INL/MIS-20-57194-Revision-0

INL Radiation Chemistry Research Capabilities: CAES Winter Collaboration Meeting

January 2020

Changing the World's Energy Future

Christopher A Zarzana

Idaho National Laboratory

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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

INL Radiation Chemistry Research Capabilities

CAES Winter Collaboration Meeting

January 23-24, 2020

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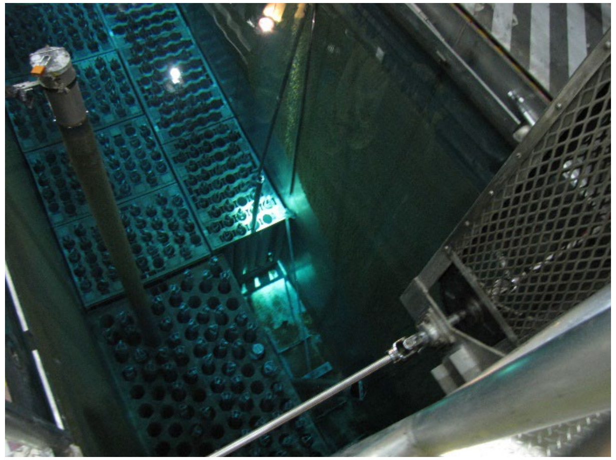
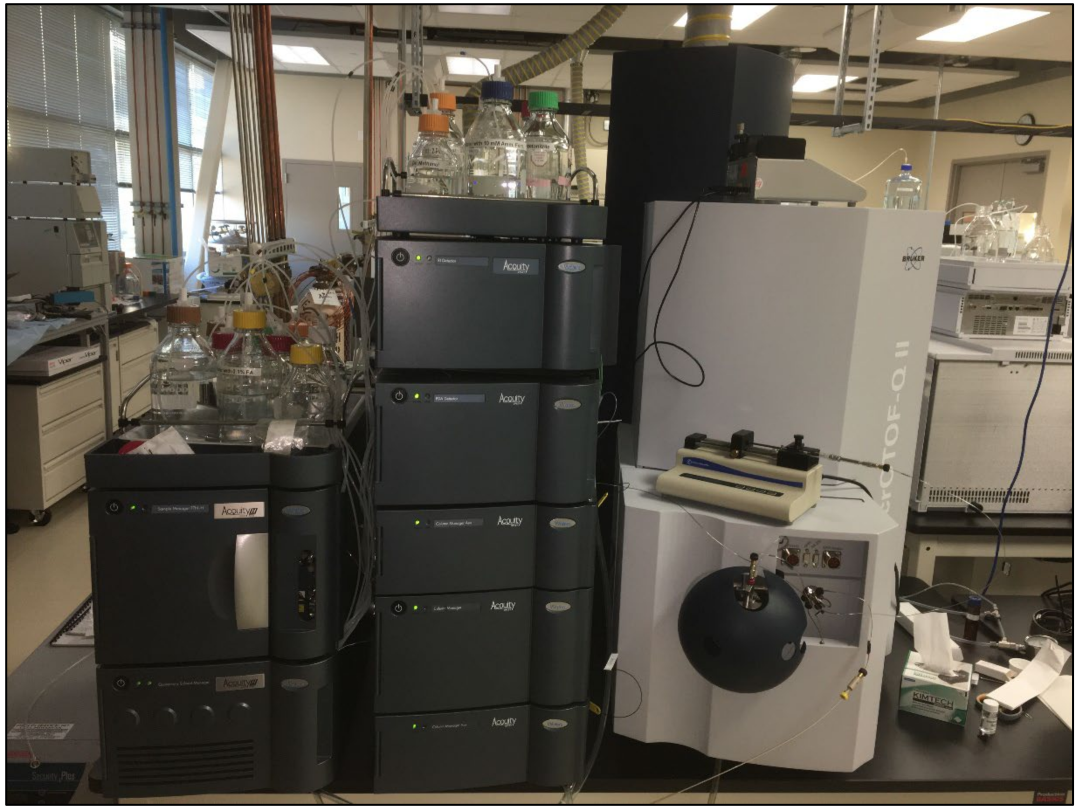
Gamma Irradiation Capabilities

- **Gammacell 220 ^{60}Co Gamma Source**
  - ~ 2.5 kGy h^{-1}
  - ~ 6 in diameter x 8 in tall sample chamber
  - Highly characterized dose rate
- **Gamma Tube in the ATR Fuel Canal**
  - ~25-50 kGy h^{-1}
    - Depends on fuel age and position
  - ~ 5 in diameter x 6 m (19' 8") useable length
  - *In situ* dose measurement
- **Both sources available through the Nuclear Science User Facility (NSUF)**
  - Technical POC: Simon Pimblott:
    simon.pimblott@inl.gov or 208-526-7499

