INL/CON-25-84754-Revision-1

Overview of the Magnetic Resonance Capabilities at INL

June 2025

Corey David Pilgrim

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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Corey Pilgrim
Staff Scientist

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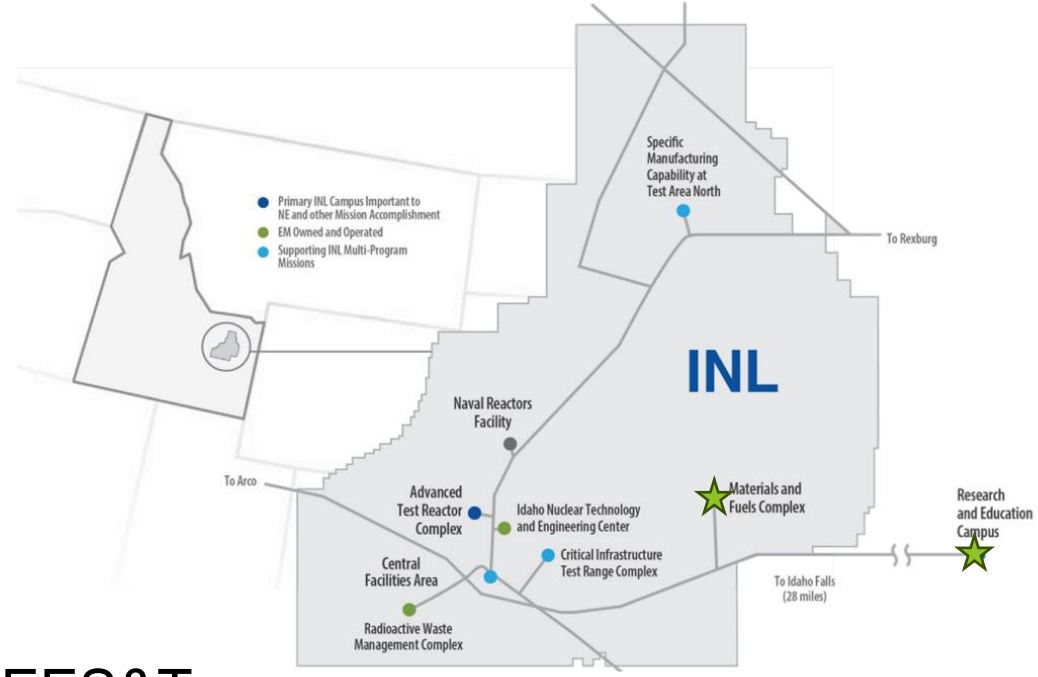
Battelle Energy Alliance manages INL for the
U.S. Department of Energy's Office of Nuclear Energy

Idaho National Laboratory

Brief Overview of INL

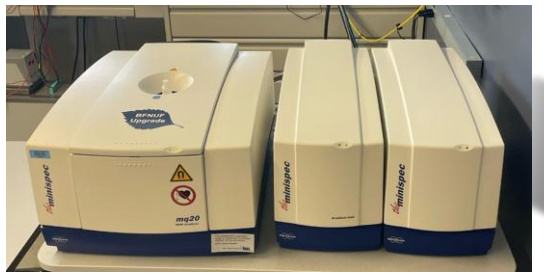
- Five main research directorates
  - Advanced Test Reactor (ATR)
  - Materials and Fuels Complex (MFC)
  - Nuclear Science and Technology (NS&T)
  - National and Homeland Security (N&HS)
  - Energy and Environment Science and Technology (EES&T)



- High-field instrumentation historically used by EES&T
  - Primarily for characterization of synthesized materials

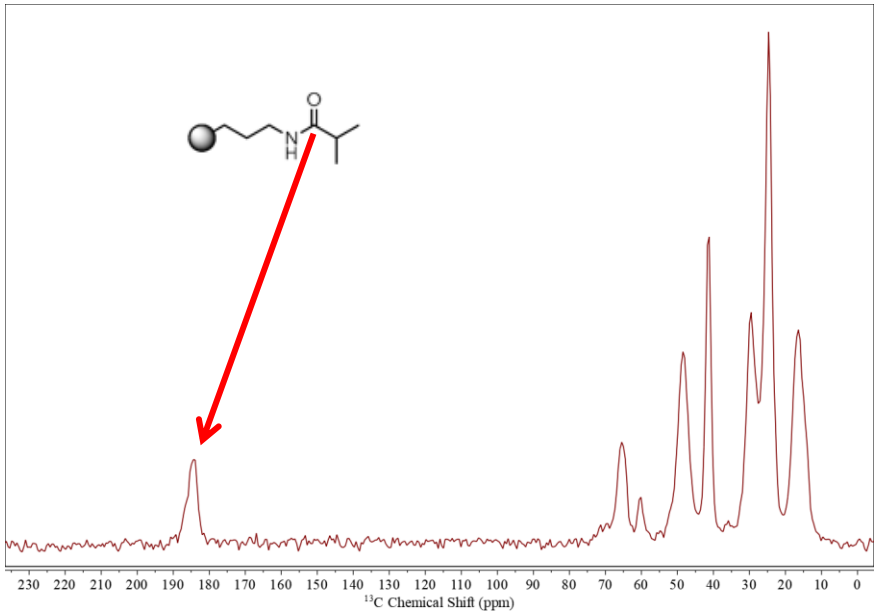
Available instrumentation at INL

- Five (5) spectrometers at INL
  - **NMR:**
    - 600 MHz (14.1T) *Bruker AVANCEIII* system
    - 400 MHz (9.4T) *Bruker AVANCEIII* system
    - 20 MHz (0.47T) *Bruker minispec* system
    - 90 MHz (2.1T) *Anasazi* system
      - Only NMR in a radiological facility
  - **EPR:**
    - X-Band (0.65T) *Bruker ESR5000* system
      - Housed with our ^{60}Co irradiator

