

U.S. DEPARTMENT OF
ENERGY

Office of
NUCLEAR ENERGY



Laser-Induced Breakdown Spectroscopy Isotope Ratio Measurements

Hunter B. Andrews
Oak Ridge National Laboratory

Annual MSR Campaign Review Meeting April 2024

ORNL is developing LIBS for nuclear technology across the board



micromachines

Article
Monitoring Xenon Capture in a Metal Organic Framework Using Laser-Induced Breakdown Spectroscopy
Hunter B. Andrews^{1,*}, Praveen K. Thallapally² and Alexander J. Robinson²

Special Issue

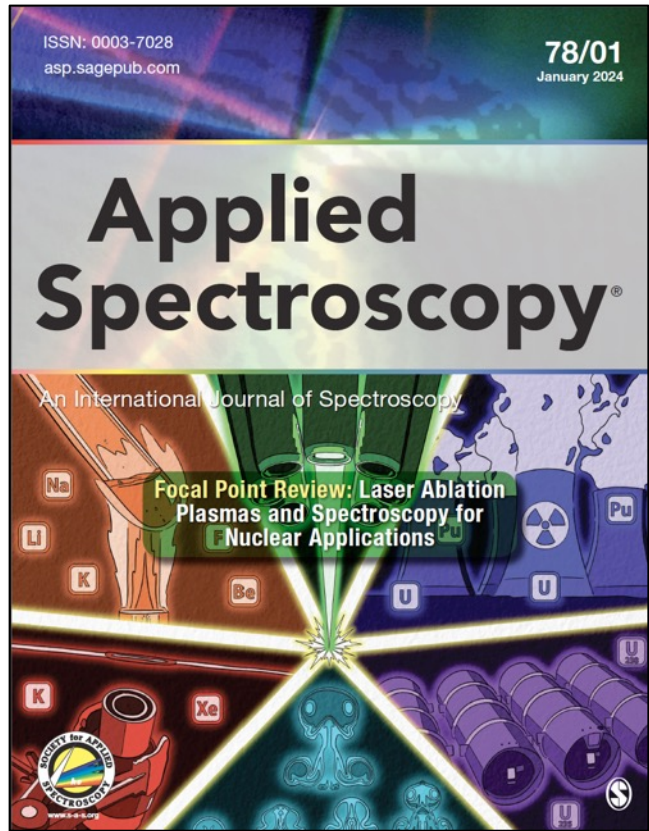
Quantification of Lanthanides in a Molten Salt Reactor Surrogate Off-Gas Stream Using Laser-Induced Breakdown Spectroscopy
Hunter B. Andrews^{1,*} and Kristian G. Myhre

Applied Spectroscopy
2022, Vol. 000 1-10
© The Author(s) 2022
Article reuse guidelines:
sagepub.com/journalsPermissions.nav
DOI: 10.1177/00037028211070323
journals.sagepub.com/home/asp
SAGE

Special Issue: Laser-Induced Breakdown Spectroscopy

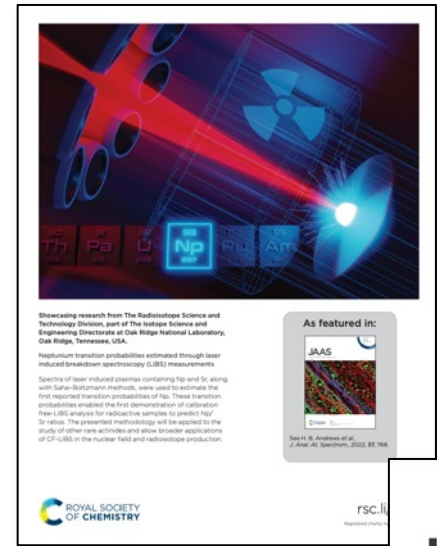
Monitoring Noble Gases (Xe and Kr) and Aerosols (Cs and Rb) in a Molten Salt Reactor Surrogate Off-Gas Stream Using Laser-Induced Breakdown Spectroscopy (LIBS)
Hunter B. Andrews^{1,*}, Joanna McFarlane² and Kristian G. Myhre¹

