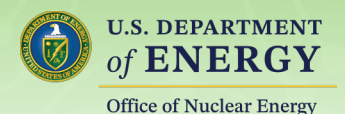




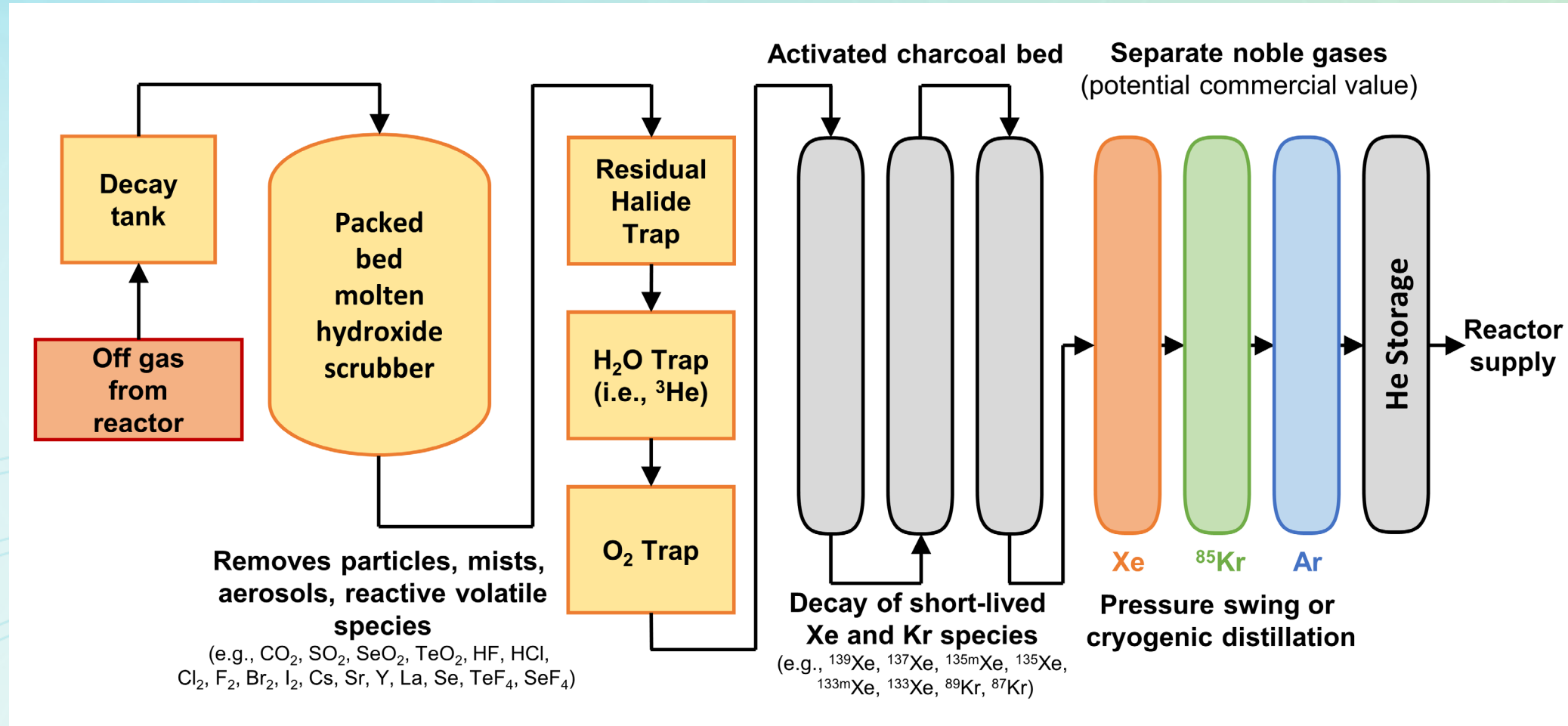
LIBS for elemental monitoring of MSR off-gas streams

Hunter B. Andrews, Zechariah Kitzhaber, Daniel Orea, Kevin Robb, Joanna McFarlane

Oak Ridge National laboratory



To aid deployment we are developing technology for off-gas treatment



- Quantify fission and activation products in off-gas system
- Monitor off-gas treatment component efficiency

An integrated off-gas system will be developed and demonstrated by FY30



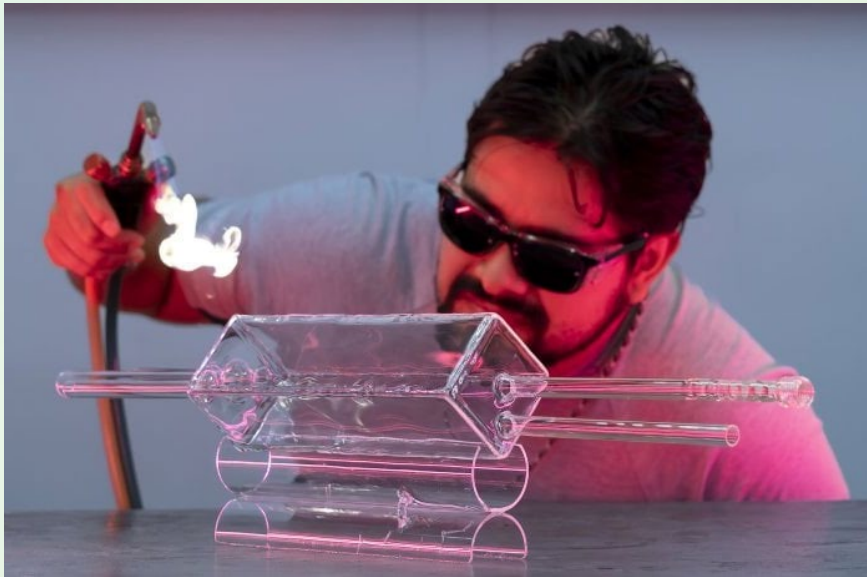
FY26
Develop
roadmap

FY27
Construct
integrated
off-gas
system

FY28
Perform cold
testing on
salt loop

FY29
Modify
design
based on
cold tests

FY30
Start
radiological
tests



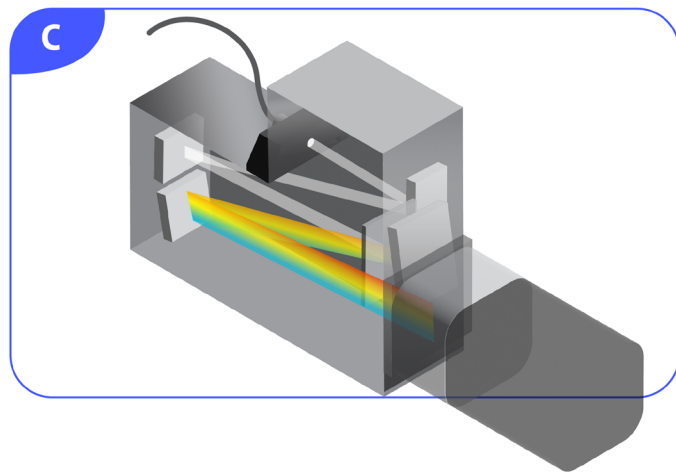
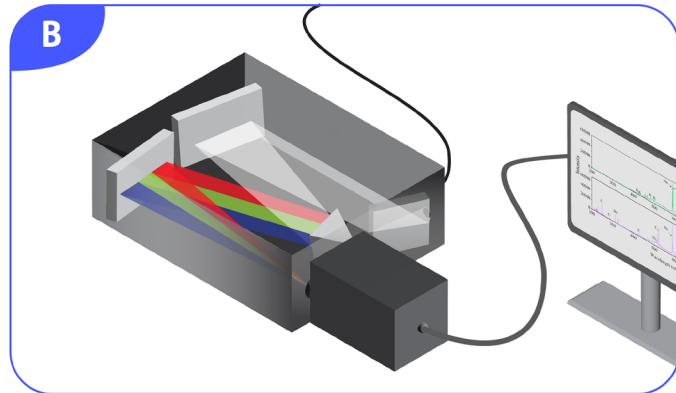
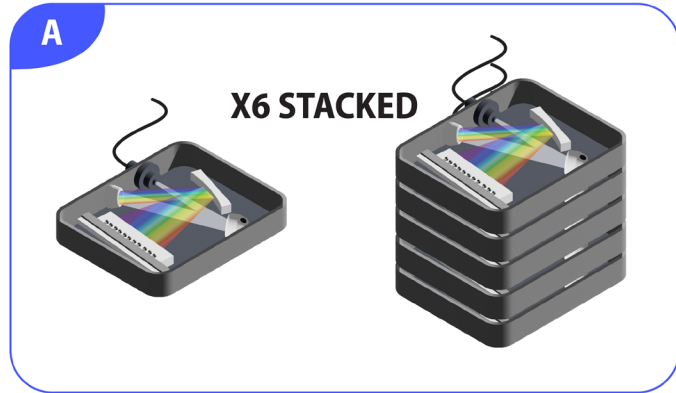
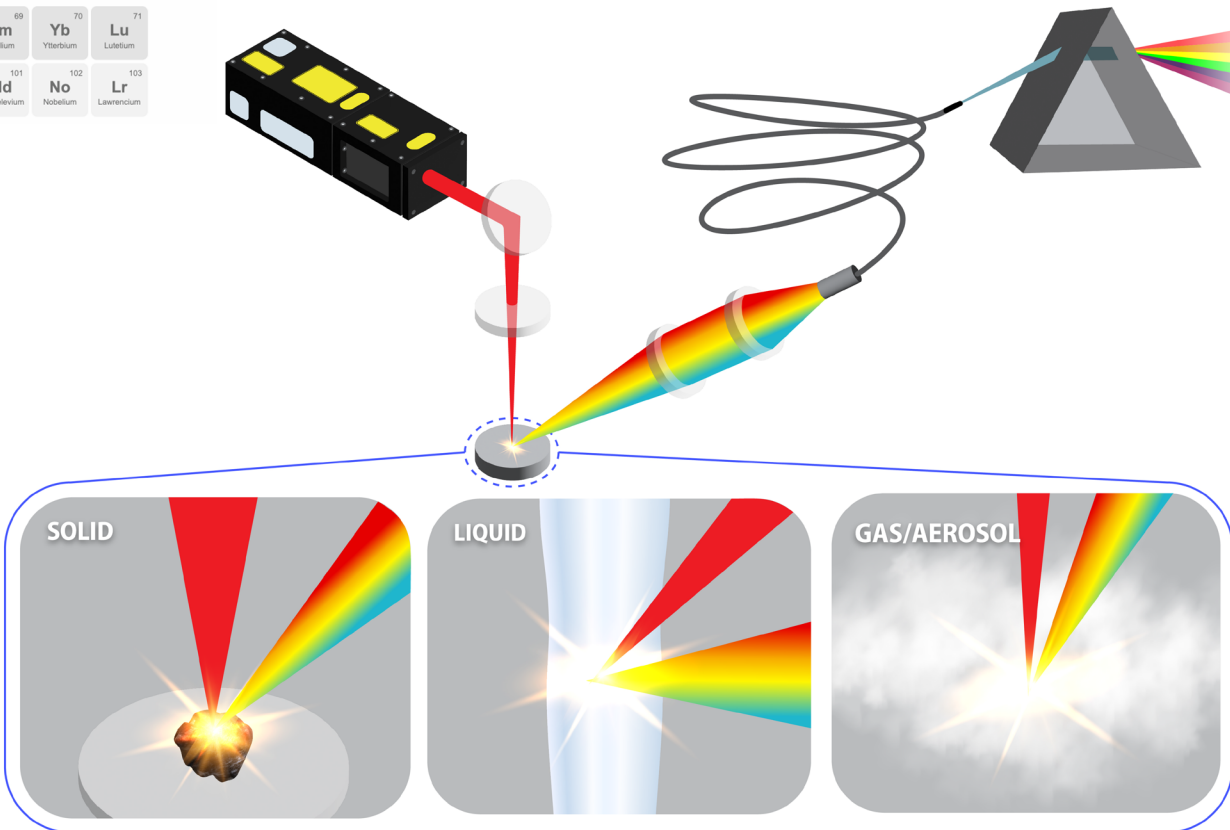
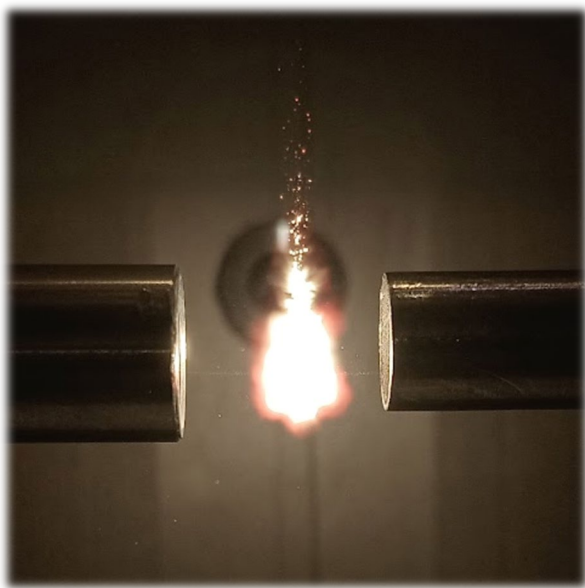
Molten Salt Reactor
P R O G R A M



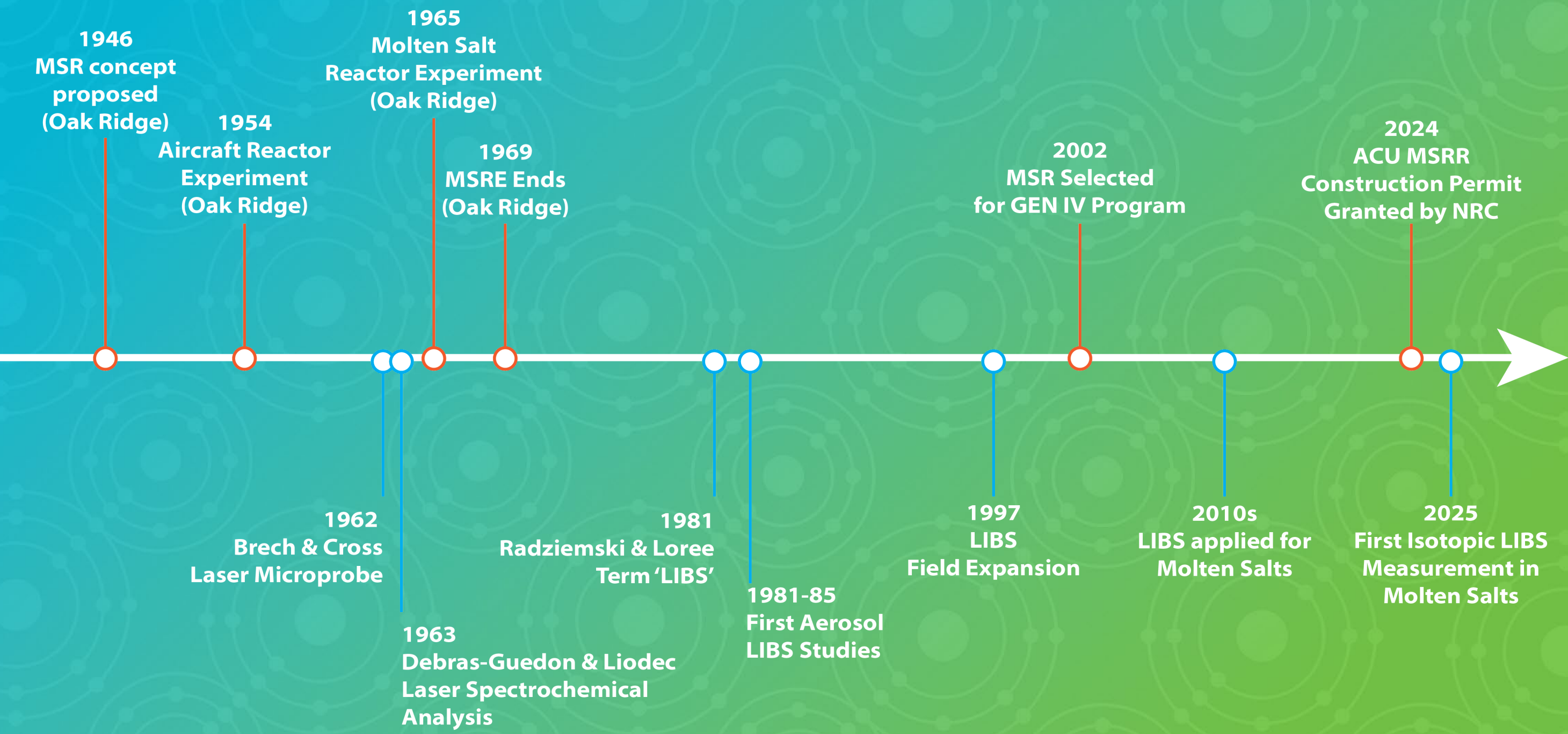
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Laser-Induced Breakdown Spectroscopy (LIBS) is a powerful tool for online monitoring complex systems

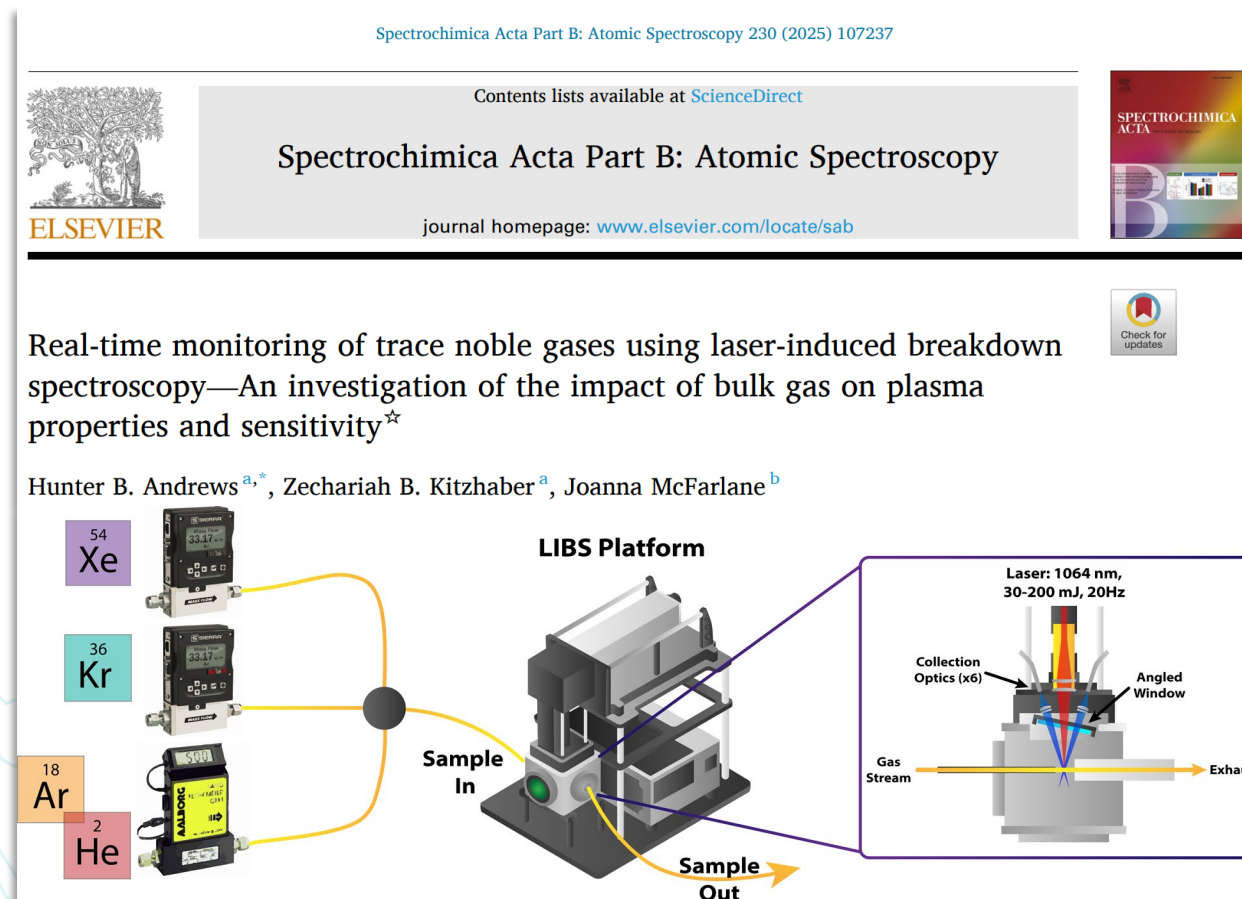
1 IA																	18 VIIIA
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium															9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium															17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Caesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson
58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium				
90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium				



Molten salt and LIBS, an interesting history



Several fundamental LIBS advancements were made in FY25



Kitzhaber et al. ACS Omega. 2025

Andrews et al. Spectrochimica Acta Part B: Atomic Spectroscopy, 2025.

