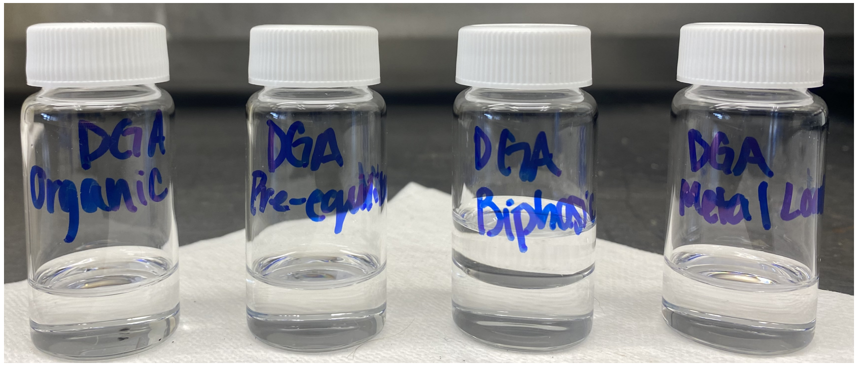


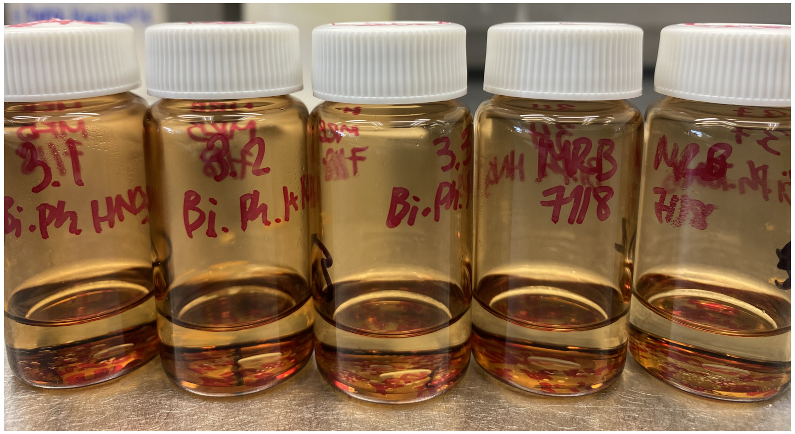
+3 +4 +5 +6 +5 +4 +3 +3 +3 +3 +3 +3 +3 +2 +3

Periodic Table with Radioactive Elements Highlighted. Environmental Protection Agency.

- Metals of choice:
  - Neodymium (Nd)
  - Europium (Eu)
  - Gadolinium (Gd)
  - Ytterbium (Yb)

Gamma Irradiation Experiments





DGA Irradiator Sample Prep

Organic Phase
(n-dodecane, DGA)

Aqueous Phase
(HNO_3 or HNO_3 w/ metal)

- 50 mM DGA
- n-dodecane

- Organic solvent system
- 3 M HNO_3
- 3x contact w/ 1:1 org. to aq.

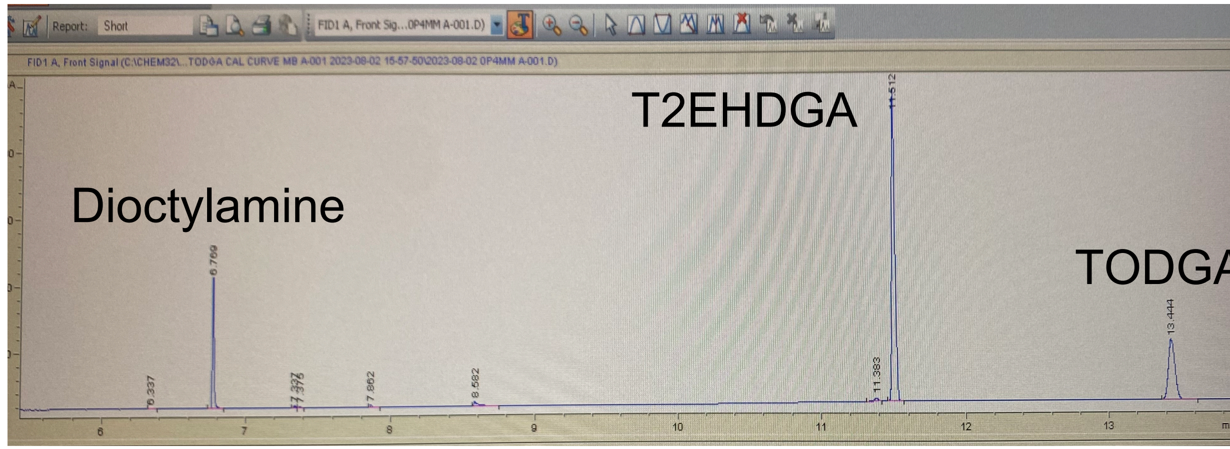
- 1 equiv. pre-equilibrated solvent system
- 1 equiv. 3 M HNO_3

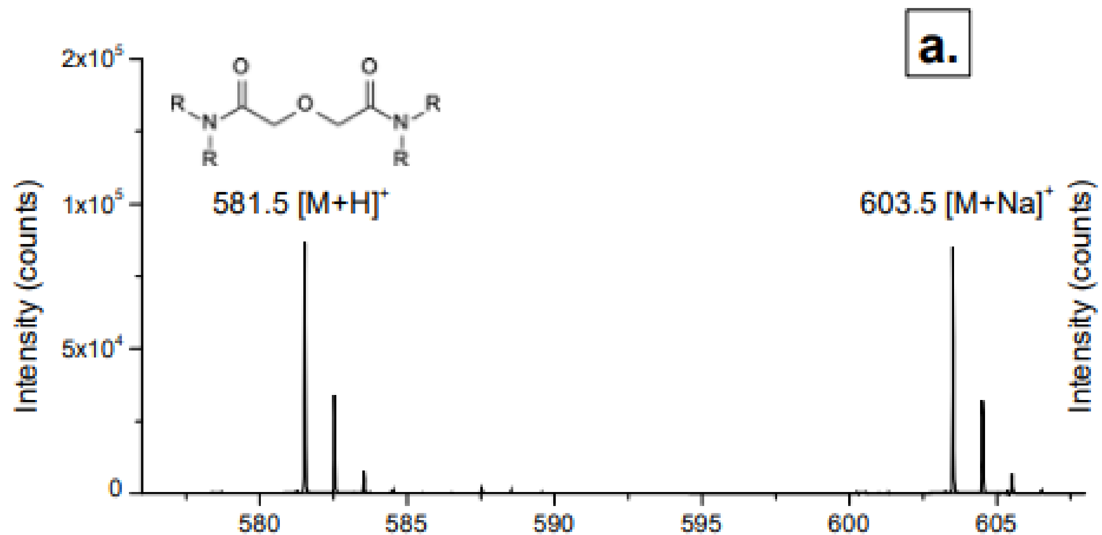
- Pre-equilibrated solvent system
- 20 mM Ln(III) in 3 M HNO_3
- 1 contact w/ 1:1 org. to aq.