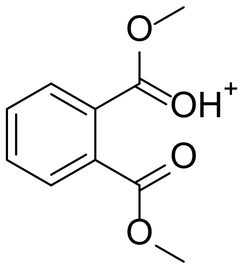


Characterization of Irradiated Organics: Identification

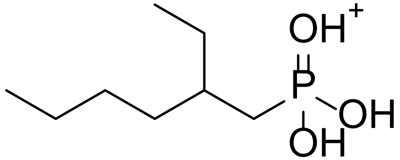
- **High Resolution High Mass Accuracy Mass Spectrometry**
  - Bruker micrOTOF-Q II:
    - quadrupole time-of-flight
    - Mass range: 3000 *m/z*
    - Resolution: ~15,000 (full-width half-max)
    - Mass Accuracy: ~±0.002 Da
    - ESI, APCI, APPI ion sources
    - Waters Acquity H-Class Plus UPLC front-end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



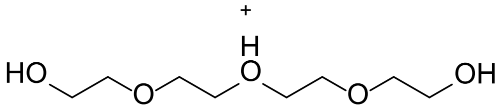
High Mass Accuracy Yields Molecular Formula



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

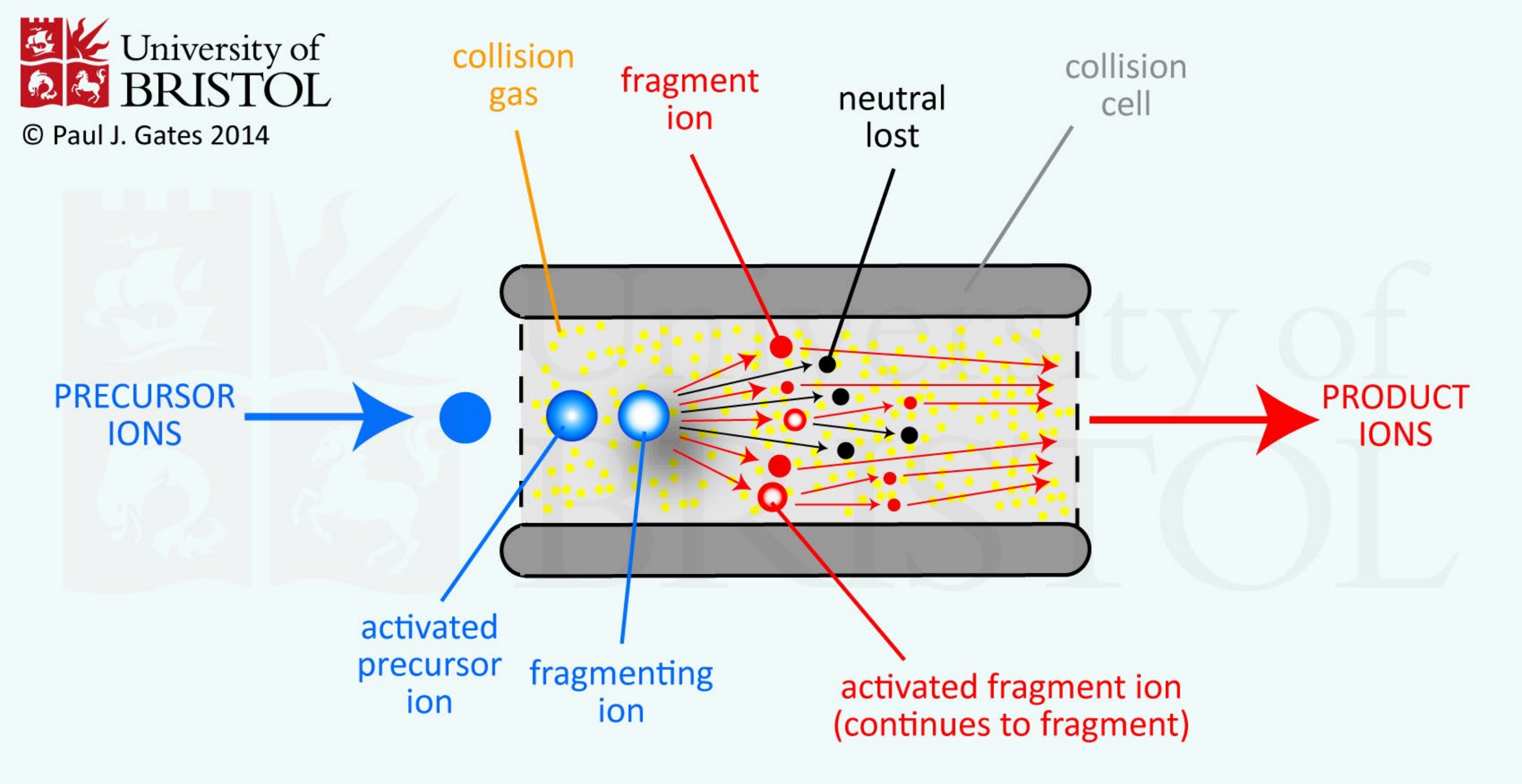


2-ethylhexyl phosphonic acid
$C_8H_{20}O_3P^+$
m/z: 195.1145



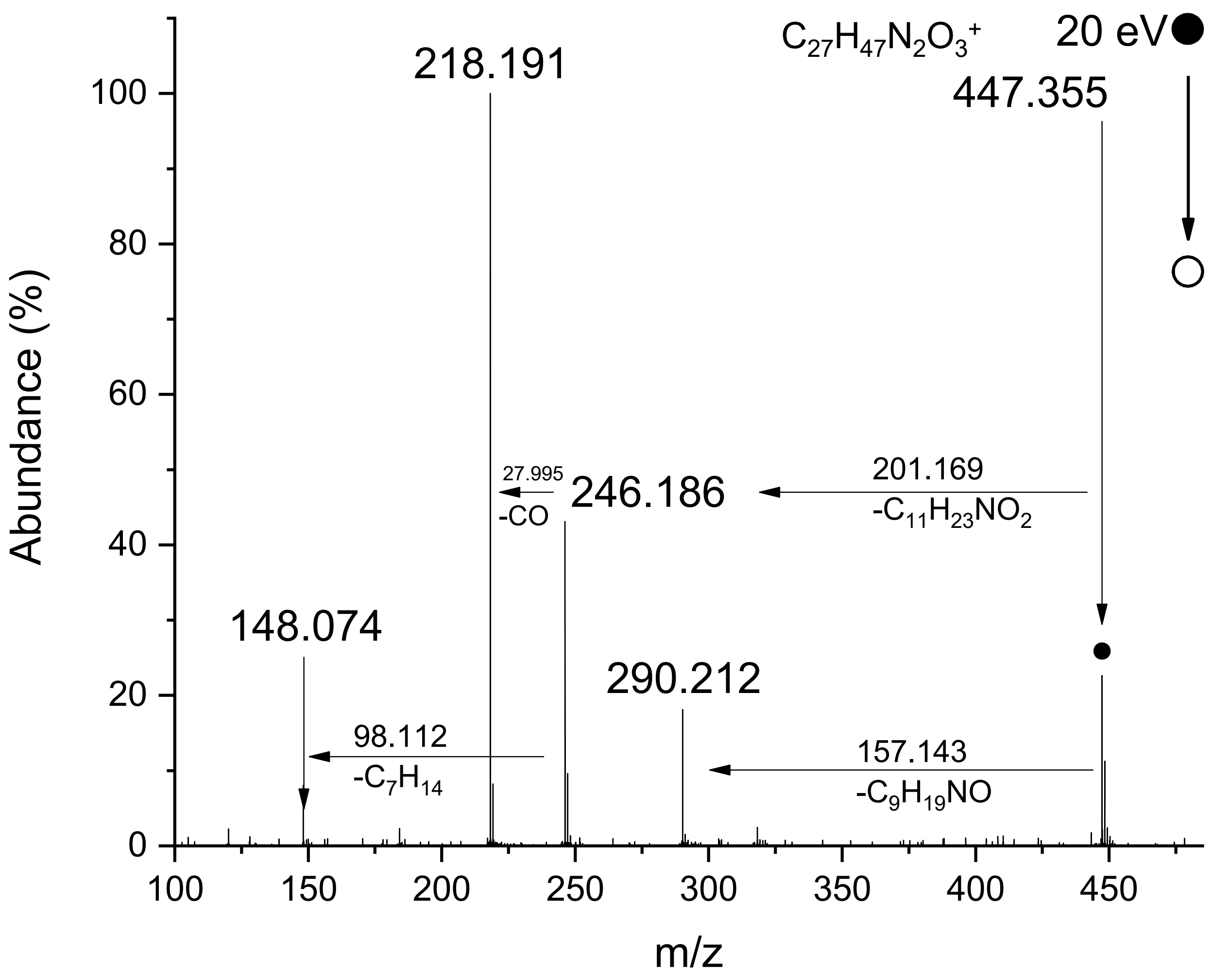
Polyethylene glycol (n=4)
$C_8H_{19}O_5^+$
m/z: 195.1227
Δm: +0.0082
+42 ppm

