Molten Salt Reactor
PROGRAM

Laser-Induced Breakdown Spectroscopy for Elemental Monitoring of MSR Off-Gas Streams

Hunter Andrews, Zechariah Kitzhaber, Daniel Orea, Joanna McFarlane

Oak Ridge National Laboratory

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Los Alamos NATIONAL LABORATORY
OAK RIDGE National Laboratory
Pacific Northwest NATIONAL LABORATORY
Sandia National Laboratories
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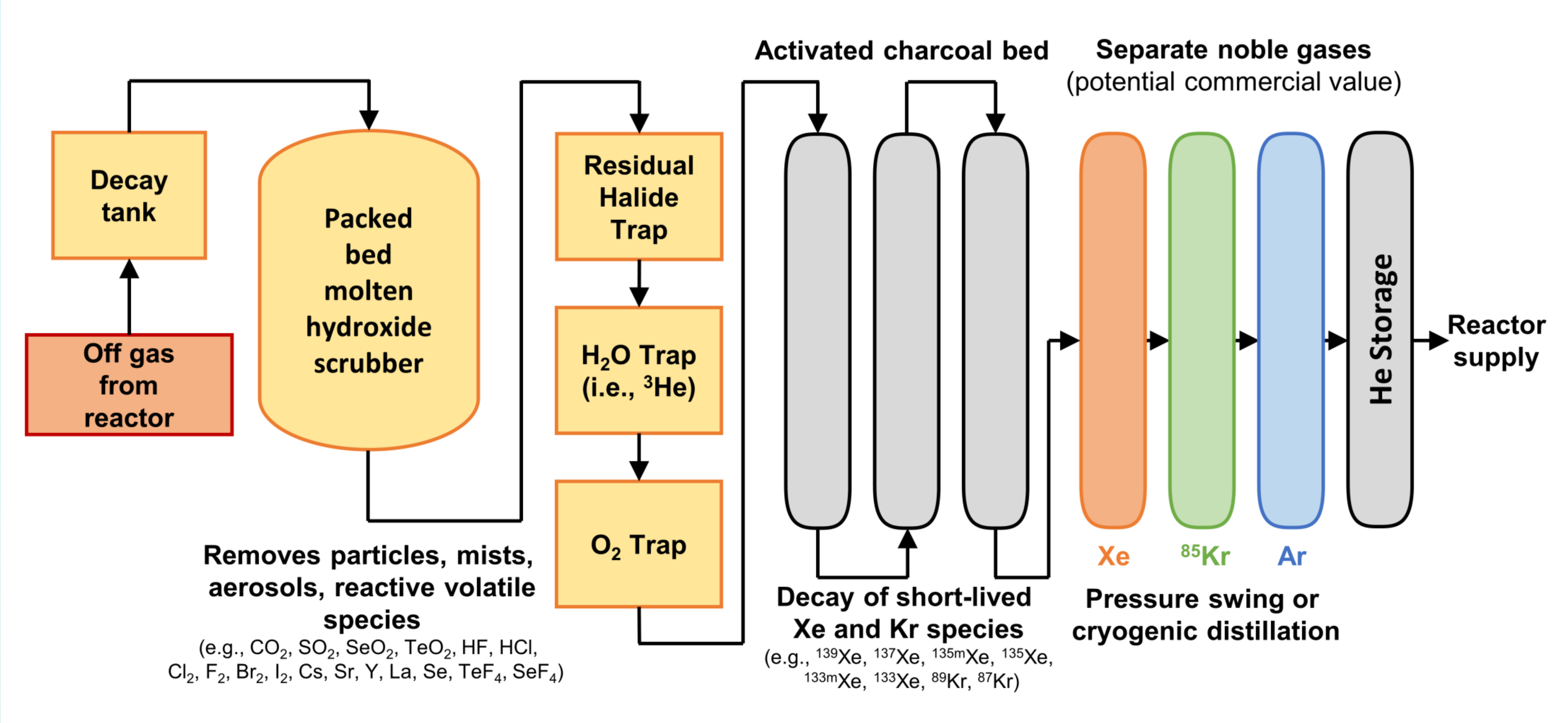
To aid deployment we are developing technology for off-gas treatment



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

Riley et al. Nuclear Engineering and Design, 2019, 345, 94-109.
Andrews et al. Nuclear Engineering and Design, 2021, 385, 111529.

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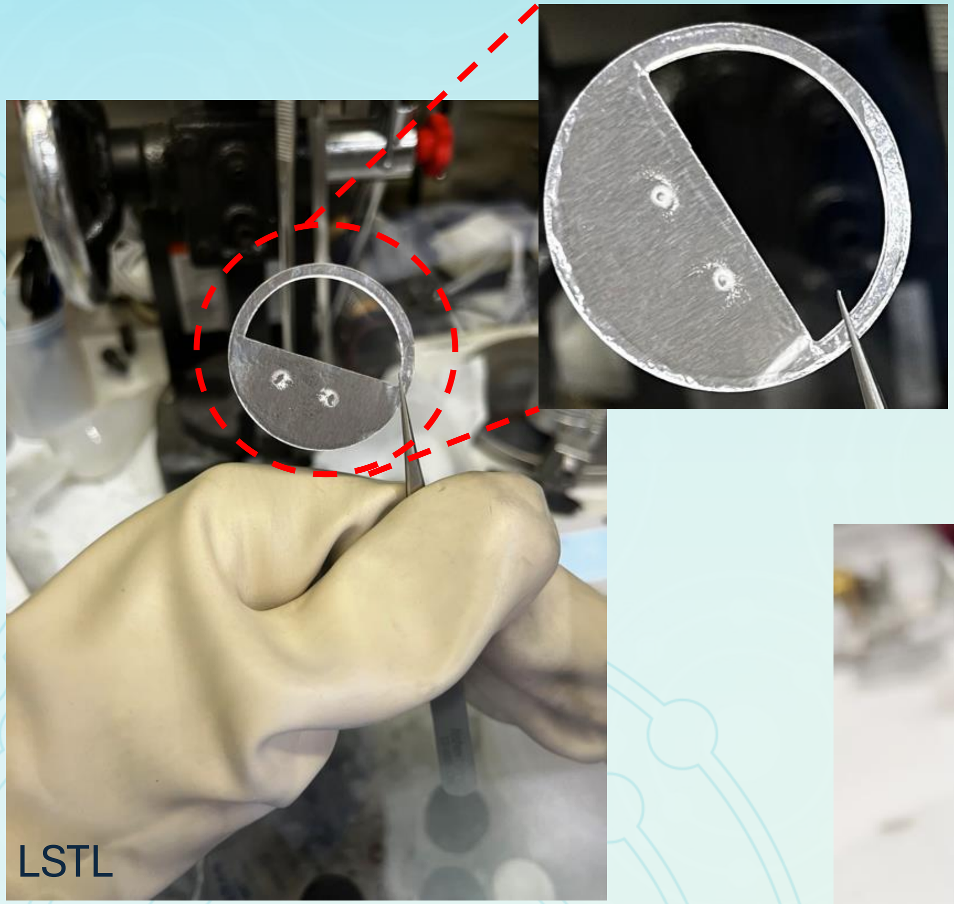
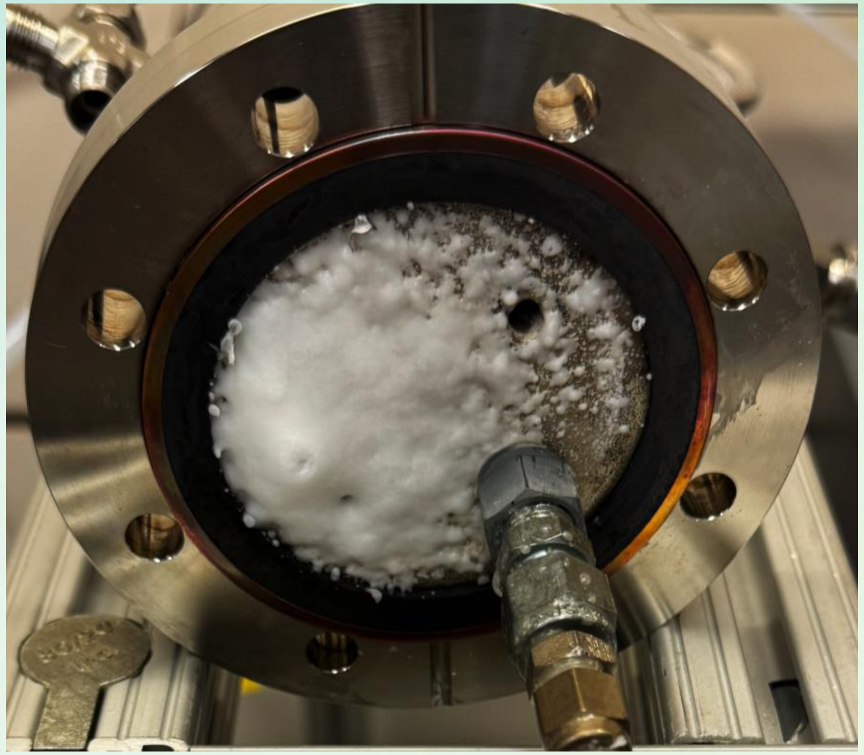
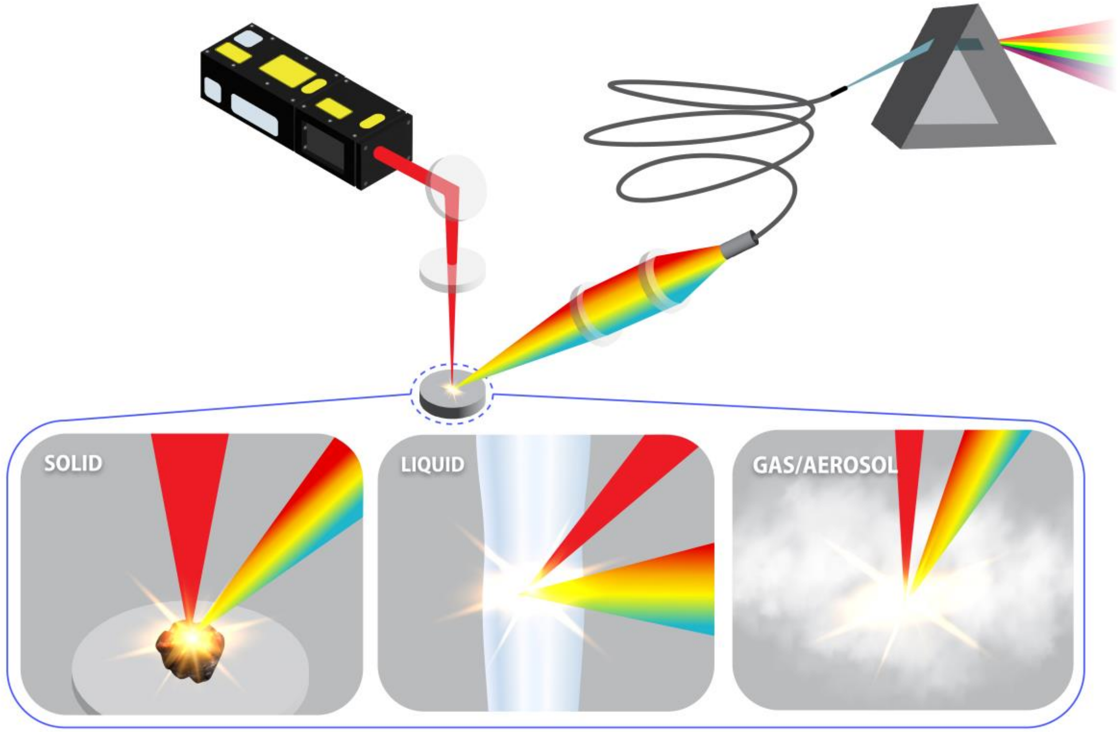
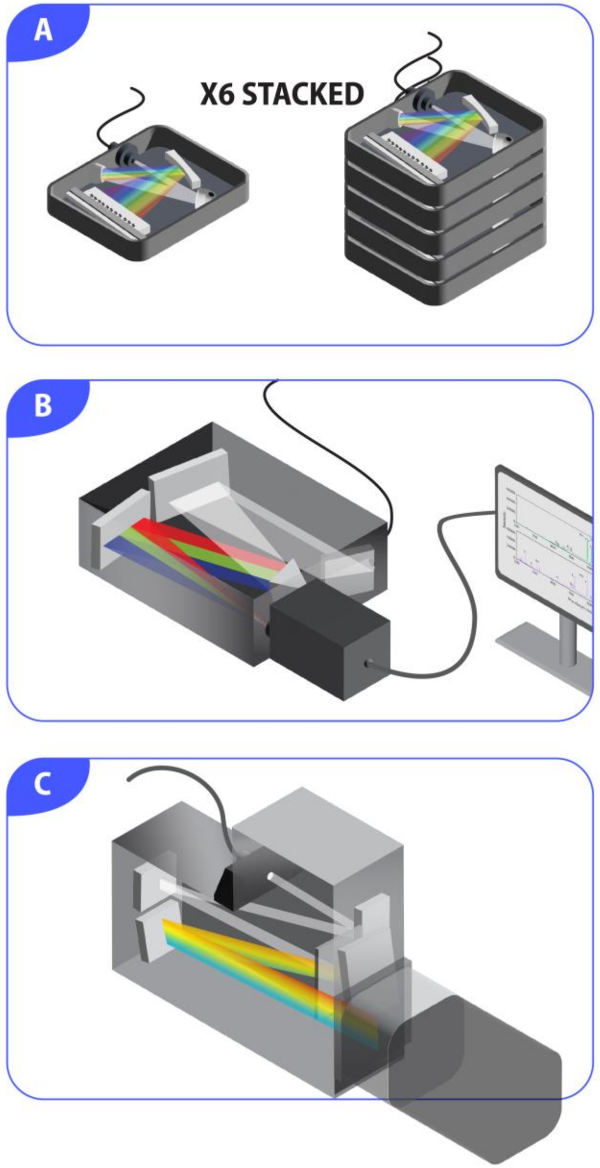
MSRs offer great benefit and challenges