- 1 equiv. Pre-equilibrated w/ Ln(III) solvent system
- 1 equiv. 3 M HNO_3

Horne et al. *Phys. Chem. Chem. Phys.* **2020**, *22* (43), 24978–24985.

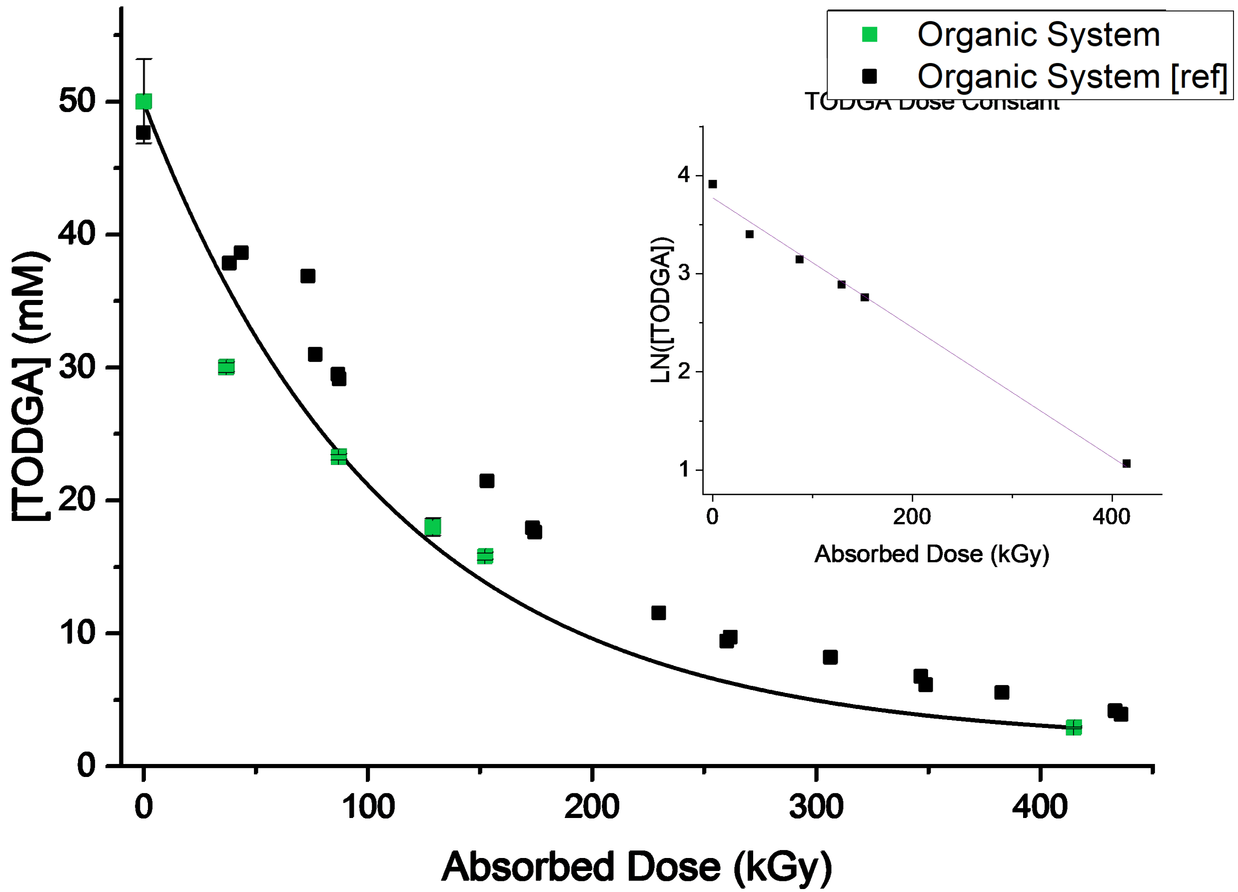
Post Irradiation Analysis





Zarzana et al. *Solvent Extr. Ion Exch.* **2015**, *33* (5), 431–447.