Collision-induced Dissociation (CID)

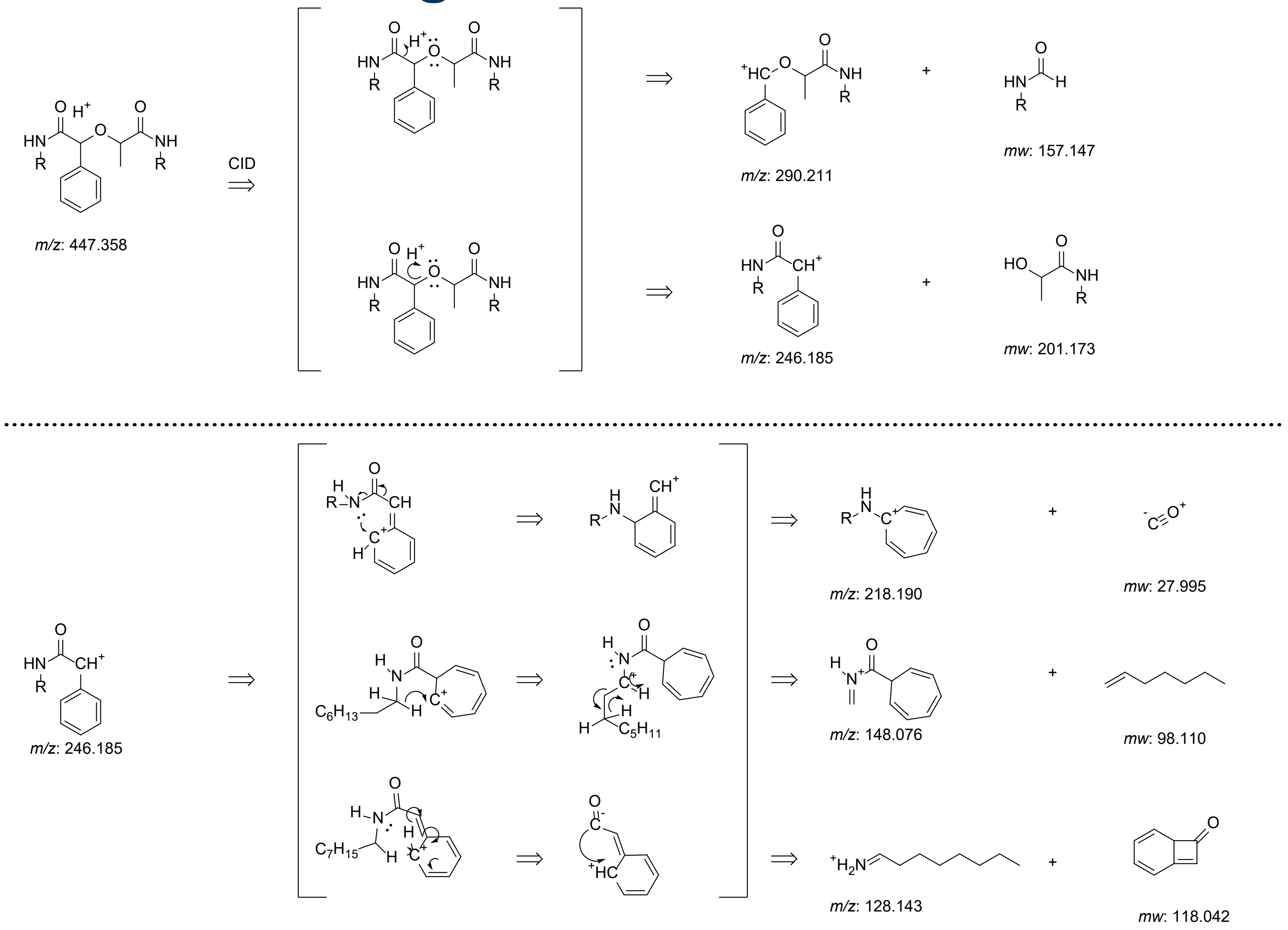


http://www.chm.bris.ac.uk/ms/cid.xhtml

Example for PhMeTODGA Cmpd 6

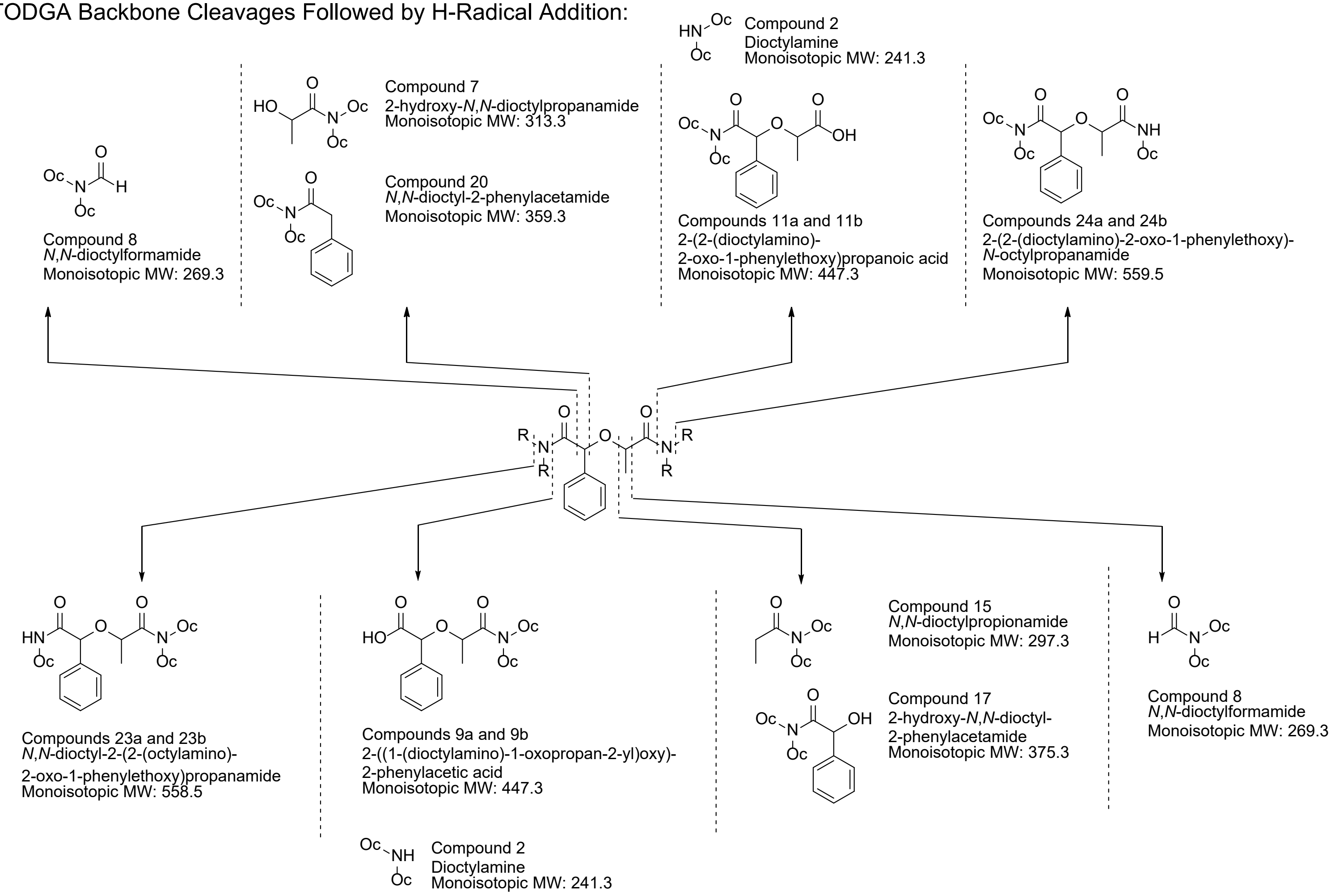


Proposed Gas-Phase Fragmentation Mechanisms



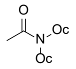
Complex Example: PhMeTODGA Degradation Product Analysis

PhMeTODGA Backbone Cleavages Followed by H-Radical Addition:

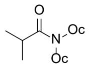


But wait, there's more……

PhMeTODGA Backbone Bond Cleavage Followed by CH_3-Radical Addition:

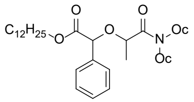


Compound 10
N,N-dioctylacetamide
Monoisotopic MW: 283.3

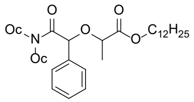


Compound 18
N,N-dioctylisobutyramide
Monoisotopic MW: 311.3

Dodecanol Esterification:

