



ADVANCED REACTOR SAFEGUARDS & SECURITY

Hybrid MC&A Tools for MSRs

Multimodal Sensor Assessment in MSR-Relevant Flow System

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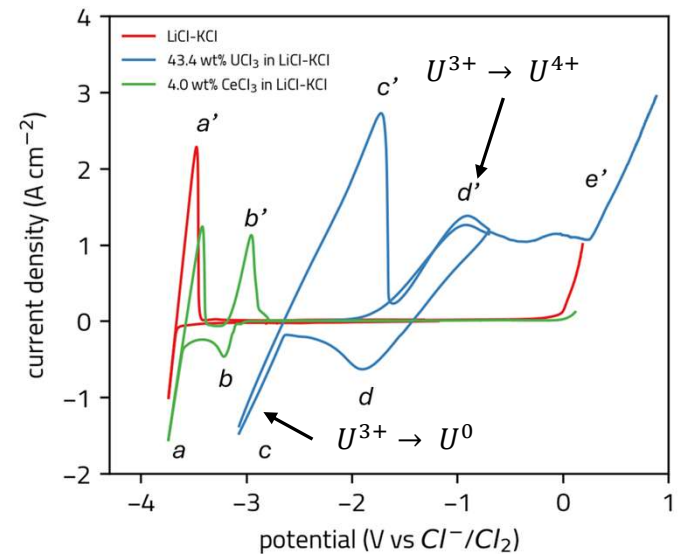
Hybrid MC&A approach for molten salt reactors



Combining voltammetry and optical methods improves actinide measurements in mixed salts.

Technique	Advantages	Limitations
Voltammetry	Robust; sensitive to redox-active species; speciation and kinetics	Less effective for minor actinides in complex, high-concentration salts
Raman spectroscopy	Non-contact; sensitive to bonding and speciation	Weak signal; fluorescence; matrix effects; not ideal for all species
Laser induced breakdown spectroscopy (LIBS)	Non-contact; elemental and multi-element analysis	Strong matrix effects; shot-to-shot variability; self-absorption

- **Voltammetry measures UCl_3 concentration in salt.**
- **Optical methods target minor actinides using ratiometric analysis.**
- **Combined measurements improve performance in complex, mixed-actinide salts.**



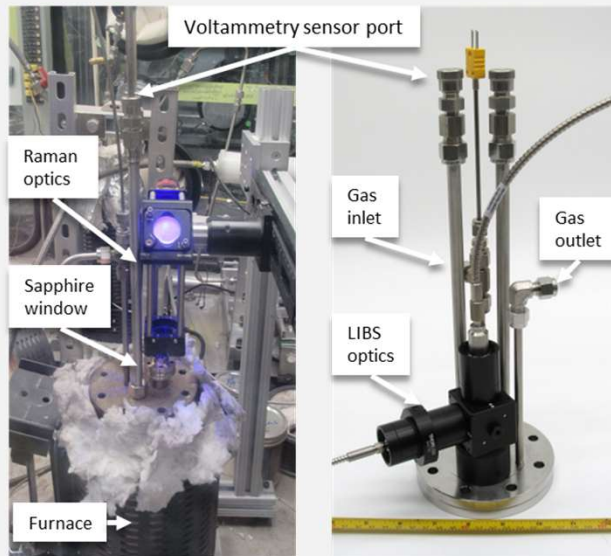
Voltammetry of LiCl-KCl with UCl_3 and CeCl_3 at 550 °C.