Applied Spectroscopy
2022, Vol. 000 1-10
© The Author(s) 2022
Article reuse guidelines:
sagepub.com/journalsPermissions.nav
DOI: 10.1177/00037028211088425
journals.sagepub.com/home/asp
SAGE



sensors MDPI

Article
Novel Calibration Approach for Monitoring Aerosol Hydrogen Isotopes Using Laser-Induced Breakdown Spectroscopy for Molten Salt Reactor Off-Gas Streams
Hunter B. Andrews^{1,*} and Joanna McFarlane²



frontiers | Frontiers in Energy Research

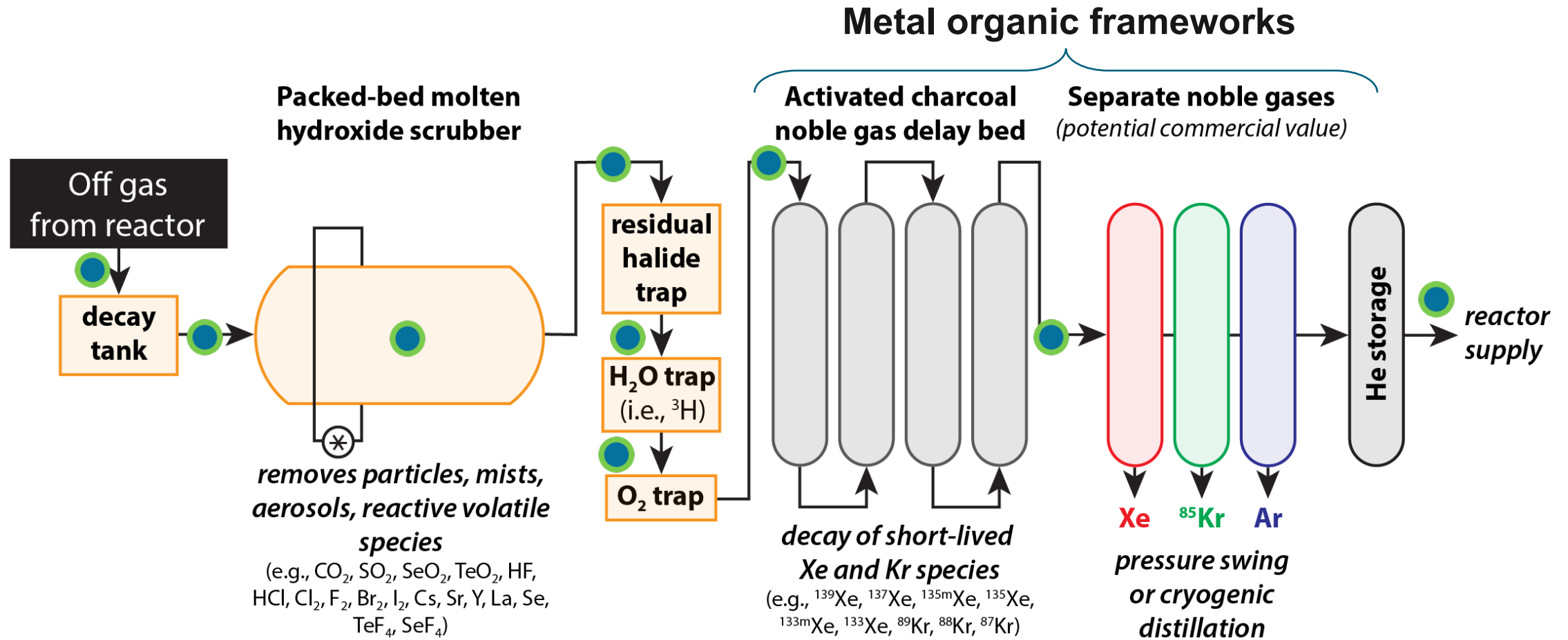
OPEN ACCESS
EDITED BY
Palash Kumar Shroemik, Idaho National Laboratory (INEL), United States
REVIEWED BY
Mehmet Şahinli, Duzluk University, Bangladesh
A. B. M. Shaukat Ali Daultan, Missouri University of Science and Technology, United States

ORIGINAL RESEARCH
PUBLISHED 09 January 2023
DOI: 10.3389/feen.2022.1005556

Concept for an irradiation experiment to test a laser-induced breakdown spectroscopy off-gas sensor for molten salt systems
Hunter B. Andrews*, Kristian G. Myhre and Joanna McFarlane
Oak Ridge National Laboratory, Oak Ridge, TN, United States