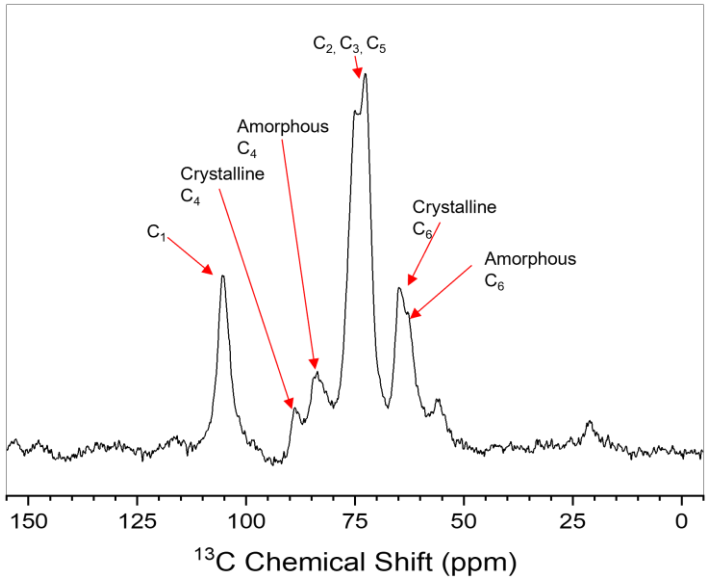


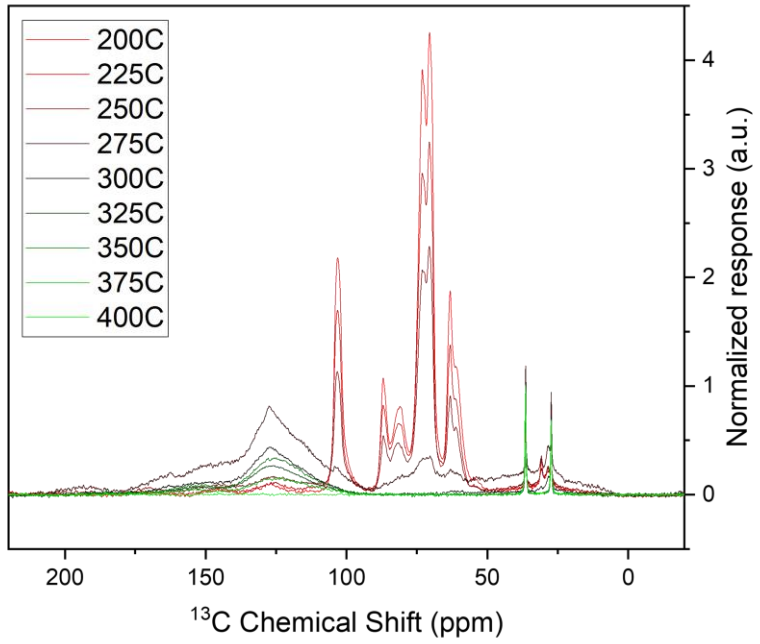
Typical magnetic resonance experiments at INL

- Heavy focus on solution-state NMR
  - Compositional and purity analyses of new compounds
  - Determination of the thermodynamics and bonding character of metal-ligand complexes in solution
  - Degradation analysis of materials
    - Thermal and radiolytic
  - Fast-turnaround analyte quantification
  - Relaxometric analysis of water content
- Building a portfolio for solid-state NMR
  - Still highly useful for purity analysis and confirmation of successful synthesis
  - Torrefaction of biomass