Laser-Induced Breakdown Spectroscopy (LIBS)



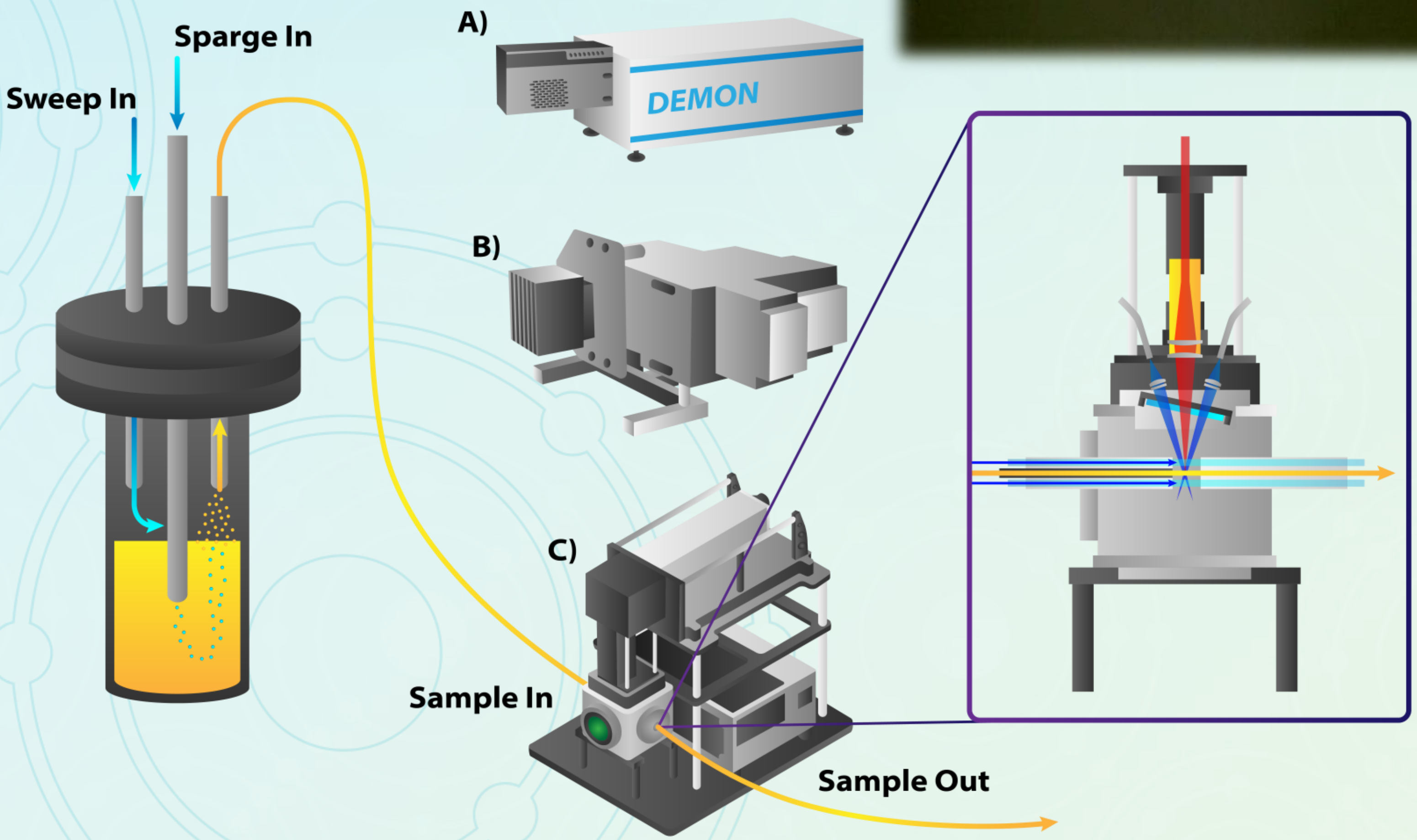


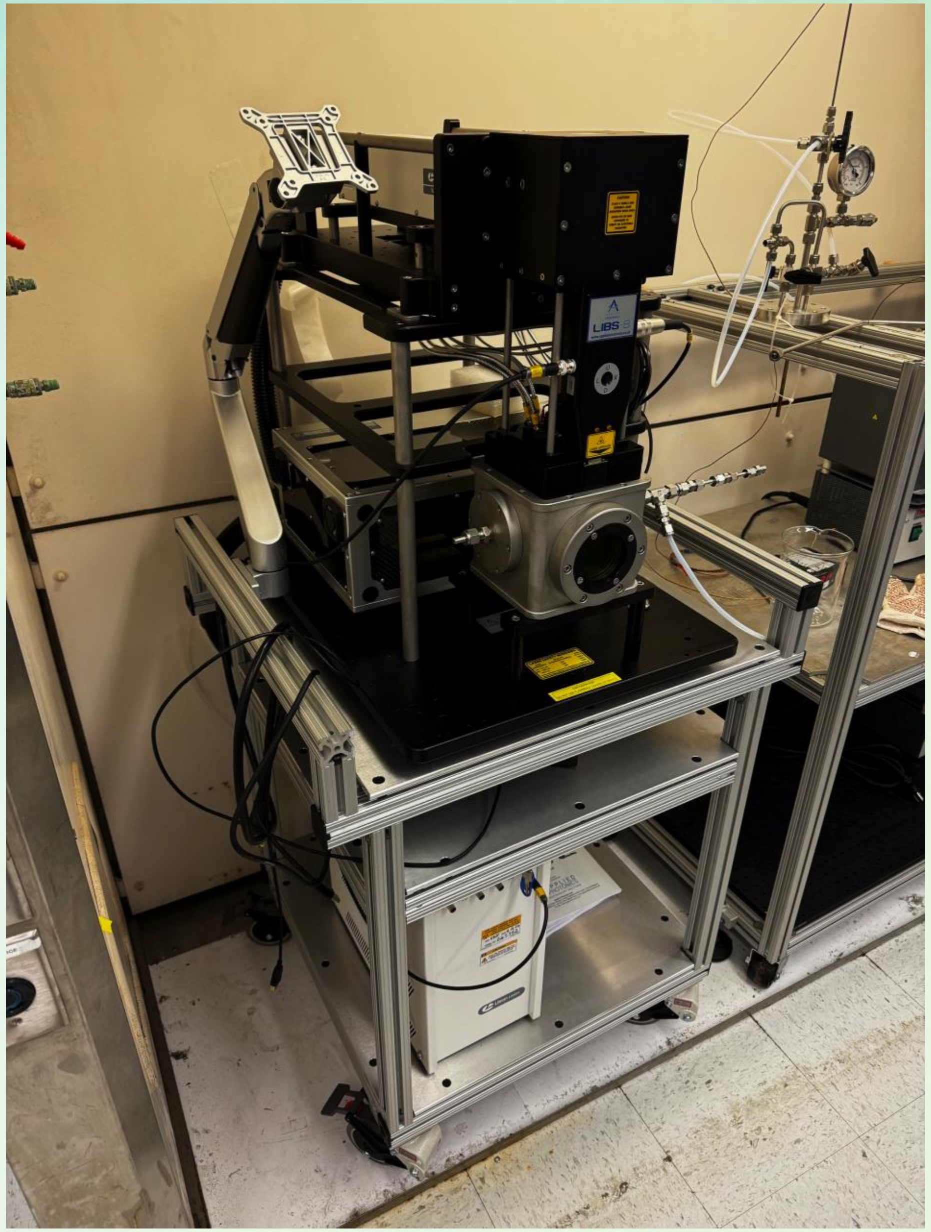
Taking things one step further…

- Mobile LIBS platform for deployment
- Investigating molten aerosol transport
- Correlation between aerosol concentration and signal
- Elemental and isotopic monitoring
- Continuous gas monitoring

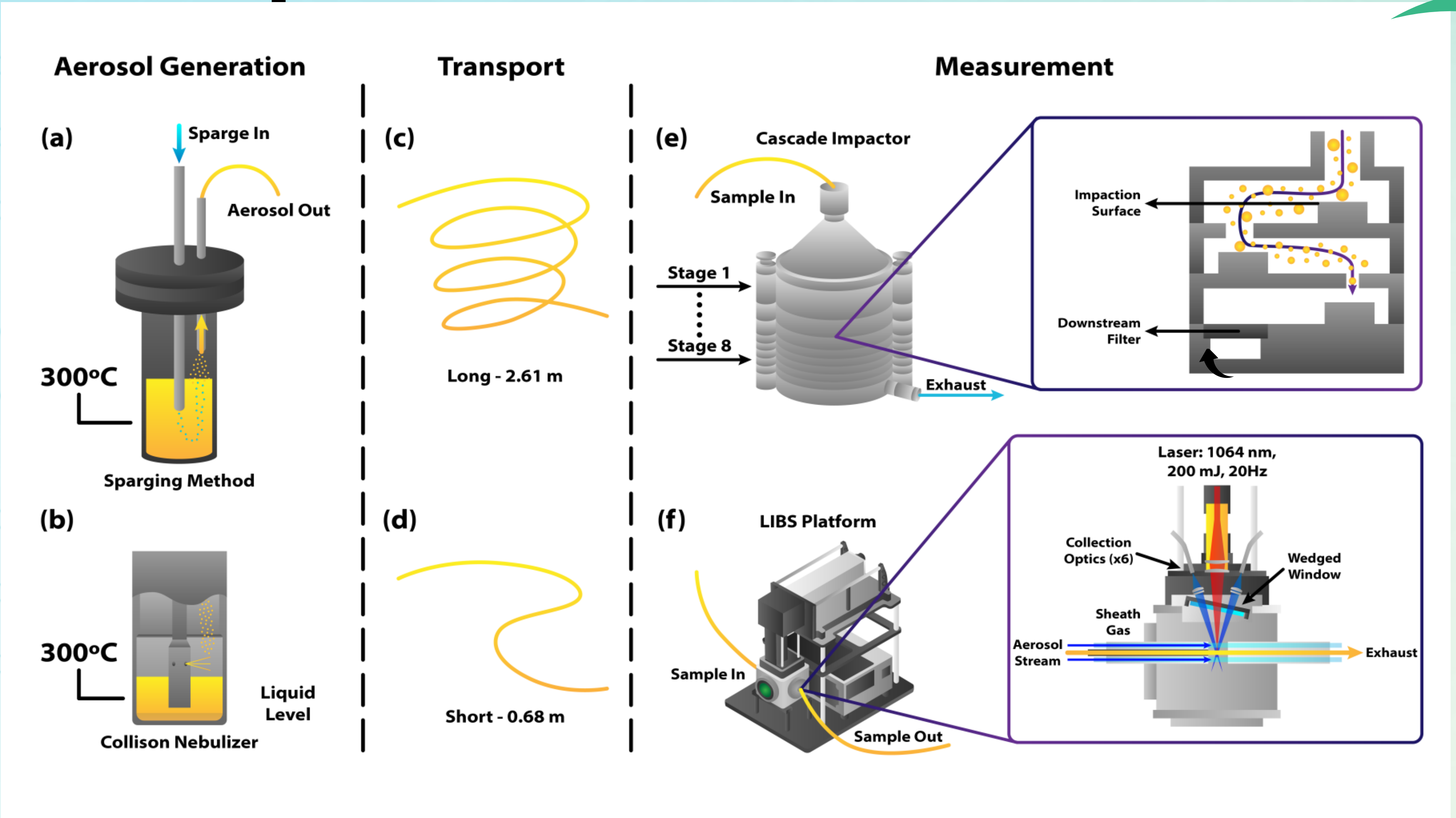
Andrews et al. *JACS*. 2025. *147* (1), 910-917.
Kitzhaber et al. 2025. *Under review.*
Andrews et al. 2025. *Under review*

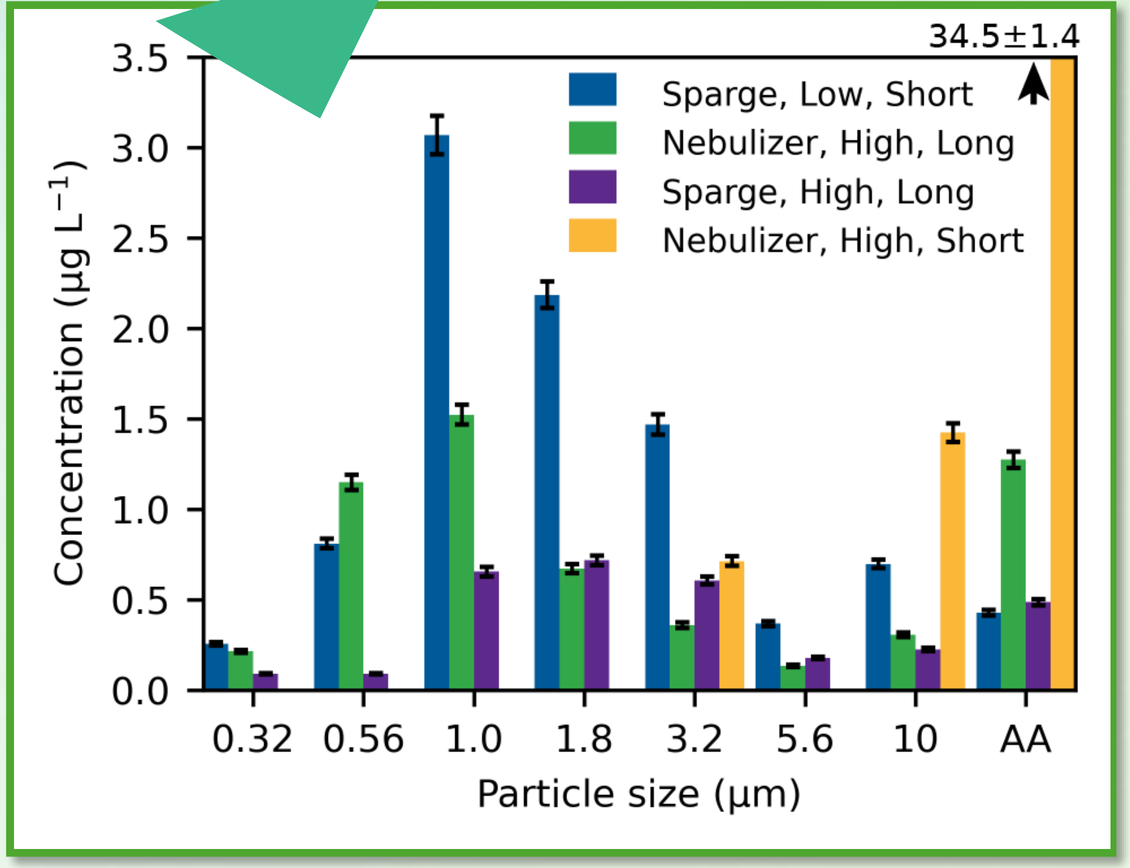
Molten salt aerosol stand and mobile LIBS platform