Impact of Metal Ion Complexation on TODGA



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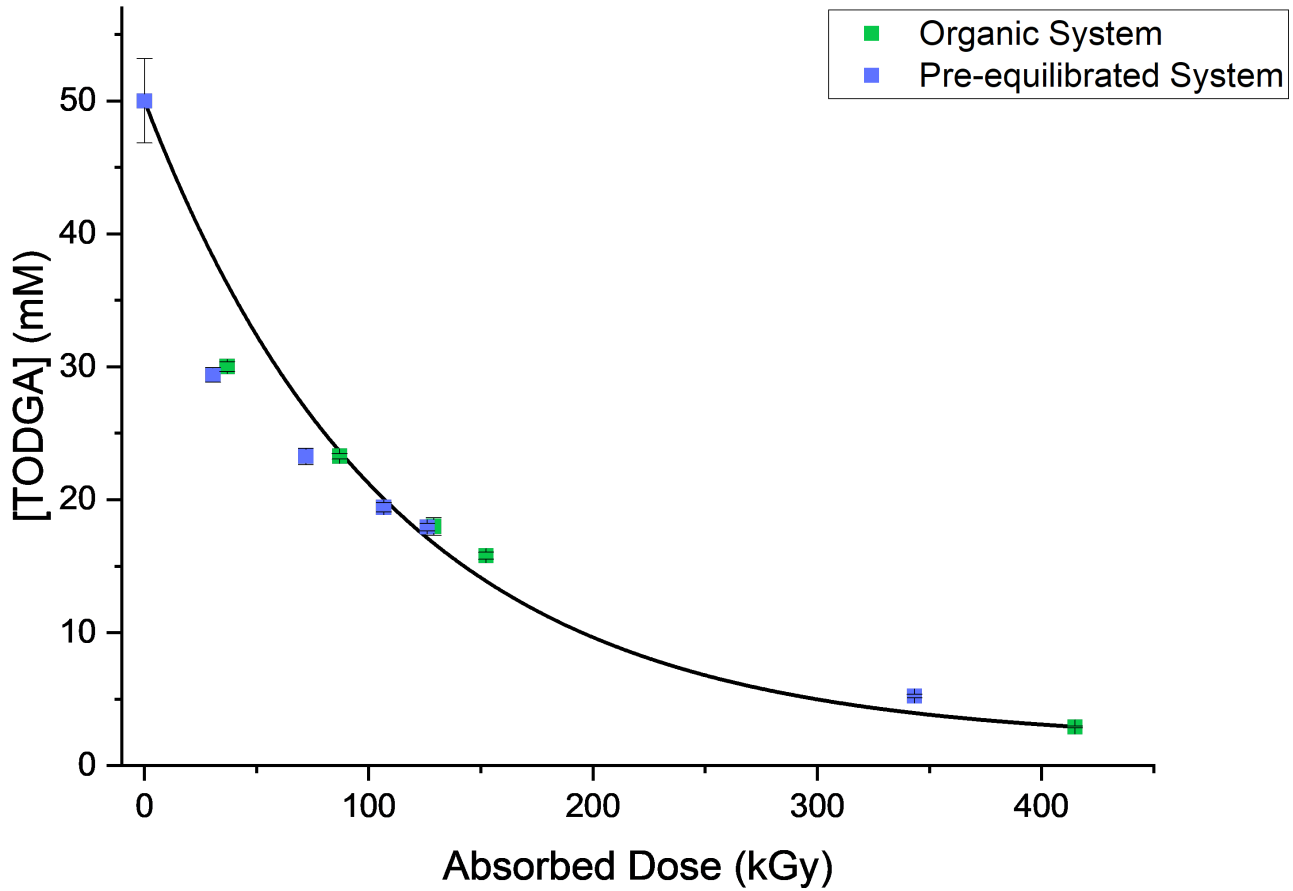
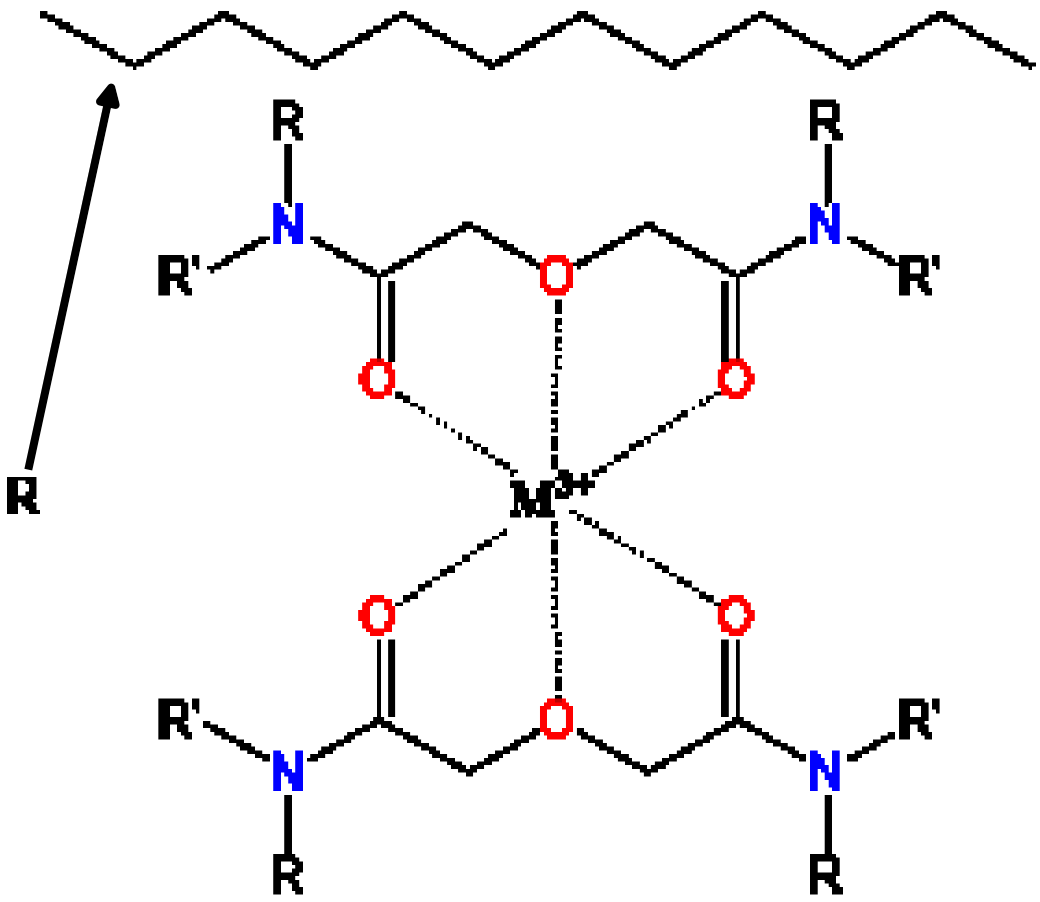
Impact of Metal Ion Complexation on TODGA