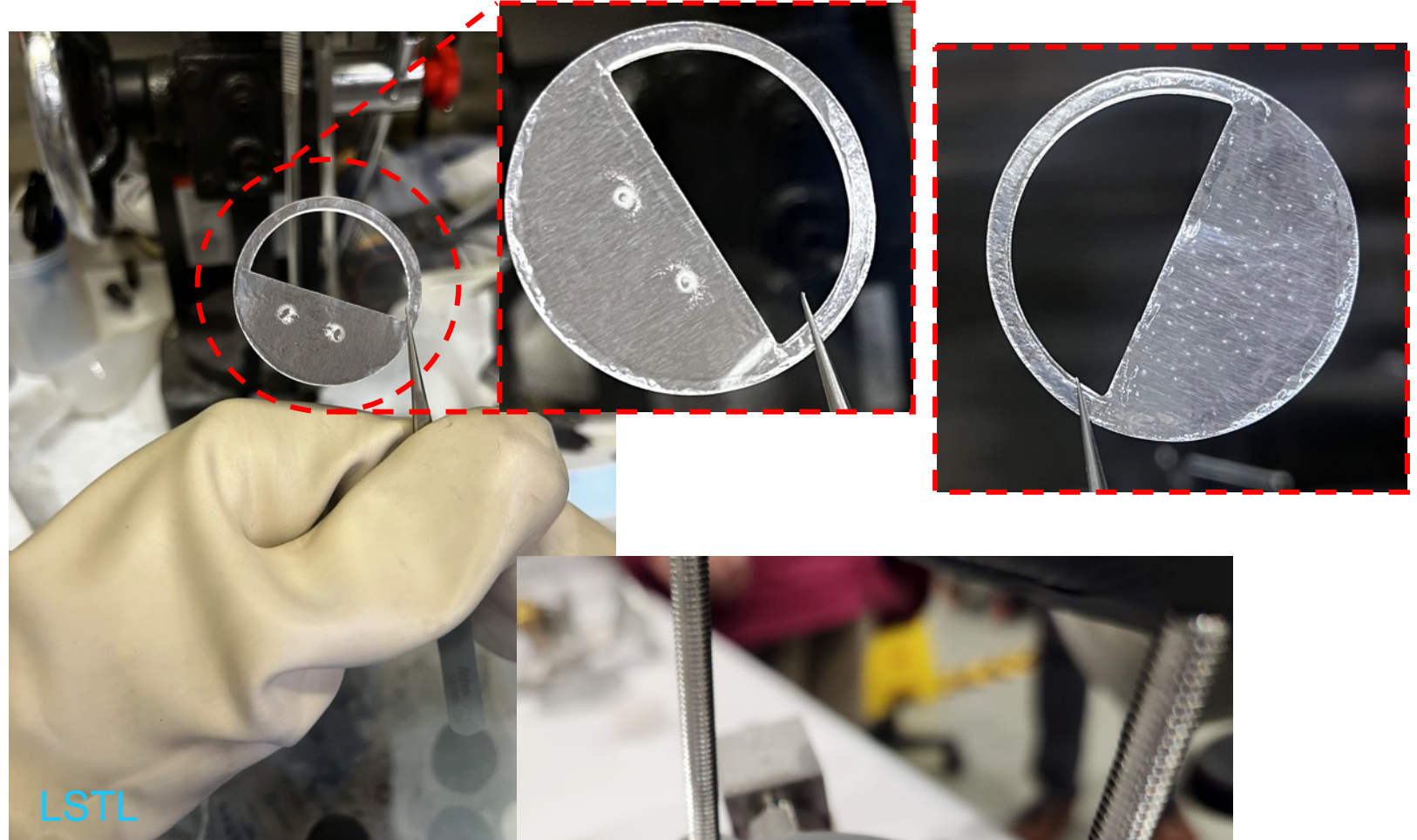


The off-gas treatment system development is critical for continued MSR development