Hybrid MC&A tool integration into MSR-representative environments

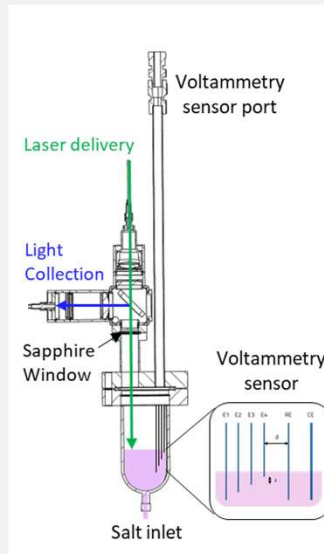


Hybrid voltammetry and optical tools

Voltammetry and optical sensor flange



Online salt sampler concept



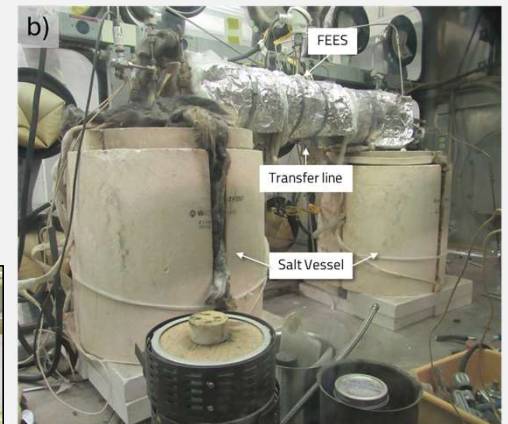
- Supports voltammetry, Raman spectroscopy, and LIBS.
- Can be coupled to flow systems and salt samplers.

MSR-representative environments

Engineering-scale UCl_3 salt production system (5 liters)



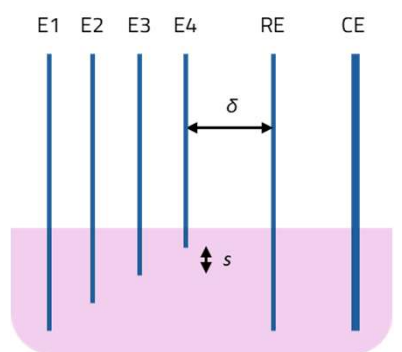
Radiological flow systems
Modular flow instrumentation testbeds(MFIT)



- Sensors will be deployed in engineering-scale and radiological molten salt systems.
- Salts containing >70 wt% UCl_3 , operated at 450–800 °C, with and without surrogate fission products.

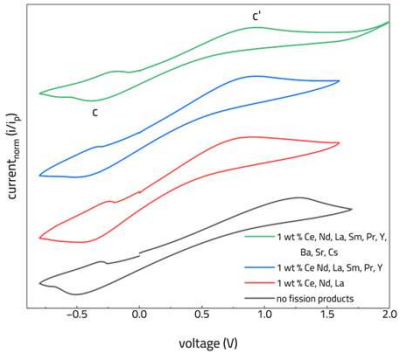


FY25 voltammetry measured UCl_3 accurately in high-loading salts with fission product surrogates

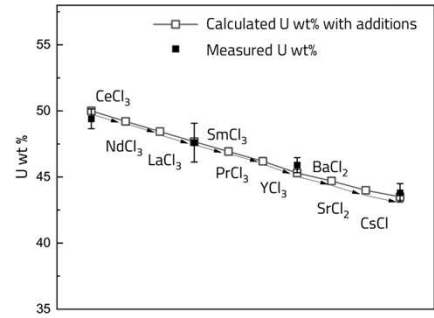


Multielectrode array voltammetry sensor

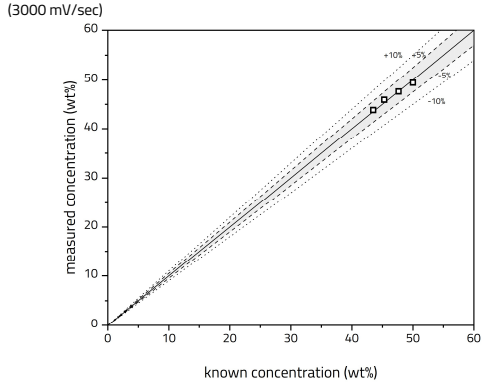
- ANL previously developed methods to measure UCl_3 in salts containing >70 wt% UCl_3 .
- Surrogate fission products Rb, Sr, Y, Zr, Ba, La, and Ce remain soluble and do not prevent uranium quantification.
- The mean absolute relative error for uranium concentration was 0.8%, even with up to nine surrogate fission products present.