Andrews et al. Journal of the American Chemical Society. 2025.



Molten Salt Reactor
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Moving from lab-scale to engineering-scale systems



Mobile LIBS Platform

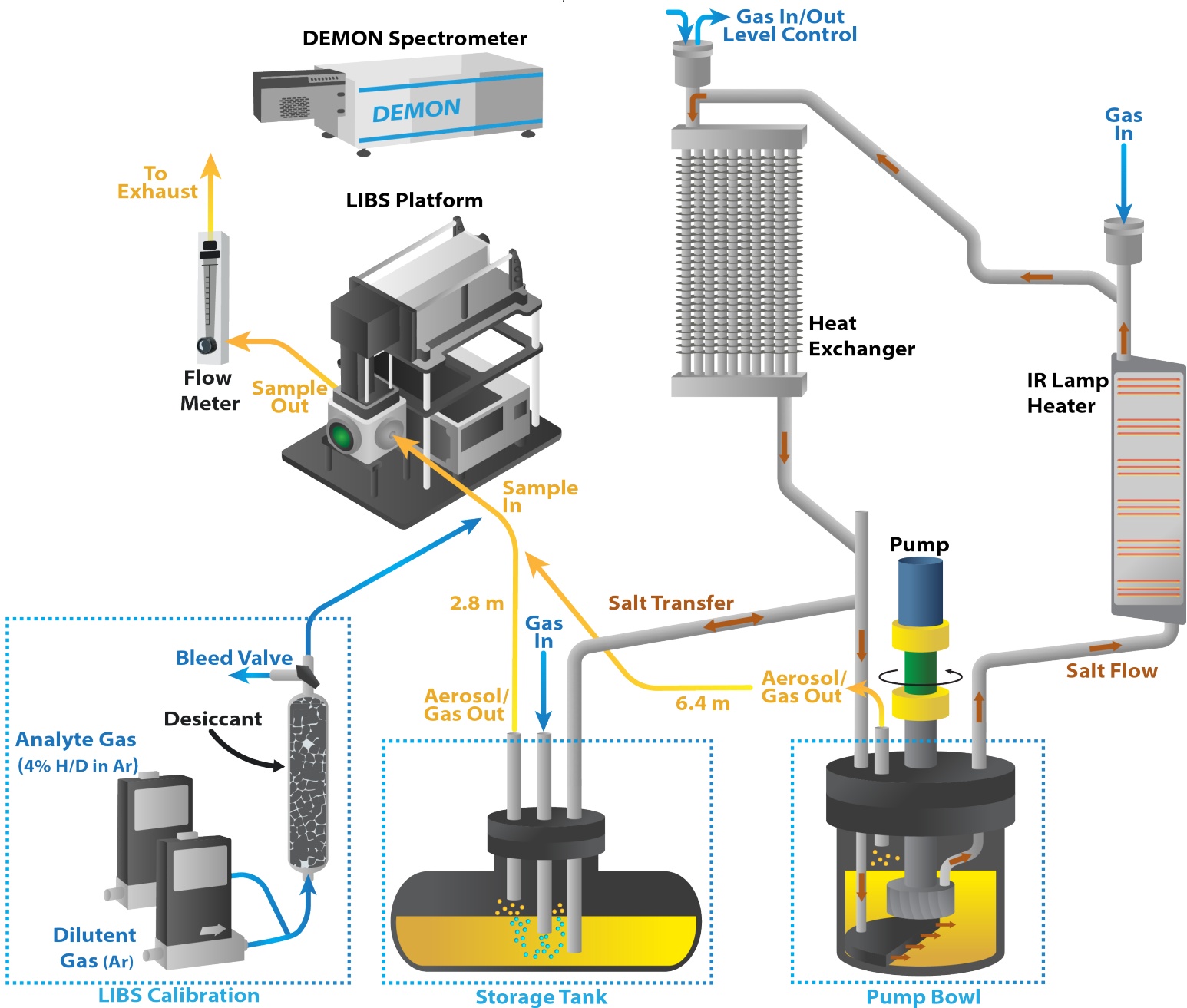
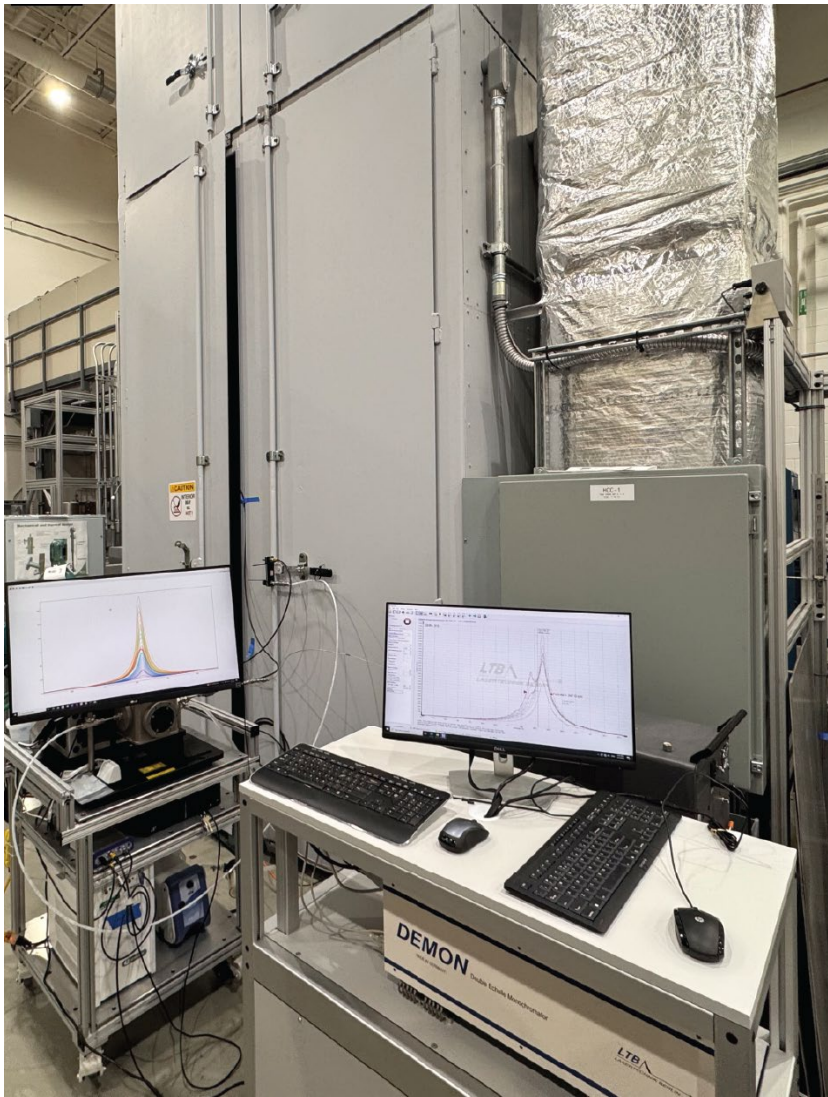
Mobile DEMON
Spectrometer



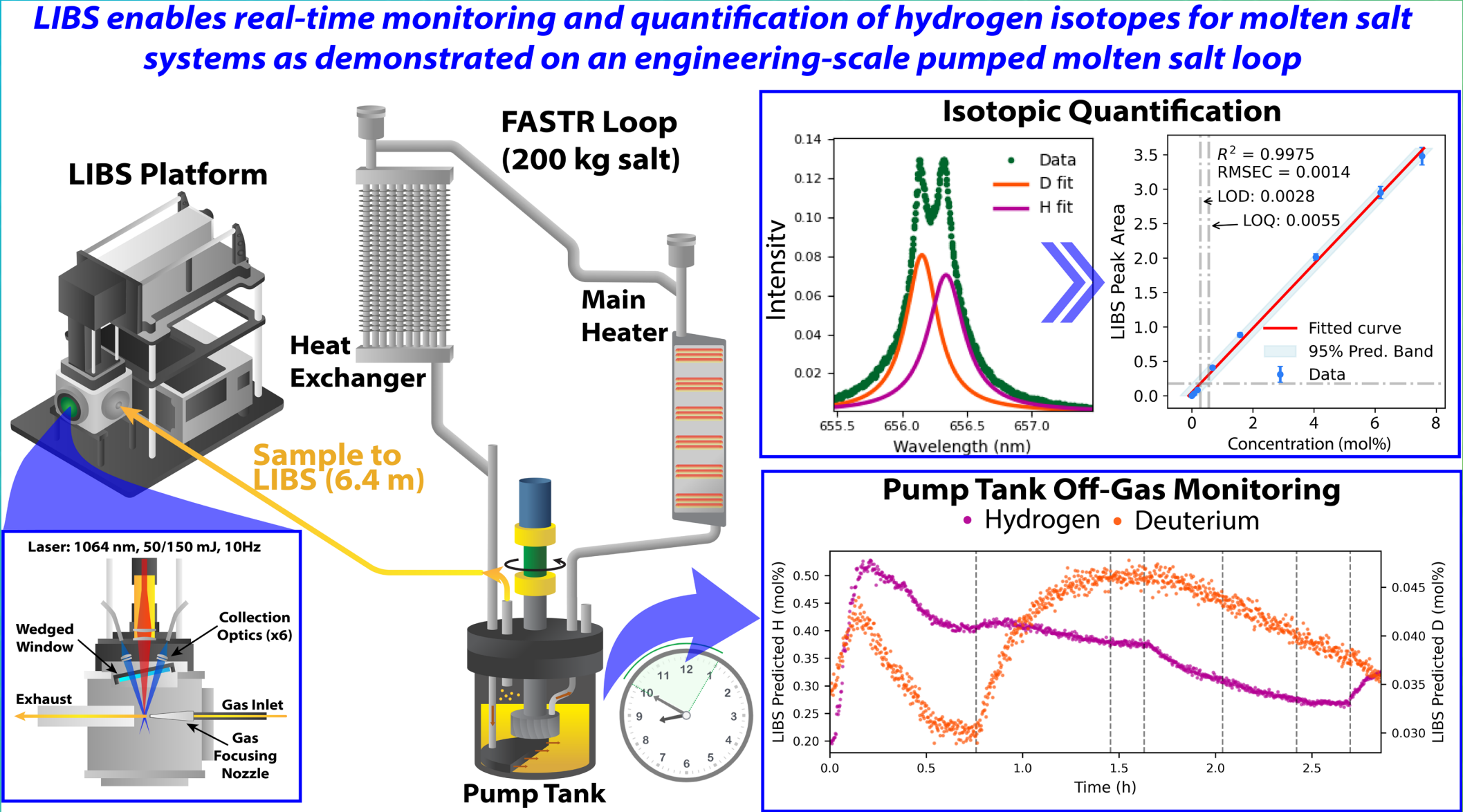
Facility to Alleviate Salt Technology Risk
(FASTR)

200 kg chloride ($\text{MgCl}_2\text{-KCl-NaCl}$) pumped loop

The LIBS unit was tested on FASTR over the course of 2 weeks



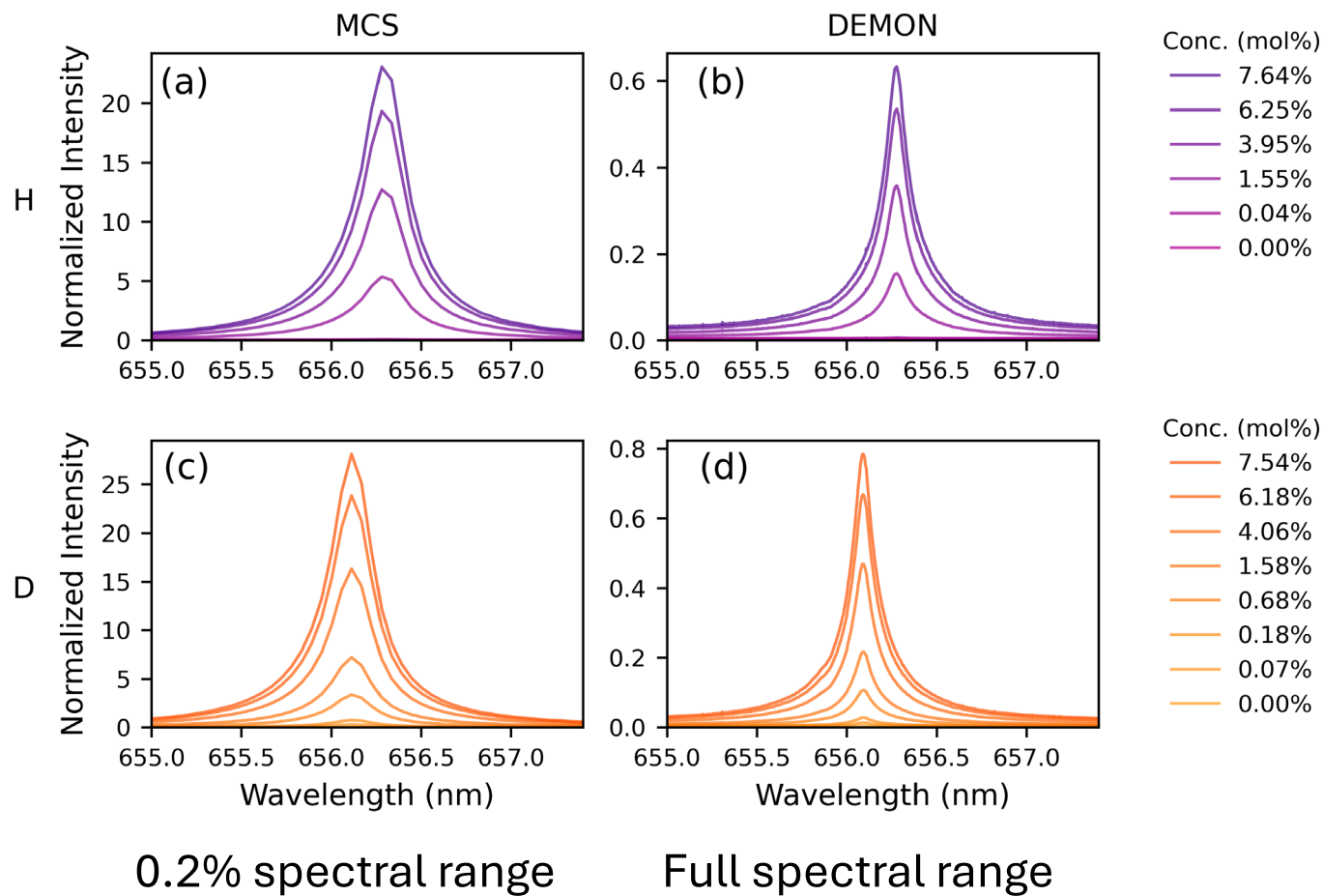
Quantification of hydrogen isotopes was the first focus of the FASTR tests



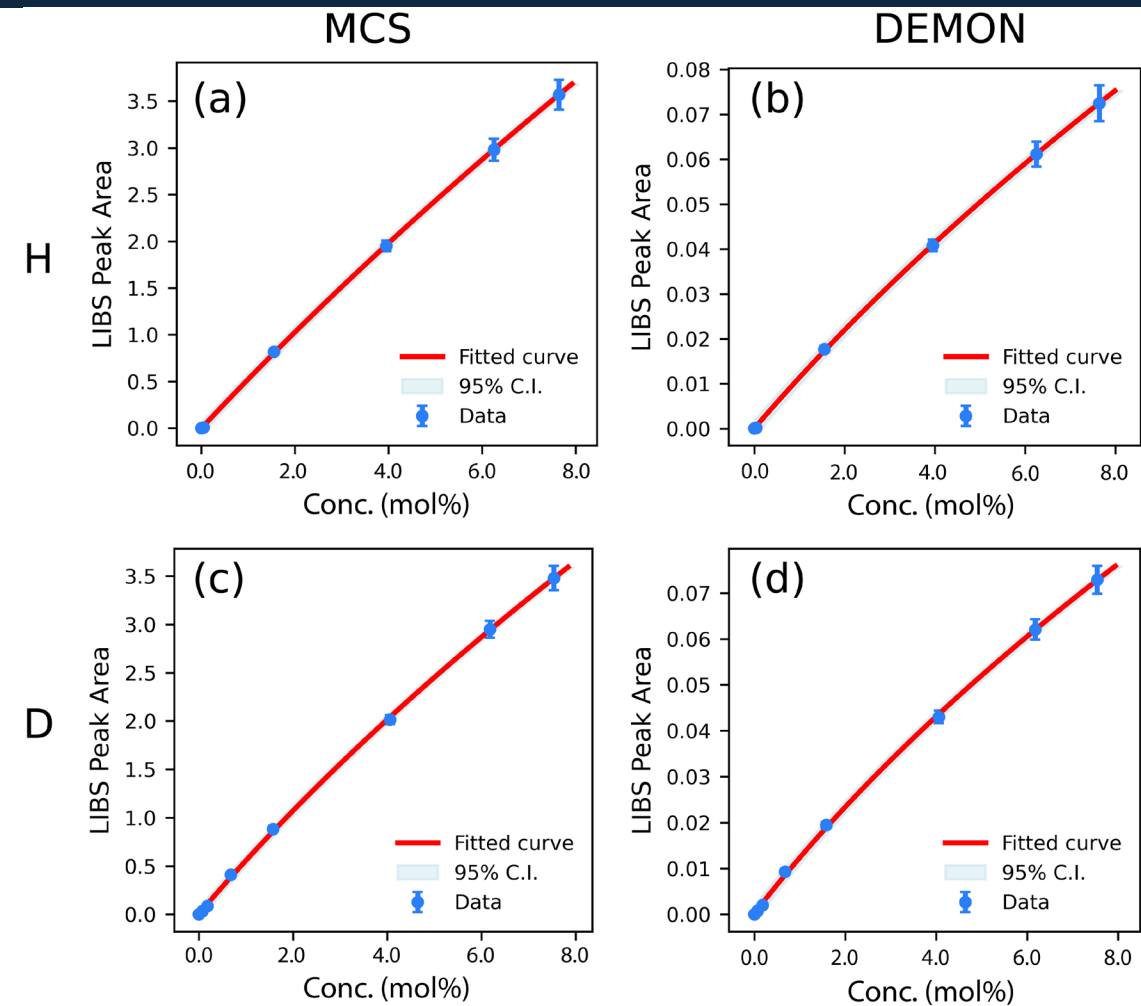
*PNNL Raman and an ORNL RGA were in-line with LIBS measurements.
Manuscript in preparation.