Sparge sampling and nebulization were compared





Sparging at low flow rates appears optimal

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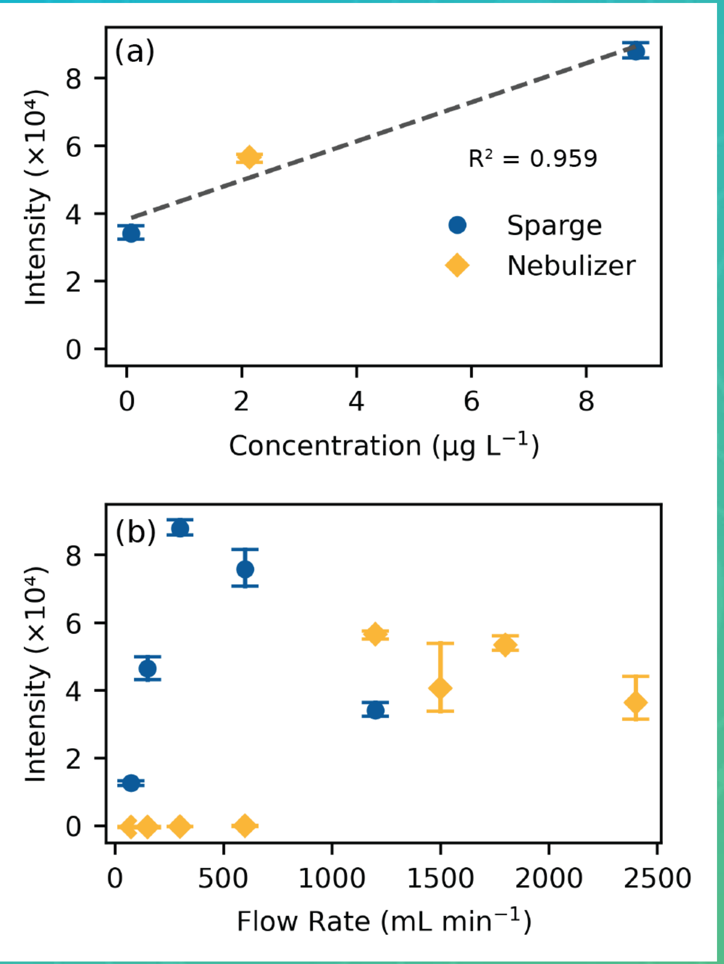
Kitzhaber et al. 2025. *Under review.*

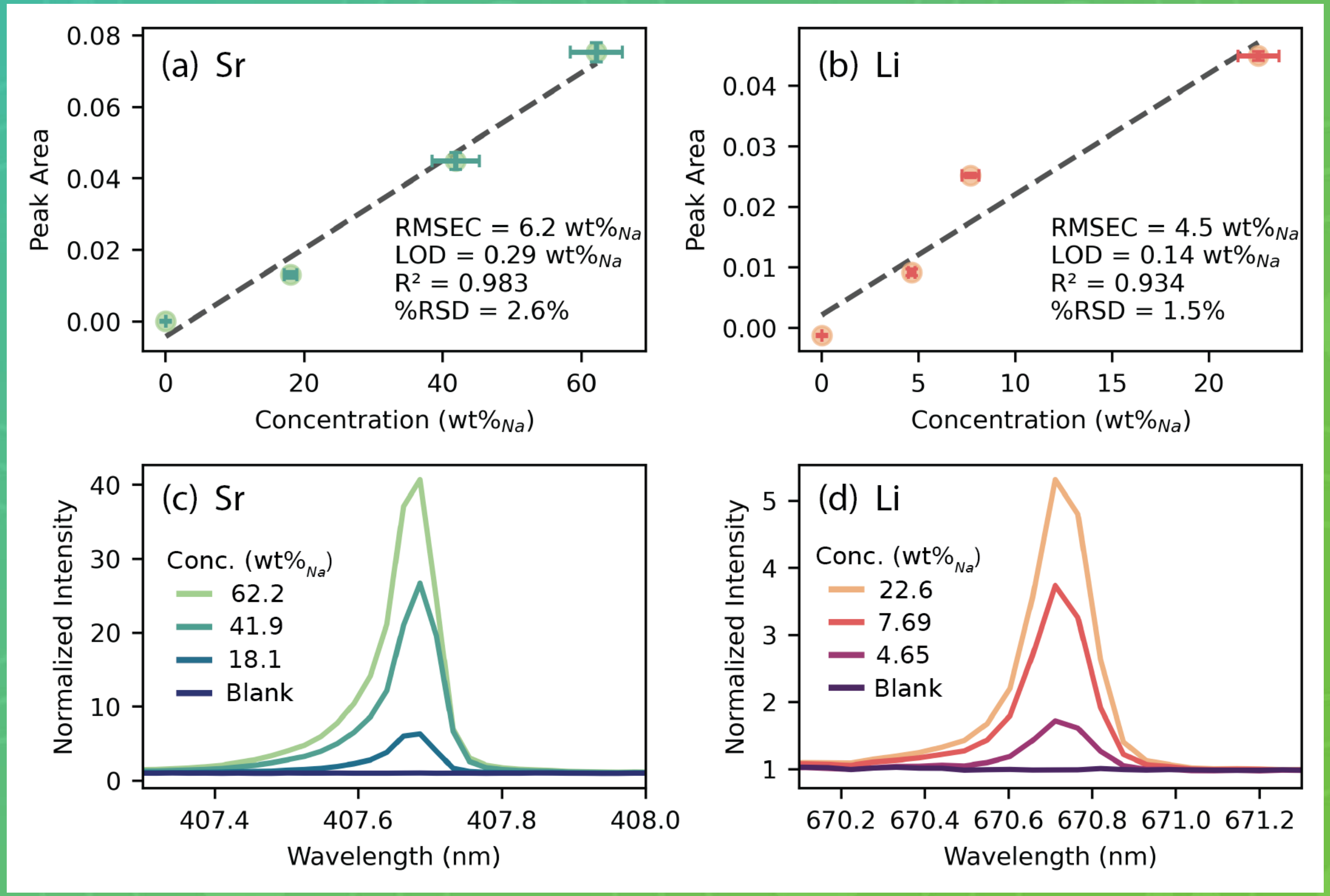
LIBS signal is related to aerosol concentration and the composition of the salt itself

Signal vs Aerosol Concentration / Sparge Rate



LIBS signal measured > 0.08 μg L^{-1}

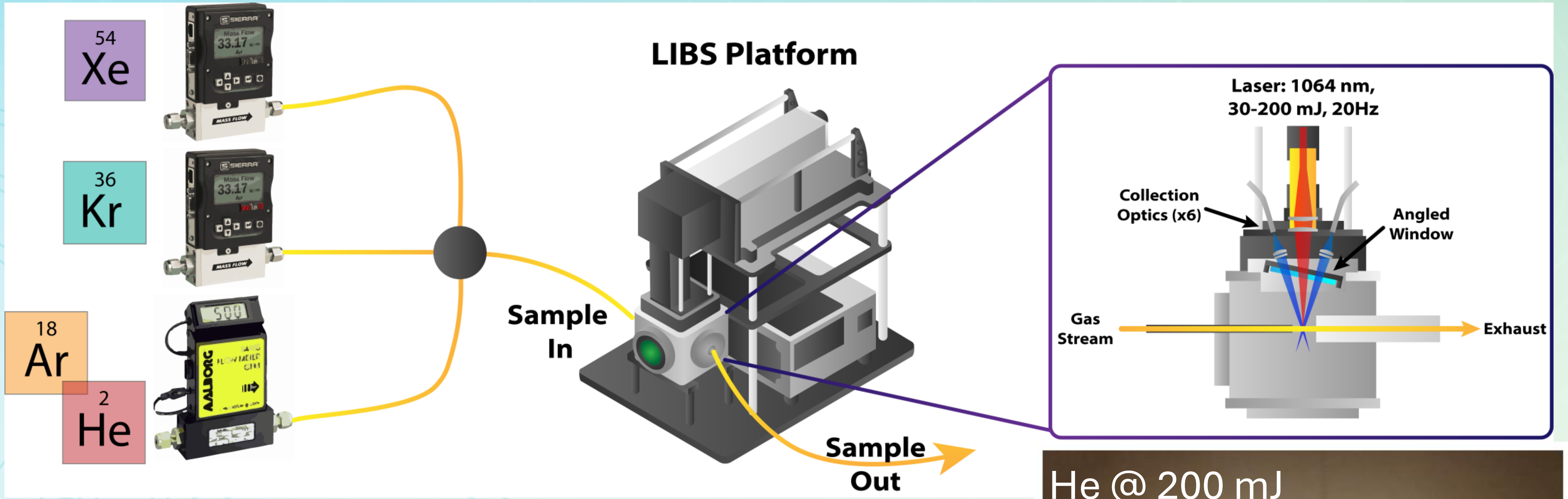
Signal vs Trace Analyte Composition

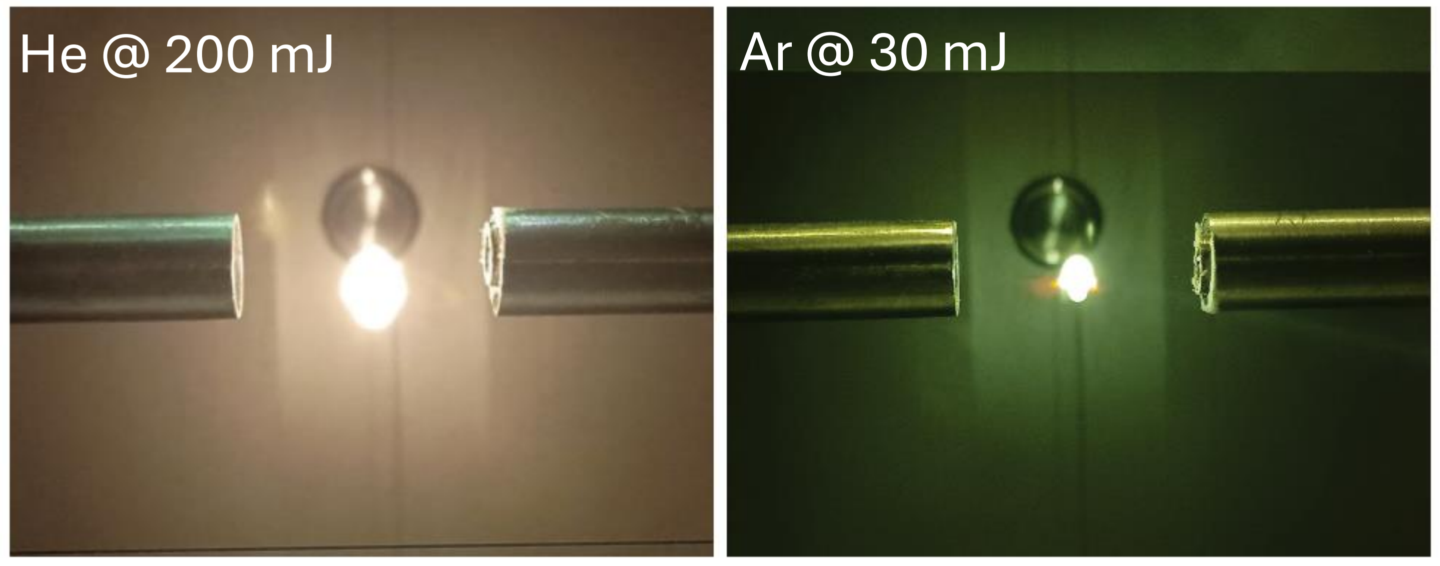


LOD_{Sr} = 0.29 $wt\%_{Na}$ ~ 350 μg mL^{-1} in the bulk
LOD_{Li} = 0.14 $wt\%_{Na}$ ~ 170 μg mL^{-1} in the bulk