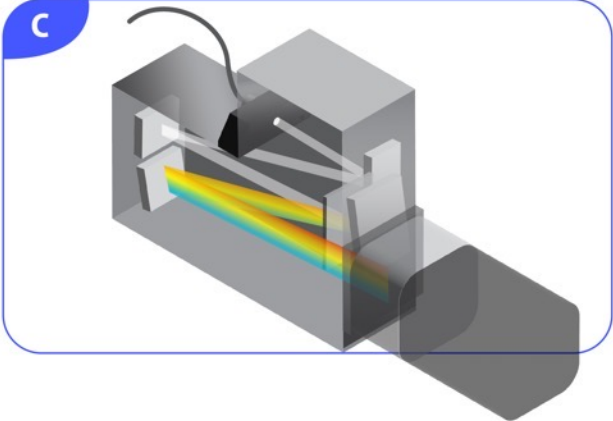
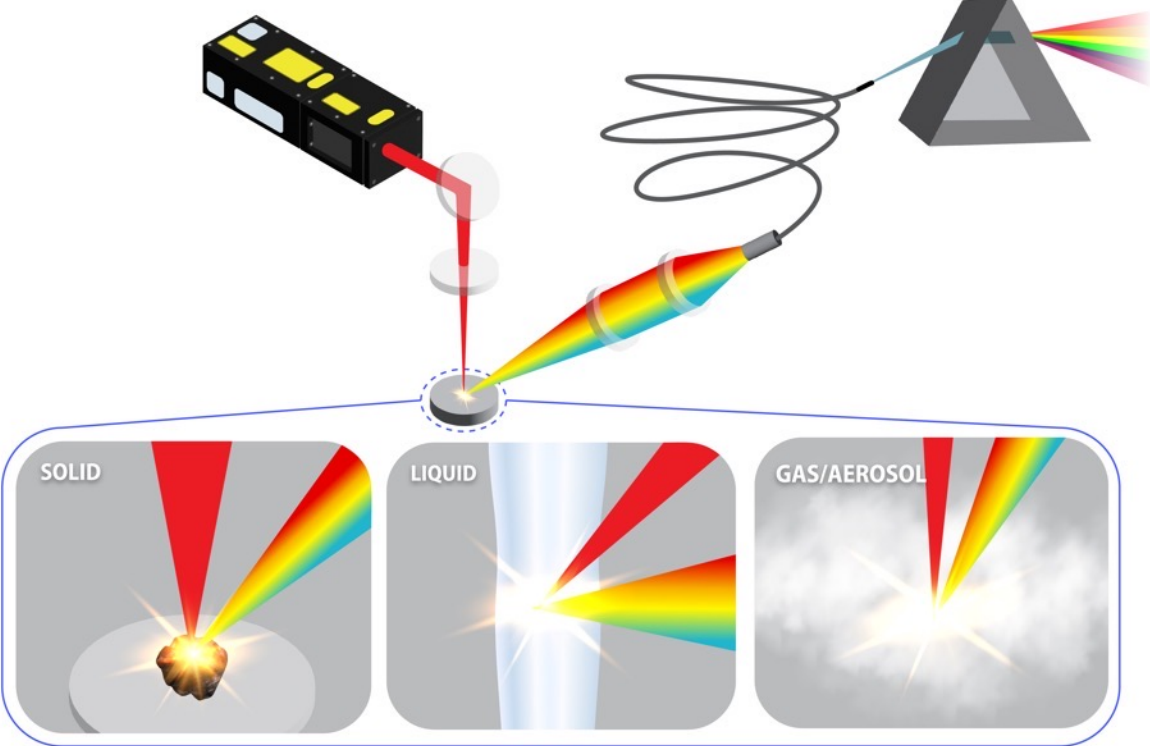
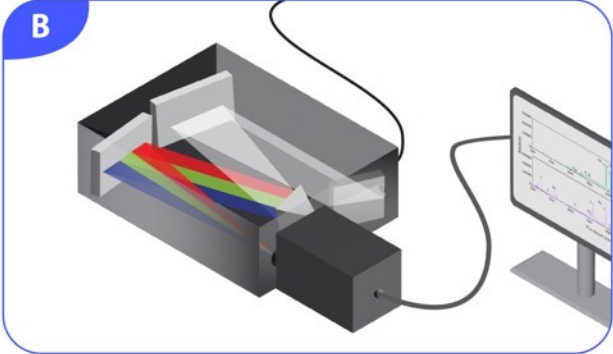