The multichannel and DEMON spectrometers were run in parallel to compare the trade-off between wavelength coverage and resolution

H/D Calibration Spectra

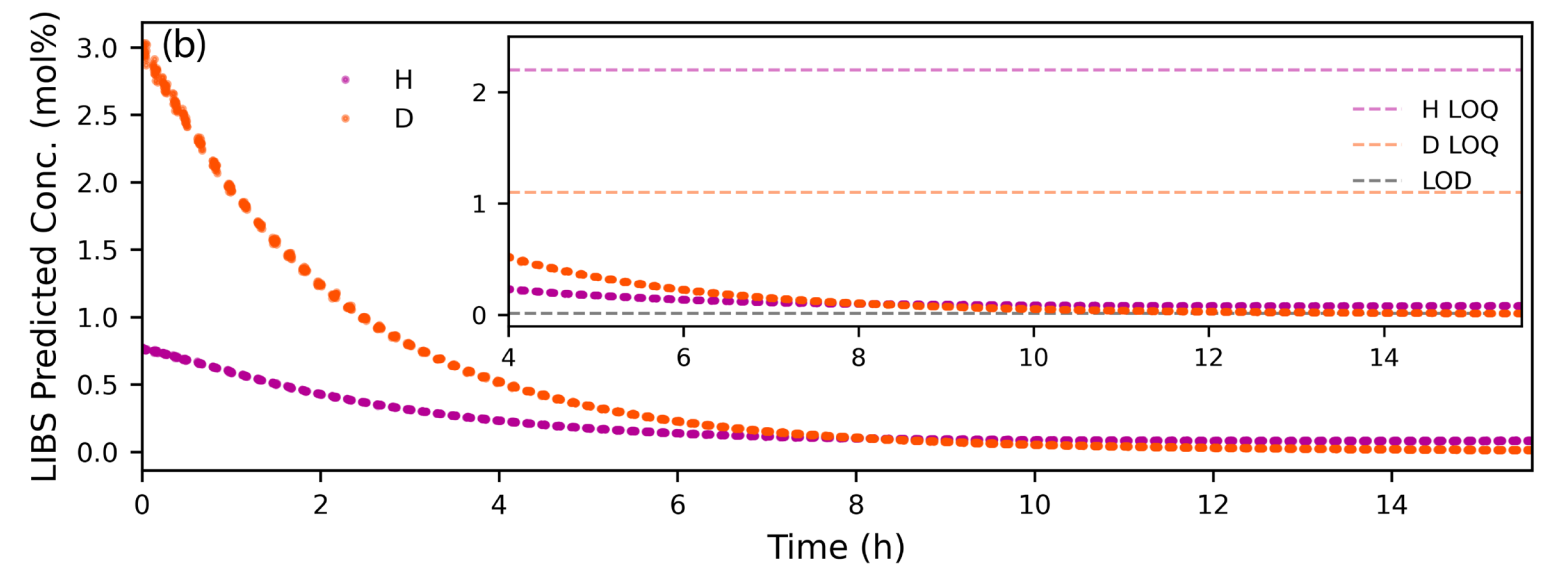
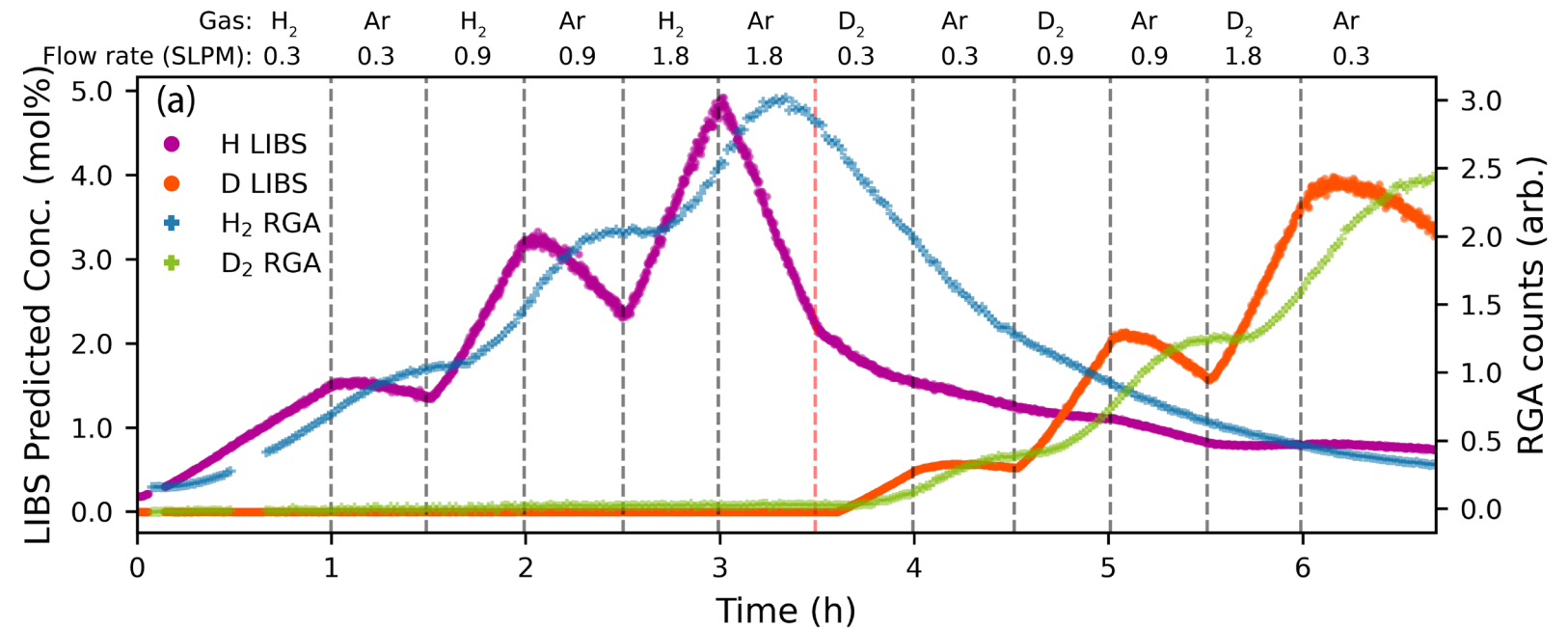
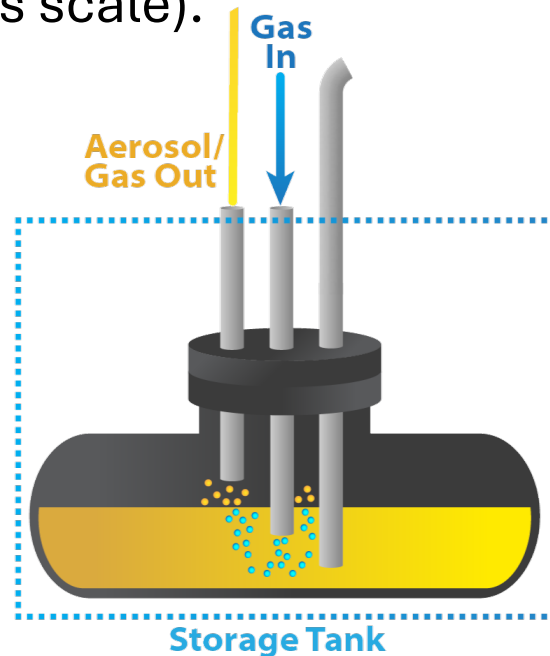


H/D Calibration Models

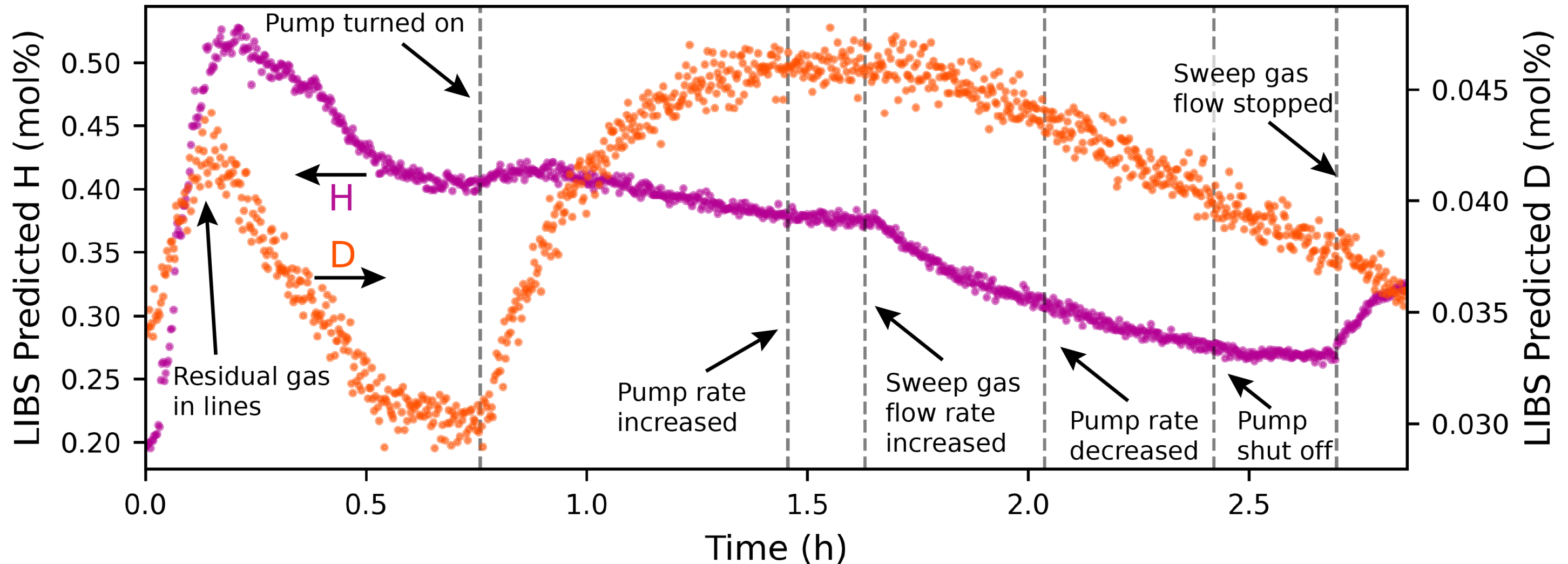


H and D were quantified during controlled, real-time tests on the storage tank

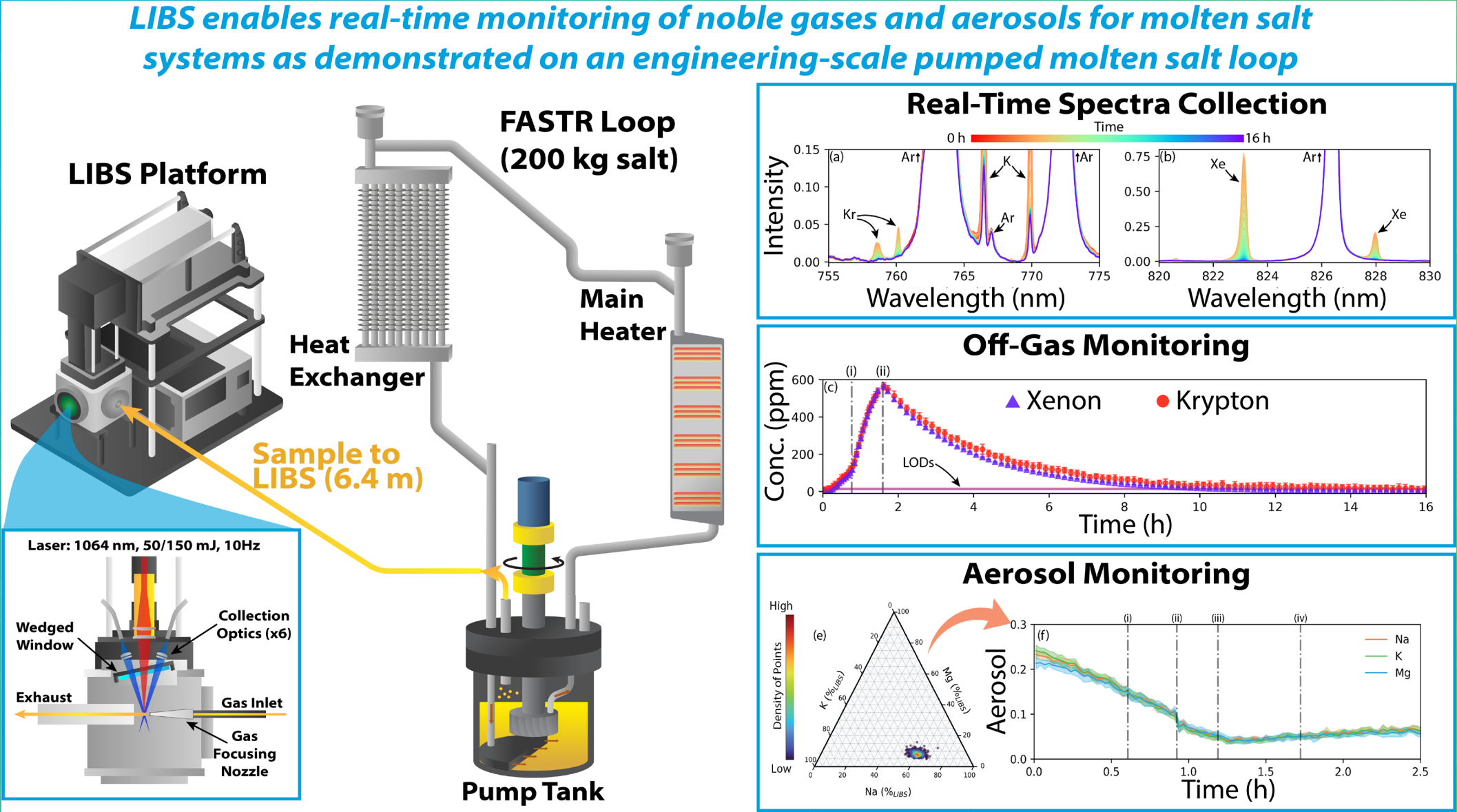
- (a) LIBS-predicted H and D concentrations using the MCS OLS model versus RGA signal for the test on the FASTR storage tank.
- (b) Predicted H and D concentrations monitored overnight. The expanded region shows detection of H and D at concentrations below the LOQ and approaching the LOD (the H and D LODs are indistinguishable on this scale).



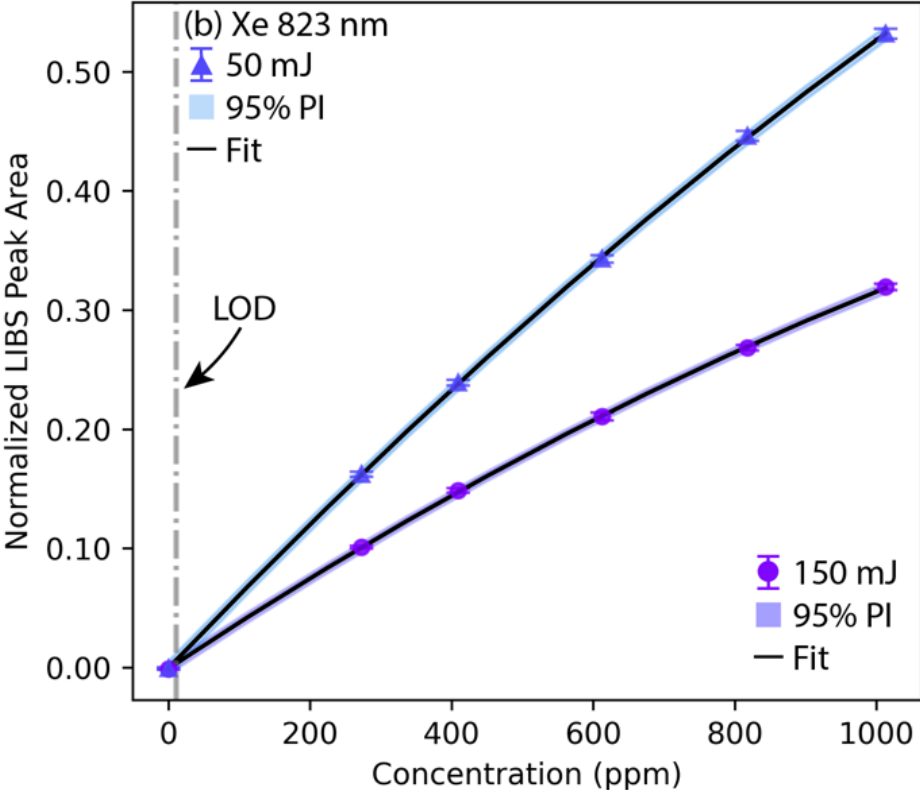
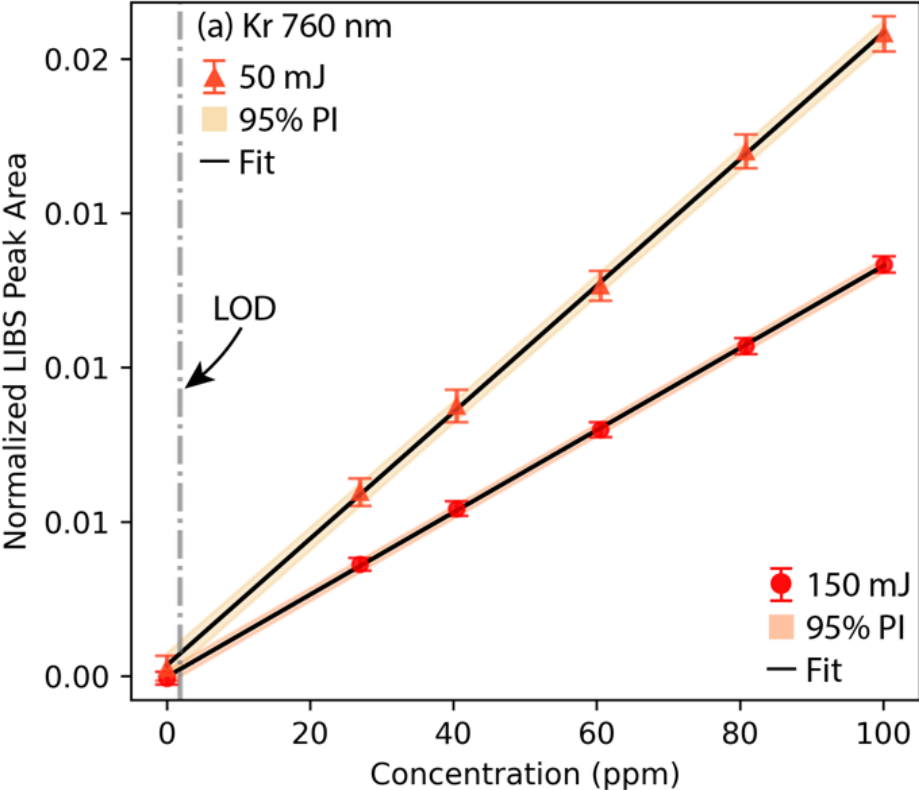
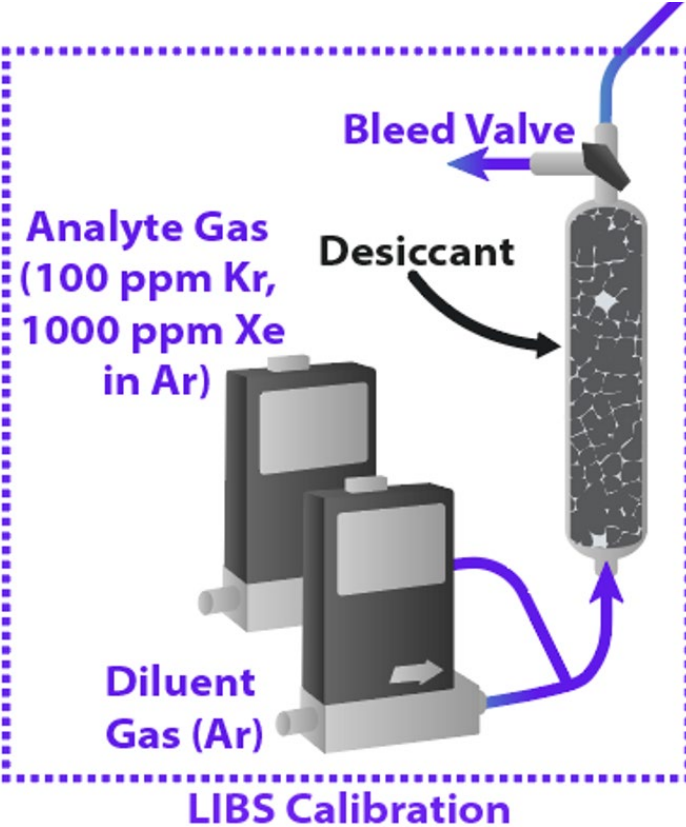
Pumped salt circulation leads to release of dissolved H and D, quantified during real-time tests on the pump bowl