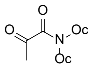


Compound 25
dodecyl 2-((1-(dioctylamino)-1-oxopropan-2-yl)oxy)-2-phenylacetate
Monoisotopic MW: 615.5

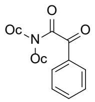


Compound 26
dodecyl 2-(2-(dioctylamino)-2-oxo-1-phenylethoxy)propanoate
Monoisotopic MW: 615.5

Oxidation of Primary PhMeTODGA Radiolysis Products:

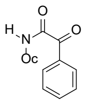


Compound 12
N,N-dioctyl-2-oxopropanamide
Monoisotopic MW: 311.3



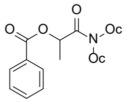
Compound 19
N,N-dioctyl-2-oxo-2-phenylacetamide
Monoisotopic MW: 373.3

Oxidation of Secondary PhMeTODGA Radiolysis Products:



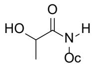
Compound 4
N-octyl-2-oxo-2-phenylacetamide
Monoisotopic MW: 261.2

Oxidation of OH-Radical Addition:

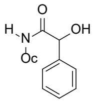


Compound 22
1-(dioctylamino)-1-oxopropan-2-yl benzoate
Monoisotopic MW: 417.3

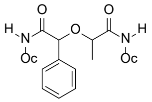
Primary PhMeTODGA Radiolysis Product Bond Cleavages Followed by H-Radical Additions:



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

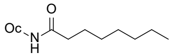


Compound 3
2-hydroxy-N-octyl-2-phenylacetamide
Monoisotopic MW: 263.2



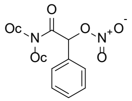
Compounds 6a and 6b
N-octyl-2-(2-(octylamino)-2-oxo-1-phenylethoxy)propanamide
Monoisotopic MW: 446.4

Unknown Formation Mechanism:

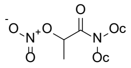


Compound 5
N-octyloctanamide
Monoisotopic MW: 255.3

Nitrate-Radical Additions:

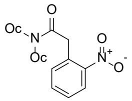


Compound 21
2-(dioctylamino)-2-oxo-1-phenylethyl nitrate
Monoisotopic MW: 420.3



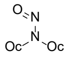
Compound 14
2-(dioctylamino)-2-oxo-1-phenylethyl nitrate
Monoisotopic MW: 358.3

Aromatic Nitration:



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

Nitrosamine Formation:



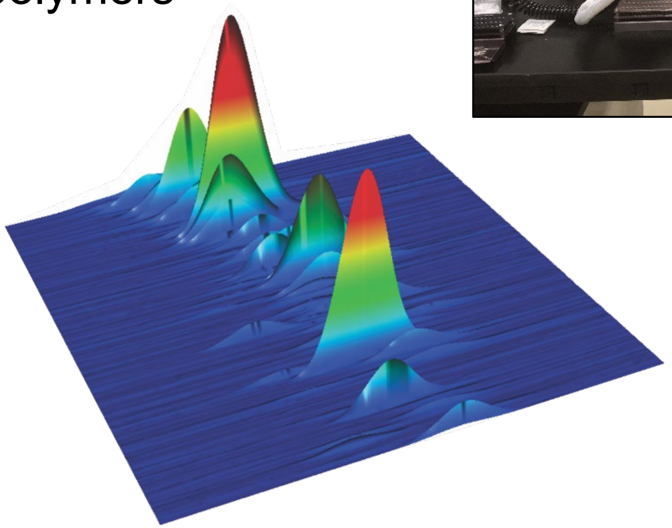
Compound 13
N,N-dioctylnitrous amide
Monoisotopic MW: 270.3

Characterization of Irradiated Organics: Identification

- **Gas Chromatography - Mass Spectrometry**
  - Shimadzu GC-TQ8040:
    - Triple-quadrupole
    - Mass range: 1250 *m/z*
    - Resolution: A little better than unit mass
    - EI, PCI, NCI ion sources
- **Some structural information from tandem MS**