Biomass characterization using $^{13}C\{^{1}H\}$ NMR

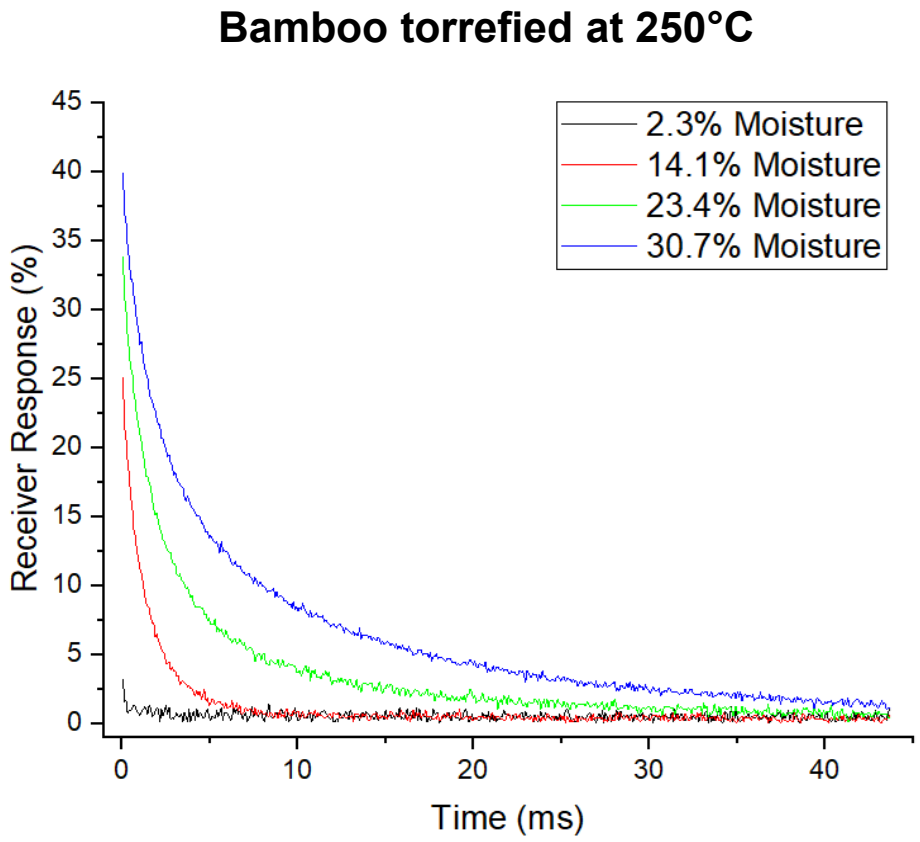




- A continuing series of various biomass materials and associated chars/torrefactions have been run using solid-state NMR
- Cellulose has a distinct ^{13}C shift pattern (top)
  - Sensitive to crystalline environments
- Used to study the impact of the torrefaction process on the biomass, and to understand changes in the material structure at varying temperature (bottom)

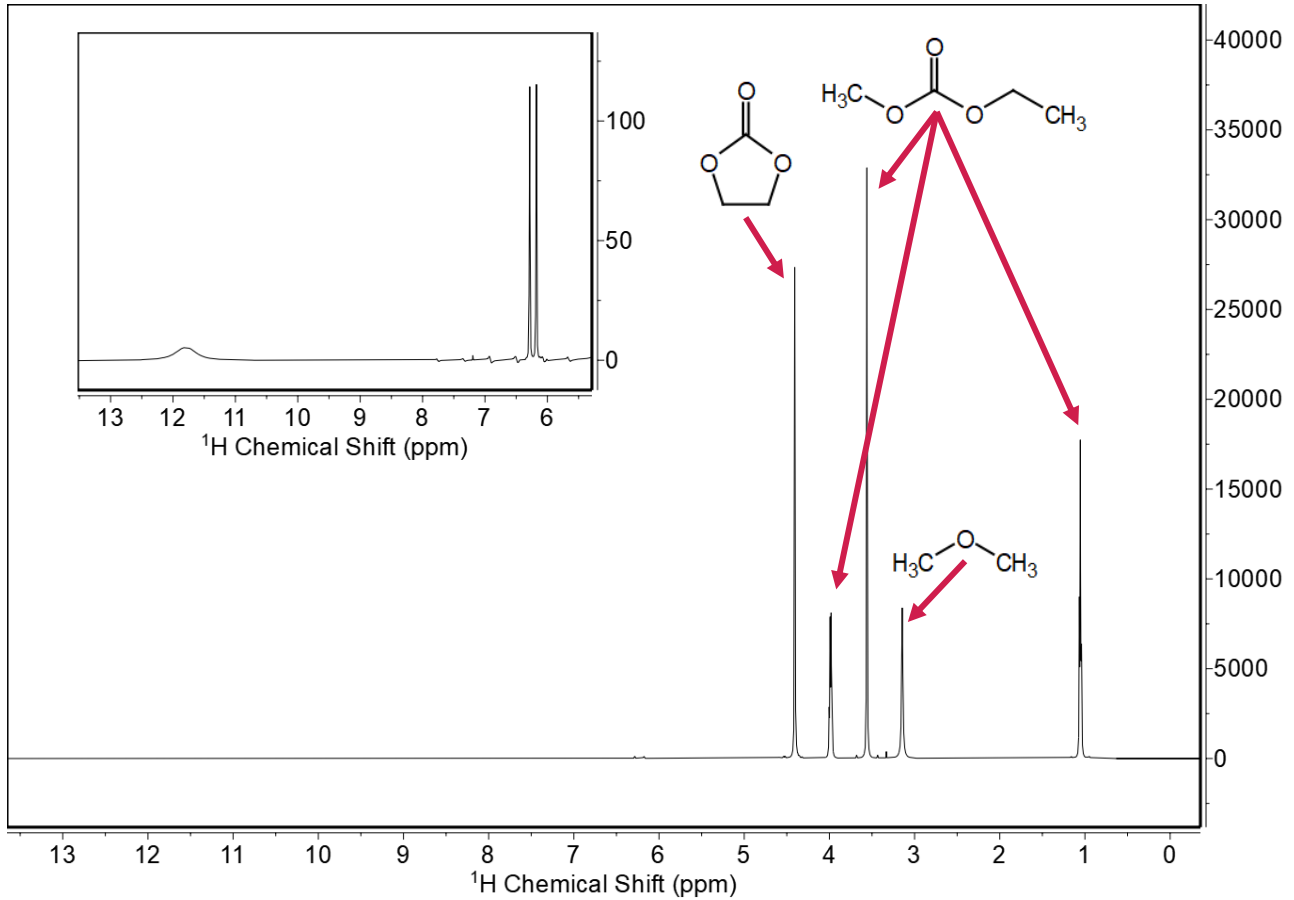
Determination of water content in solid biomass via relaxometry

- Low-field spectroscopy, focusing on the proton signal of water in torrefied biomass samples
- Able to ascertain bulk vs. adsorbed water
- *Carr-Purcell-Meiboom-Gill* (CPMG) pulse sequence used
- Deconvolution and population analysis by exponential fitting
  - Typically multicomponent in nature



Characterization of extracted electrolytes from spent battery cells

- The project aims to recycle electrolyte materials via a proprietary dimethyl ether extraction process
- Examining the uptake of ethylene carbonate (EC), ethyl methyl carbonate (EMC), $LiPF_6$, and assorted degradation products in solution