Kitzhaber et al. 2025. *Under review.*

The LIBS Platform allows for easy changing between the monitored sample lines





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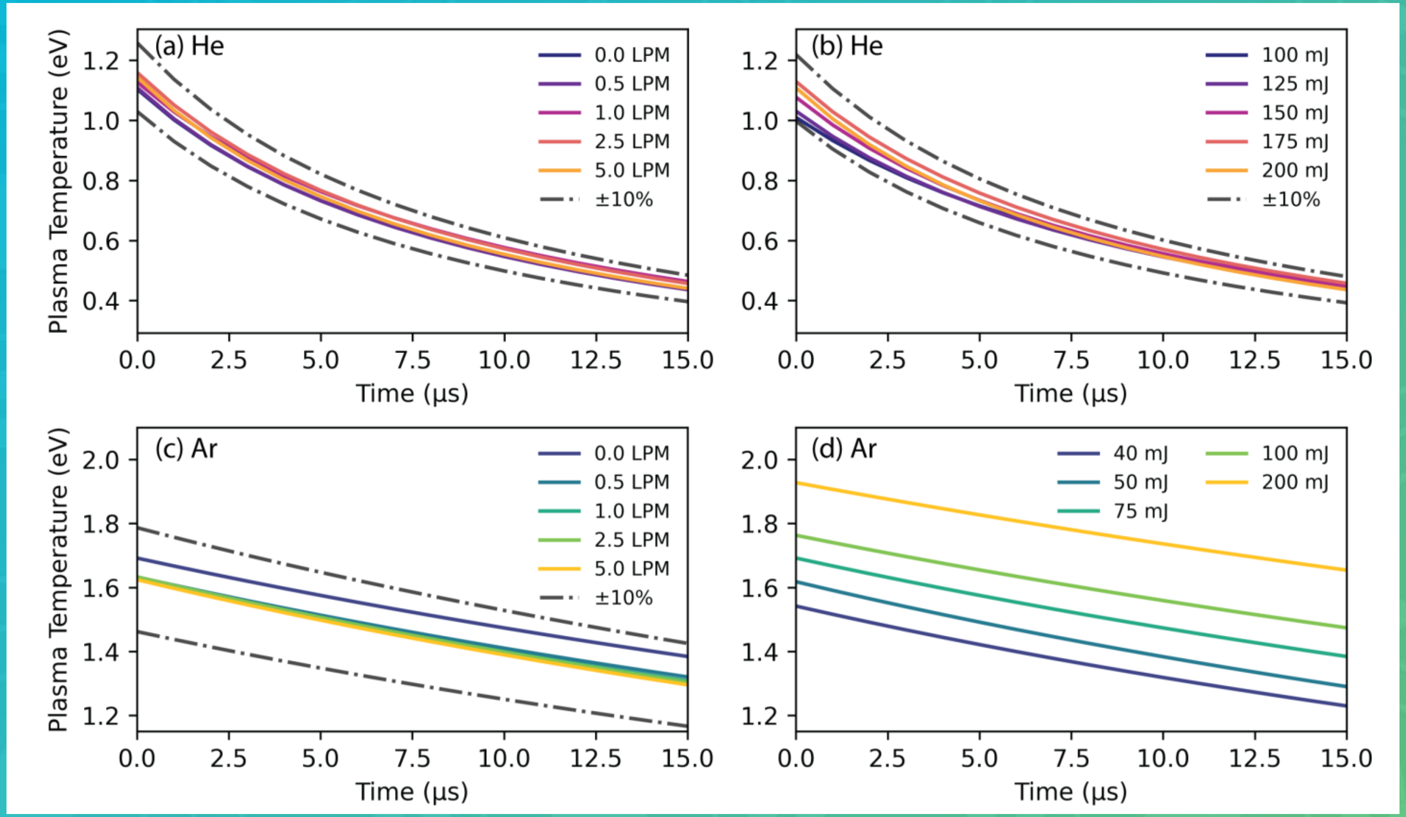
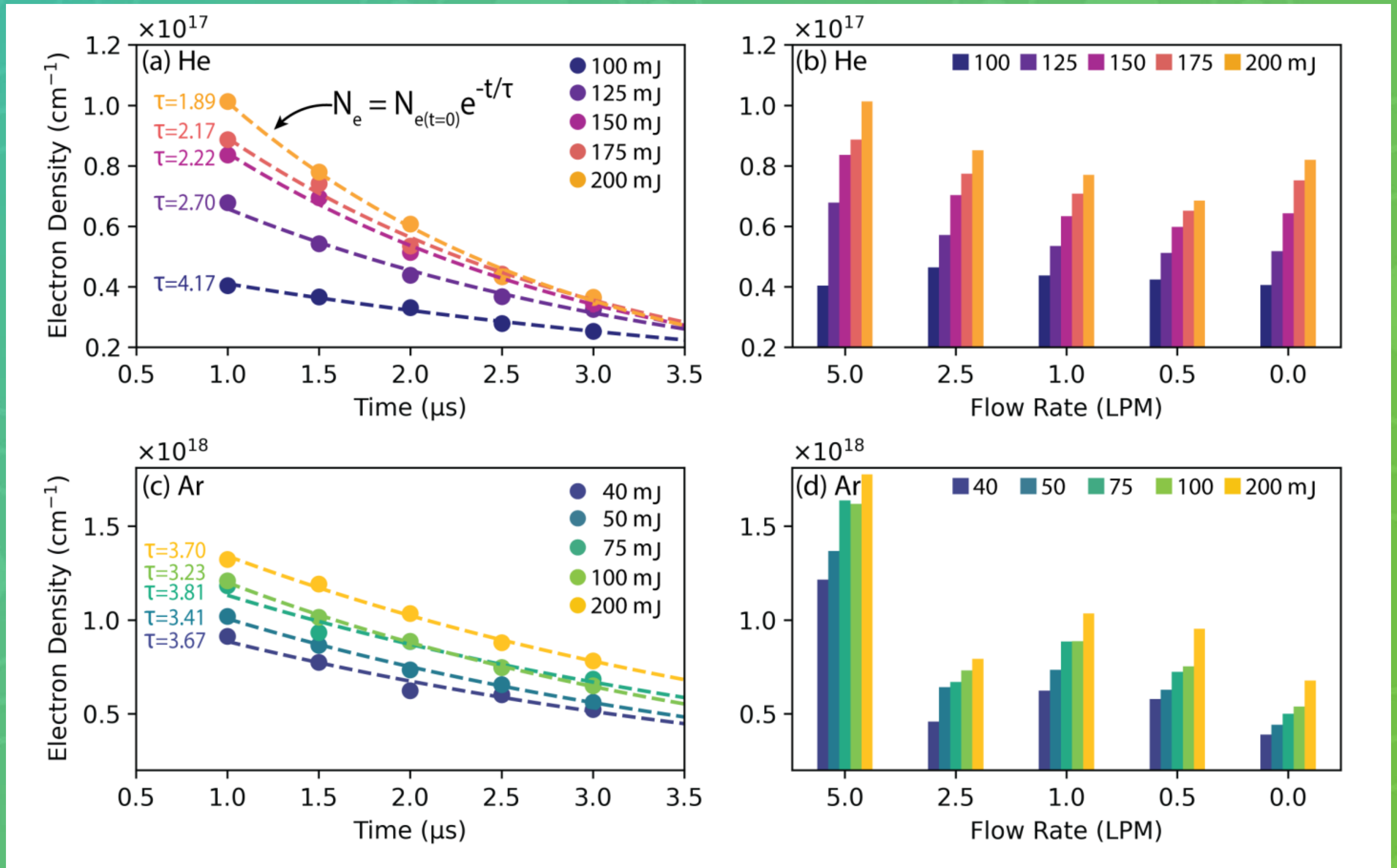
Andrews et al. 2025. *Under review.*