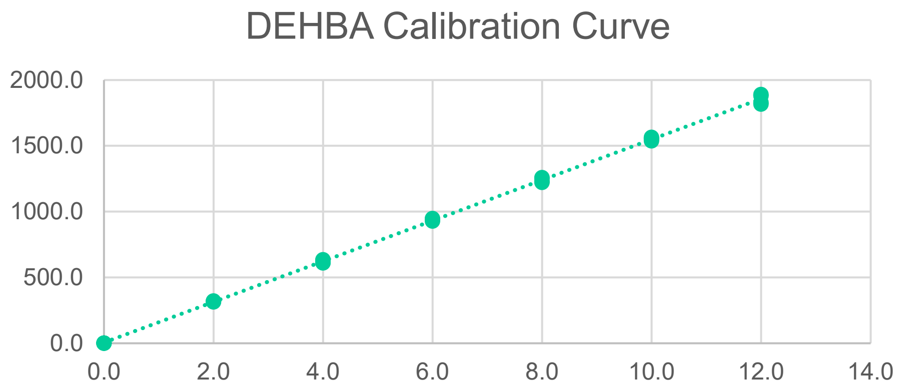
Characterization of Irradiated Organics: Identification

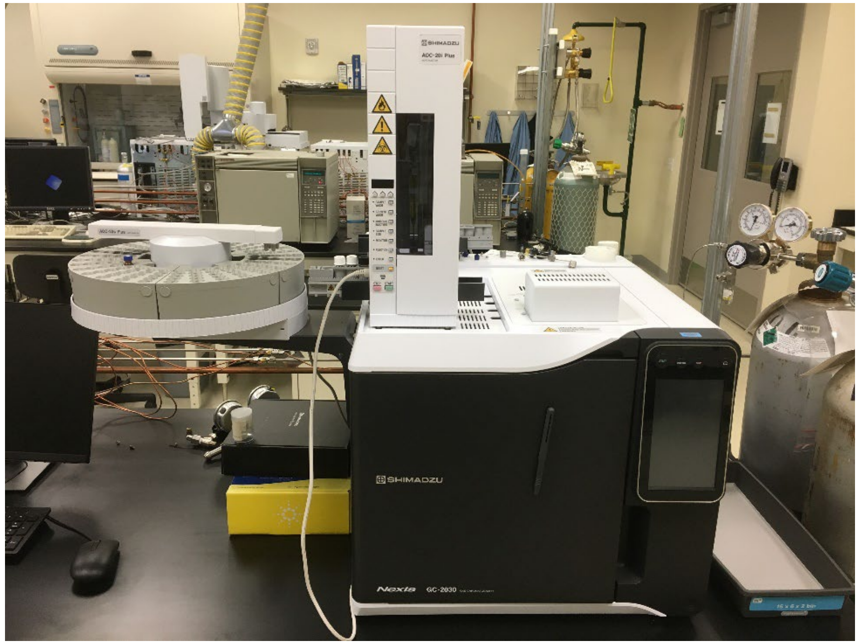
- **Two-Dimentional Gas Chromatography - Mass Spectrometry**
  - Leco Pegasus 4D GCxGC-ToF:
    - Time-of-Flight
    - Mass range: 1250 *m/z*
    - Resolution: unit
    - EI ion sources
- **CDS Analytical pyrolyser front end**
  - Good for large molecules like biomass, coal, polymers
- **Good for complex mixture analysis**



Characterization of Irradiated Organics: Quantification

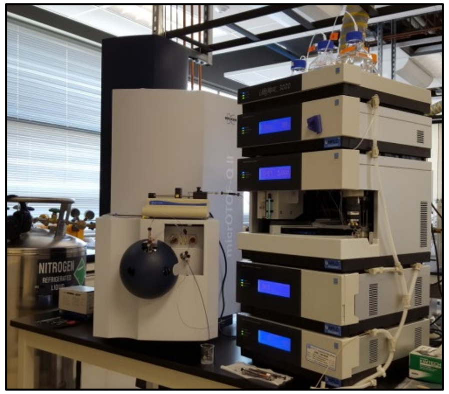
- **Gas chromatography with flame ionization detection (GC-FID)**
  - Very stable detector: High precision
    - Usually < 2% relative standard deviation