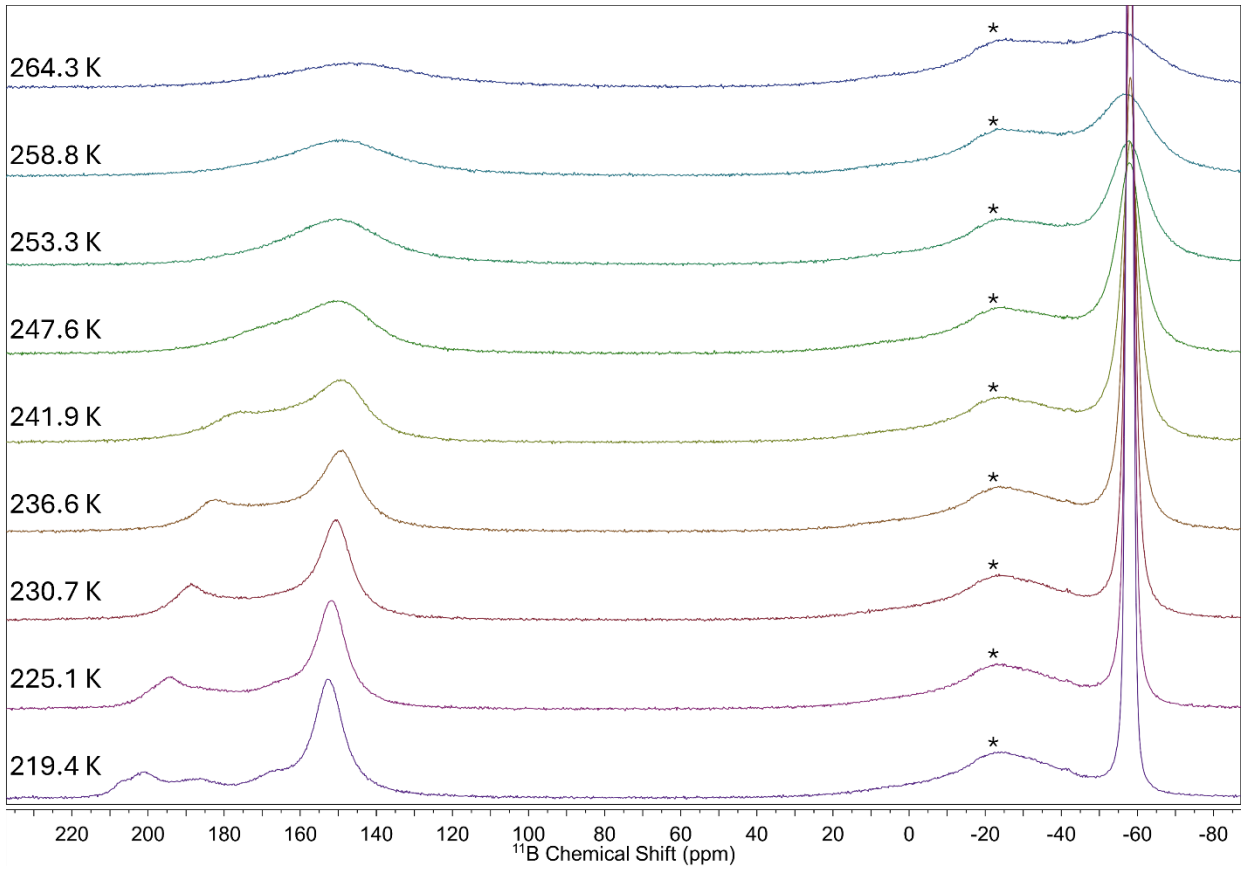
Understanding the speciation of Nd-borohydrides in a non-aqueous environment

- Metathesis reactions of $Nd(BH_4)_3$

$$LiBH_4 + NdCl_3 \longrightarrow LiCl_{(s)} + Nd(BH_4)_3$$

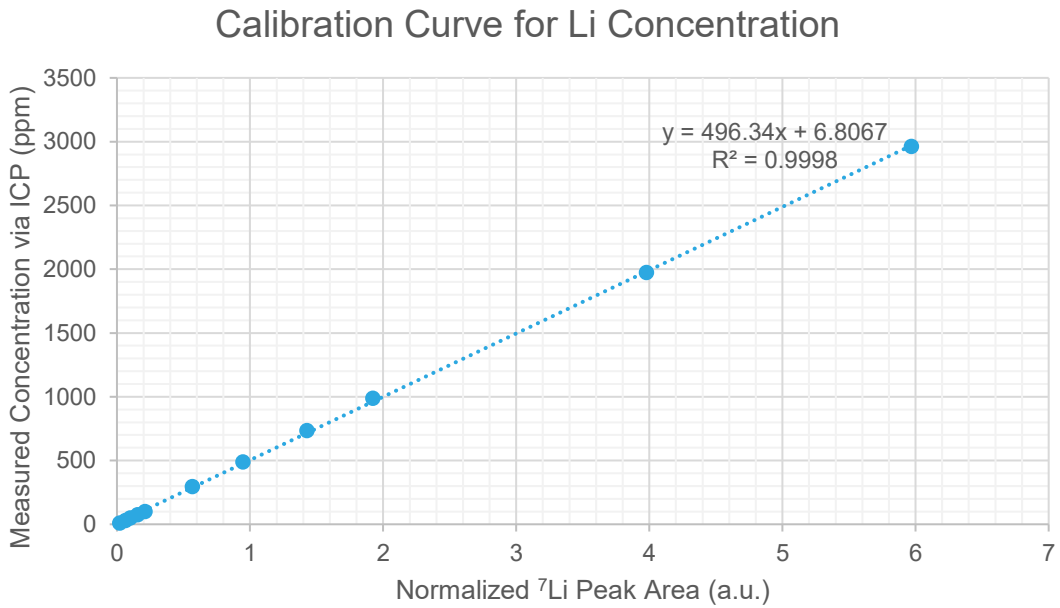
- Paramagnetic Nd^{3+} can be problematic, but lowering the temperature helped