Switching between He and Ar bulk gases will directly impact the LIBS plasma

Plasma Temperature vs Flow Rate / Laser Power



Electron density vs Flow Rate / Laser Power



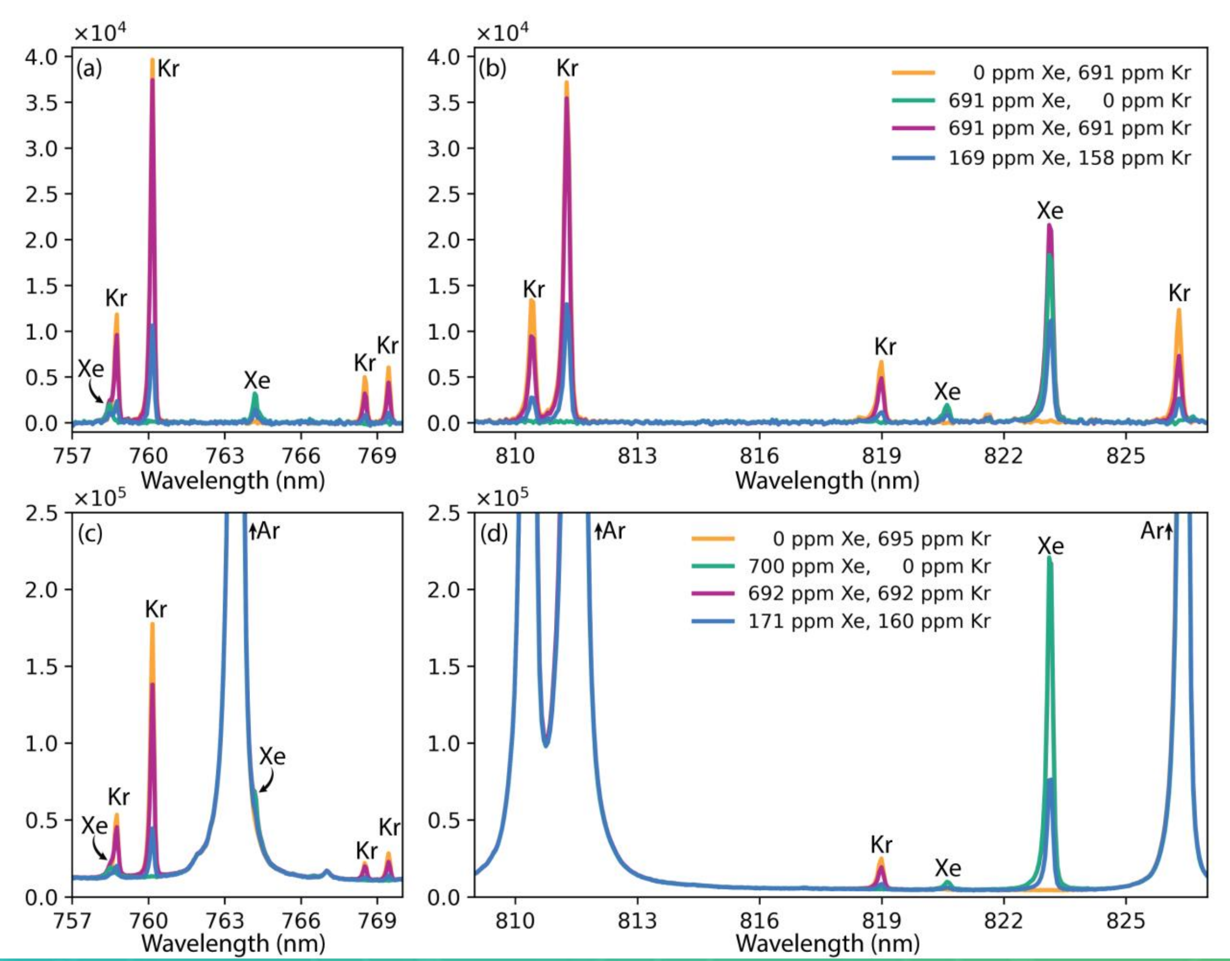
Andrews et al. 2025. *Under review.*

Not only does the bulk gas impact the signal, but so do other analytes

Xe and Kr in He and Ar Bulk Gases

He

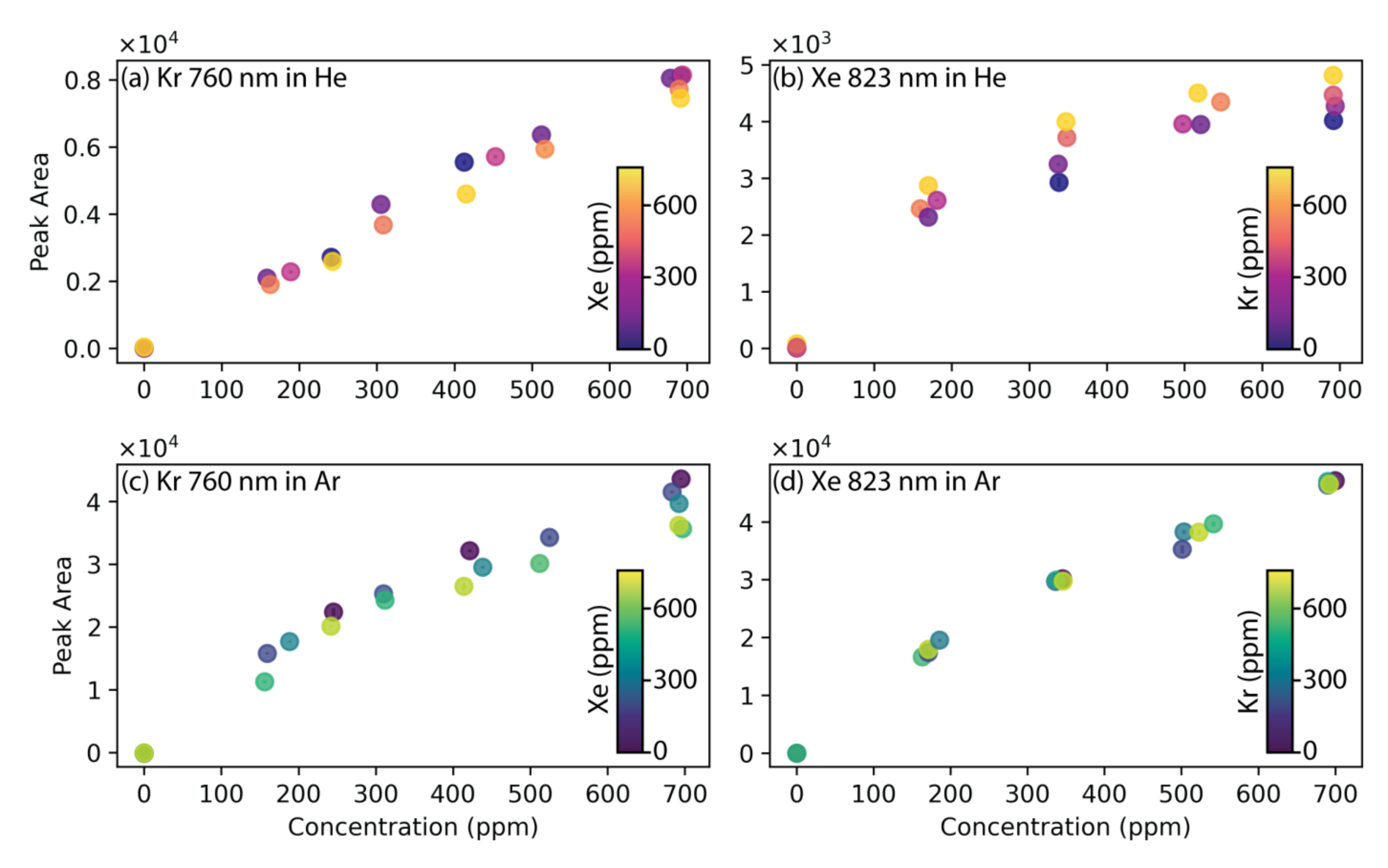
Ar



A Closer Look at Matrix Effects

He

Ar



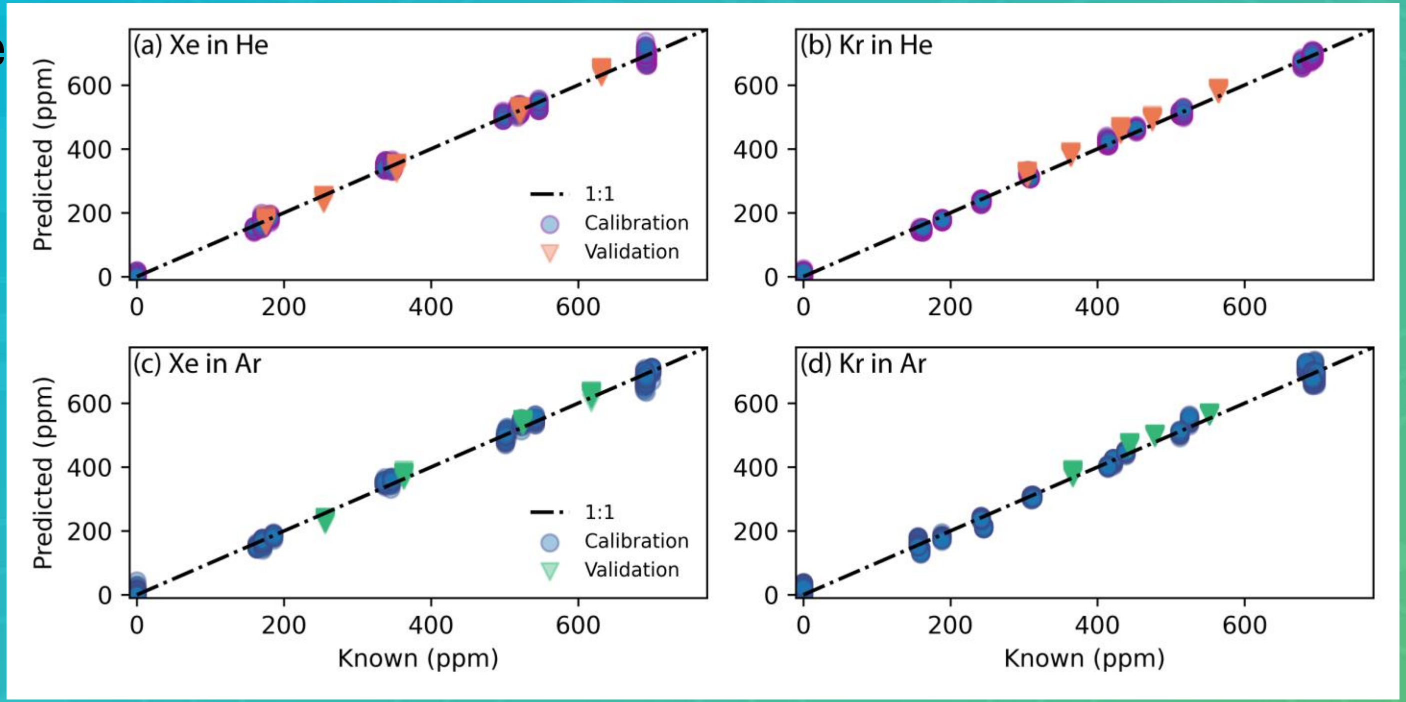
Andrews et al. 2025. *Under review.*

Fortunately, we can handle matrix effects using multivariate modeling methods

Parity Plots Showing Prediction Accuracy

He

Ar



Parity plots for PLSR models of (a) Xe in He, (b) Kr in He, (c) Xe in Ar, and (d) Kr in Ar. Note, the black 1:1 line represents a perfect prediction.

Detection Limits

Calculated LOD values for Xe and Kr in various bulk gases as a function of the number of shots accumulated.

		Limits of Detection			
Shots	**Time Resolution (s)**	**Xe in He (ppm)**	**Kr in He (ppm)**	**Xe in Ar (ppm)**	**Kr in Ar (ppm)**
50	2.5	55.0	40.9	57.6	63.1
100	5.0	43.4	36.6	51.6	62.0
200	10	36.1	34.8	48.0	61.3
500	25	30.5	34.4	46.5	61.1
1000	50	28.4	33.8	45.7	61.2
5000	250	22.9	30.4	42.5	54.7

Andrews et al. 2025. *Under review.*

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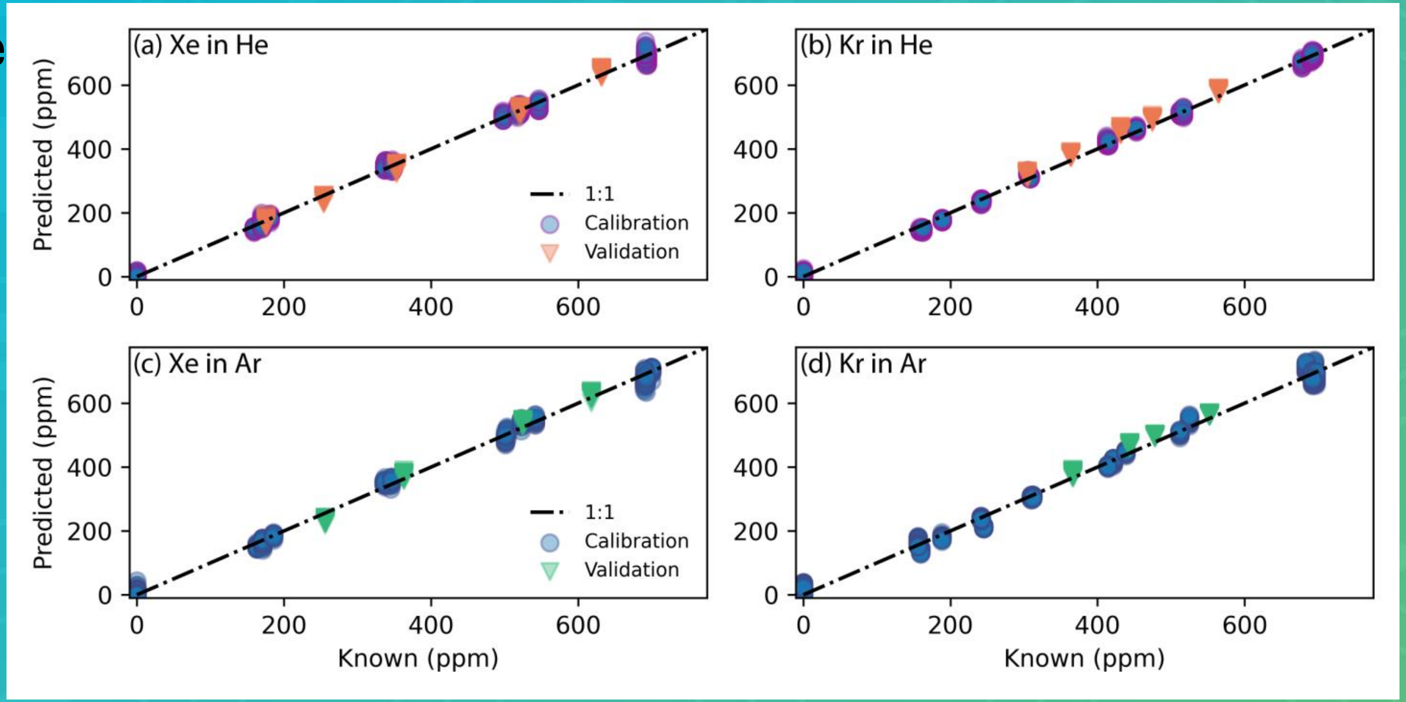

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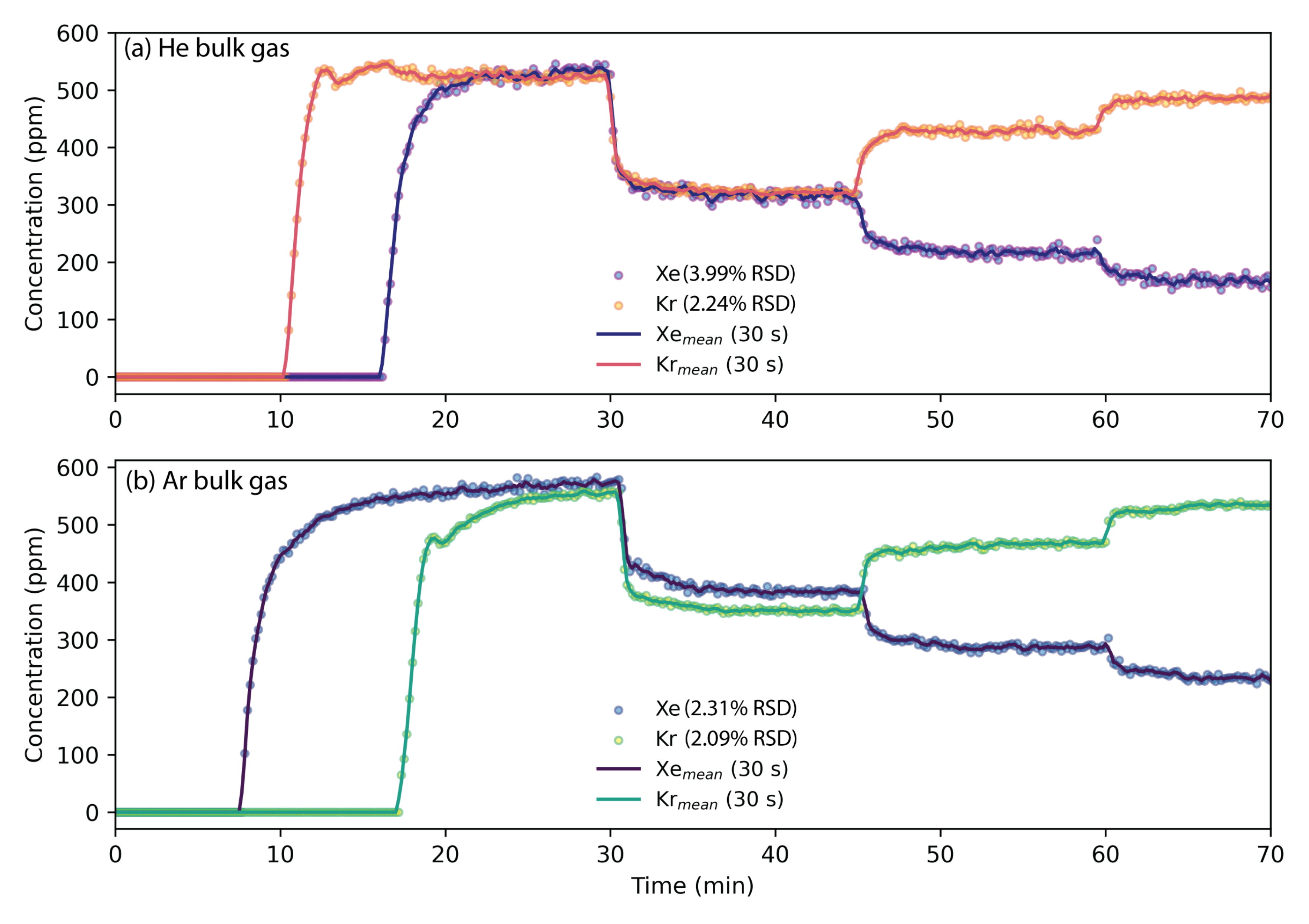
Andrews et al. 2025. *Under review.*

Despite all these differences we can still accurately track noble gases in real-time



Andrews et al. 2025. *Under review.*

Elemental and Isotopics

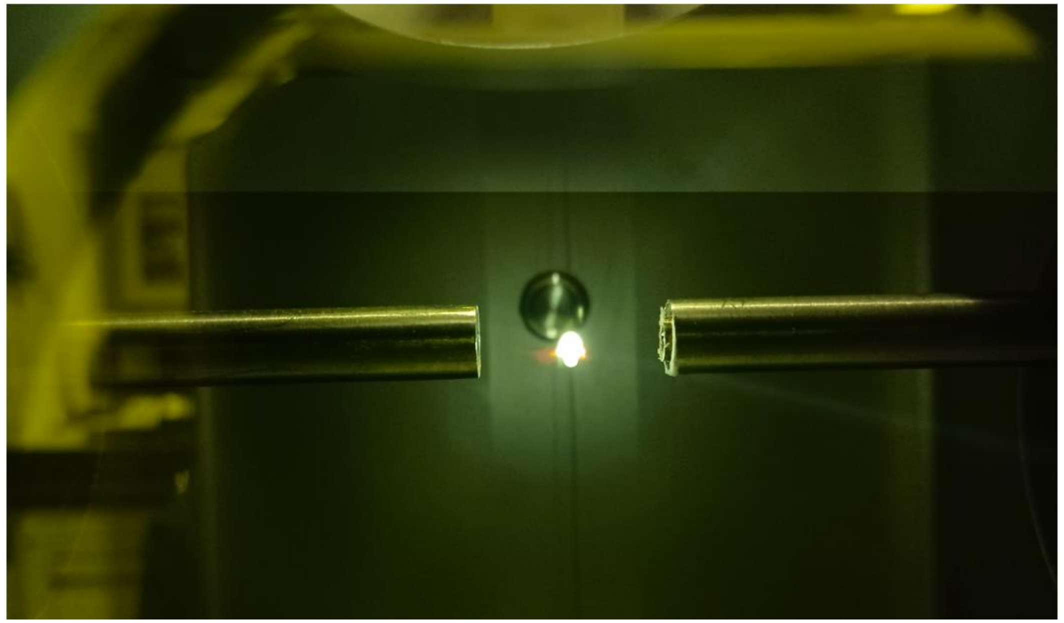
- The full power of LIBS is realized when combining aerosol detection, gas monitoring, and extending compositional measurements to isotopic ratios