CVs of 72 wt% UCl_3 -LiCl-KCl with various additions of Ce, Nd, La, Sm, Pr, Y, Ba, Sr, & Cs. All species added as 1 wt %.

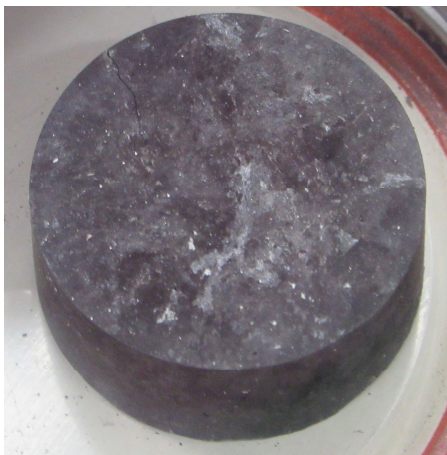


Measured and calculated concentrations of U in 72 wt% UCl_3 -LiCl-KCl with sequential additions of surrogate fission products.

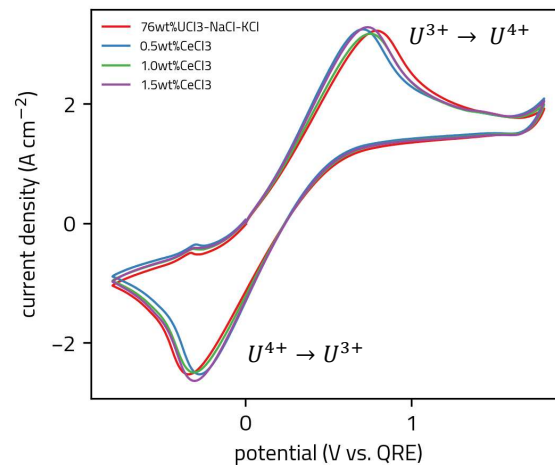


Measured and known uranium concentrations during additions of fission product surrogates.

FY26 voltammetry measured U in 76 wt% UCl_3 salt with 1% random uncertainty during CeCl_3 additions



76 wt% UCl_3 -NaCl-KCl (52.5 wt% U)



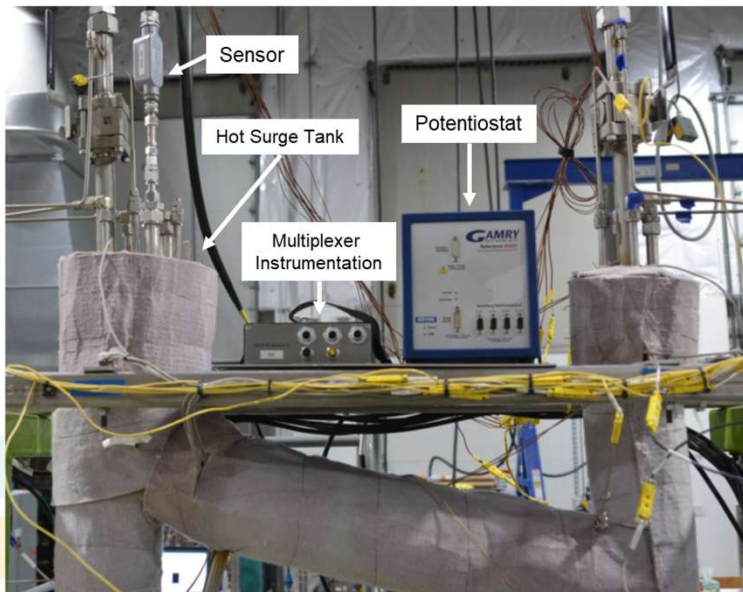
U(III)/U(IV) current response during additions of CeCl_3 fission product surrogates. (3000 mV/sec)



Salt compositional analysis to be performed in Q3 to confirm sensor total uncertainty.