- Multiple ^{11}B species seen in solution (corroborated by ^{1}H spectra as well)
  - Likely mix of $Li_x[Nd(BH_4)_y(Cl)_z]^{3+x-y-z}$ species in solution



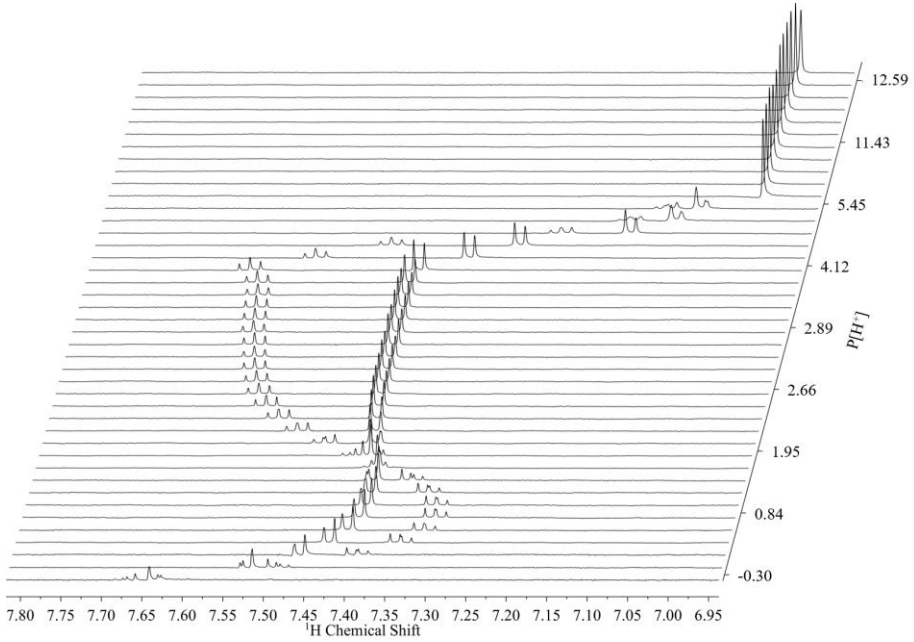
Short experiments for high-speed quantification of ^{7}Li and ^{23}Na in critical material extractions

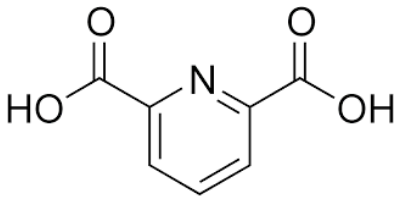
- Needed a fast-throughput quantification technique for measuring unextracted Li^{+} from brines
- Due to the nature of the project, ICP was run by collaborators at another lab
- ^{7}Li and ^{23}Na NMR proved highly useful for quick analysis of samples during extraction runs
  - Used single-scan ^{7}Li experiments to decrease the analysis time
  - Mixture of LiCl and NaCl in D_2O coaxial insert as reference standard

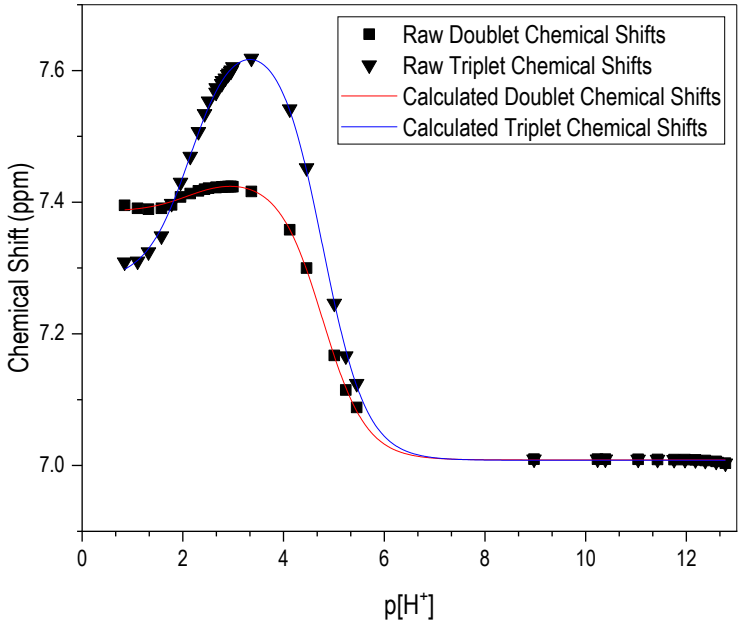


Determination of thermodynamic parameters in solution

- Titration of chelators used in the nuclear fuel cycle to extract acid-dissociation constants (pK_a)
  - Dipicolinic acid (DPA) shown as an example
- Also useful for stability constant determination of metal-ligand complexes