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Article

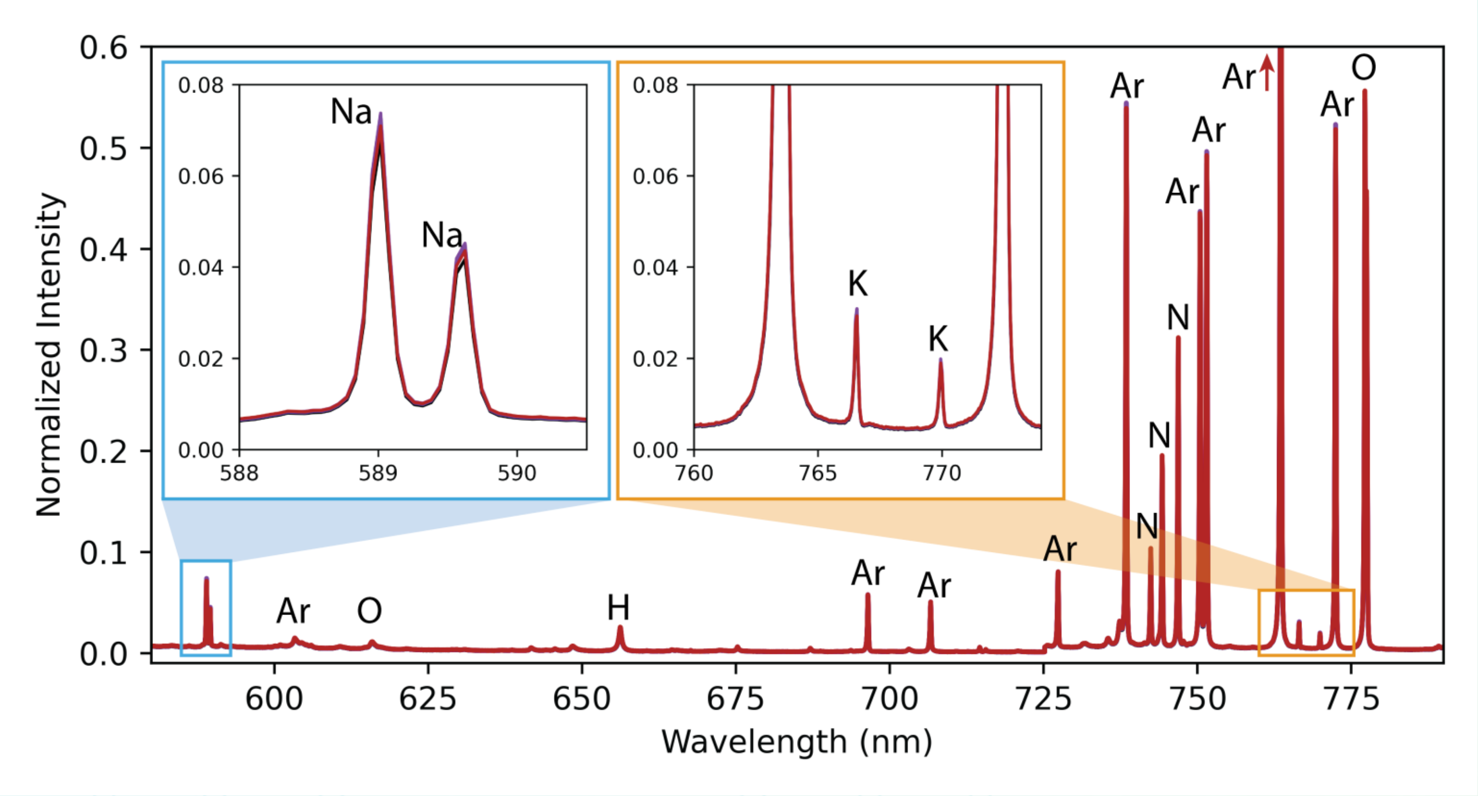
Real-Time Elemental and Isotopic Measurements of Molten Salt Systems through Laser-Induced Breakdown Spectroscopy

Hunter B. Andrews,* Zechariah B. Kitzhaber, Daniel Orea, and Joanna McFarlane

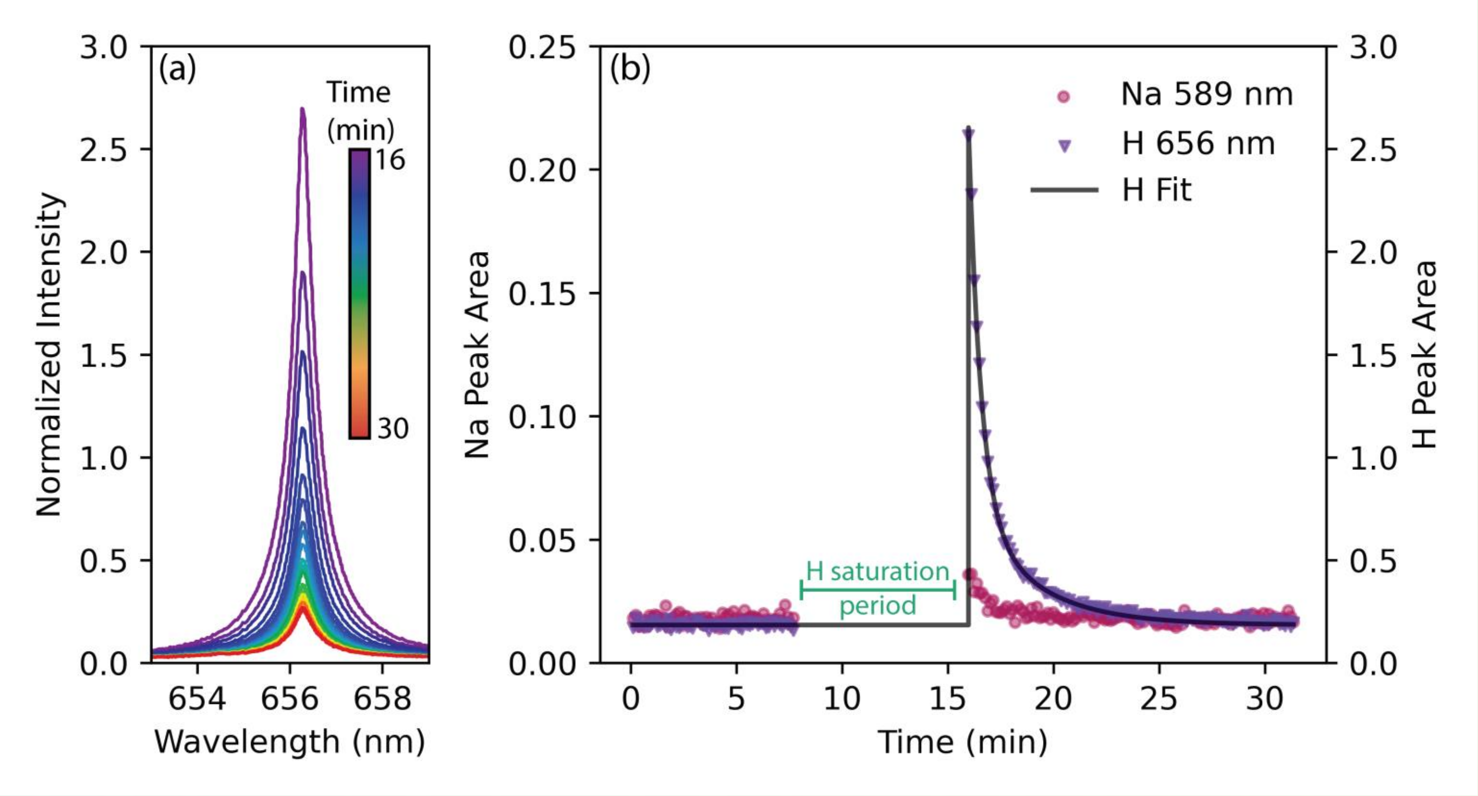
NUCLEAR MILESTONES



The power of LIBS can truly be seen when we monitor mixed-phase sample streams



KNO$_3$-NaO$_3$ Eutectic salt at ~450 deg C



Monitoring the release of H after saturation

Andrews et al. *JACS*. 2025.

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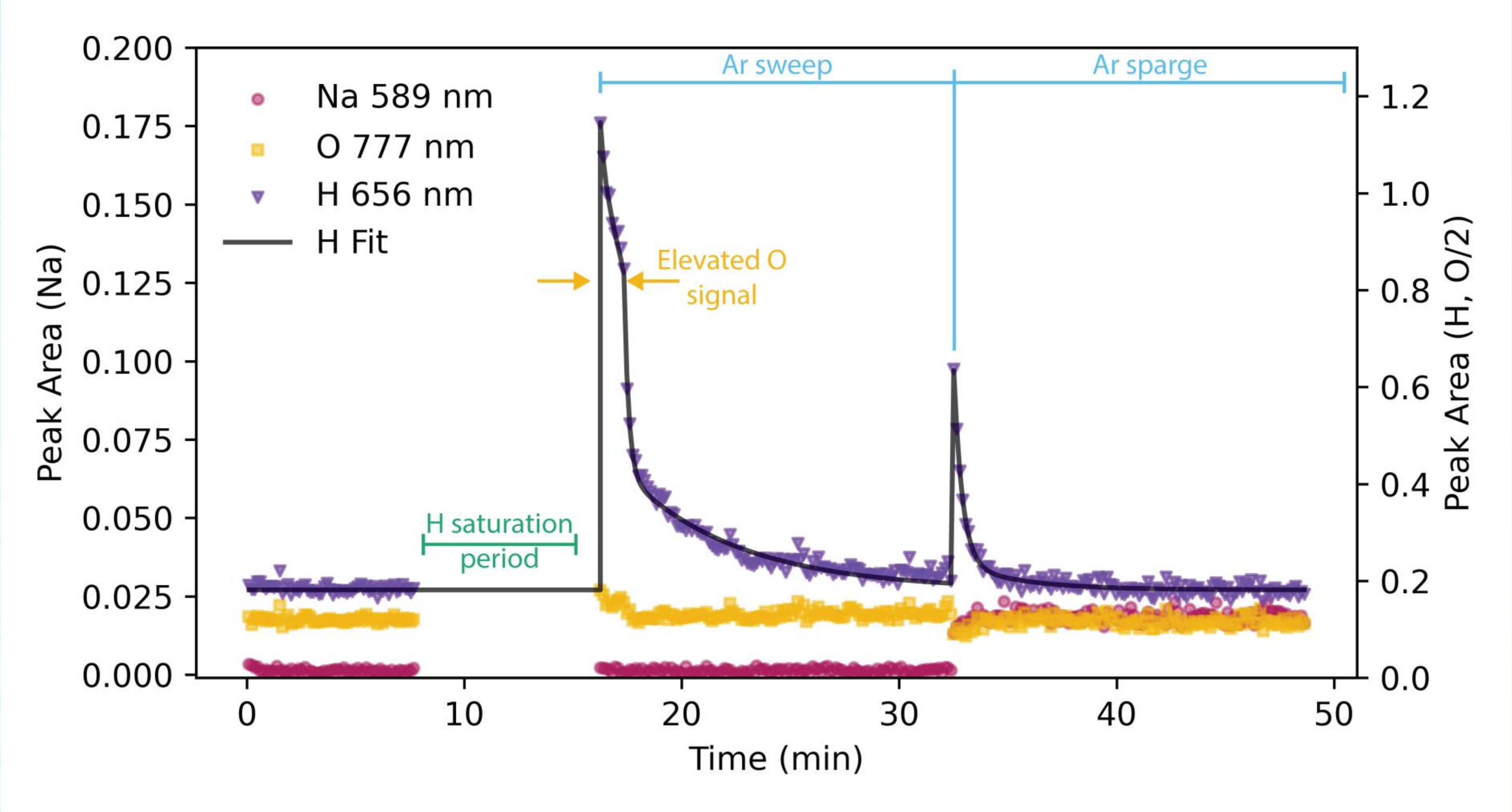
LIBS allows us a unique inspection of our molten salt experiments

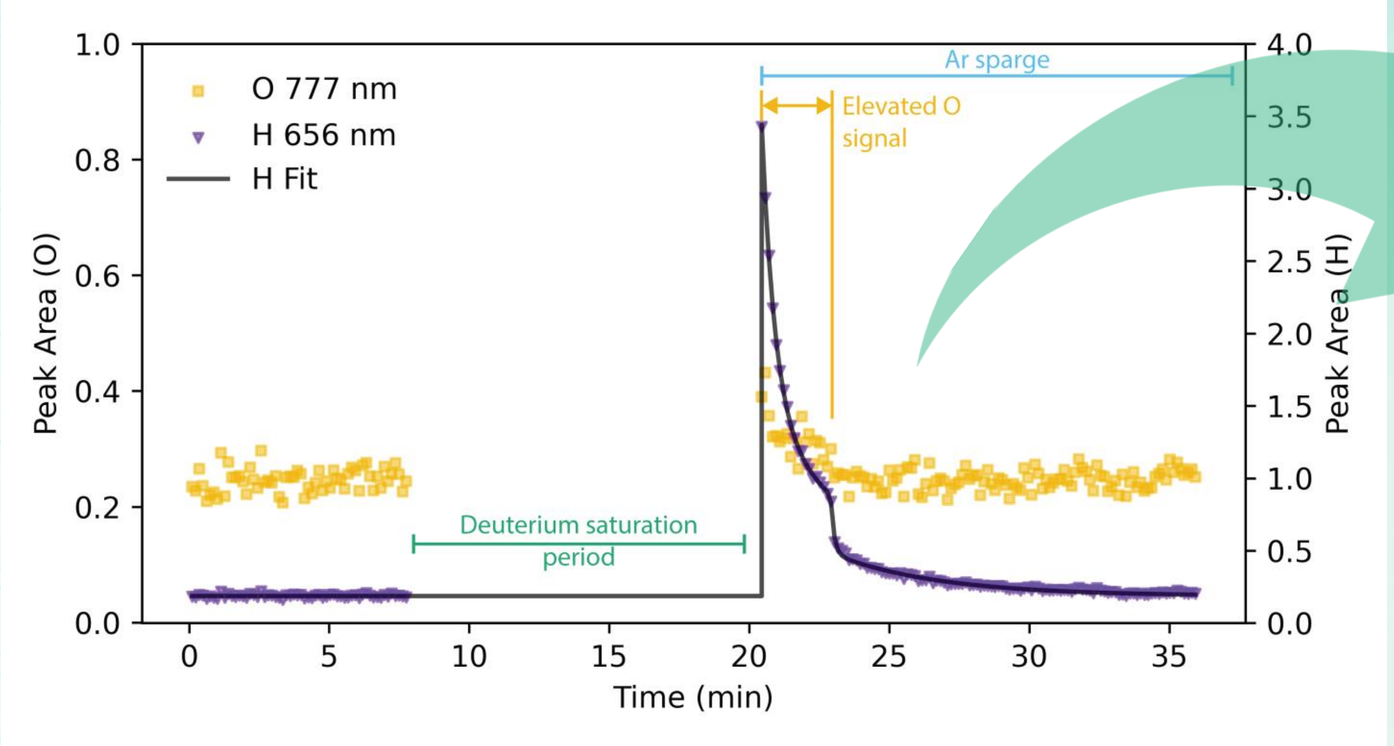


Monitoring the release of H after saturation when the salt vessel is swept with Ar vs sparged with Ar.