Monitoring noble gases and aerosols was the second focus of the FASTR tests



Xe and Kr noble gases were also monitored on FASTR

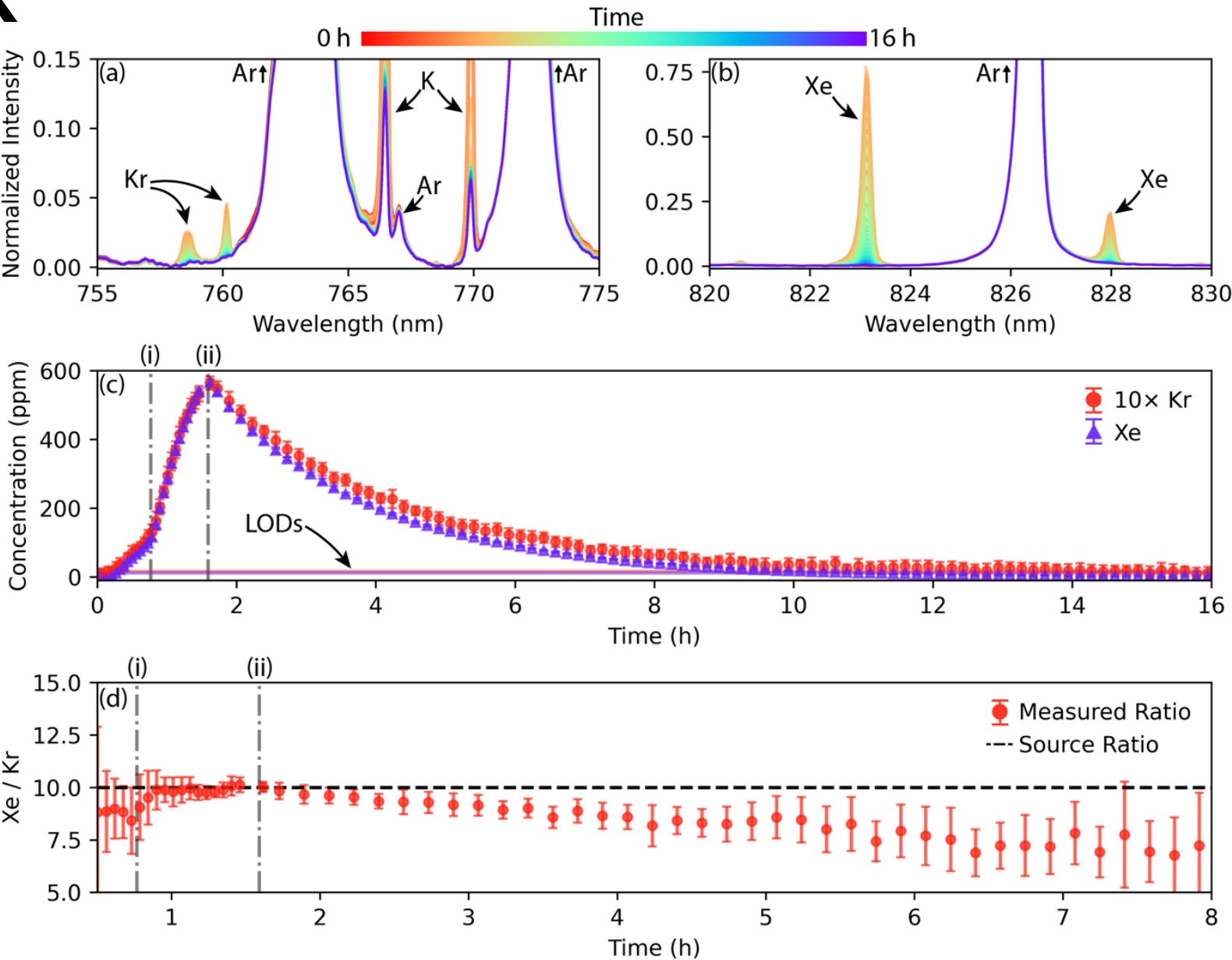
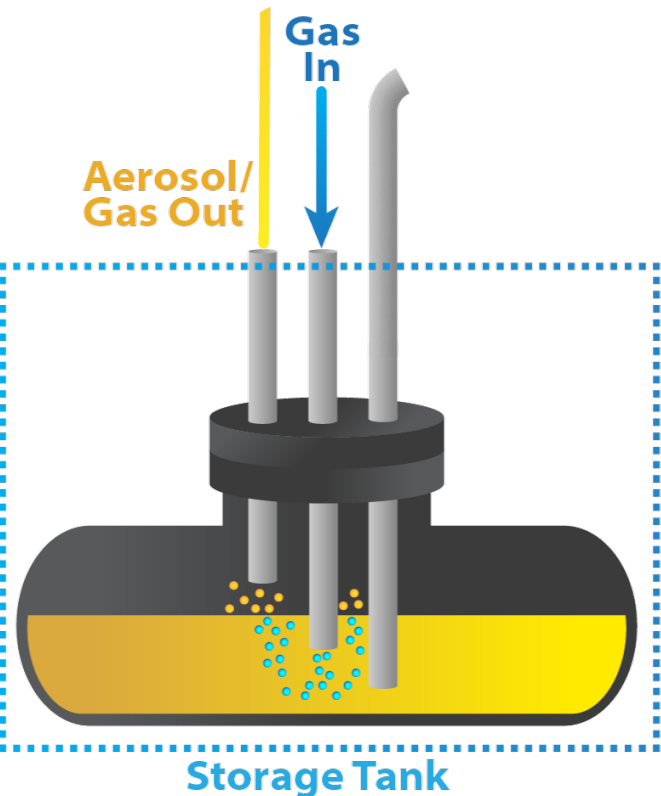


Univariate calibration models for (a) 760 nm Kr and (b) 823 nm Xe at 50 and 150 mJ.

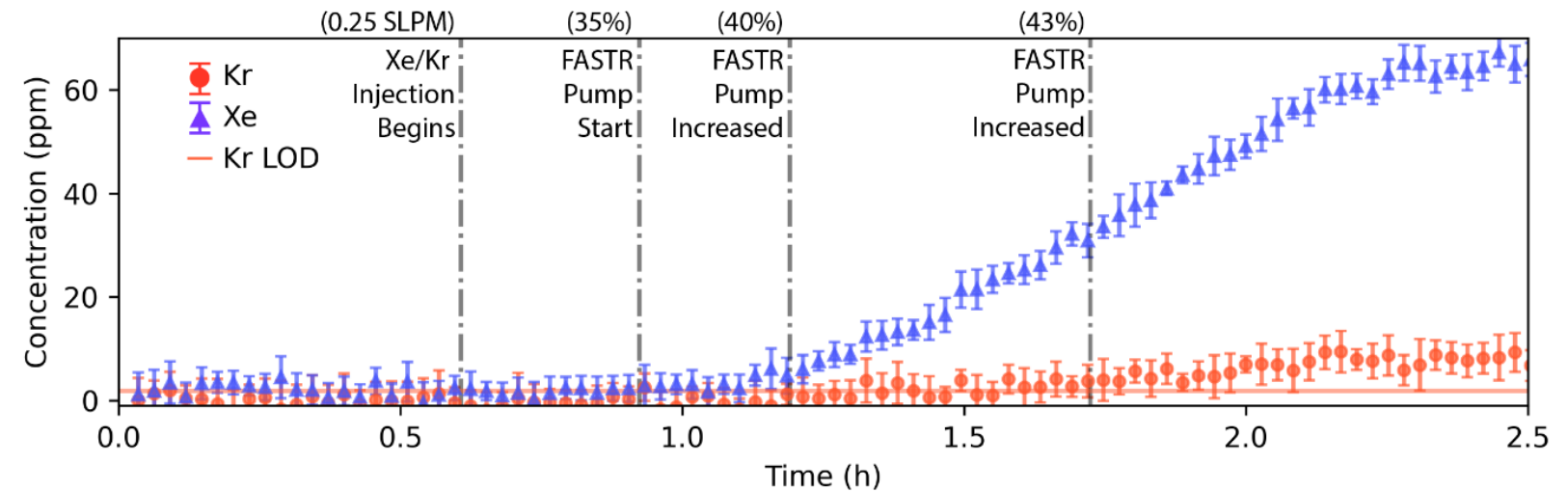
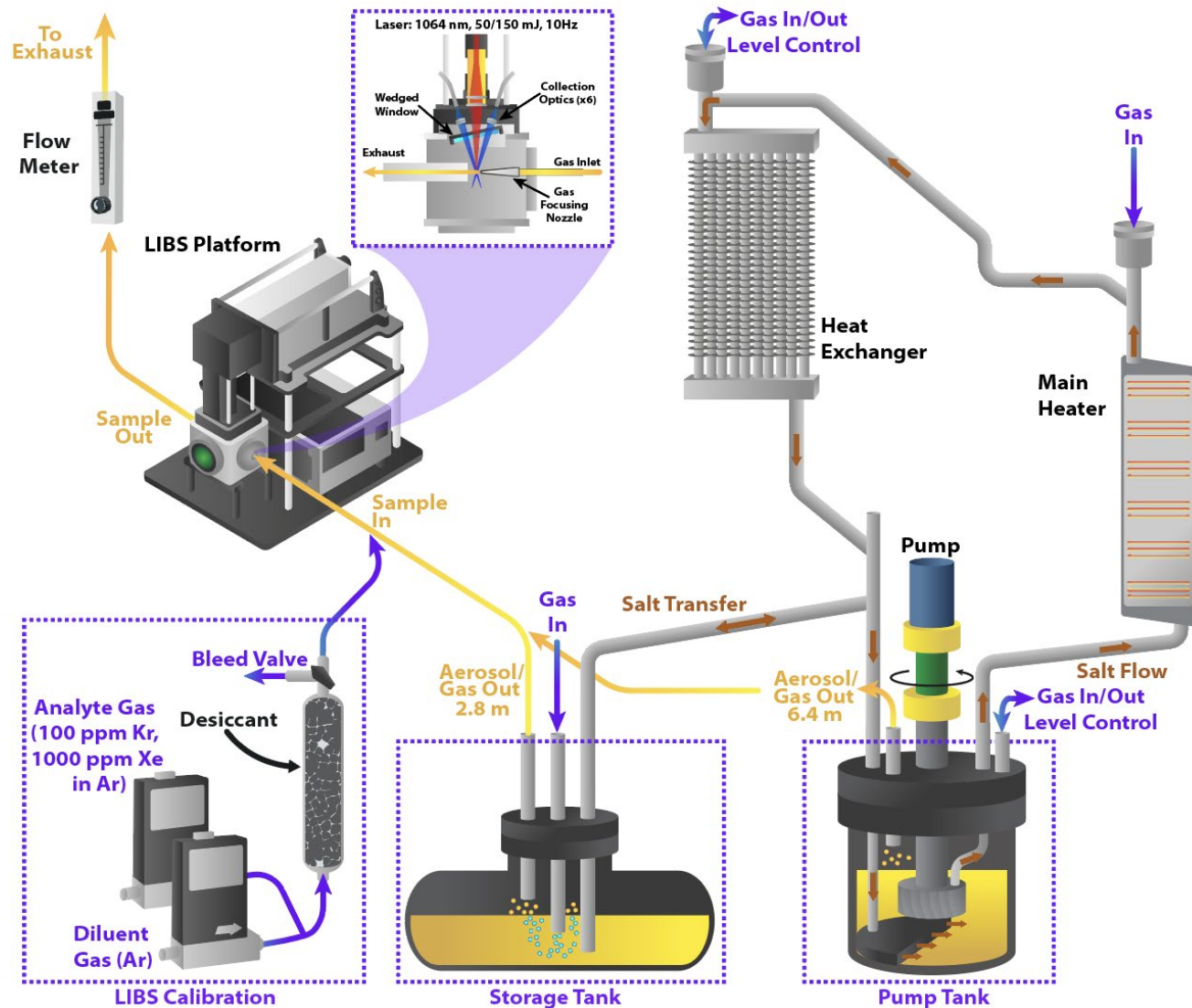
	50 mJ		150 mJ	
	Kr 760 nm	Xe 823 nm	Kr 760 nm	Xe 823 nm
Model	1 st Order	2 nd Order	1 st Order	2 nd Order
R ²	0.9998	0.9999	0.9999	0.9999
%RSD	4.6	0.99	3.5	1.1
%RMSEC	0.90	0.53	0.79	0.33
LOD	1.92	9.78	1.69	11.7

Time evolution of Kr and Xe were recorded on the Ar-swept FASTR storage tank

	Kr	Xe
Measured (mmol)	0.205	1.78
Expected (mmol)	0.219	2.19
Recovery (%)	93.6	81.0