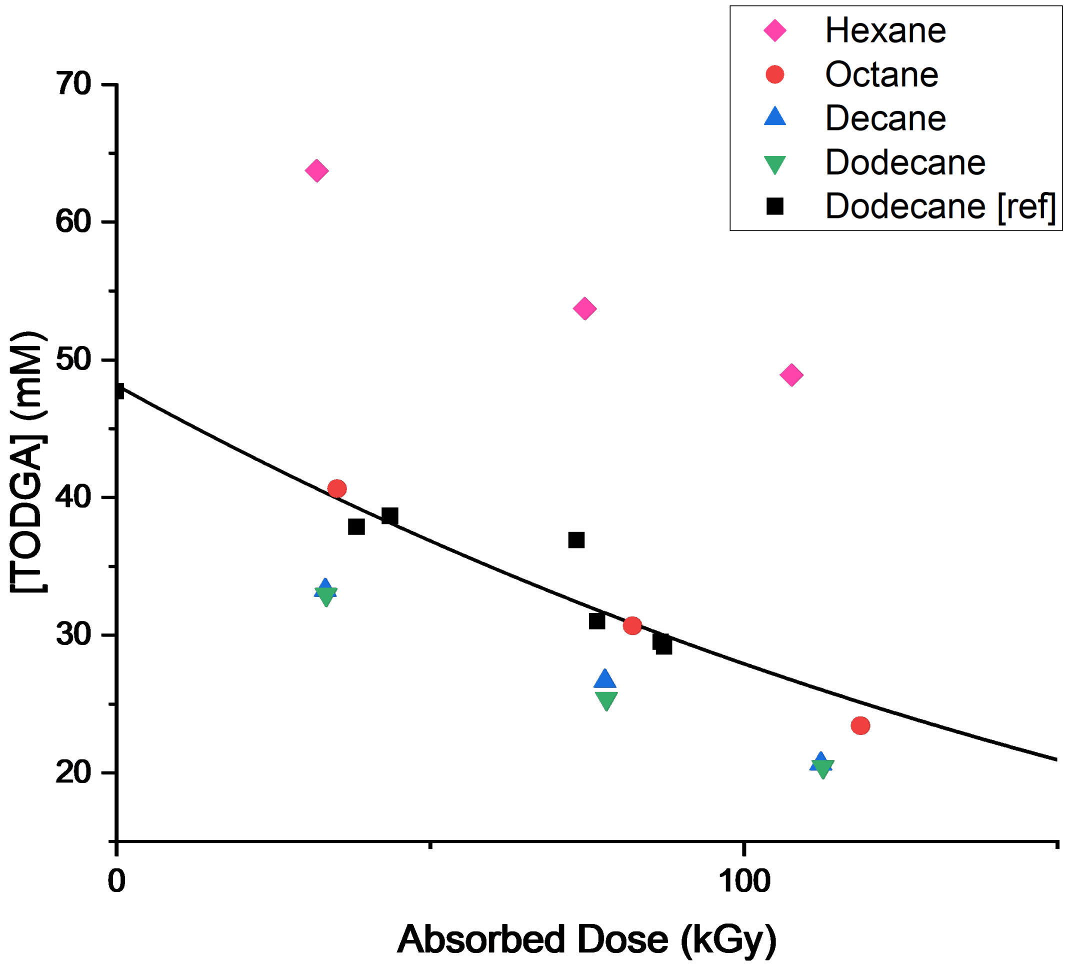


TODGA Solvent Matrix Studies

- Solvents:
  - Hexane
  - Octane
  - Decane
  - Dodecane

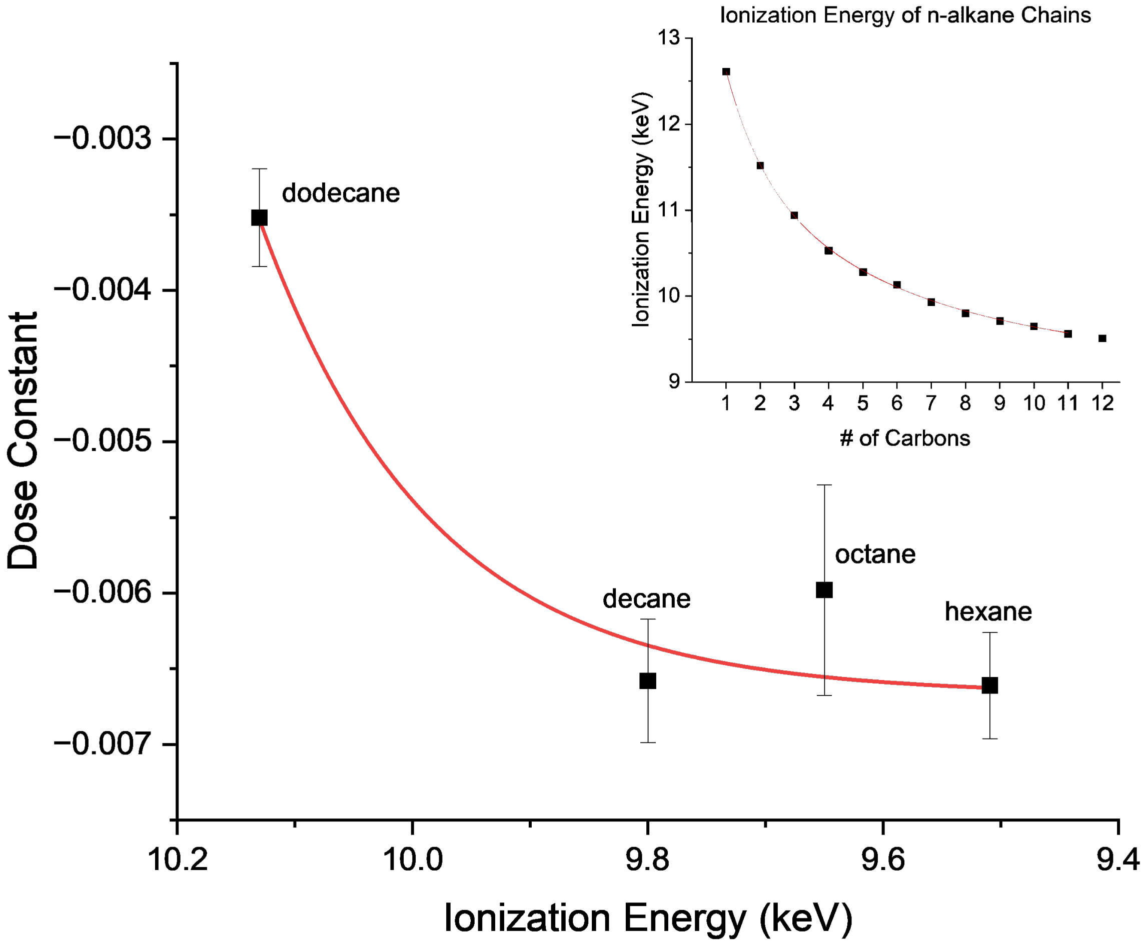


Impact of Solvent Variation on TODGA



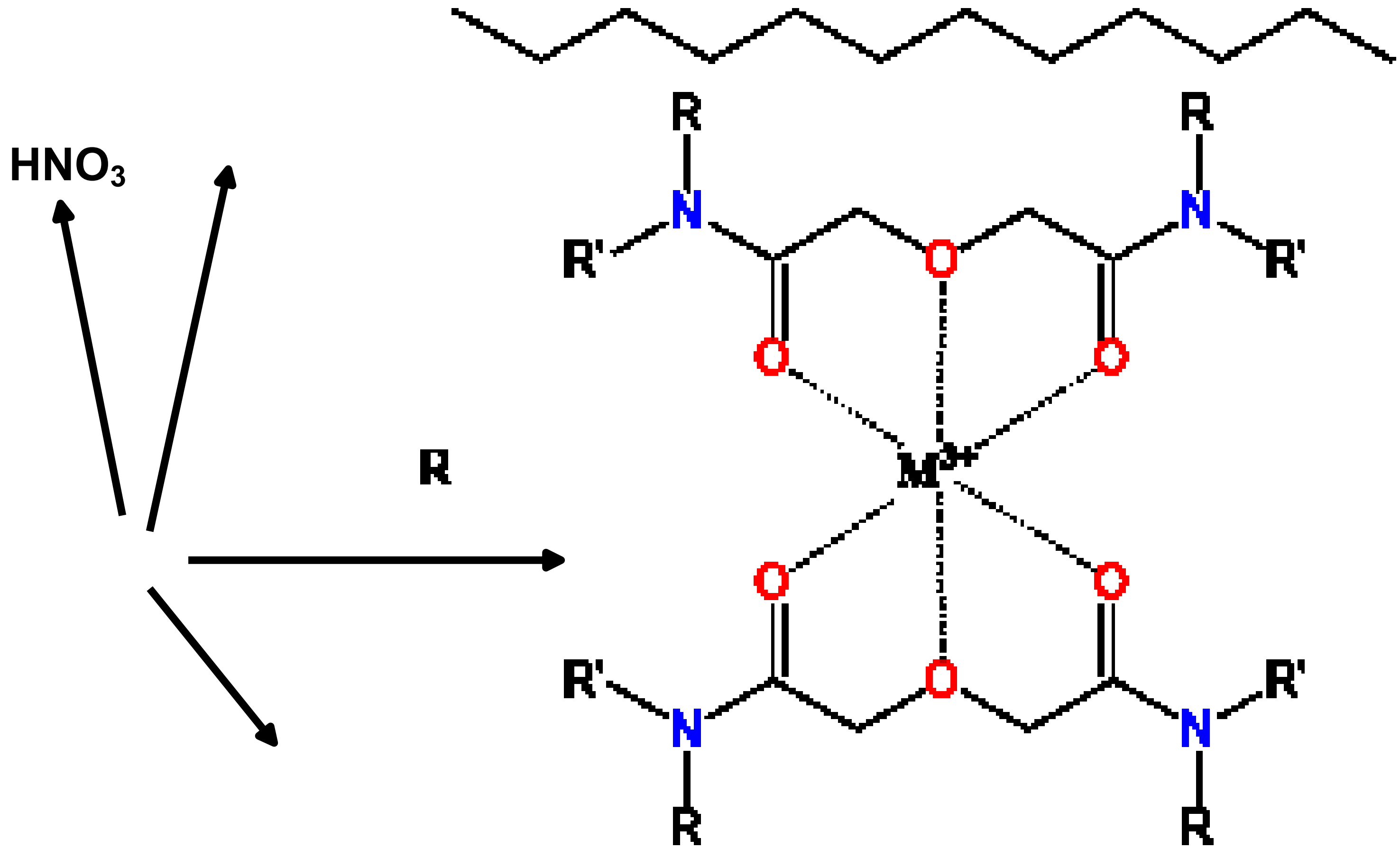
Horne et al. *Phys. Chem. Chem. Phys.* **2020**, *22* (43), 24978–24985.