- Ratio of sparge and sweep areas indicated ~14% holdup of H_2 in the salt
- The fitted mass transfer profiles are proportional to diffusion
- Elevated O regions indicate differences in H_2O and H_2 removal

Andrews et al. *JACS*. 2025.

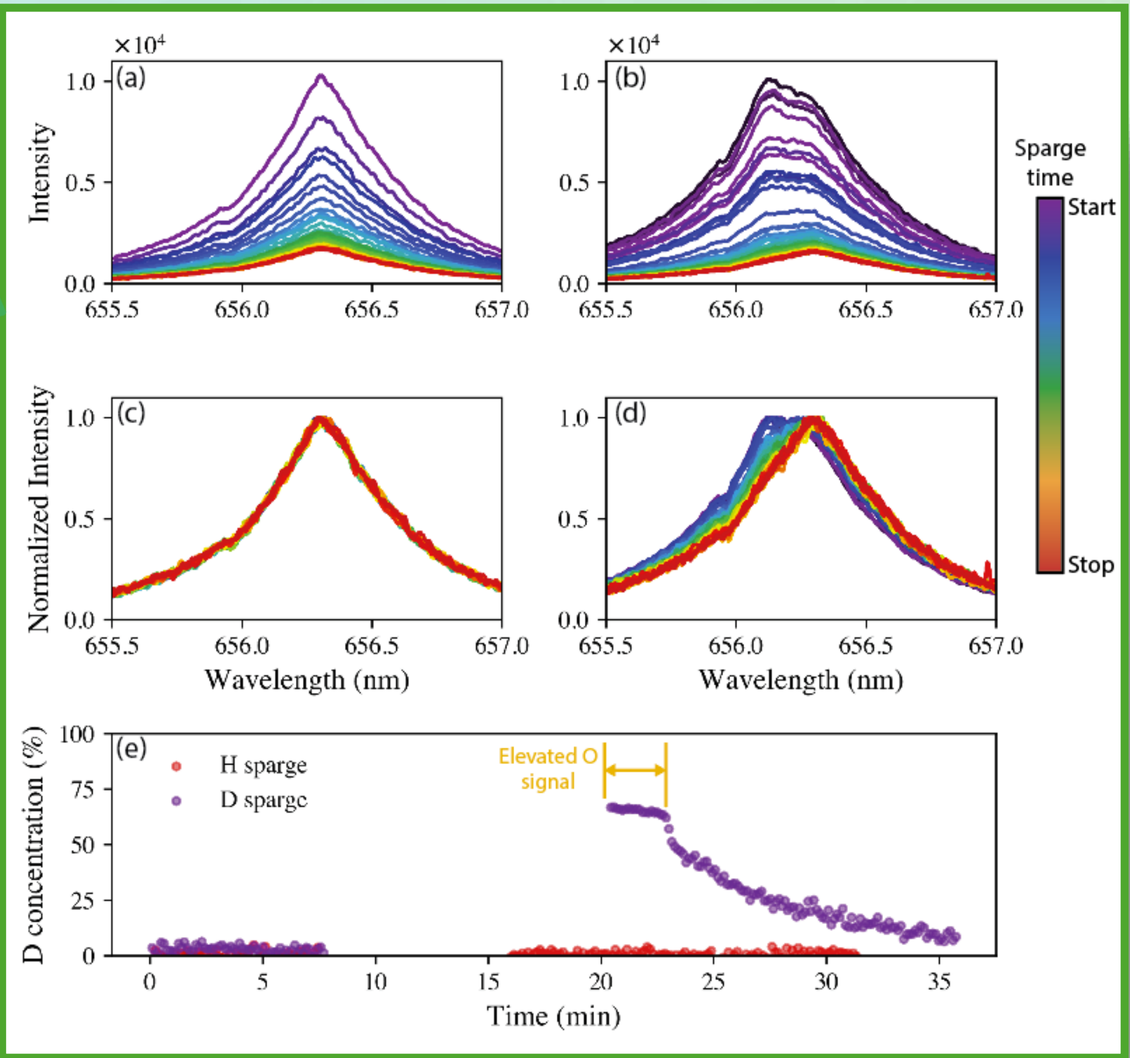
Pushing LIBS resolution to the limit provides isotopic information



Salt was saturated in D_2 and then sparged

Using a previous model, transferred using the pure H sparge data, H/D ratios could be quantified!

Mass transfer profiles indicate mass differences in H_2 and D_2 gasses of 67%. The quantified H/D levels via LIBS match this.



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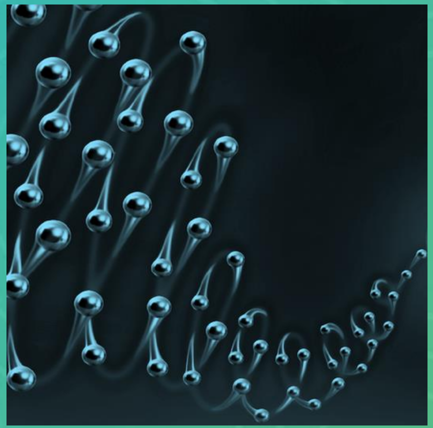
Andrews et al. *JACS*. 2025.

Ever forward – where do we go from here?

How does the aerosol signal change with bulk gas?

How low can we push our detection limits?



How can we optimize aerosol transport for remote sampling?

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P R O G R A M

Thank you

Reach out via e-mail: andrewshb@ornl.gov

The MSR Campaign team is making headway in deployable sensors and wants to work together with academia and industry to enable the continued development and deployment of MSRs.

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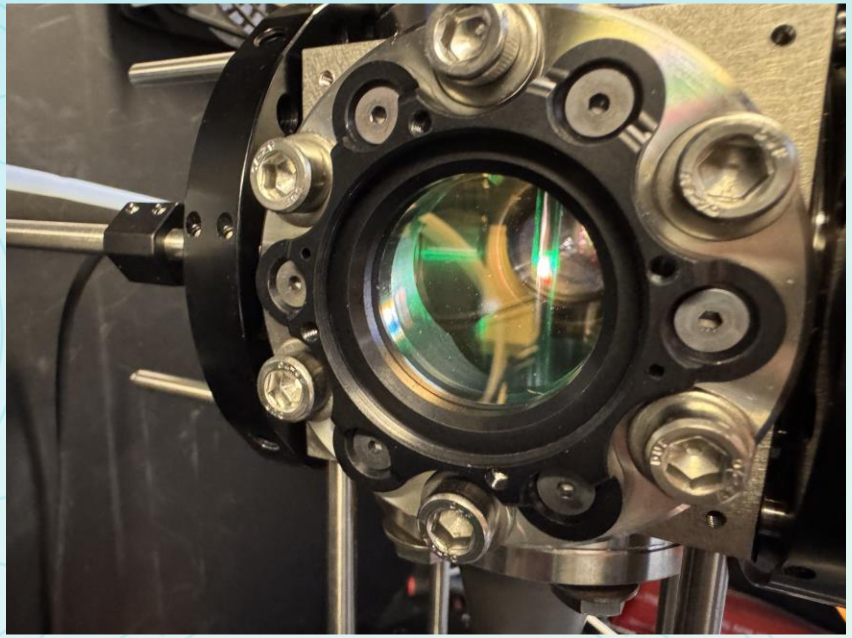
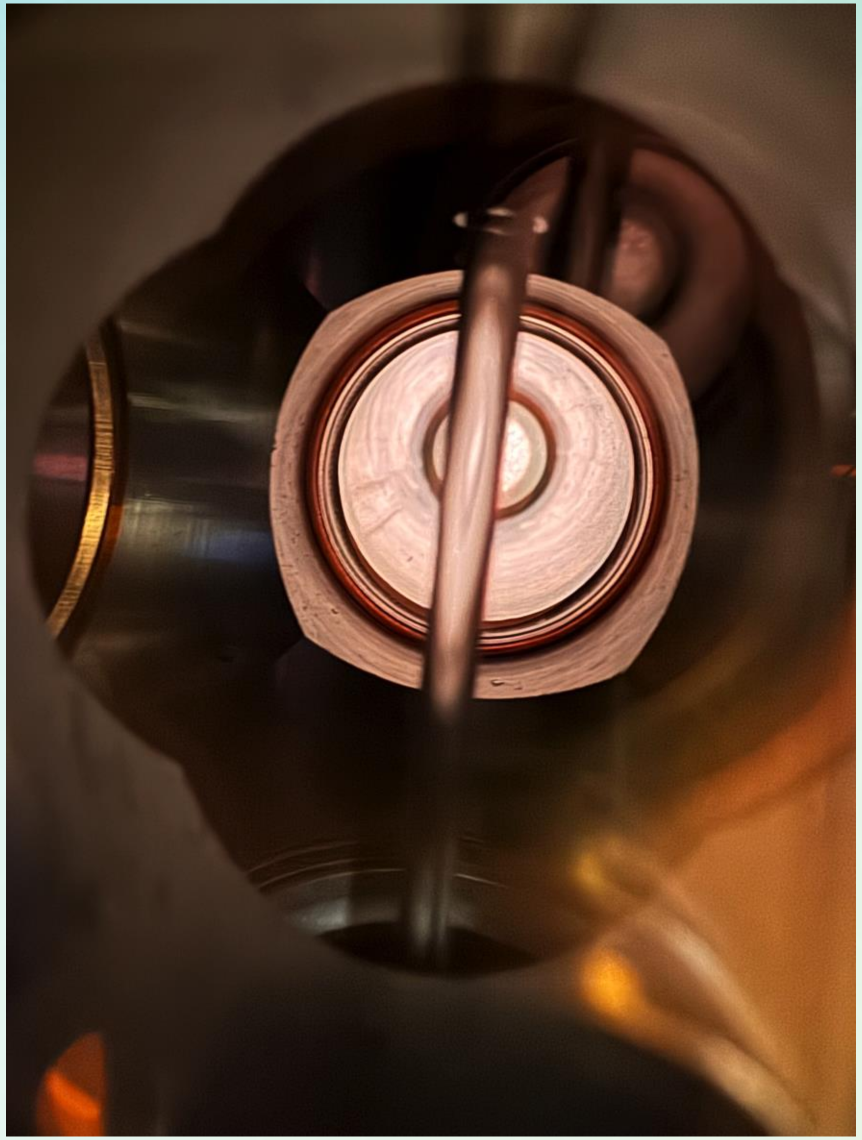
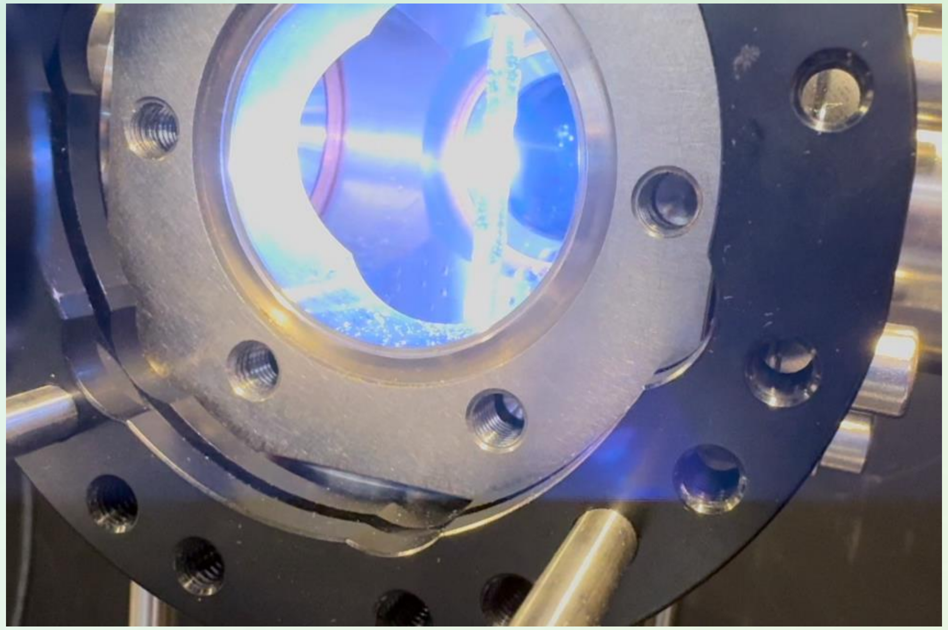
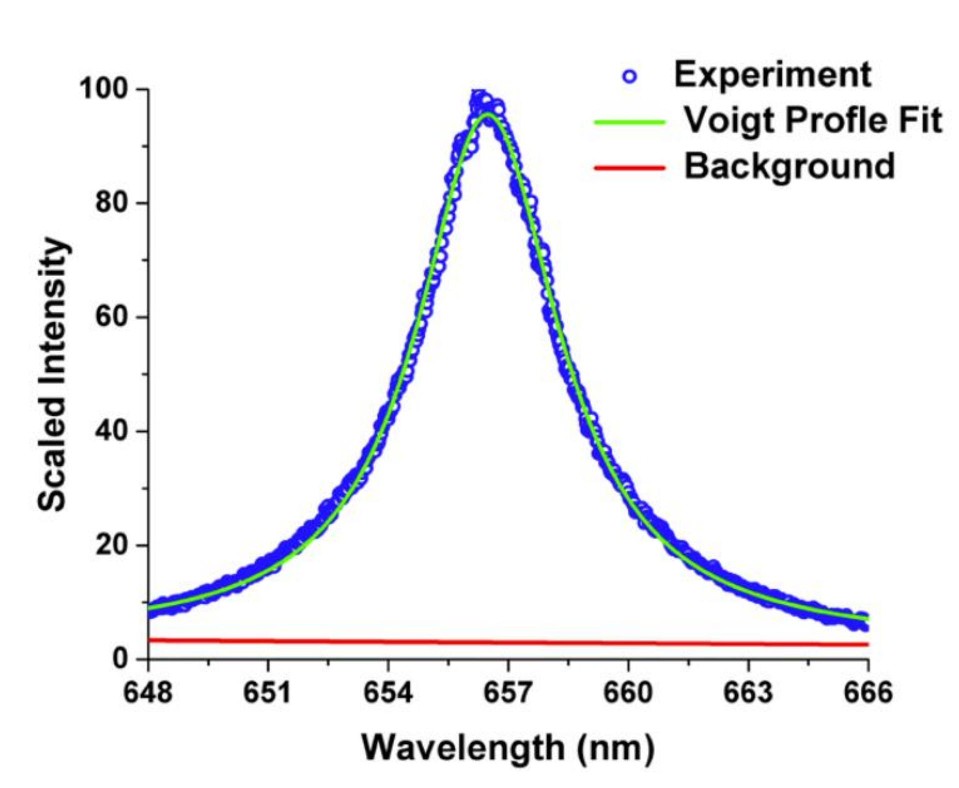
Liquid LIBS flow cell for molten salts is in development