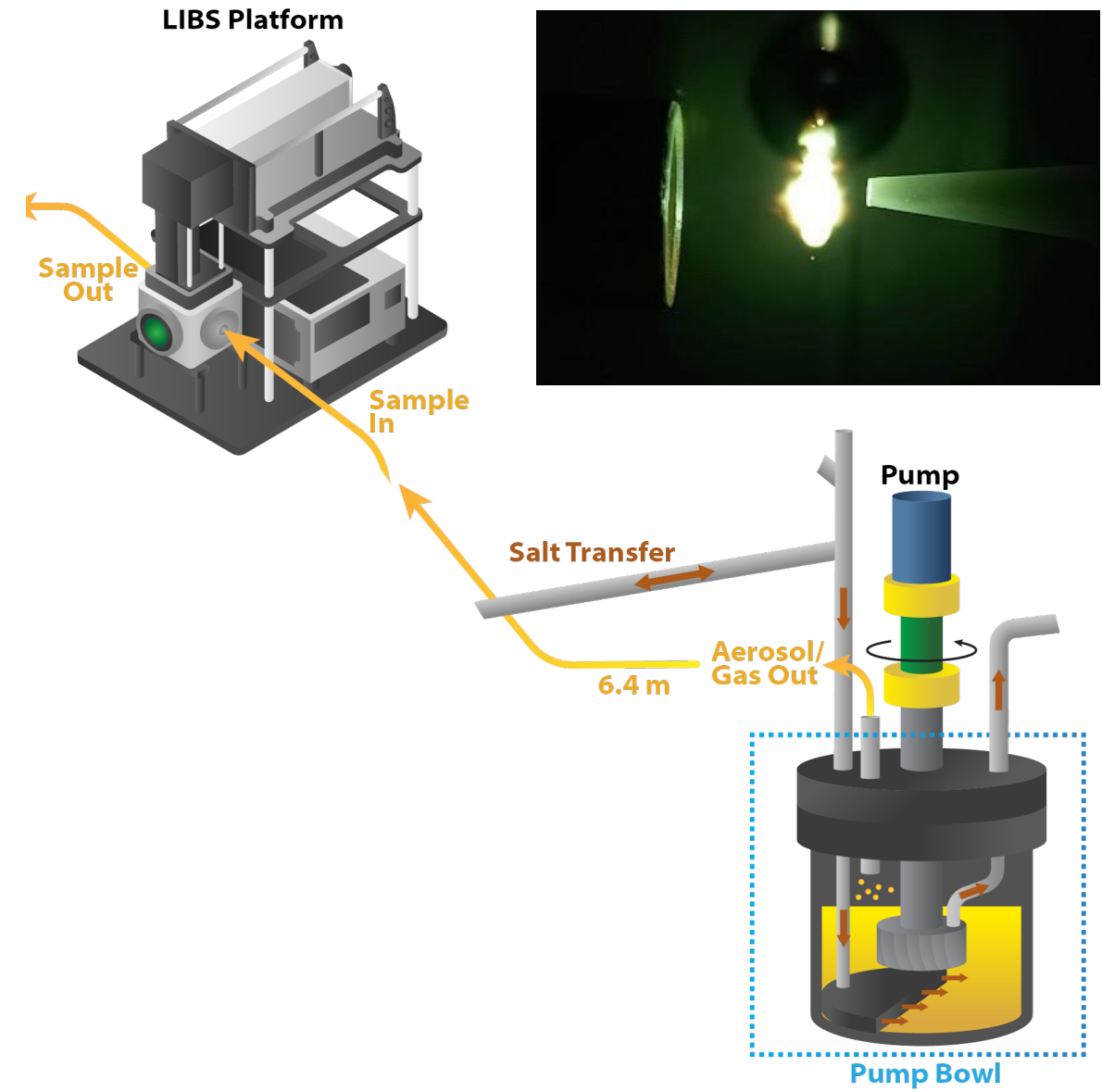
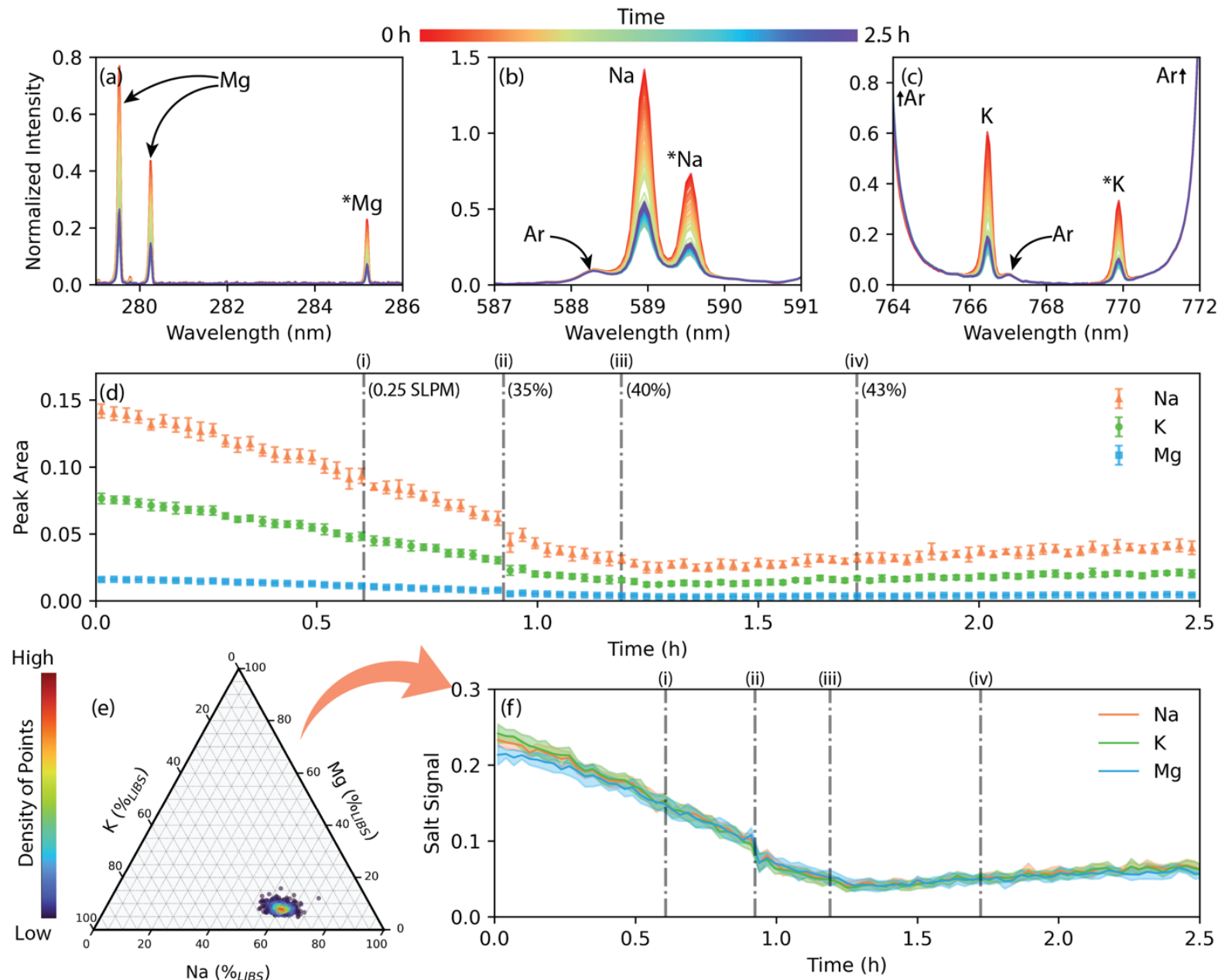


Noble gas transport was also monitored on a flowing salt loop



Quantified Kr and Xe concentrations over time from the LIBS monitoring of the off-gas from the FASTR pump tank during and Kr and Xe additions. Data point markers correspond to the average of 10 spectra, and the error bars represent one standard deviation.

Aerosols detected over 6 m from the pump bowl were indicative of salt composition



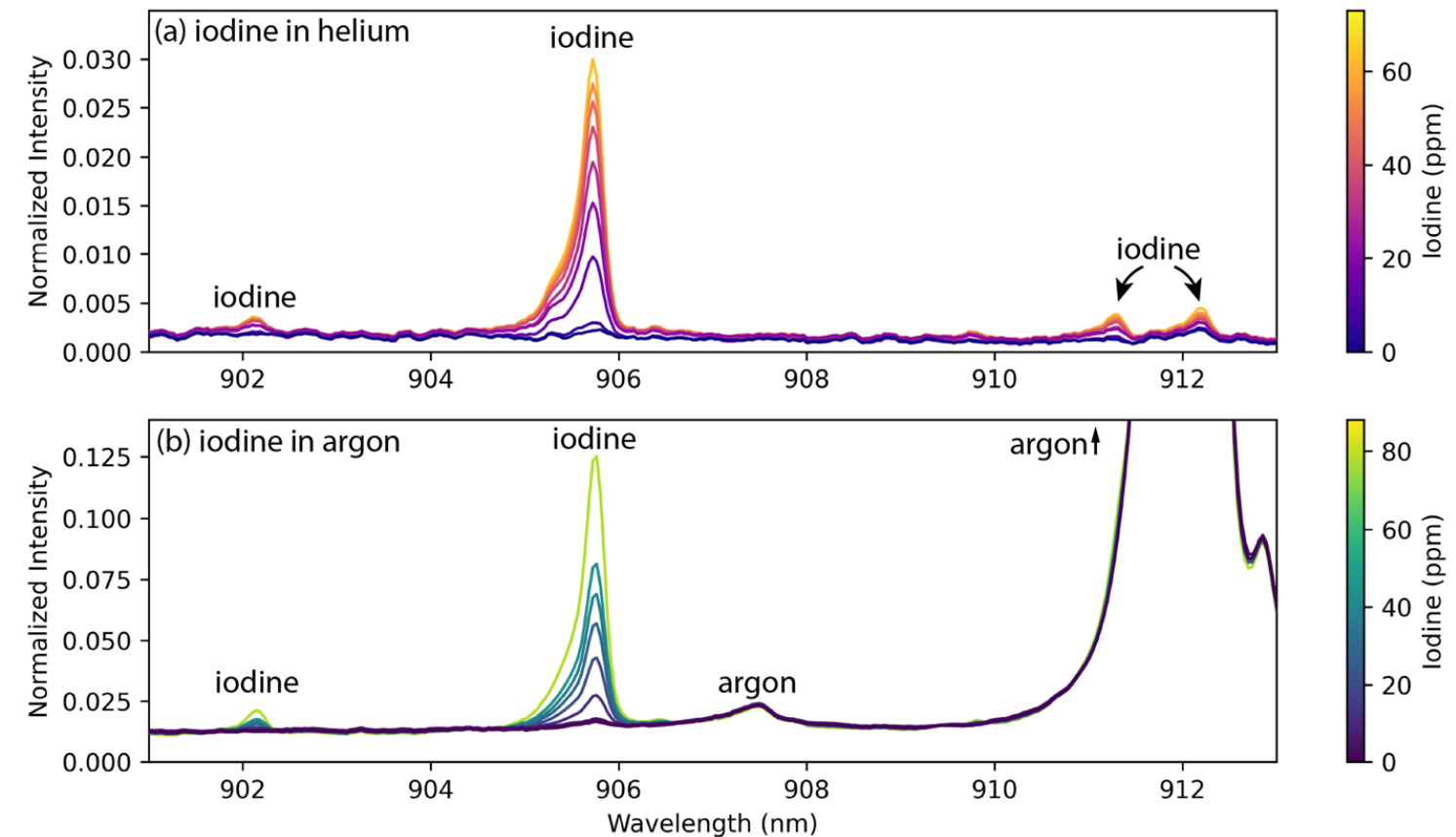
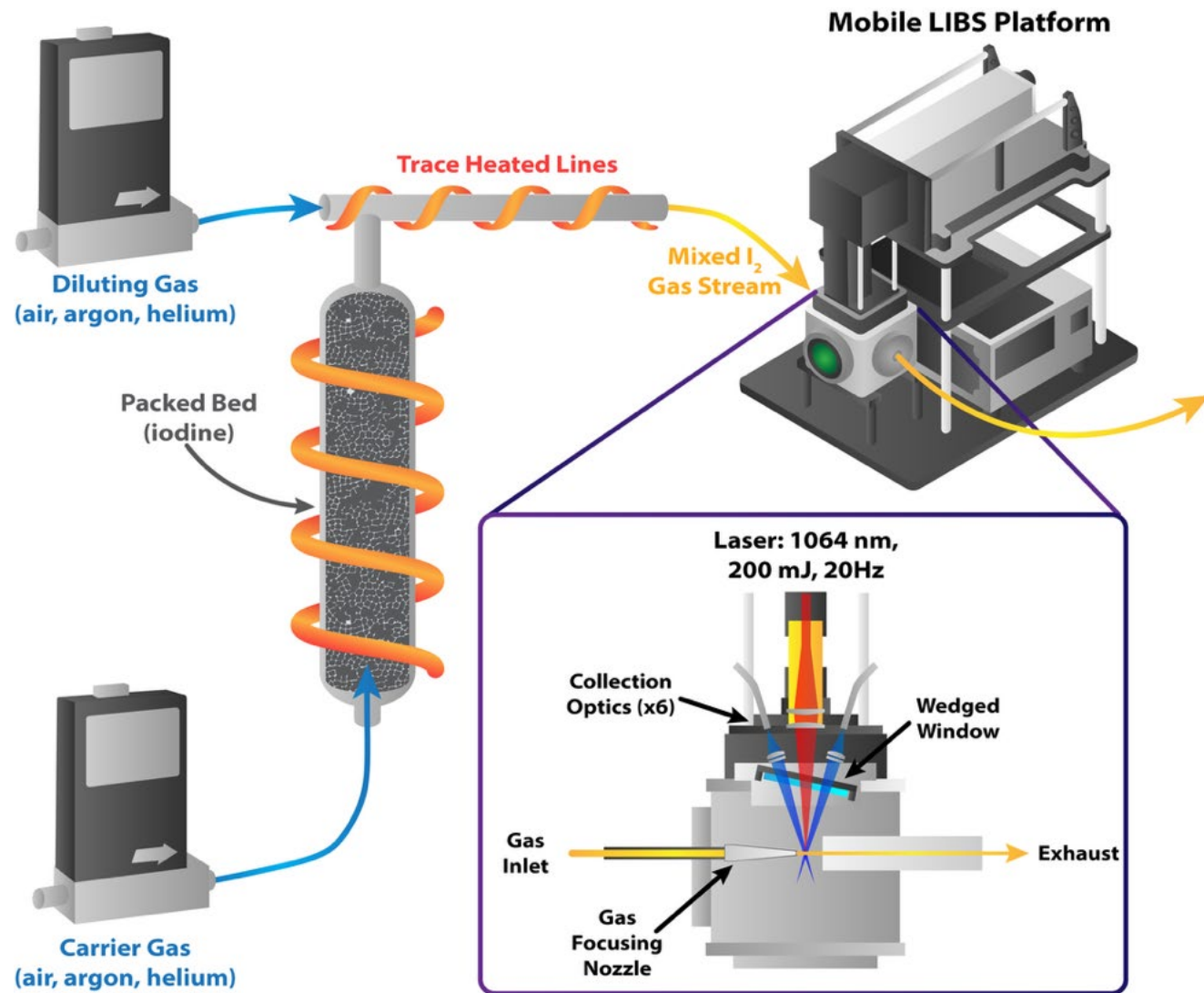
Monitoring iodine release is vital to meeting government regulations

- Radioactive iodine (iodine-129) is of significant interest in off-gas streams
- high volatility
- high biological activity
- long half-life (1.57×10^7 years).
- The US Environmental Protection Agency regulations for nuclear power operations in Title 40 of the *US Code of Federal Regulations* (CFR), Part 190, necessitate efficient capture of krypton-85 and iodine-129 before releasing gas streams to the environment.

Andrews et al. Journal of Analytical Atomic Spectrometry. 2026.

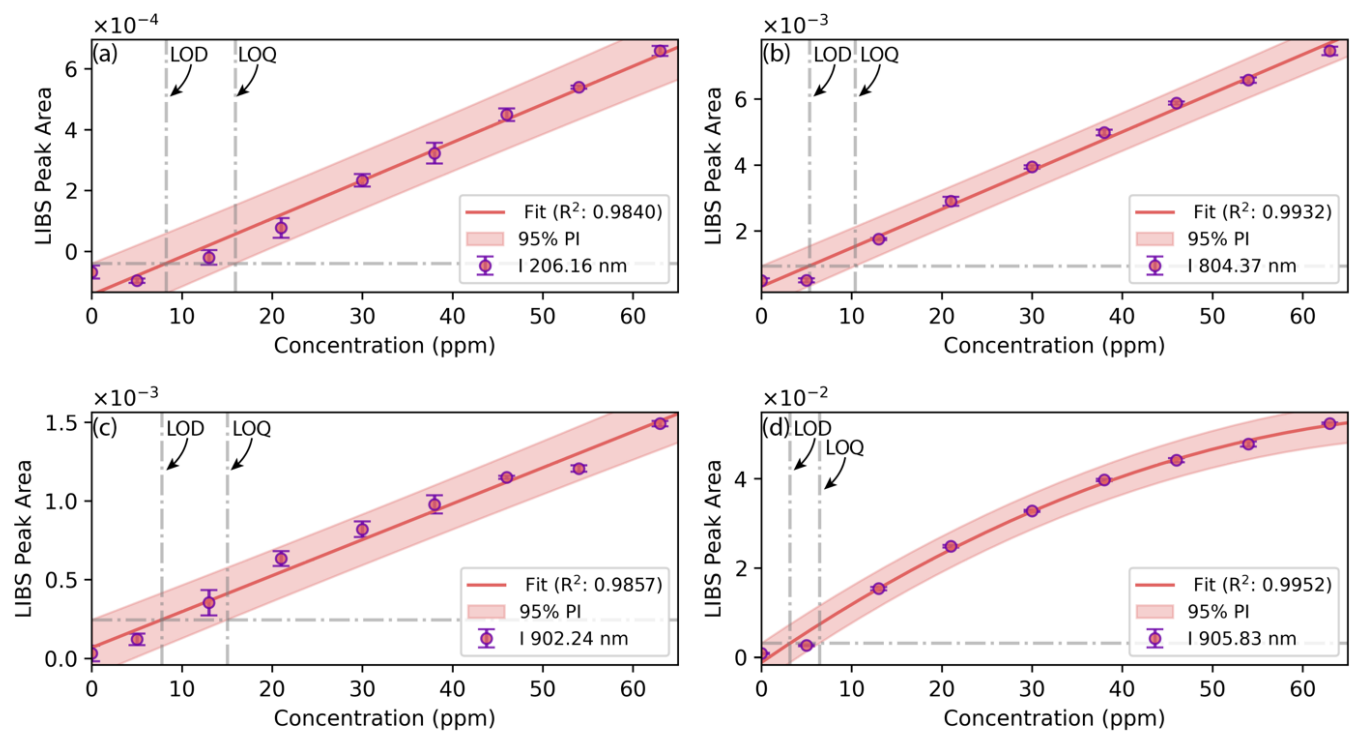


LIBS detection of iodine was evaluated at the Iodine Off-Gas Testing and Abatement (IOTA) Laboratory



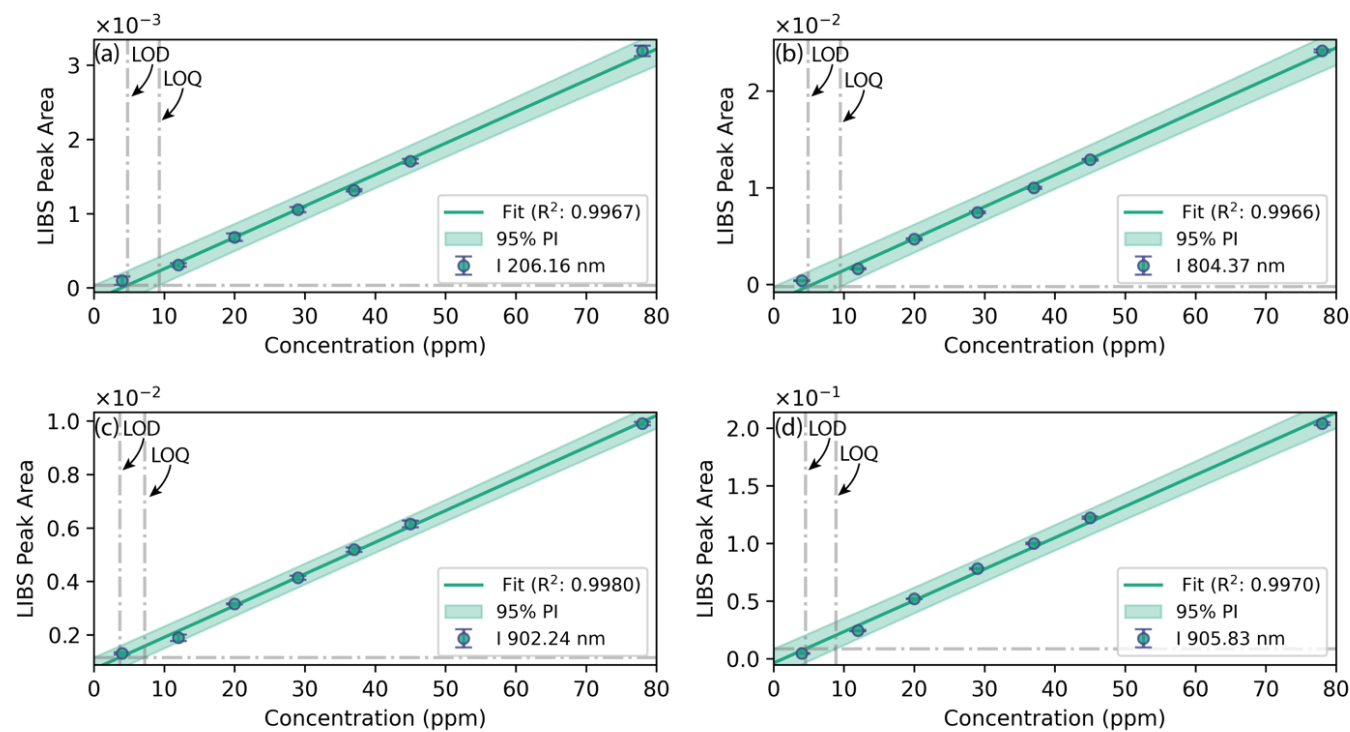
LIBS models result in iodine LODs down to 3 ppm in helium and 5 ppm in argon