Impact of Solvent Variation on TODGA



Search for Species Data by IE Value. National Institute of Standards and Technology (NIST).

Conclusion



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  - David Todd
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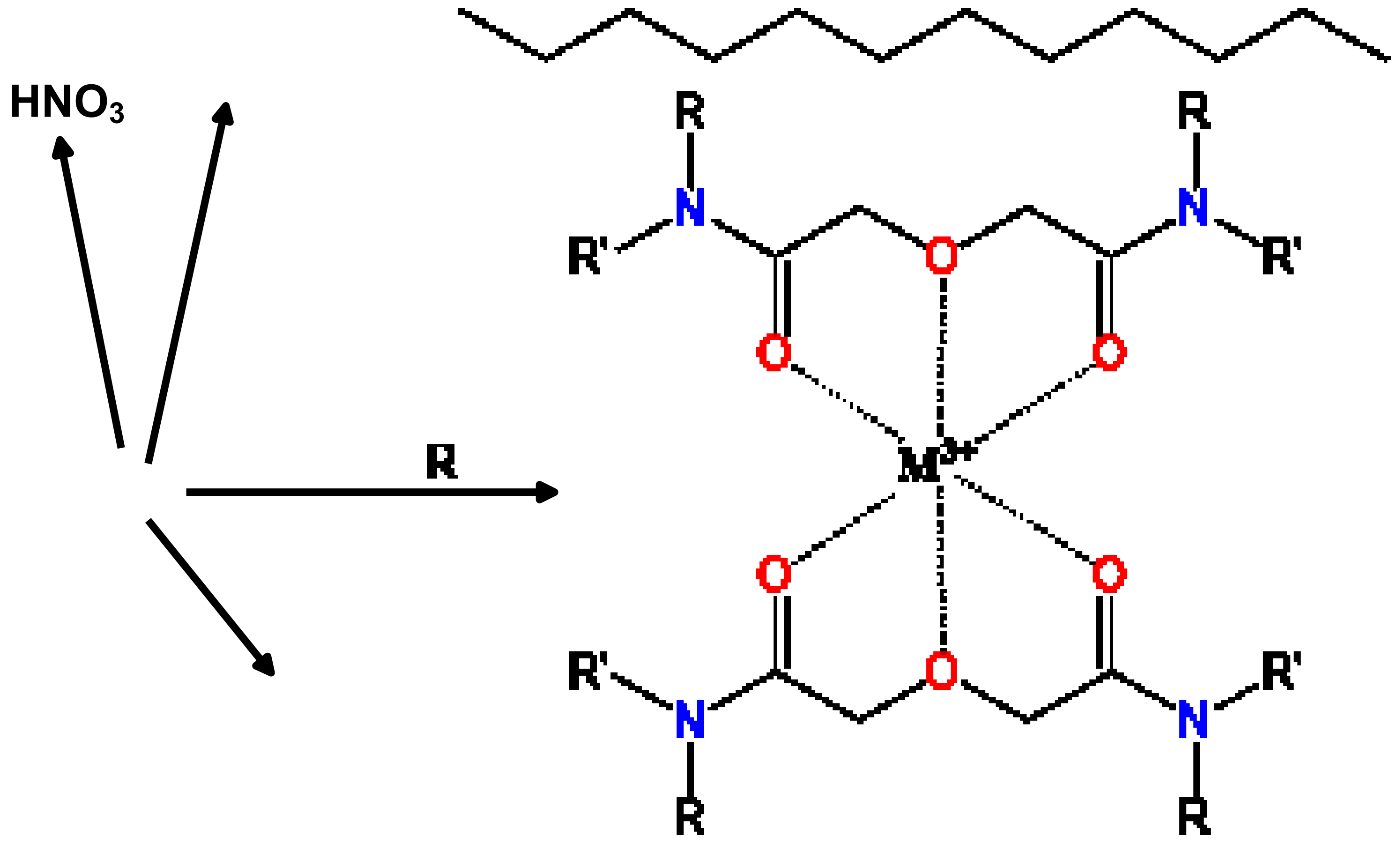
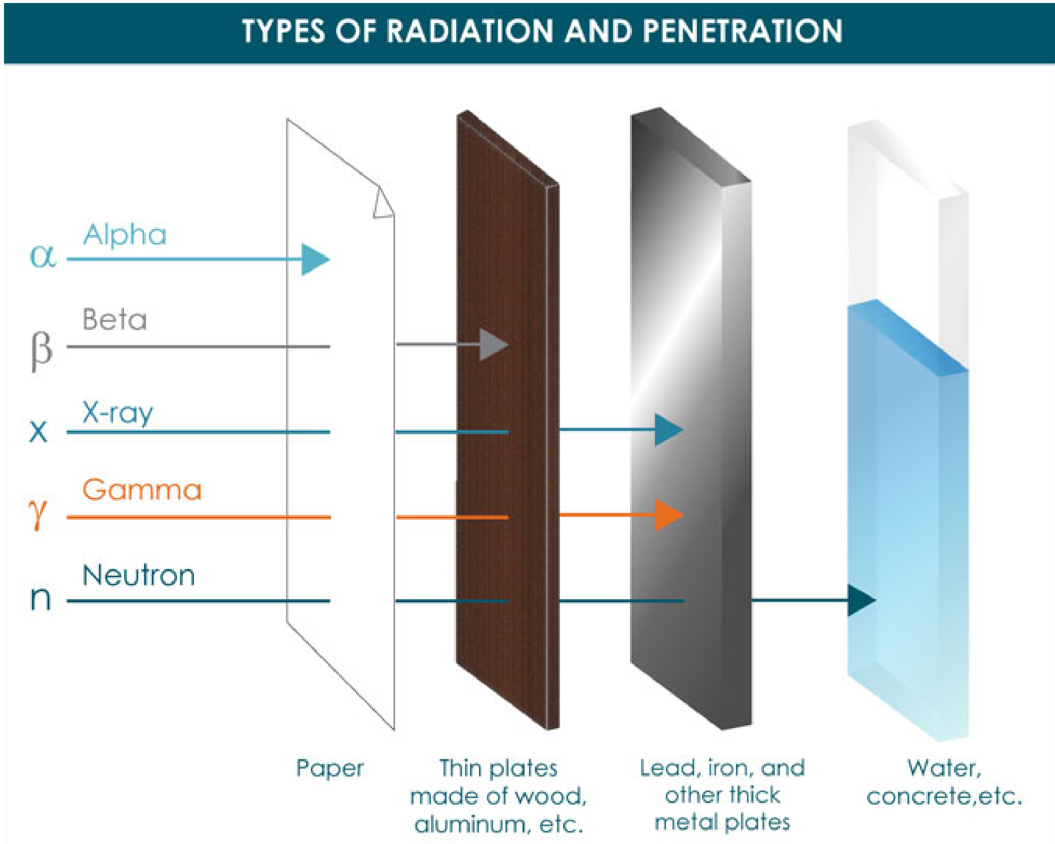
Thank you!