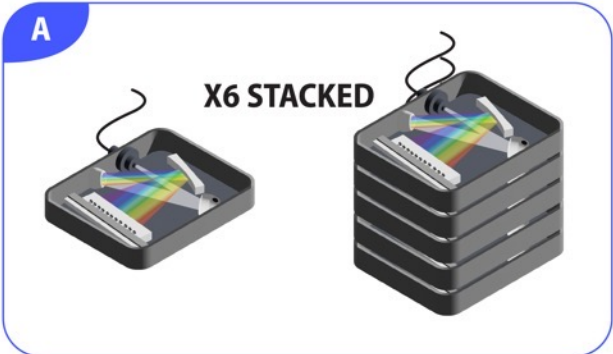
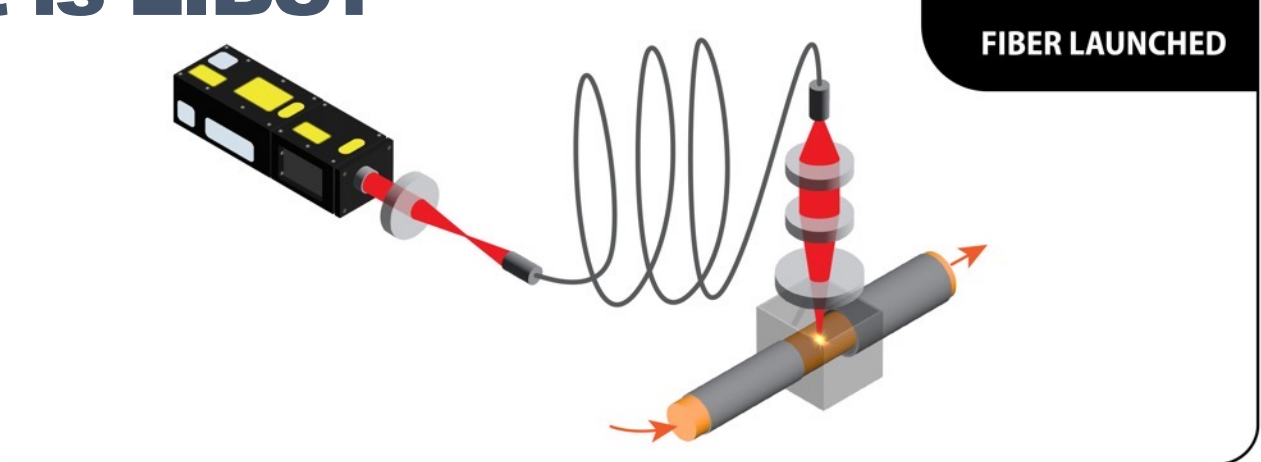