Detection of iodine in He



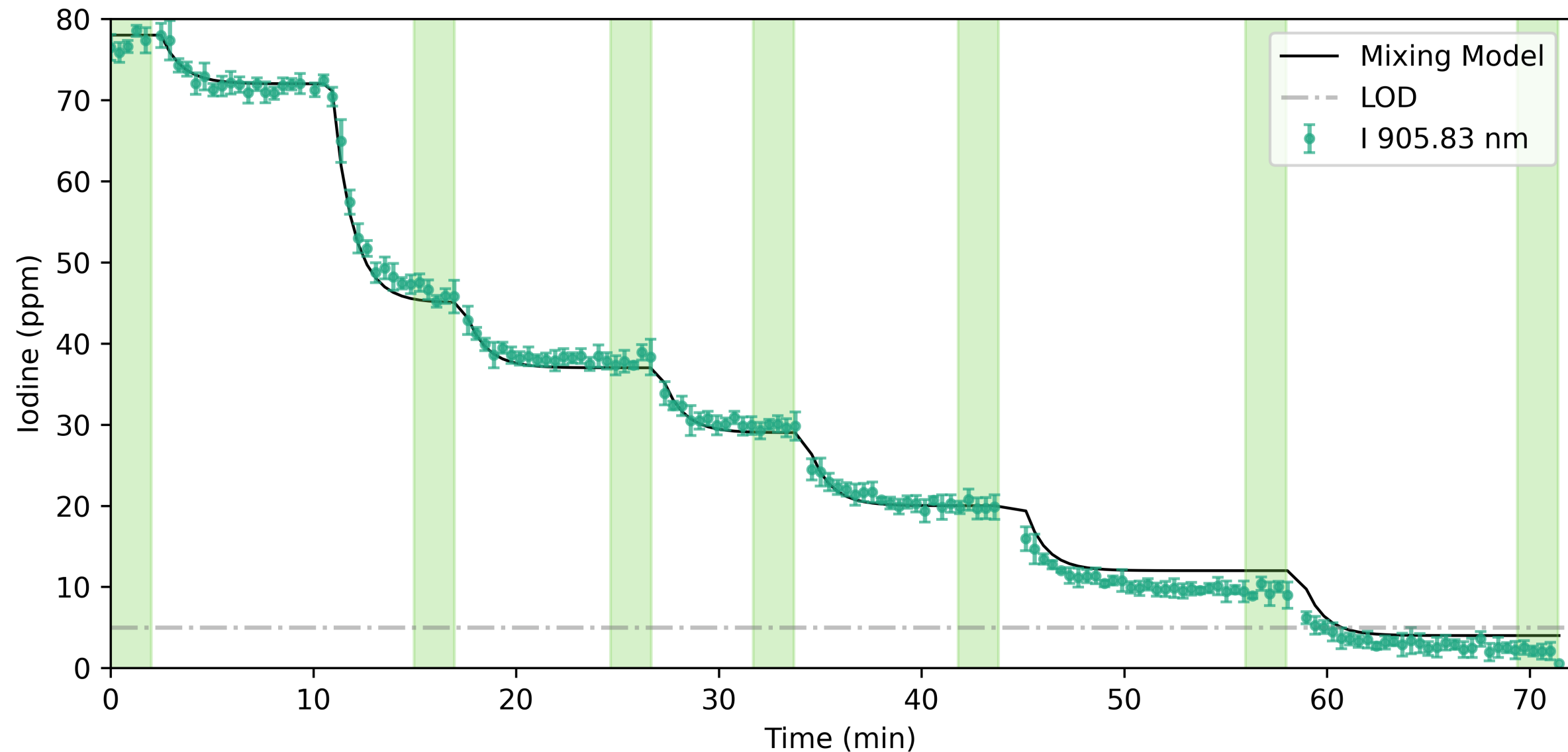
Calibration models for trace iodine quantification in a helium bulk gas. LIBS measurements were performed using a delay time of 1 μ s and a gate width of 1 ms.

Detection of iodine in Ar



Calibration models for trace iodine quantification in an argon bulk gas. LIBS measurements were performed using a delay time of 10 μ s and a gate width of 1 ms.

We can accurately track iodine gas in real-time



Green regions indicate calibration samples
Mixing Model is based on plug flow theory

Andrews et al. Journal of Analytical Atomic Spectrometry. 2026.



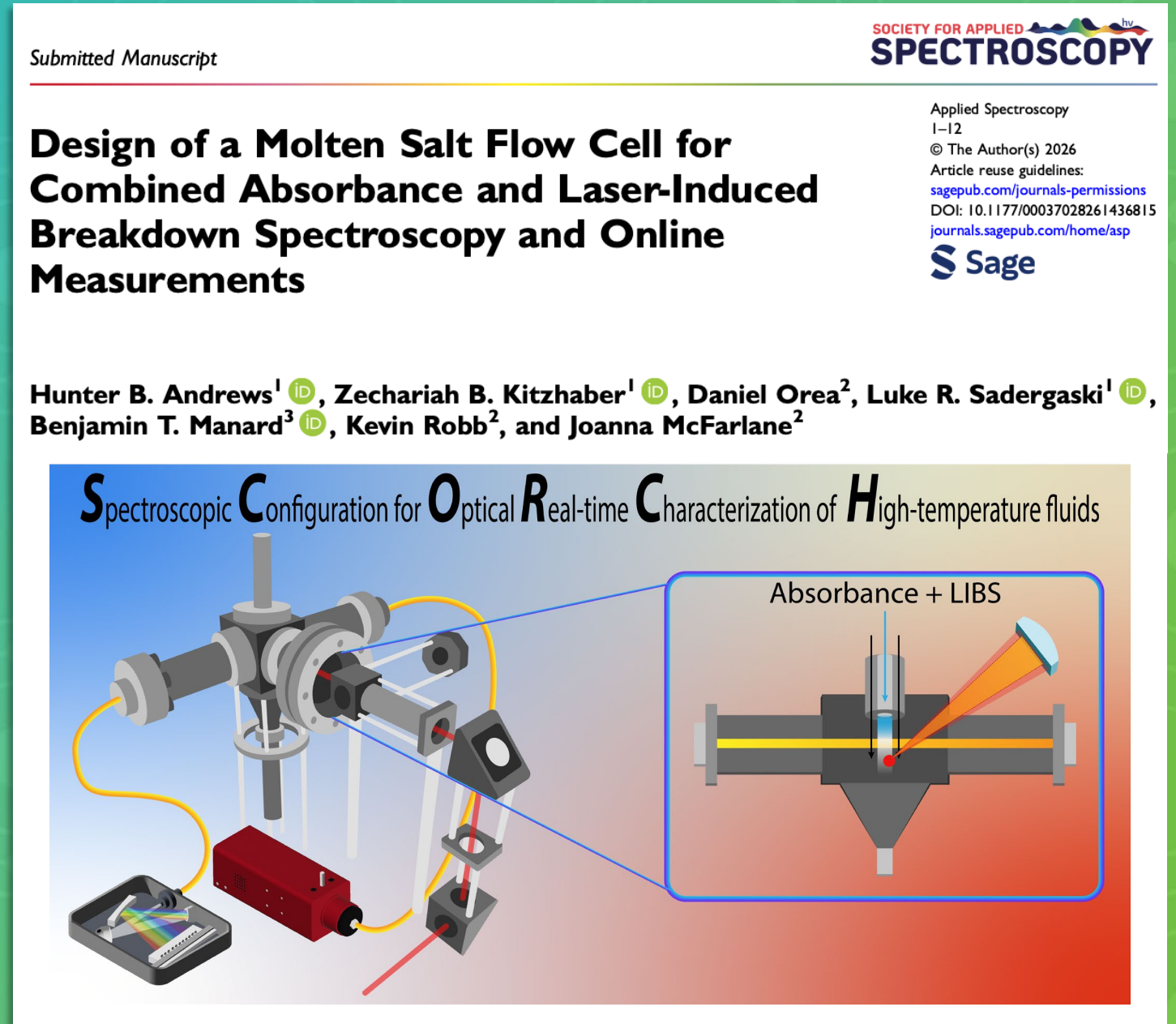
Molten Salt Reactor
P R O G R A M



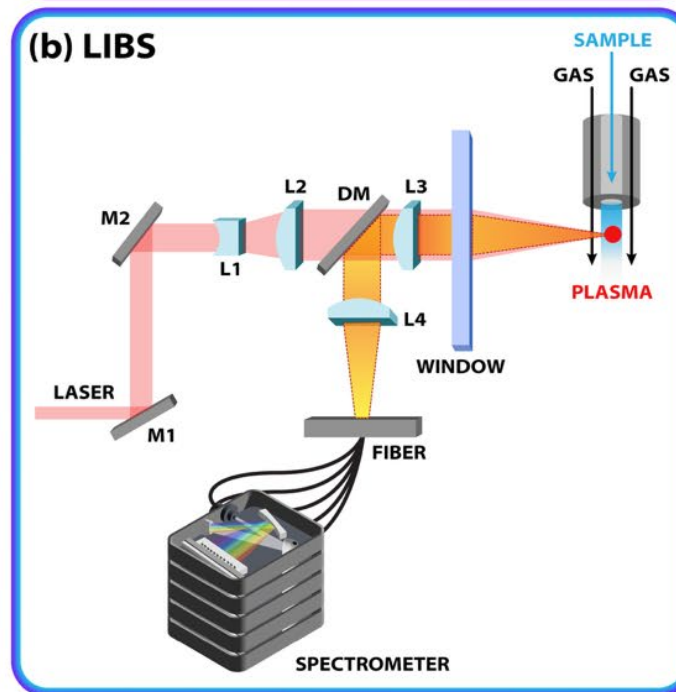
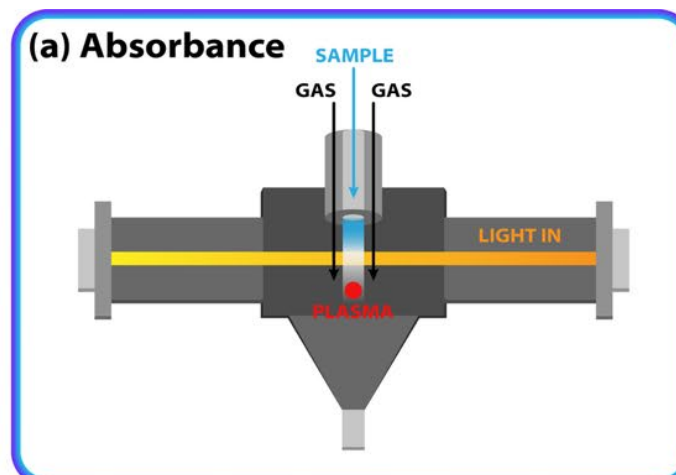
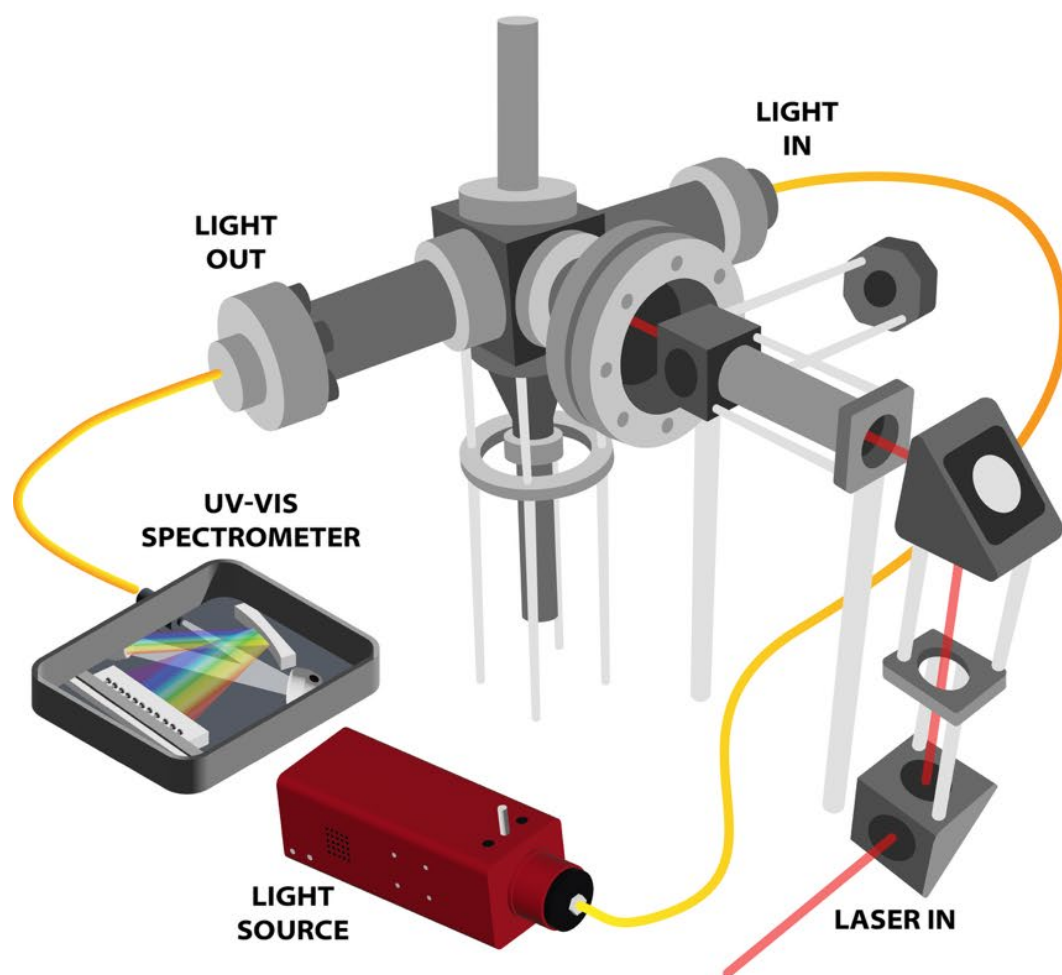
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A focus for FY26 is demonstrating LIBS on flowing molten salt systems

- LIBS on liquids is traditionally challenged by splashing effects, unstable sample location, and plasma quenching
- High temperature, corrosive salts limit optical access
- Online measurements of flowing salts can aid in understanding transport of species from the bulk salt to the off-gas

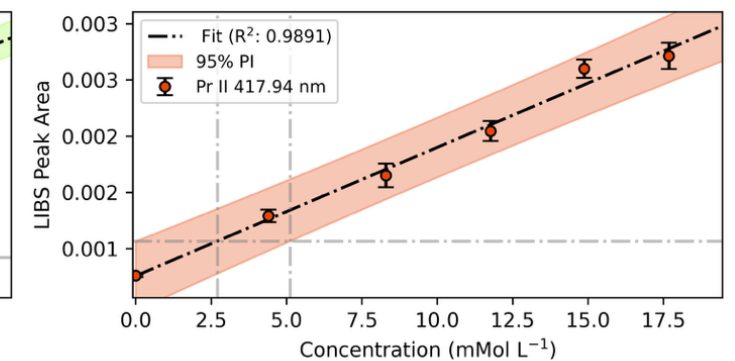
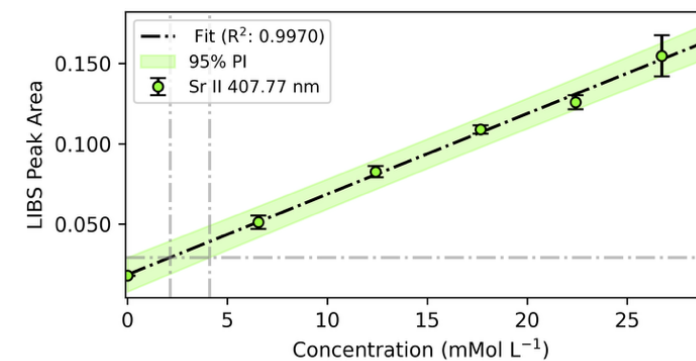
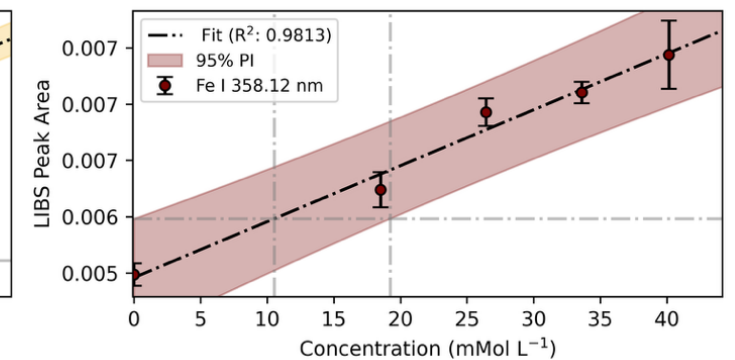
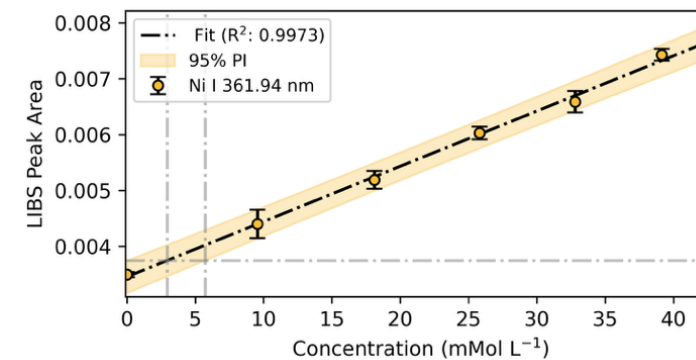
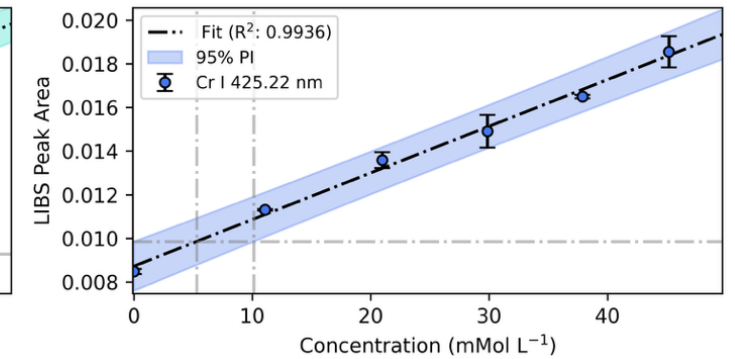
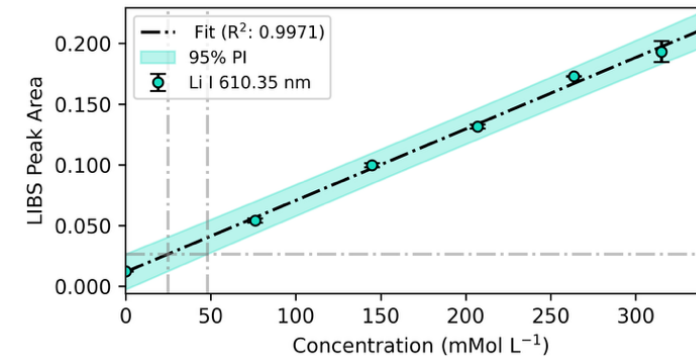
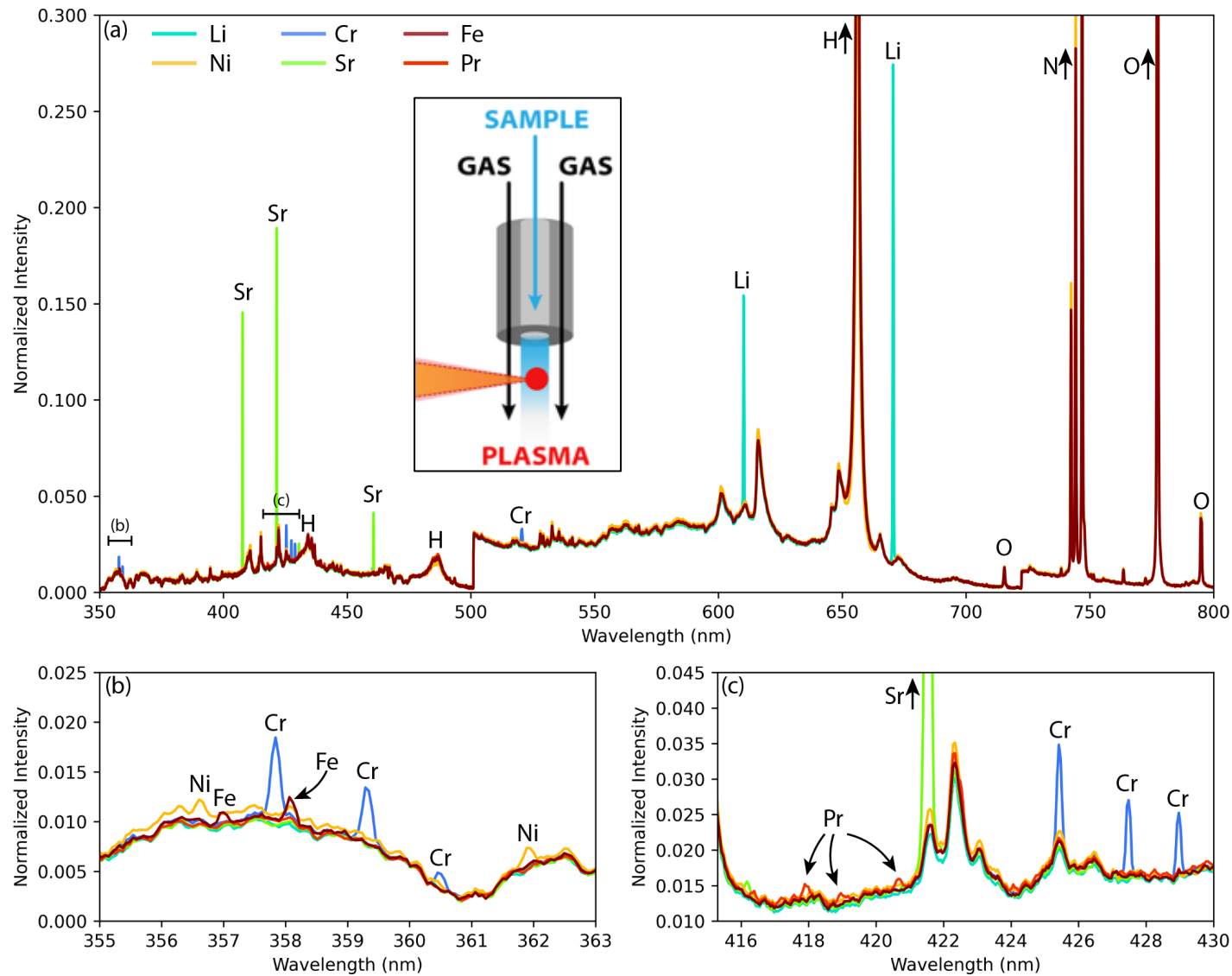