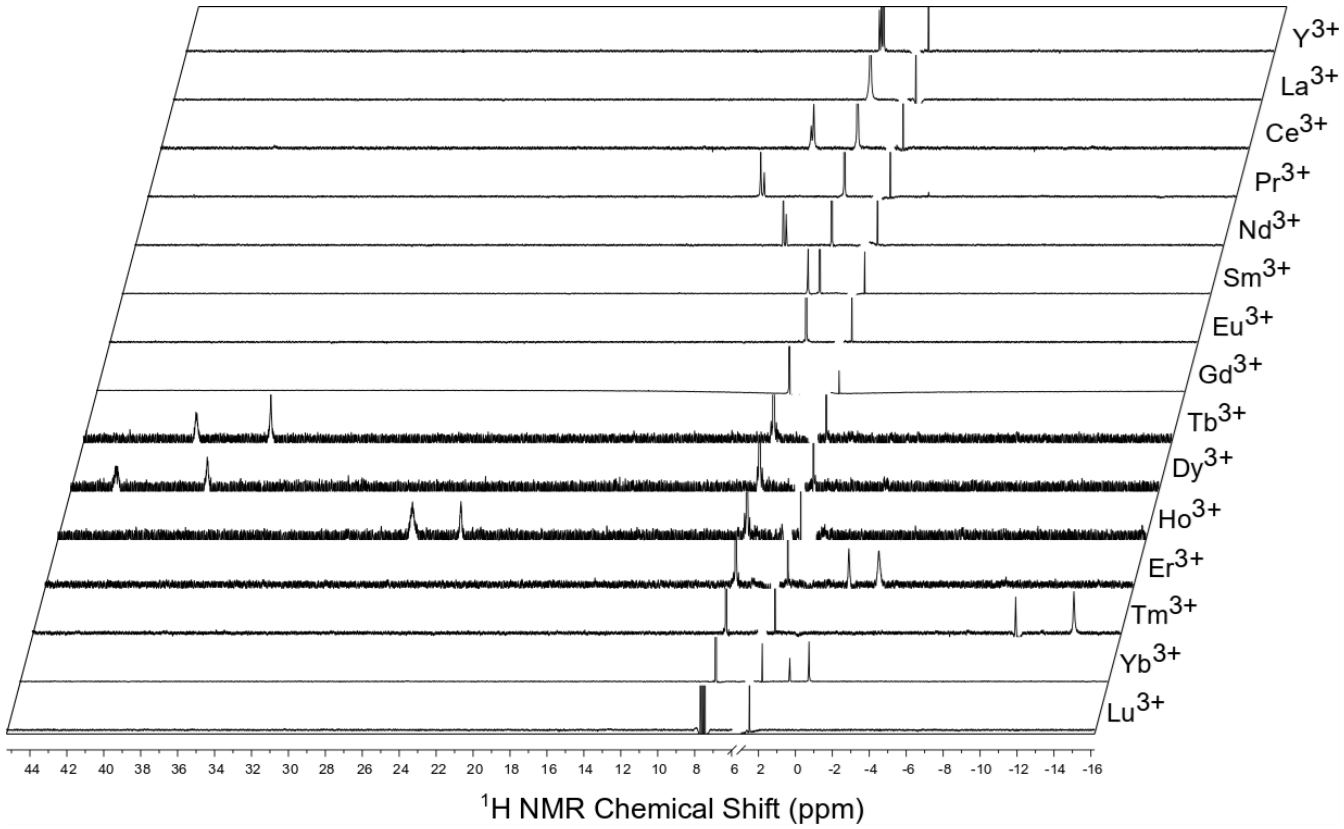




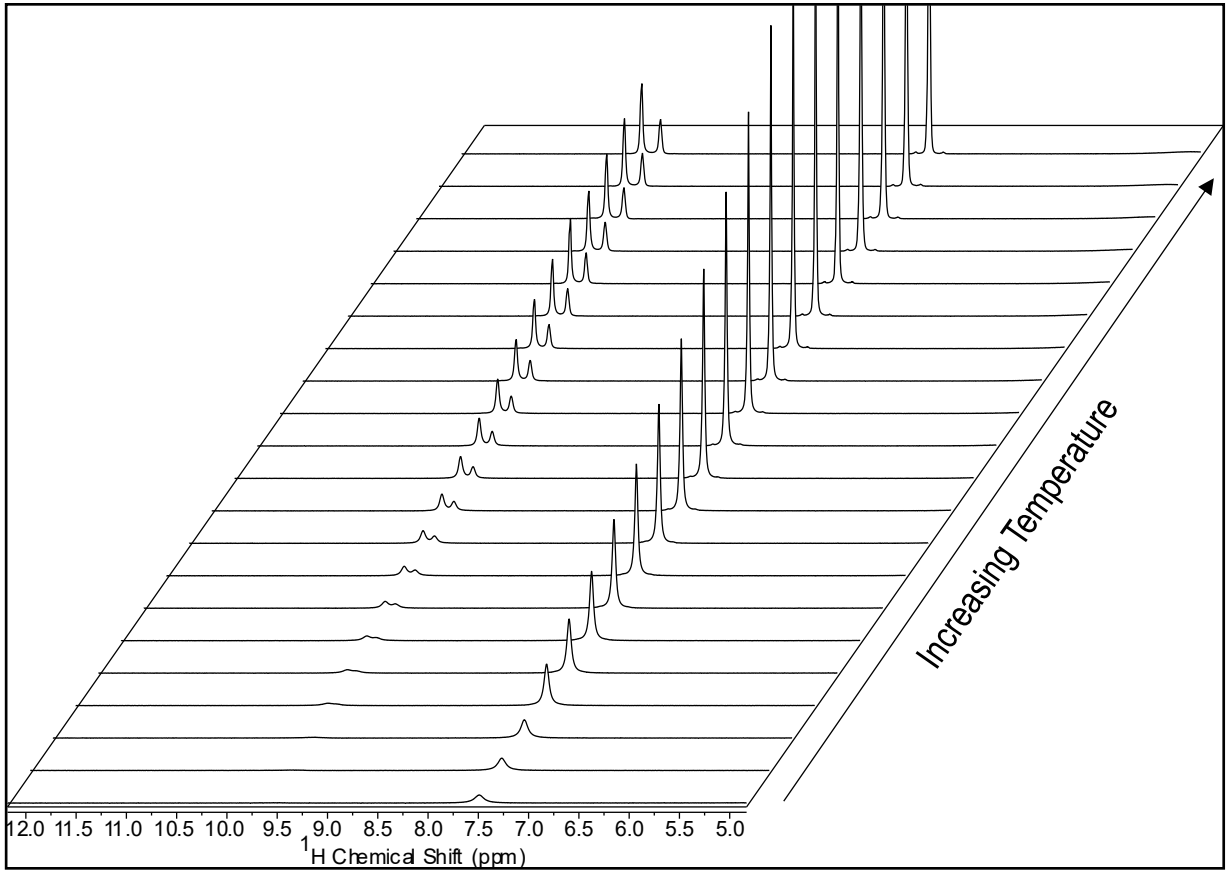


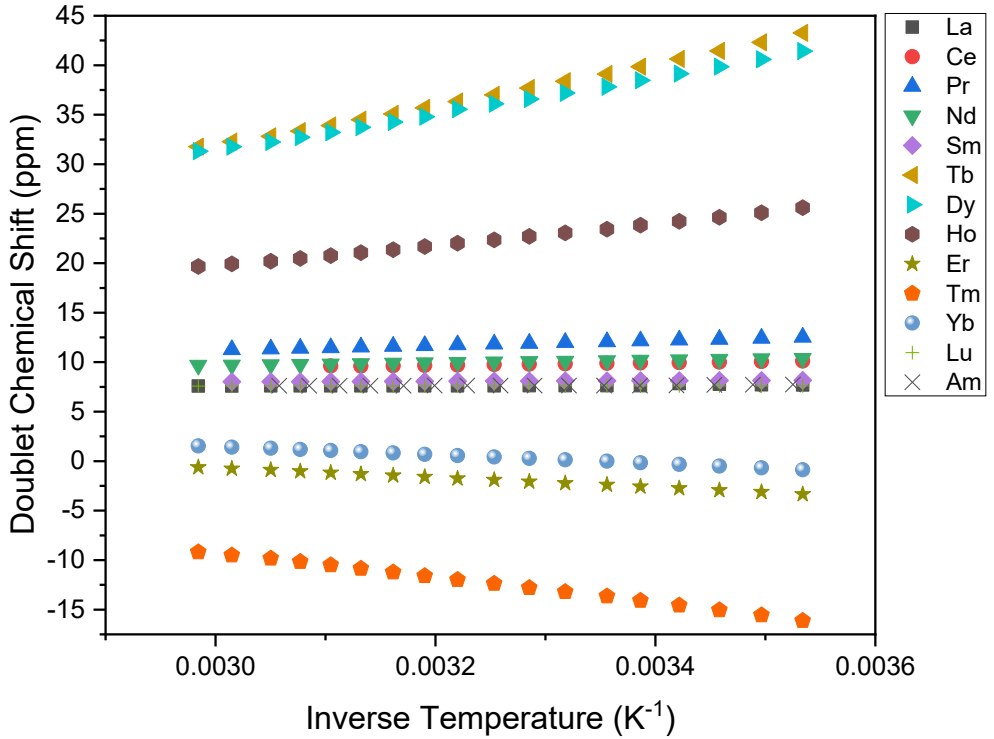
Probing the bonding environment of *f*-block elements in solution

- Measurement of lanthanide-induced shifts (LIS) and actinide-induced shifts (AIS) of ligand-metal complexes in solution
- LIS have been characterized since the 1970s; AIS characterization is lagging considerably
- Paramagnetic centers cause shifts through contact (Fermi contact, FCS) and through space (pseudocontact, PCS)
  - $\delta^{hf} = \delta^{para} - \delta^{dia} = \delta^{pcs} + \delta^{Fcs}$
- FCS and PCS can be teased out by variable temperature studies