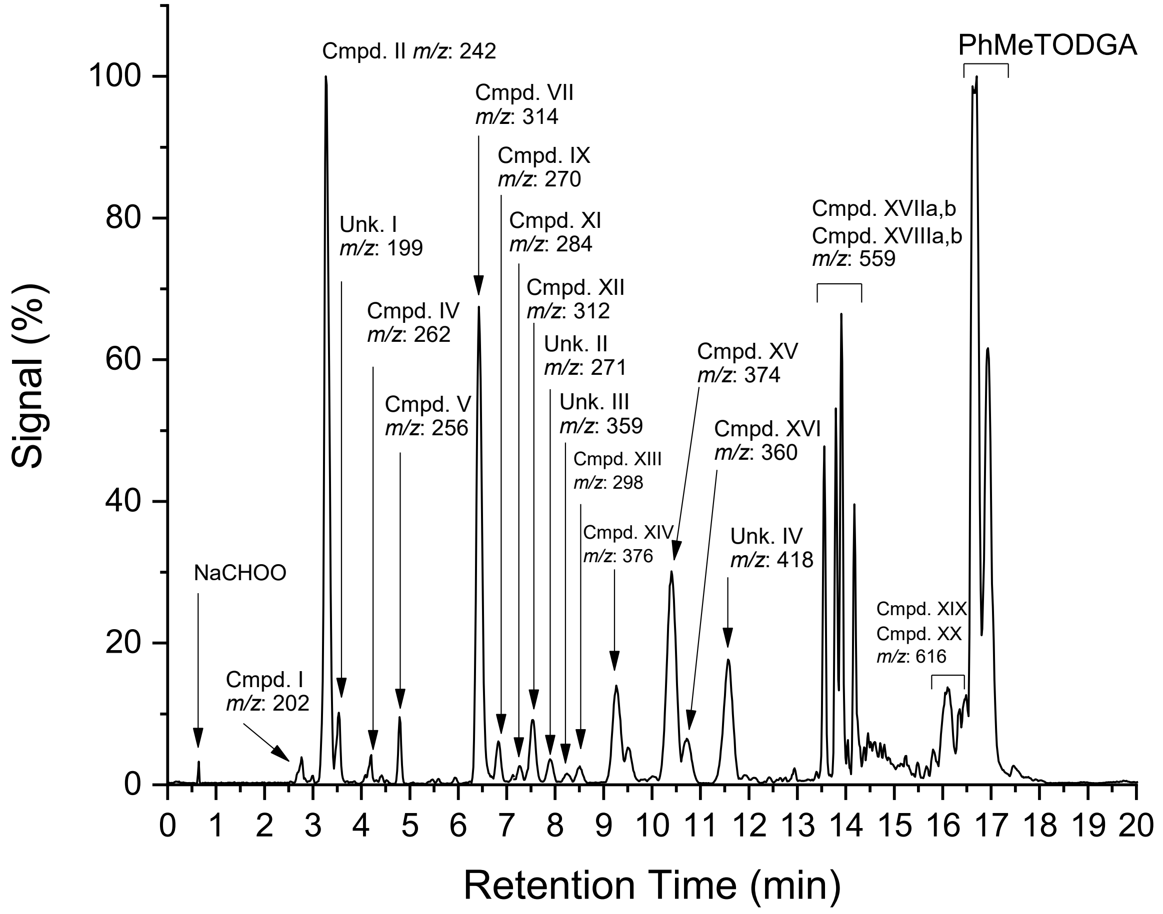
Emerging Capabilities

- **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



Emerging Capabilities, cont.....

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



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

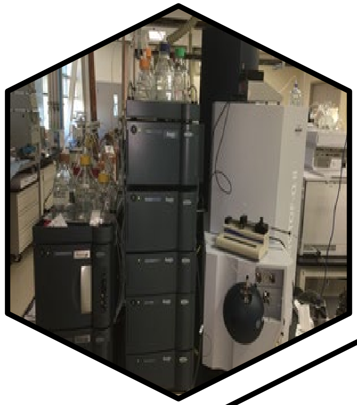
Travis Grimes

Elizabeth Parker-Quaife

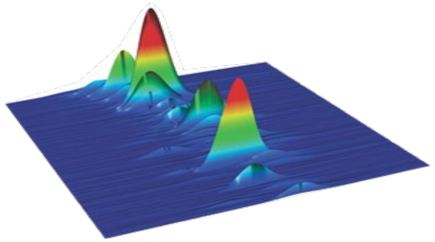
Corey Pilgrim

David Meeker

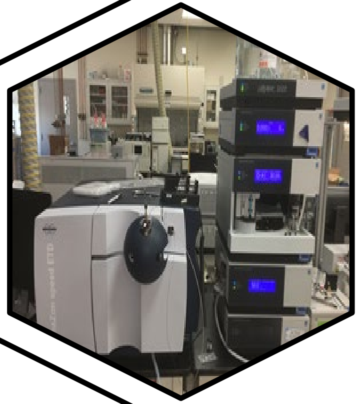
Molecular Chromatography and Mass Spectrometry Group



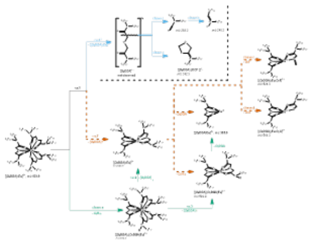
Molecular Identification and Quantification



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