Introducing the SCORCH cell (Spectroscopic Configuration for Optical Real-time Characterization of High-temperature fluids)

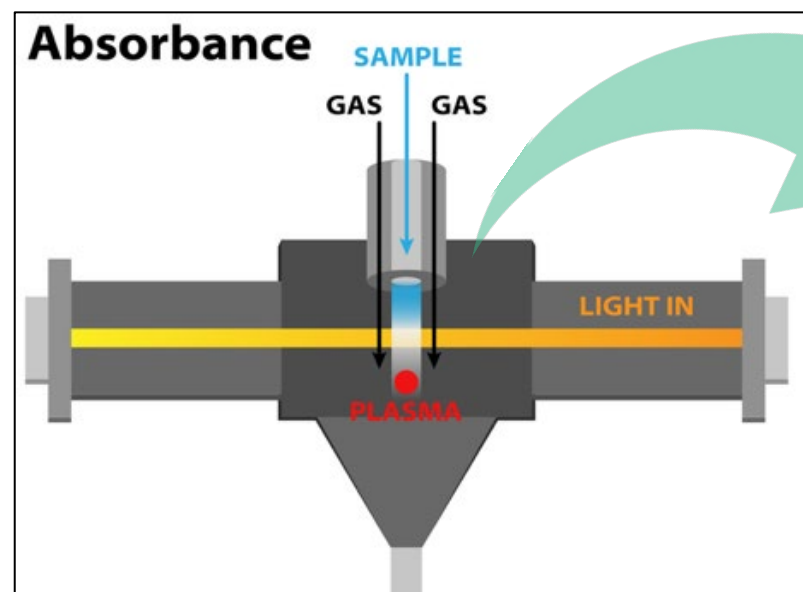


- The design allows for continuous fluid movement for online monitoring.
- The flow + gravity + sheath gas mitigates splashing effects
- The gas flow through the space around the sample stream allows optical windows to operate at lower temperatures.
- Orthogonal optical access allows for multiple measurement techniques.

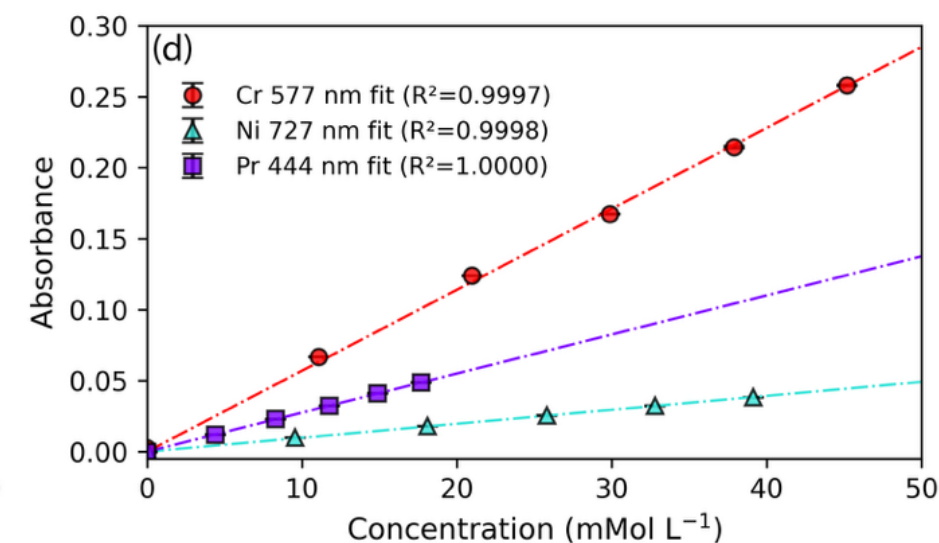
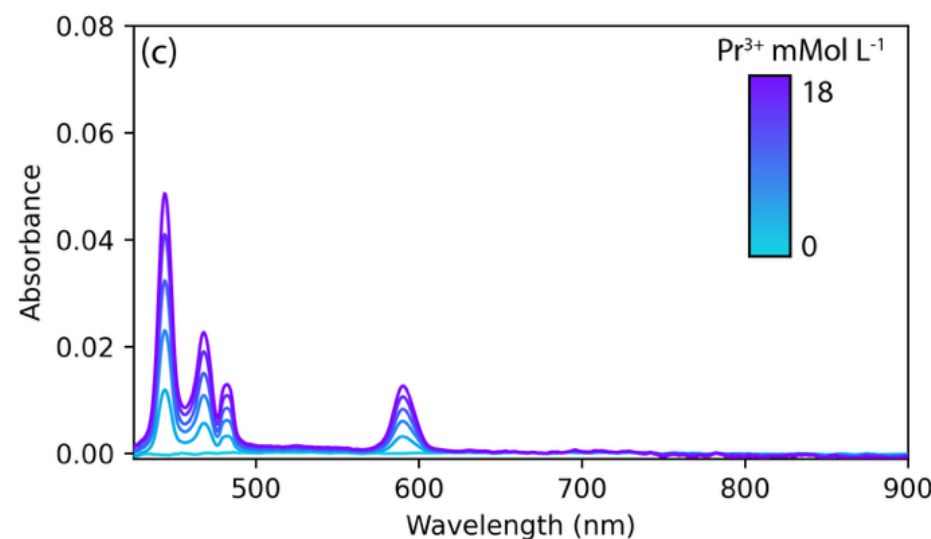
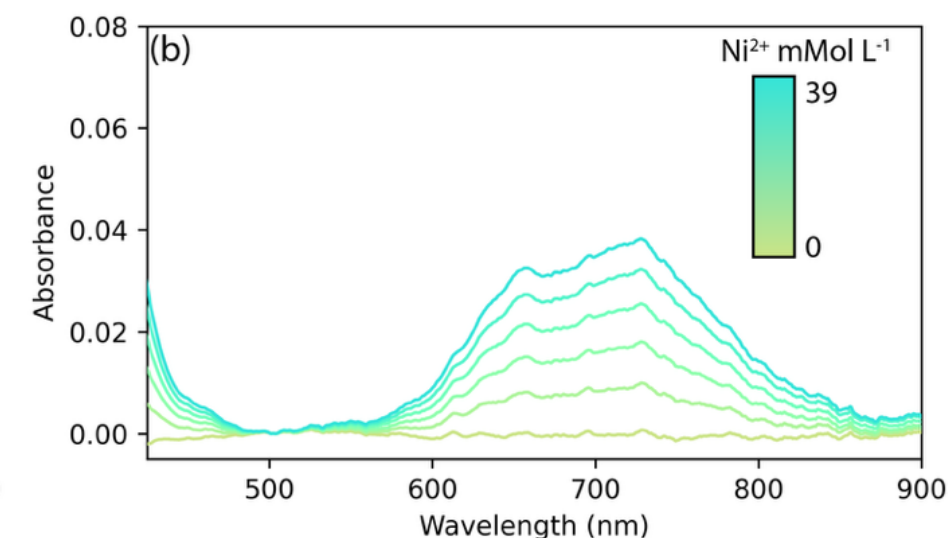
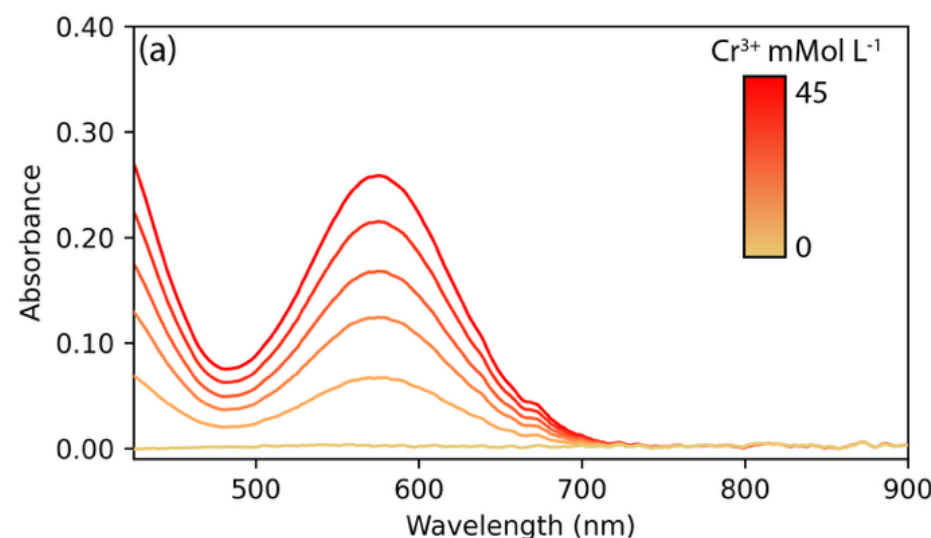
Proof-of-principle tests performed with room temperature samples flowing at 1 L min⁻¹



The SCORCH cell allows for multiple techniques to be integrated for complementary monitoring



SCORCH pathlength = 4.41 ± 0.10 mm



Multiple techniques can provide an enhanced dynamic range for online monitoring

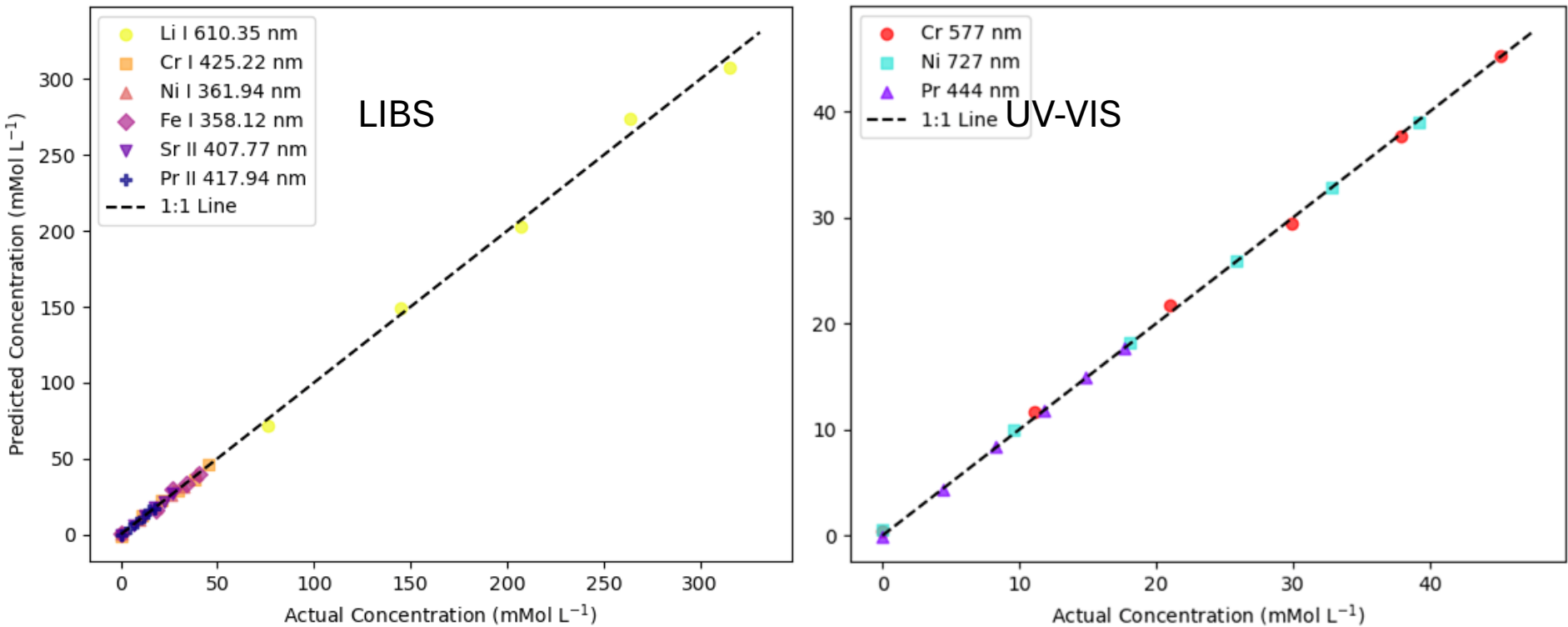
- LIBS has a larger dynamic range than UV-VIS
 - LIBS is sensitive to nearly all elements
- UV-VIS has better limits of detection (LOD)
 - Species must have an absorbance band
 - Subject to changing speciation in the sample
- The two techniques together provide greater flexibility

Table 2. LIBS calibration model figures of merit.

	Li I 610.35 nm	Cr I 425.22 nm	Ni I 361.94 nm	Fe I 358.12 nm	Sr II 407.77 nm	Pr II 417.94 nm
R^2	0.9971	0.9936	0.9973	0.9813	0.9970	0.9891
RMSEC (mmol L ⁻¹)	5.83	1.24	0.69	1.92	0.50	0.63
RMSECV (mmol L ⁻¹)	8.93	1.95	1.17	2.69	0.73	0.94
%RMSEC	1.9%	2.8%	1.8%	4.8%	1.9%	3.5%
%RMSECV	2.8%	4.3%	3.0%	6.7%	2.7%	5.2%
LOD (mmol L ⁻¹)	24.9	5.30	2.96	10.5	2.12	2.71

Table 3. Absorbance calibration model figures of merit.