- Measurements were performed in 76 wt% UCl_3 -NaCl-KCl salt containing 52.5 wt% U.
- The relative random uncertainty in uranium concentration was 1%.
- Salt compositional analysis in Q3 will confirm systematic and total uncertainty.

Voltammetry sensor deployments at TerraPower LLC's natural circulation (NC) loop



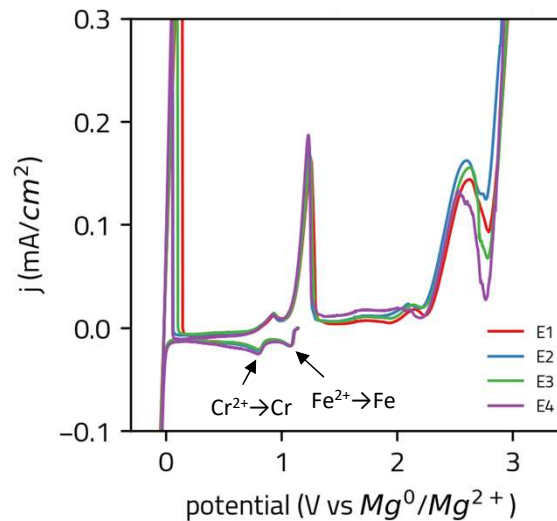
TerraPower NaCl-MgCl₂ natural circulation loop

- In FY25, ANL performed bench-scale measurements of chromium chloride in TerraPower's coolant salt.
- In FY26 Q1, TerraPower completed a 476-hour molten NaCl-MgCl₂ natural circulation loop test.
- ANL's Multielectrode Array Voltammetry Sensor (MAVS) was deployed in the hot surge tank.
- Loop salt measurements
 - Salt level
 - Redox potential
 - Corrosion product concentration

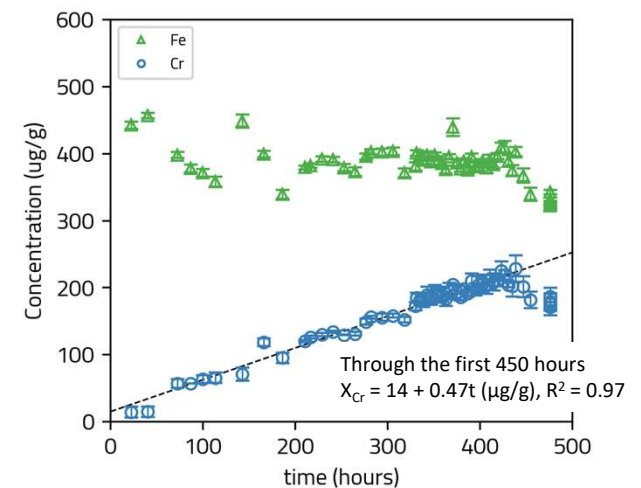
Cr²⁺ increased linearly during the first 450 hours of NC loop operation



- Corrosion caused Cr²⁺ concentration to increase linearly during the first 450 hours.
- Random error was 5.1% for Cr²⁺ and 1.5% for Fe²⁺.
- Overlap with Fe²⁺ reduced Cr²⁺ precision.
- Multiple corrosion products are an application for hybrid voltammetry-spectroscopy approaches.

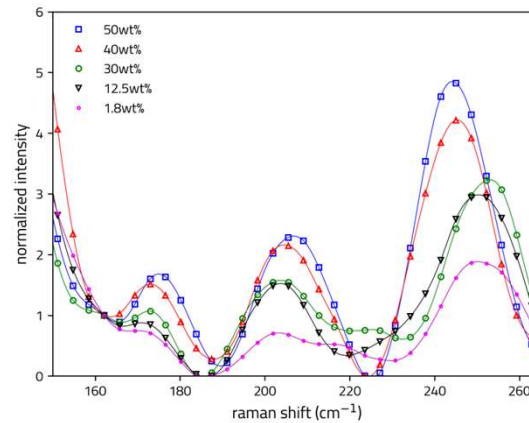


Loop surge tank voltammograms after 476 hours. (500 mV/sec)