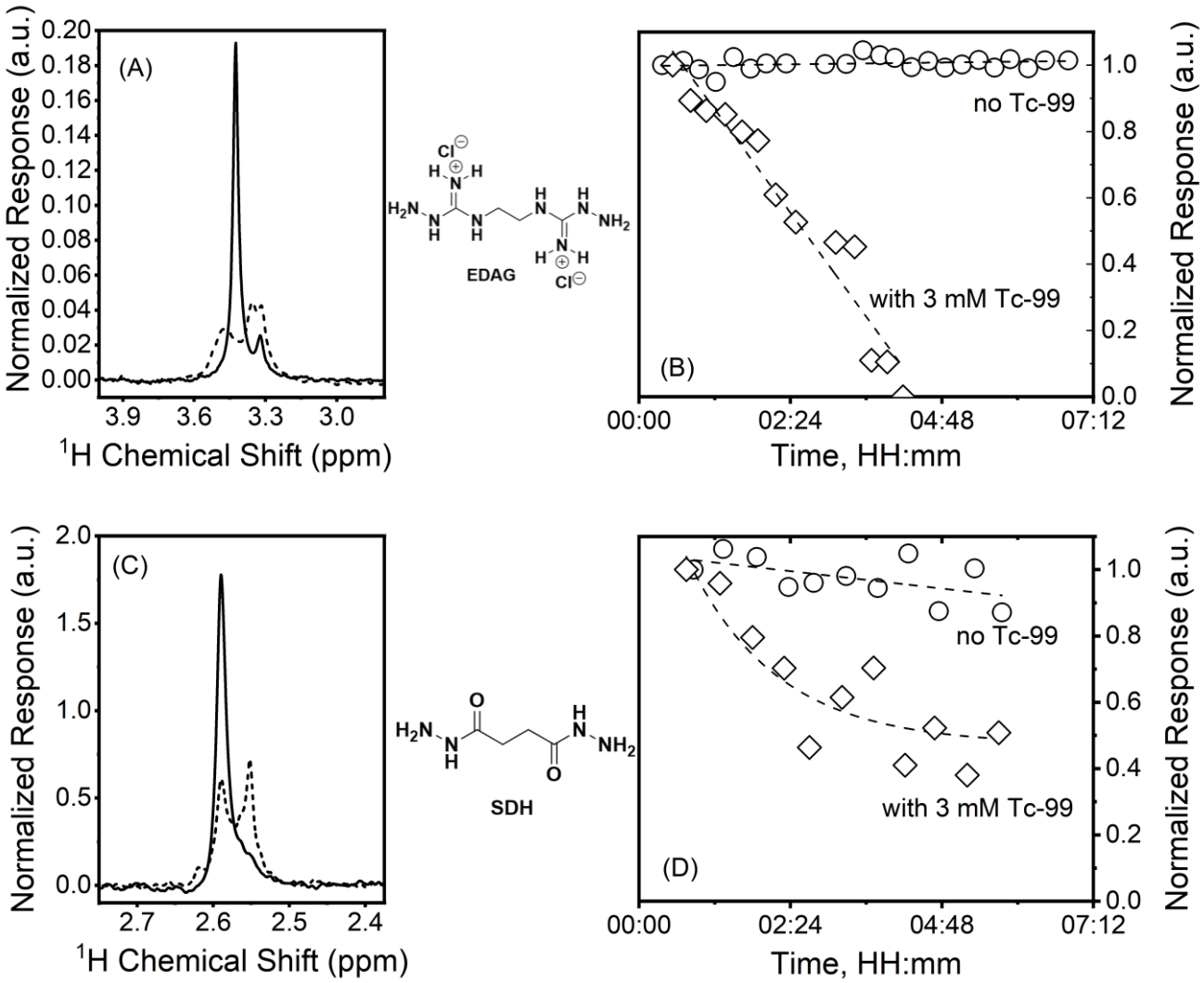


Probing the bonding environment of *f*-block elements





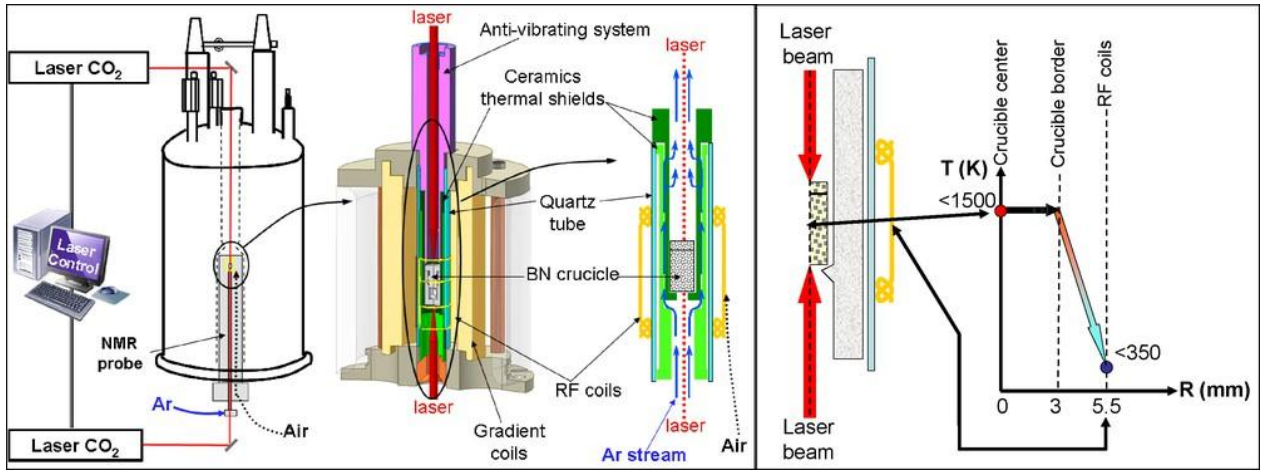
Degradation of proposed technetium holdback reagents



- Proposed holdback reagents for ^{99}Tc during reprocessing (PUREX-type)
  - Guanidinium or hydrazide based
- Ligands with Re showed stability
- However, ^{99}Tc showed an active reaction (bubbling in FEP liners)!
  - Sadly, ^{99}Tc NMR showed no deviation from a single peak (TcO_4^-)
  - Forced to follow degradation via ^{1}H NMR.

Future directions

- Continue to grow usage of the instruments within NS&T, N&HS, and EES&T
- Look for interesting projects via which to grow capabilities
  - Work with pyrochemical/molten salts (high-temperature probe?)
  - Characterization of complexes in ionic liquids
  - Work with quantum materials through C-QAST at INL



Rollet, A.-L.; Sarou-Kanian, V.; Bessada, C. Self-diffusion Coefficient Measurements at High Temperature by PFG NMR C. R. Chim. **2010**, 13, 399– 404 DOI: 10.1016/j.crci.2009.11.005

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  - Office of Nuclear Energy
  - Office of Energy Efficiency and Renewable Energy
    - Bioenergy Technologies Office
    - Vehicle Technologies Office

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