	Cr ³⁺ 577 nm	Ni ²⁺ 727 nm	Pr ³⁺ 444 nm
R^2	0.9997	0.9998	1.0000
RMSEC (mmol L ⁻¹)	0.501	0.325	0.053
RMSECV (mmol L ⁻¹)	0.556	0.354	0.056
%RMSEC	2.2%	1.7%	0.6%
%RMSECV	2.5%	1.8%	0.6%
LOD (mmol L ⁻¹)	0.080	0.397	0.209

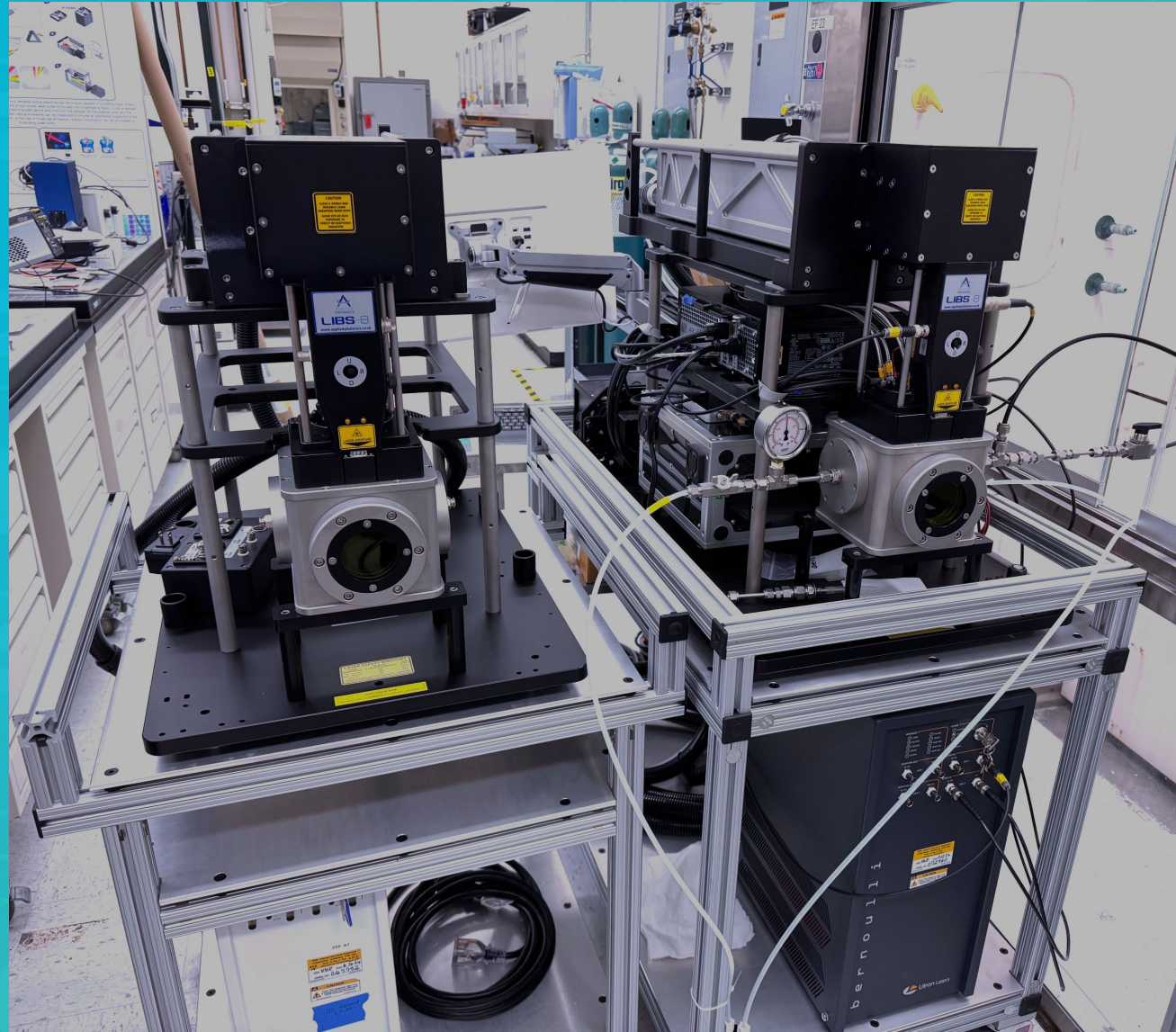


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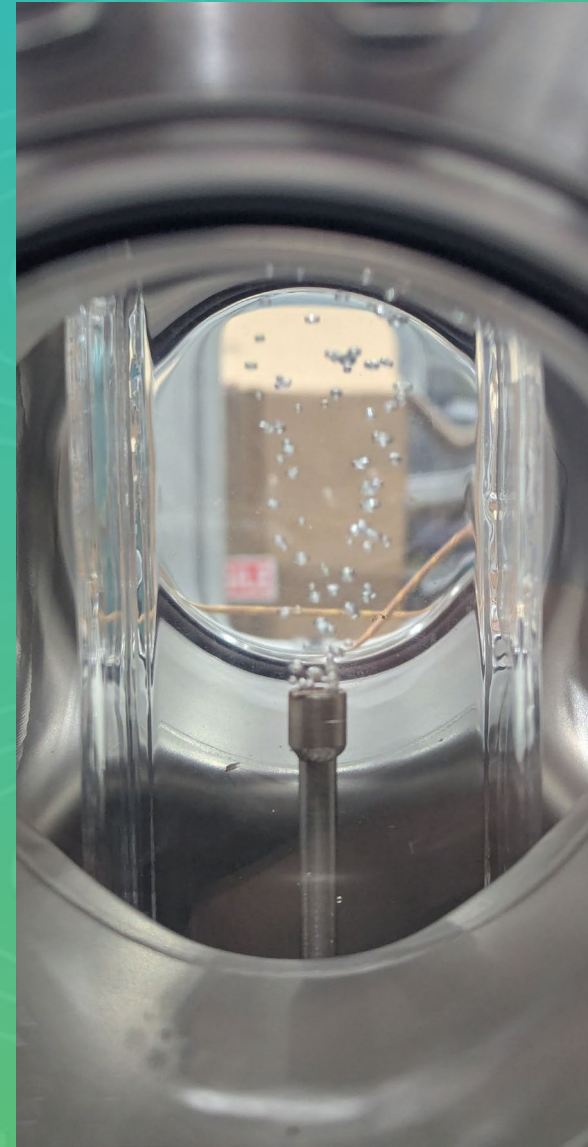


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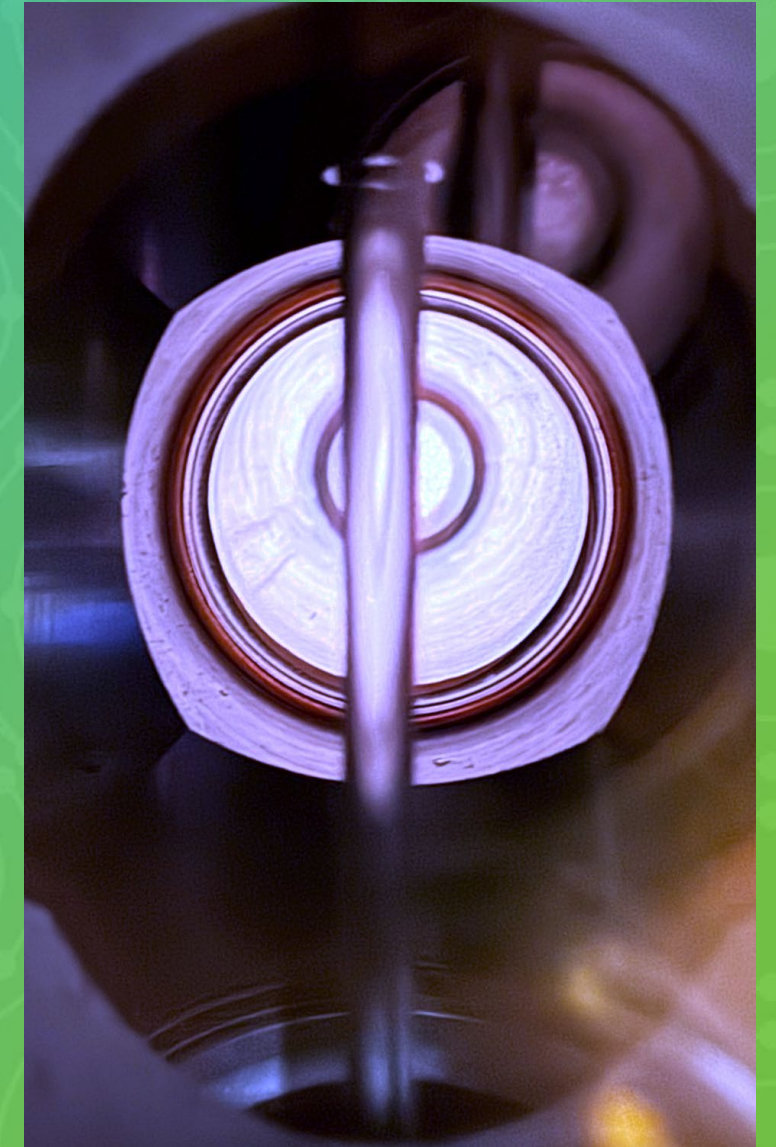
Next steps for campaign work in FY26



Two mobile LIBS platforms now complete: SP- and DP-LIBS for further integration across the lab

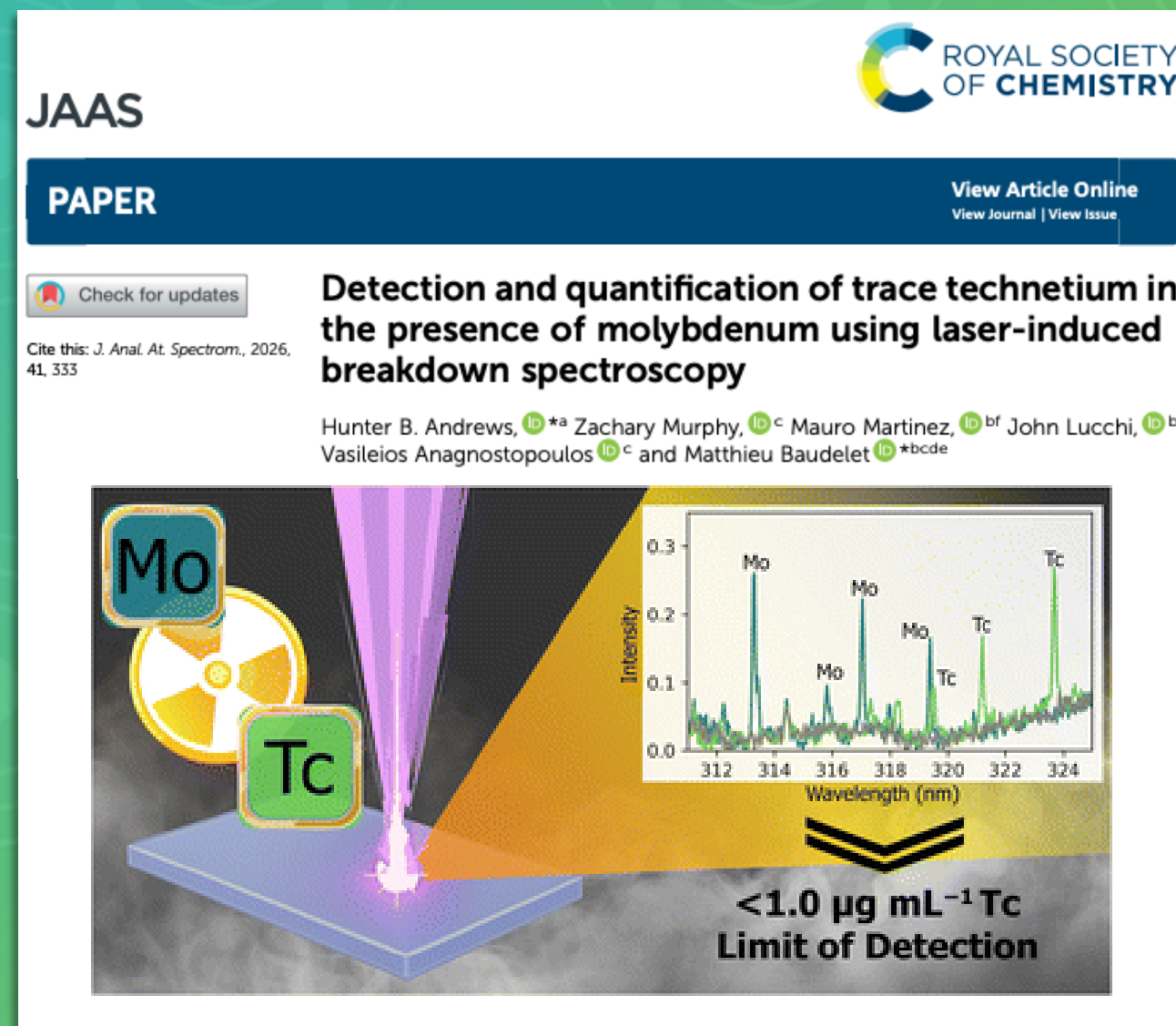
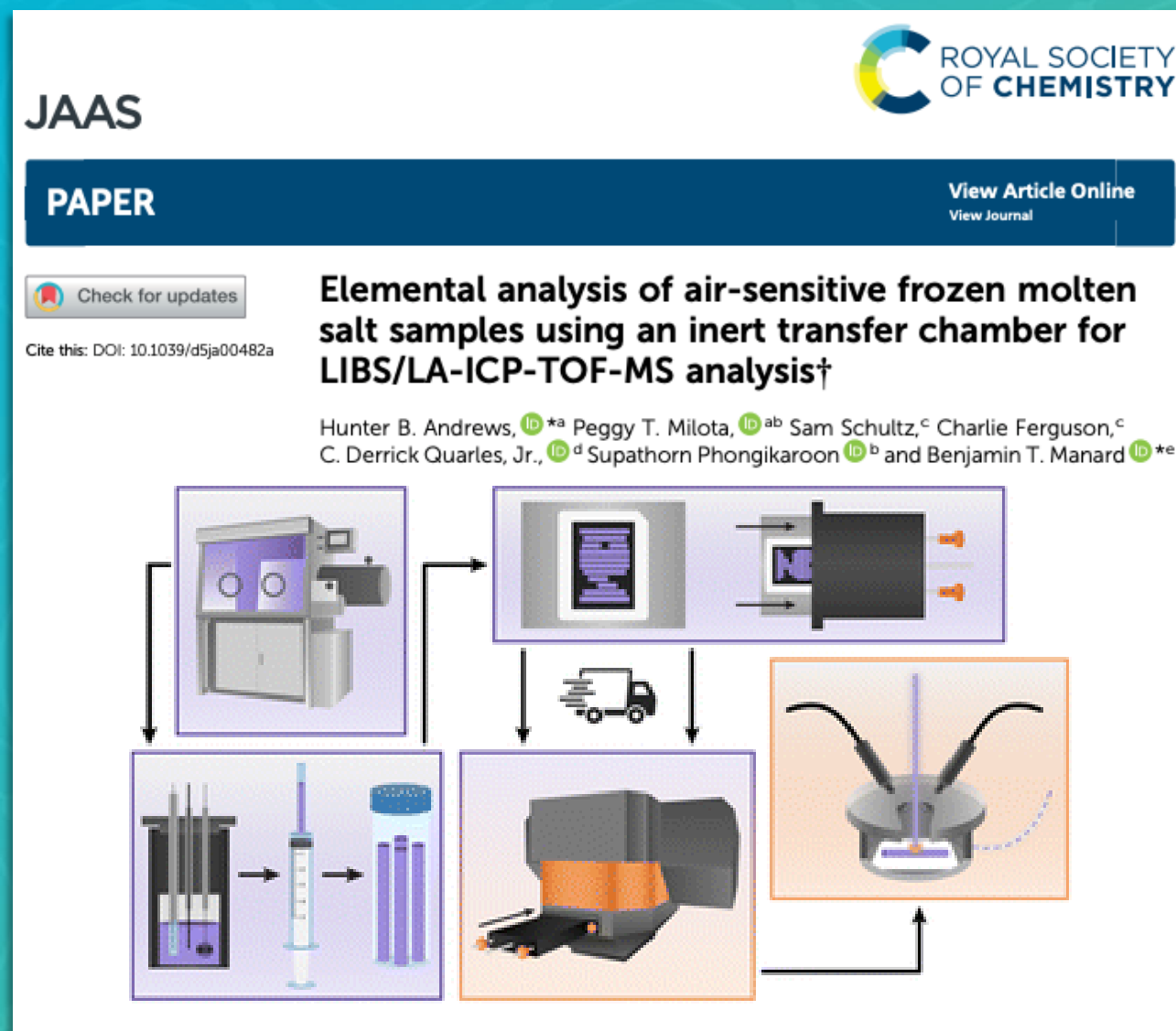


LIBS will be coupled to VISTA for gas/particle transport analysis



The SCORCH cell will be integrated into a small salt loop

Ask me about our other recently published molten salt LIBS work





Collaborators

Zechariah Kitzhaber, RSTD

Daniel Orea, FFESD

Katie Johnson, FFESD

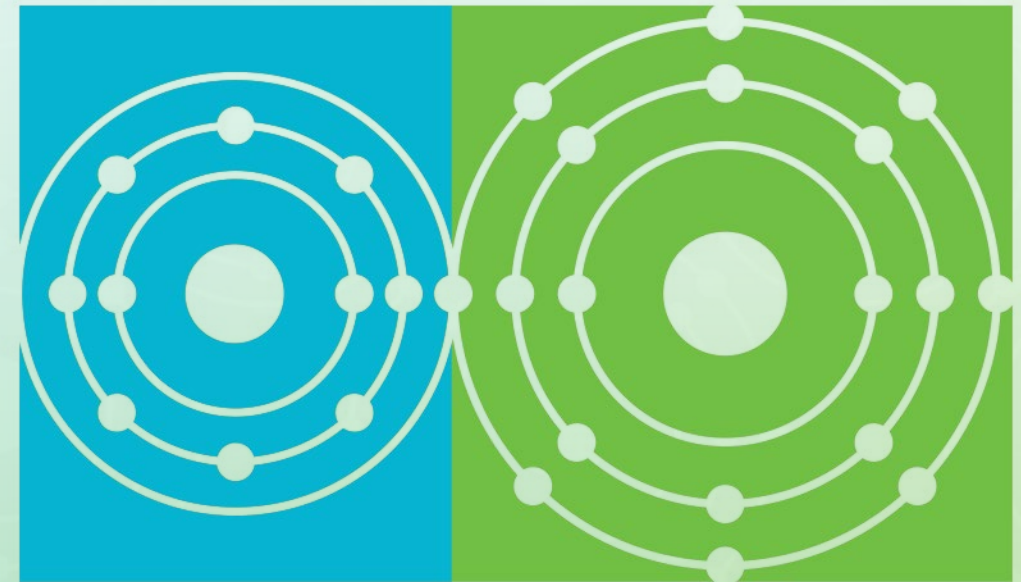
Kevin Robb, FFESD

Joanna McFarlane, FFESD

Ben Manard, CSD

Chase Coble, FFESD

Luke Sadergaski, RSTD



Molten Salt Reactor
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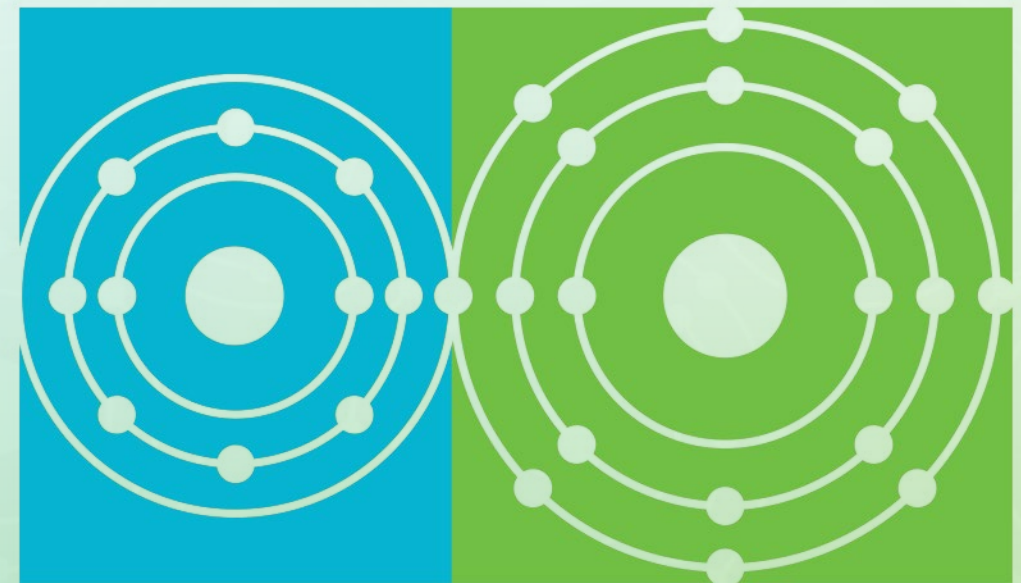
Funding

US DOE, Molten Salt Reactor Program

Recovery and Waste Form Development Program

Thank you!

andrewshb@ornl.gov



Molten Salt Reactor

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