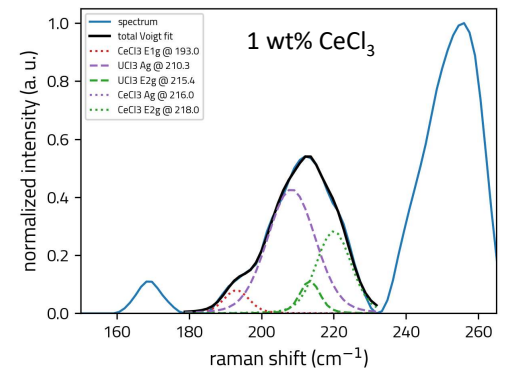
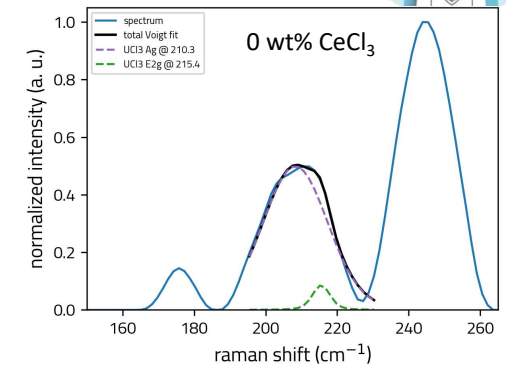
Concentration of Fe and Cr in NaCl-MgCl₂.

Raman spectroscopy resolved UCl_3 and CeCl_3 features at room temperature



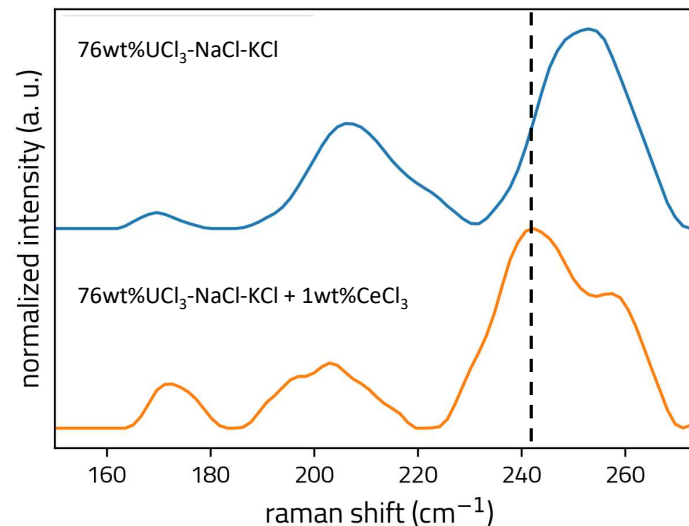
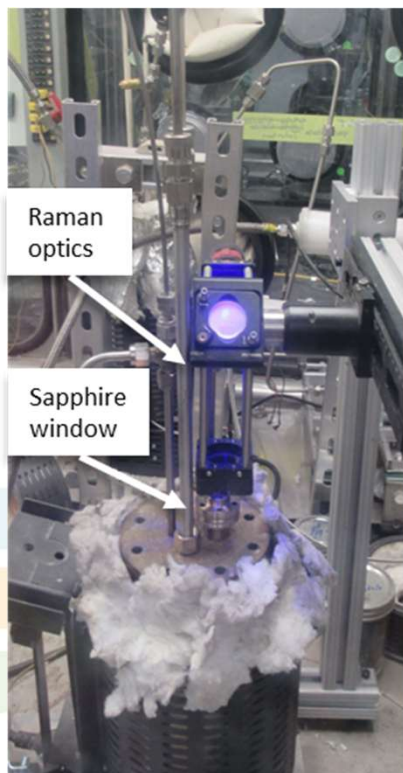
Raman spectra of LiCl-KCl with various U concentrations at room temperature.