Types of Radiation

- Alpha (+)
  - Helium nucleus
  - High energy
- Beta (-,+)
  - Electron / positron
  - High energy
- Gamma / X-ray (neutral)
  - Photon
  - Varying energies
- Neutron
  - Varying energies



Types of Ionizing Radiation. Mirion Technologies.

SNF Component Characteristics

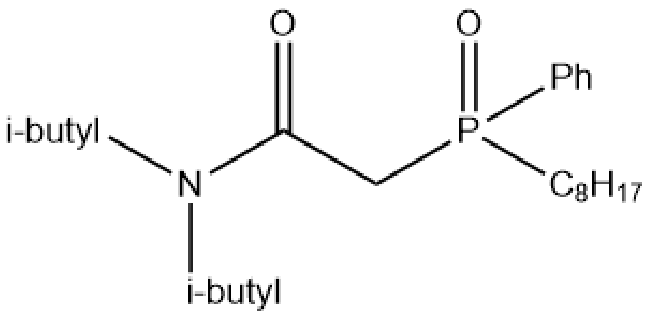
Metal	Oxidation State	Coordination Number	Ionic Radius (ppm)
Am	+2	7	121
		8	126
		9	131
	+3	6	97.5
		8	109
	+4	6	85
		8	95
Cm	+3	6	97
	+4	6	85
		8	95
Nd	+2	8	129
		9	135
	+3	6	98.3
		8	110.9
		9	116.3
		12	127
Pm	+3	6	97
		8	109.3
		9	114.4

Shannon-Prewitt Effective Ionic Radius Table. KnowledgeDoor.

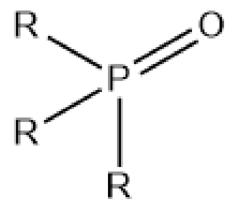
Previous Ligand Studies

- CMPO (a)
  - Pros:
    - » Bifunctionality
    - » High [HNO_3]
  - Cons:
    - » Multiple contacts needed

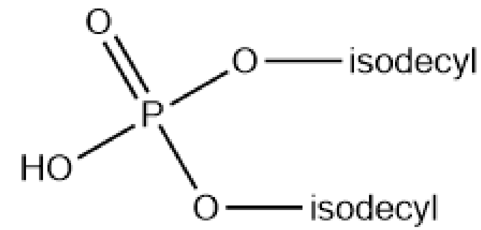
- TRPO (b) and DIDPA (c)
  - Pros:
    - » Lower acidity An partitioning
  - Cons:
    - » Low acidity use



(a) Octyl-(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide (CMPO)



(b) Trialkyl phosphine oxide (TRPO)



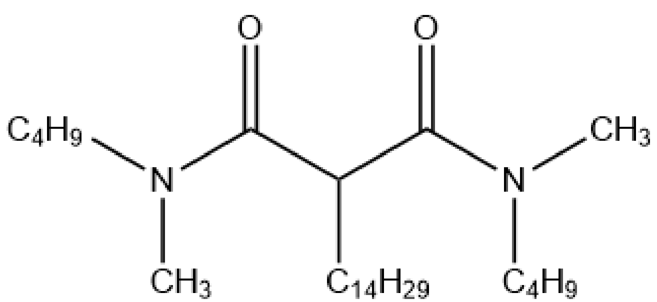
(c) Diisodecylphosphoric acid (DIDPA)

Ansari et al. *Chem Rev* **2012**, *112* (3), 1751–1772.

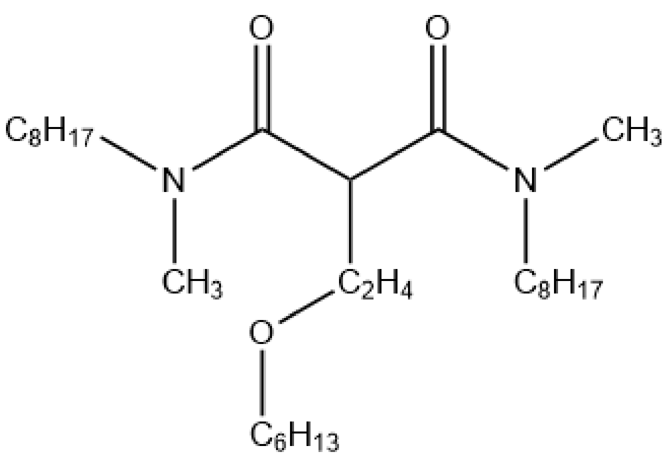
Previous Ligand Studies

- DMDBTDMA (d) and DMDOHEMA (e)
  - Pros:
    - » Back extraction
    - » Incinerable
  - Cons:
    - » D value for An(III) are low… high [ligand]

$$D_C = \frac{[\text{solute}]_{org}}{[\text{solute}]_{aq}}$$



(d) N,N'-dimethyl-N,N'-dibutyl tetra decyl malonamide (DMDBTDMA)