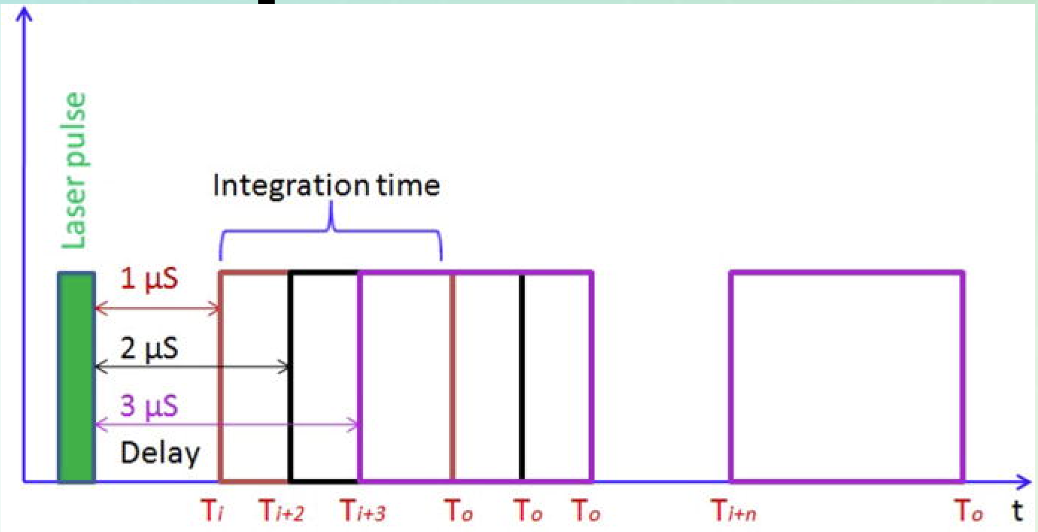


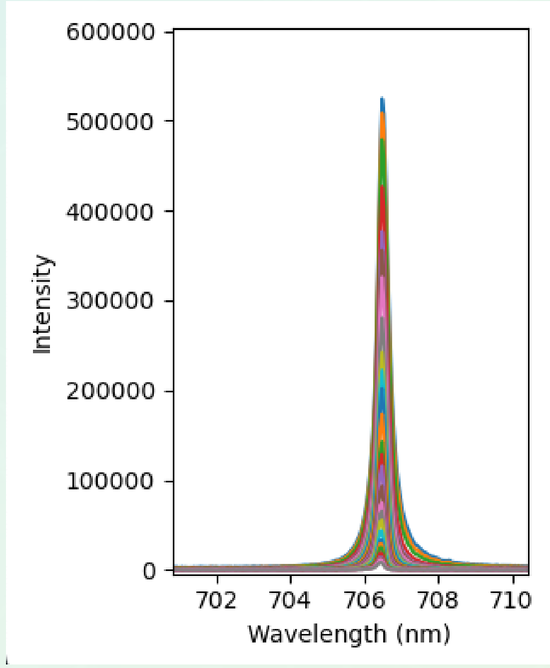


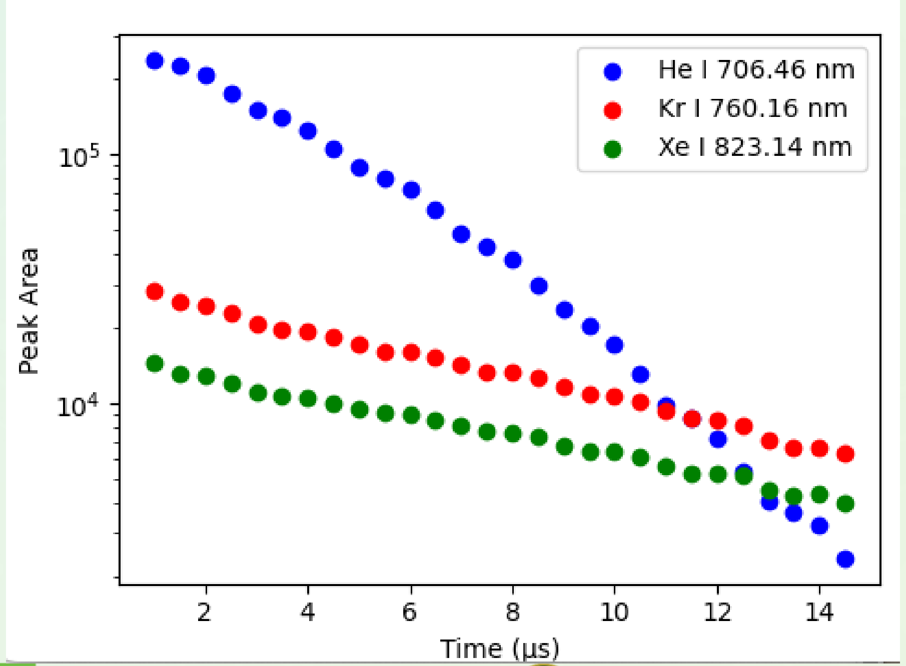
Plasma temperature and electron density can be calculated from the emission peak behavior



$N_e = 1\times10^{17} \times (\mathrm{FWHM}/0.549)^{1.4713}$







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Surmick and Parigger. *IRAMP*. 2014.

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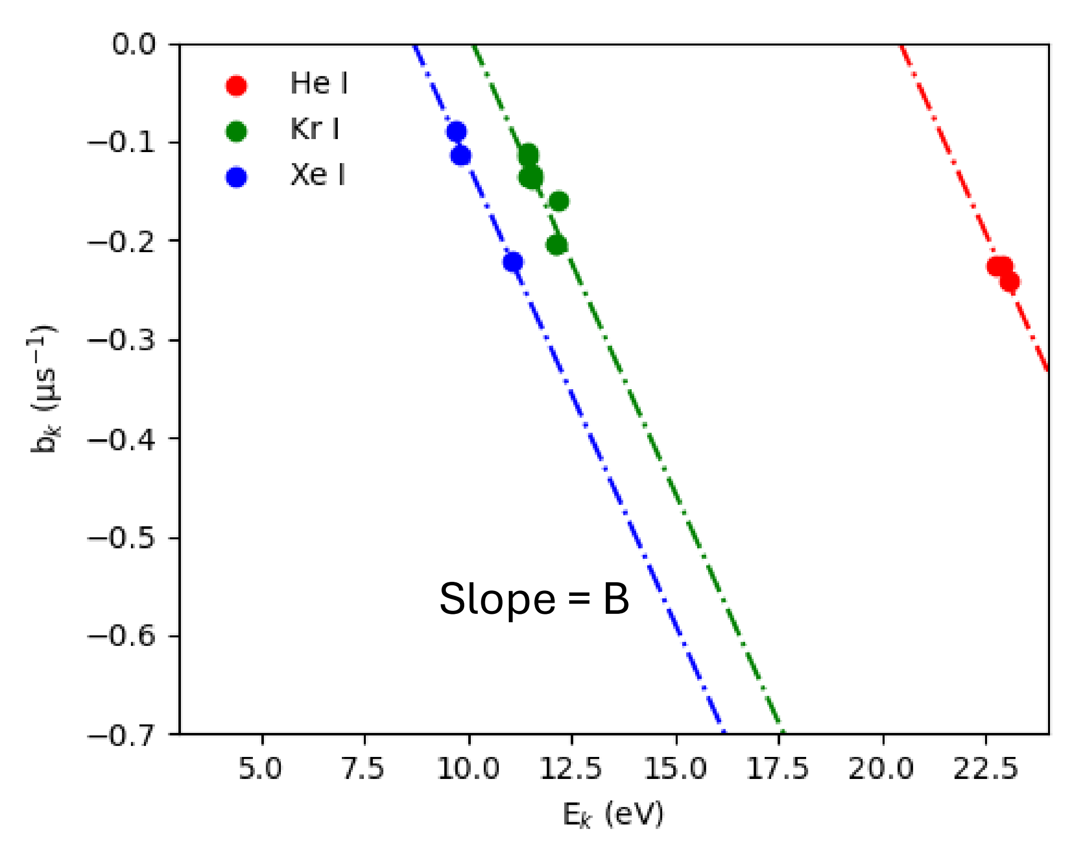
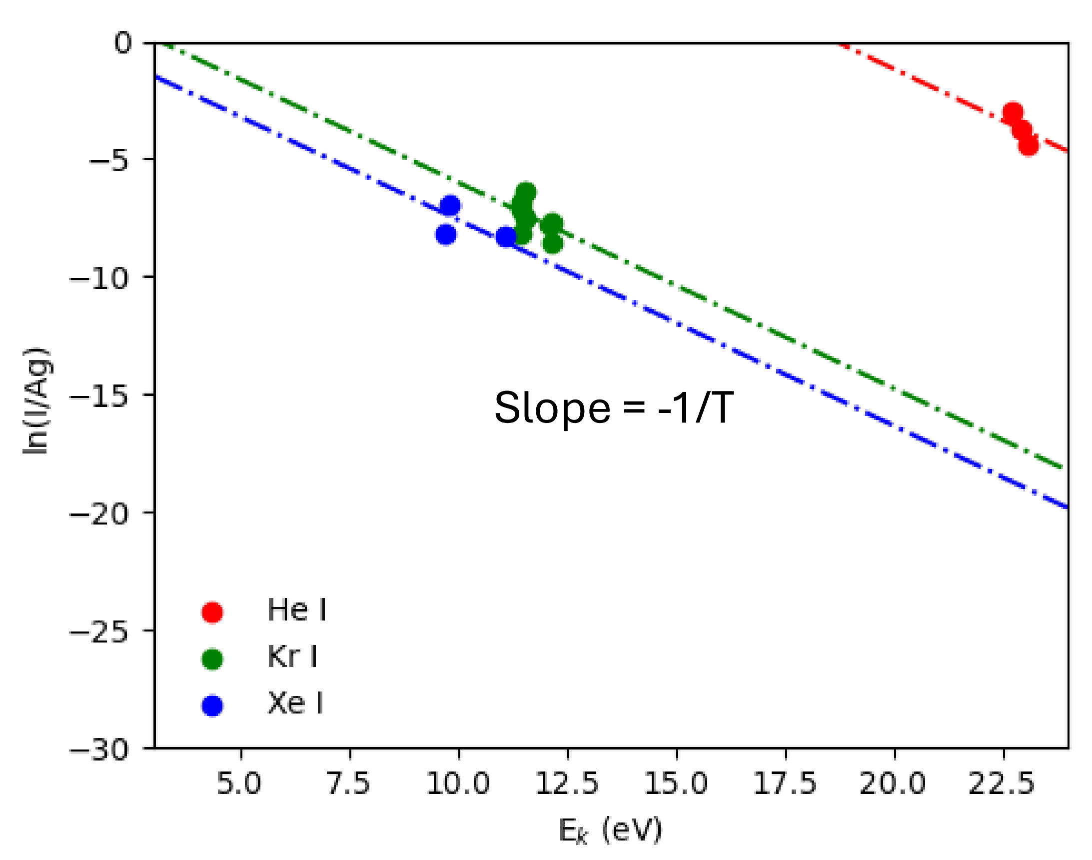


Bredice Plot provides the shape of the plasma temperature in time



Boltzmann Plot provides the temperature at time ~0

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