- Raman spectra were collected in an argon glovebox using a 457 nm, 300 mW laser.
- UCl_3 bands were observed across a wide range of salt compositions.
- UCl_3 and CeCl_3 bands matched reported vibrational modes for solid salts.



Raman spectra of 76wt% UCl_3 -NaCl-KCl at room temperature.

Online Raman spectroscopy detected CeCl_6^{3-} features in molten UCl_3 salt



Raman spectra of 76 wt% UCl_3 -NaCl-KCl with and without addition of CeCl_3 at 550 °C.

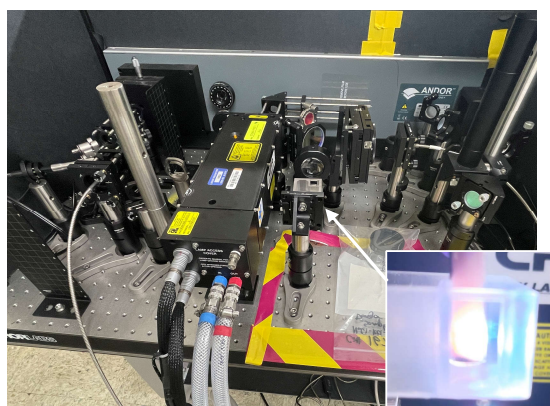
- Online Raman measurements were performed at 550 °C through a sapphire window in an argon glovebox.
- A band at 242 cm^{-1} is consistent with octahedral CeCl_6^{3-} .
- Instrument upgrades planned for Q3 will improve low-shift resolution.

Room-temperature LIBS resolved U and Ce emission lines

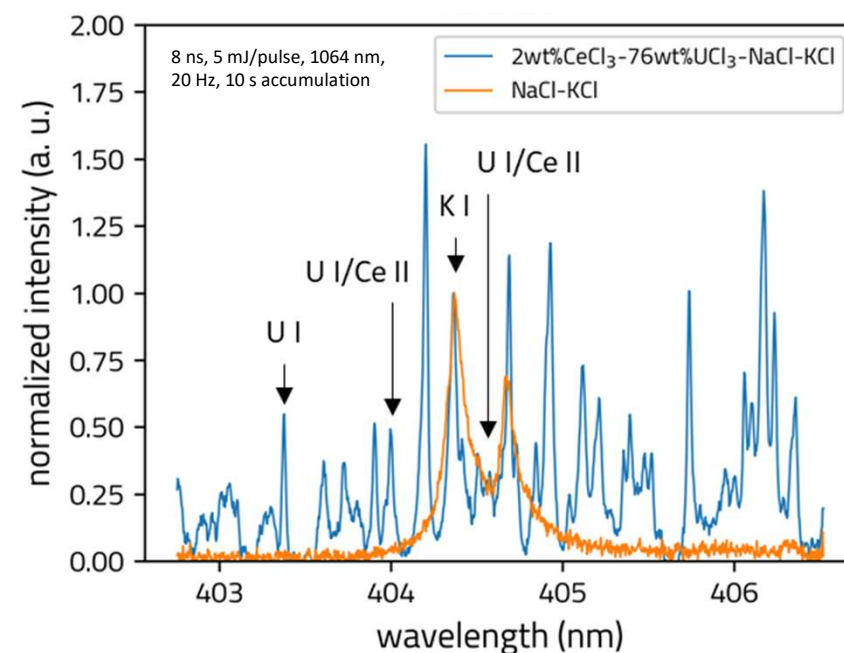
- Nanosecond LIBS was performed on LiCl-KCl and NaCl-KCl salts containing UCl_3 and CeCl_3 .
- Samples were sealed in glass vials under argon.
- Uranium's dense emission spectrum complicates line identification and fitting.