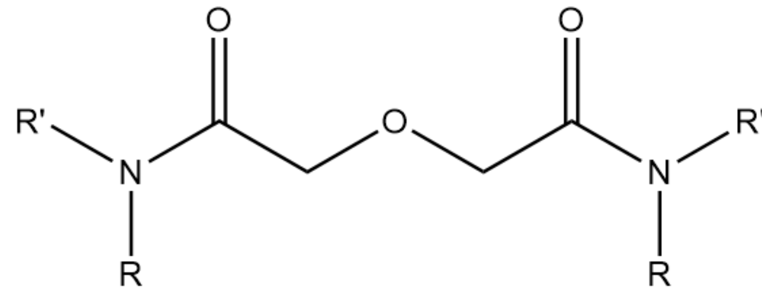


(e) N,N'-dimethyl-N,N'-dioctyl-2(2-hexyloxyethyl)malonamide (DMDOHEMA)

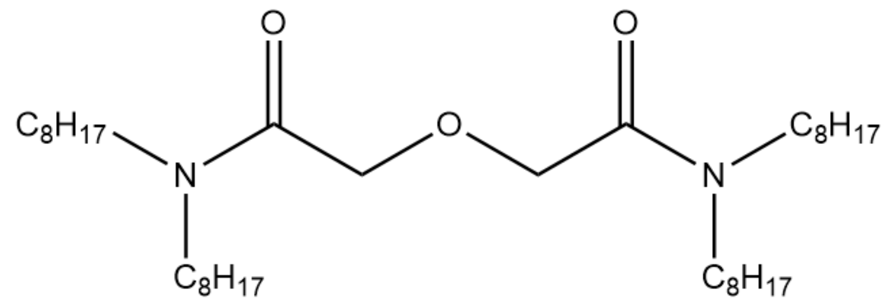
Ansari et al. *Chem Rev* **2012**, *112* (3), 1751–1772.

Previous DGA Studies

- DGAs
  - Basic studies:
    - » Aqueous complexation
    - » Theoretical calculations
    - » Spectroscopic studies
    - » Synthesis and characterization of solid complexes
  - Actinide partitioning w/ DGAs
  - Alternative separation technique extractants
  - Extraction chromatography studies
- TODGA solvent extraction studies:
  - Acid and aggregation
  - Diluent on Am extraction
  - Metal ion extraction
  - Phase modifiers
  - Stability



DGA
Diglycolamide



TODGA
N,N,N′,N′-tetraoctyldiglycolamide

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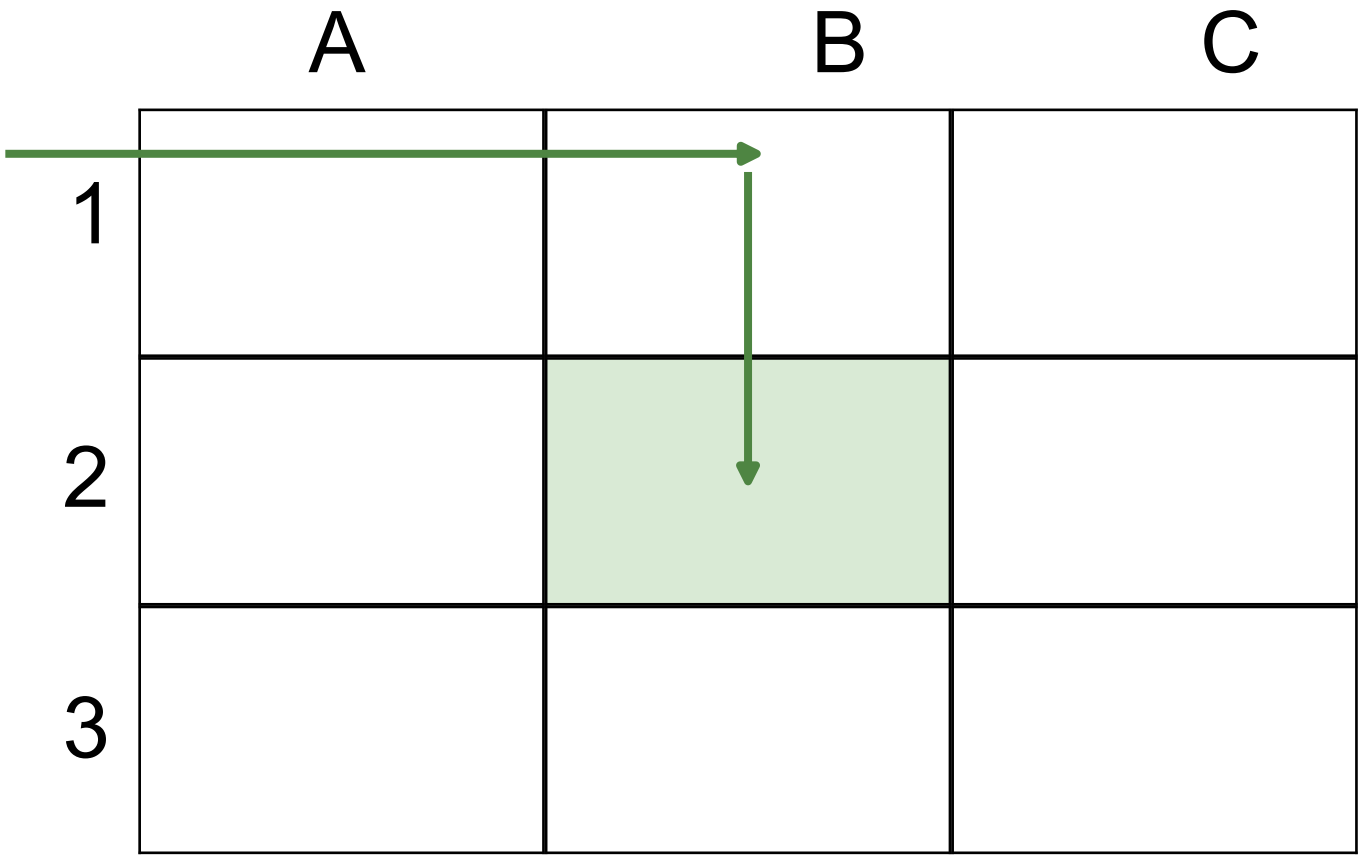
Irradiator Setup



Fricke Dosimetry

- Contains:
  - Ferrous ammonium sulfate
  - Sodium Chloride
  - Sulfuric acid

Table 1. Main reactions for ferric ion production in the radiolysis of the Fricke dosimeter, under aerated conditions.