UCl_3 -NaCl-KCl LIBS vials sealed under argon



ANL nanosecond-LIBS system

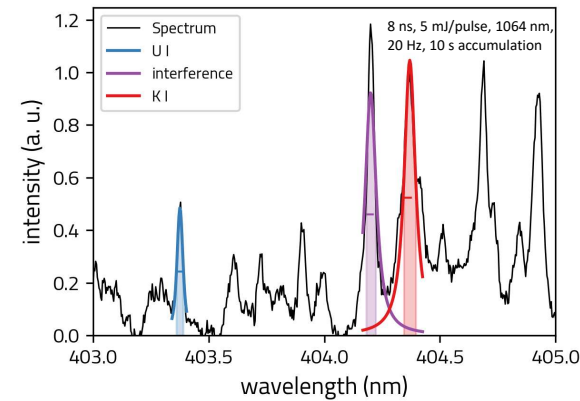


Nanosecond-LIBS of CeCl_3 and UCl_3 in NaCl-KCl at room temperature.

LIBS calibrated uranium concentration from 3 to 72 wt% UCl_3 at room temperature



- A calibration curve was developed for 3–72 wt% UCl_3 in LiCl-KCl.
- The **U I 403.4 nm line** provided the best predictive performance.
- Random error results from shot-to-shot variation, matrix effects, and self-absorption.
- The nonzero intercept likely reflects inconsistent background subtraction.

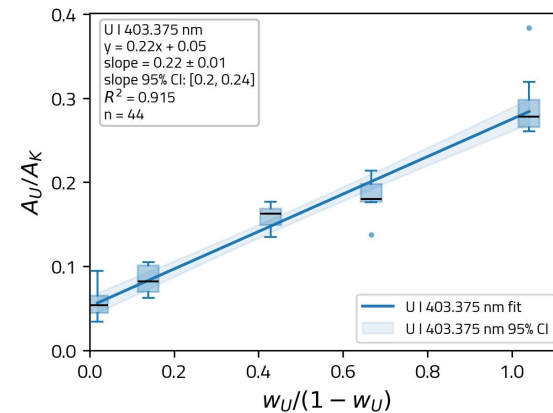


ns-LIBS of 72wt% UCl_3 -LiCl-KCl with peak Voigt fitting for area measurement.

Univariate analysis: Ratio of U & K peak areas

$$R = \frac{A_U}{A_K} \quad R = a + \hat{\beta}_{U/K} \frac{w_U}{(1 - w_U)}$$

Calibration Slope: $\hat{\beta}_{U/K} = 0.22$
(RSE = 4.7%, 95% CI: 0.20, 0.24)

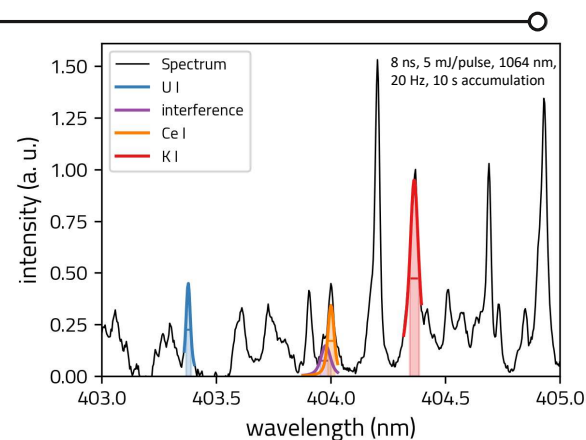


U/K peak ratio calibration curve for LiCl-KCl salts with various UCl_3 concentrations.

LIBS quantified CeCl_3 in high- UCl_3 salts using Ce/U peak ratios at room temperature



- Calibration was performed for 0.5–2.0 wt% CeCl_3 in 76 wt% UCl_3 -NaCl-KCl.
- The **Ce I 404 nm line** gave the best predictive performance when fit with two Voigt components to account for peak overlap.
- Relative standard deviation was 7.4%, with error strongly influenced by interference peak fitting.
- A multivariate approach should yield improved accuracy.

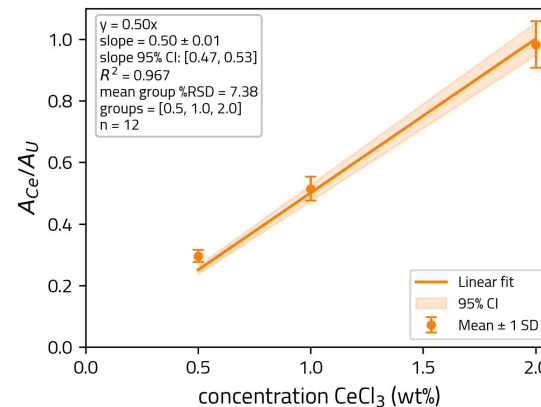


*ns-LIBS
2wt% CeCl_3 in
76wt% UCl_3 -NaCl-KCl
with peak Voigt fitting
for area measurement.*

Univariate analysis: Ratio of Ce & U peak areas

$$R = \frac{A_{\text{Ce}}}{A_{\text{U}}} \quad R = \hat{\beta}_{\text{Ce/U}} w_{\text{Ce}}$$

Calibration Slope: $\hat{\beta}_{\text{Ce/U}} = 0.50$
(RSE = 2.6%, 95% CI: 0.47, 0.53)



*Ce/U peak area ratio
calibration curve for
76wt% UCl_3 -NaCl-KCl
salts with various CeCl_3
additions*

Performance summary of multimodal MC&A sensors



Technique	Environment	Measurement	Demonstrated Uncertainty (%)	Readiness
Voltammetry (FY22-FY23)	1-5wt%UCl ₃ -NaCl-MgCl ₂	U Concentration	2.6% total	Advanced
Voltammetry (FY24)	55-72wt%UCl ₃ -LiCl-KCl, 550 °C	U Concentration	4.0% total	Advanced
Voltammetry (FY25)	55-72wt%UCl ₃ -LiCl-KCl, Various surrogate fission products, 550 °C	U Concentration	1.3% total	Advanced
Voltammetry (FY26)	76wt%UCl ₃ -NaCl-KCl, 0.5-2.0 wt% CeCl ₃ , 550 °C	U Concentration	1% random	Advanced
Raman Spectroscopy (FY26)	76wt%UCl ₃ -NaCl-KCl, 0.5-2.0 wt% CeCl ₃ , 550 °C	Ce Concentration/speciation	Quantification in progress	Emerging
Laser-induced breakdown spectroscopy (FY26)	76wt%UCl ₃ -NaCl-KCl, 0.5-2.0 wt% CeCl ₃ , Room Temperature	Ce Concentration	*7.4% random	Emerging

*Preliminary result for Ce determined by a univariate analysis approach. A multivariate approach to reduce uncertainty is under development.

- **Voltammetry currently provides the best uranium accuracy.**
- **Raman and LIBS extend sensitivity to species that voltammetry struggles to resolve.**
- **Next step: quantify optical-method total uncertainty in molten systems**

Future work will improve molten salt spectroscopy and data analysis



Experimental

- Configure the fiber-coupled LIBS systems in the glovebox. A new 532 nm laser and spectrometer will be delivered in May.
- Reconfigure the online Raman system with new spectrometer to improve small Raman shift resolution.
- Perform online measurements of additional surrogate fission products in molten salts.
- Couple hybrid techniques to engineering-scale molten salt systems

Multivariate Analysis

- Account for matrix, laser, plasma, and environmental effects.
- Principal Component Analysis (PCA): exploratory, reduces data dimensions.
- Partial Least Squares Regression (PLSR): calibration, identify components that are directly useful for regression.

Conclusions



- In FY26, ANL continued to demonstrate high-accuracy uranium measurements in molten chloride salts.
- Voltammetry performed well both with and without surrogate fission products.
- The voltammetry sensor was successfully deployed in TerraPower's non-radiological chloride loop.
- Raman spectroscopy and LIBS are being developed to strengthen hybrid MC&A measurements for minor actinides.



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