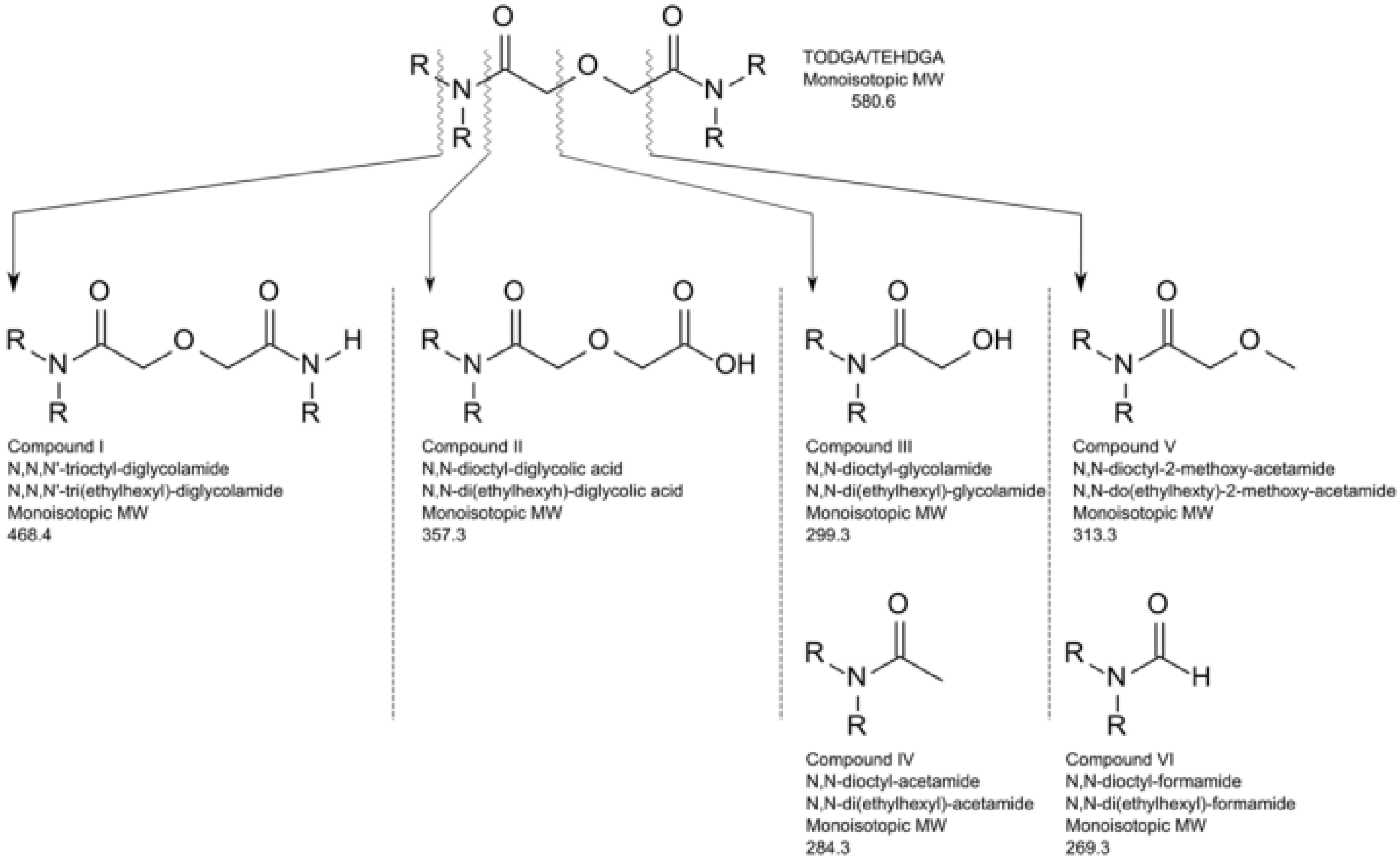
R1	$e^-_{aq} + H^+ \rightarrow H^\bullet$	$k_1 = 2.1 \times 10^{10}$ M^{-1} s^{-1}; $pK_a(H^\bullet/e^-_{aq}) = 9.59$
R2	$H^\bullet + O_2 \rightarrow HO_2^\bullet$	$k_2 = 2.1 \times 10^{10}$ M^{-1} s^{-1}
R3	$^\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$	$k_3 = 3.4 \times 10^8$ M^{-1} s^{-1}
R4	$OH^- + H^+ \rightarrow H_2O$	$k_4 = 5.97 \times 10^{10}$ M^{-1} s^{-1}; $pK_a(H_2O/OH^-) = 13.999$
R5	$HO_2^\bullet + Fe^{2+} \rightarrow Fe^{3+} + HO_2^-$	$k_5 = 7.9 \times 10^5$ M^{-1} s^{-1}
R6	$HO_2^- + H^+ \rightarrow H_2O_2$	$k_6 = 5 \times 10^{10}$ M^{-1} s^{-1}; $pK_a(H_2O_2/HO_2^-) = 11.62$
R7	$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^\bullet OH + OH^-$	$k_7 = 52$ M^{-1} s^{-1}
R8	$H^\bullet + Fe^{2+} \xrightarrow{H^+} Fe^{3+} + H_2$	$k_8 = 1.3 \times 10^7$ M^{-1} s^{-1}
R9	$^\bullet OH + HSO_4^- \rightarrow H_2O + SO_4^{\bullet -}$	$k_9 = 1.5 \times 10^5$ M^{-1} s^{-1}
R10	$SO_4^{\bullet -} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$	$k_{10} = 9.9 \times 10^8$ M^{-1} s^{-1}

Note: The rate constants given here for the reactions between ions are in the limit of infinite dilution, i.e., not corrected for the effects of the ionic strength of the solutions. Note that some $H^\bullet$ atoms can also react directly with Fe^{2+} (reaction R8). This reaction is important when no oxygen is present initially. In aerated solutions at 25 °C and a Fe^{2+} ion concentration of 1 mM, however, the contribution of this reaction to the formation of Fe^{3+} is small and may be neglected.

Zakaria, A. M.; Lertnaisat, P.; Islam, M. M.; Meesungnoen, J.; Katsumura, Y.; Jay-Gerin, J.-P. Yield of the Fricke Dosimeter Irradiated with the Recoil α and Li Ions of the 10B(n,α)7Li Nuclear Reaction: Effects of Multiple Ionization and Temperature. *Can J Chem* **2021**, *99* (4), 425–435.

deAlmeida et al. *PLoS One* **2014**, *9* (12), e115155.

MS TODGA Degradation Analysis



Zarzana et al. *Solvent Extr. Ion Exch.* **2015**, *33* (5), 431–447.