MSR Challenges

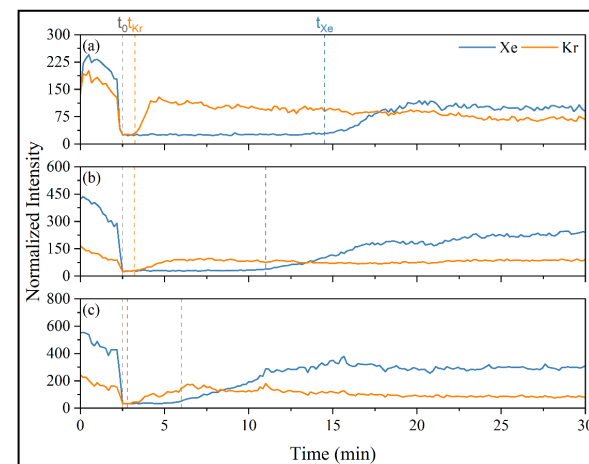
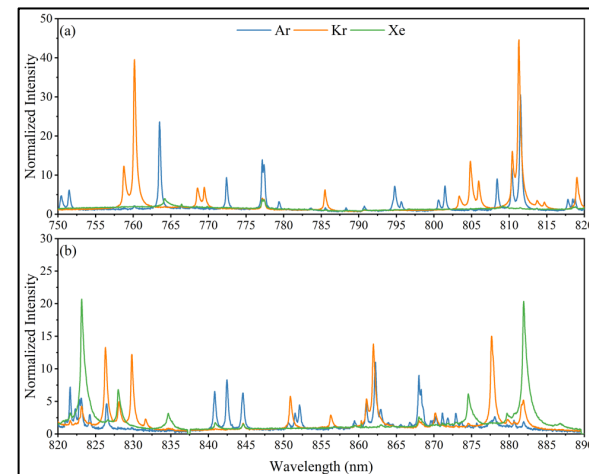
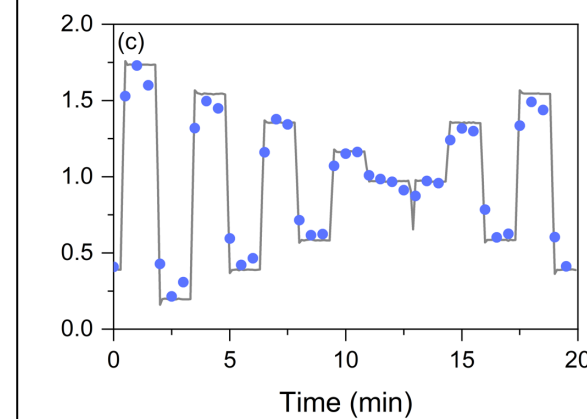
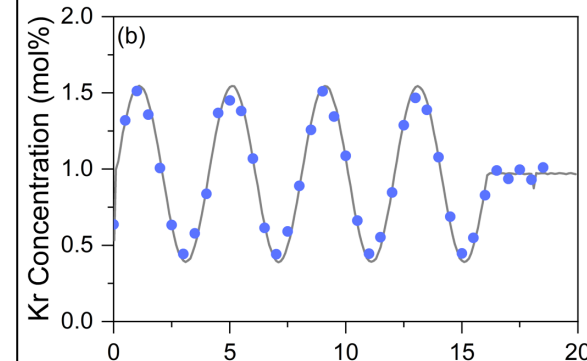
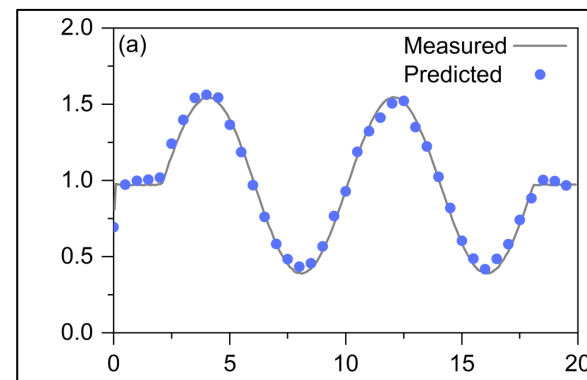
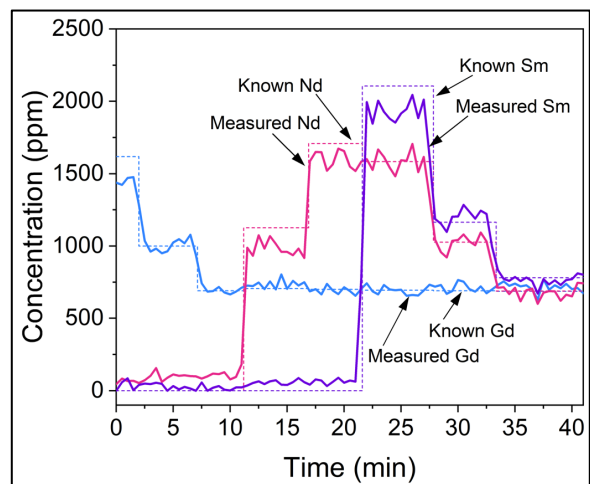
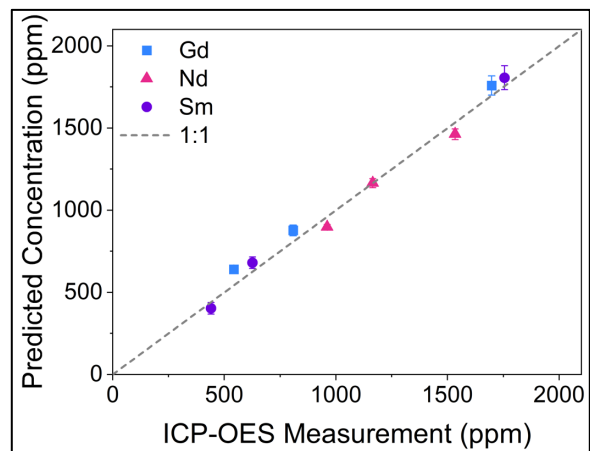
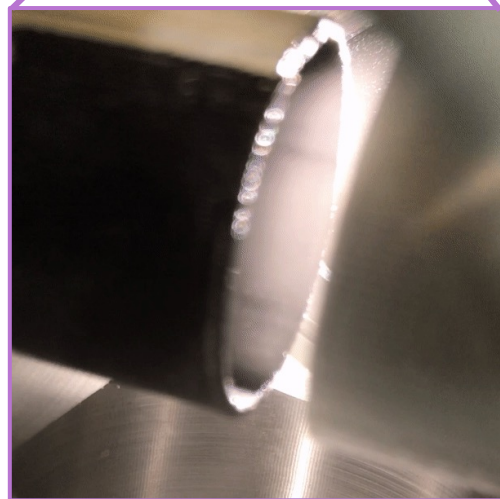
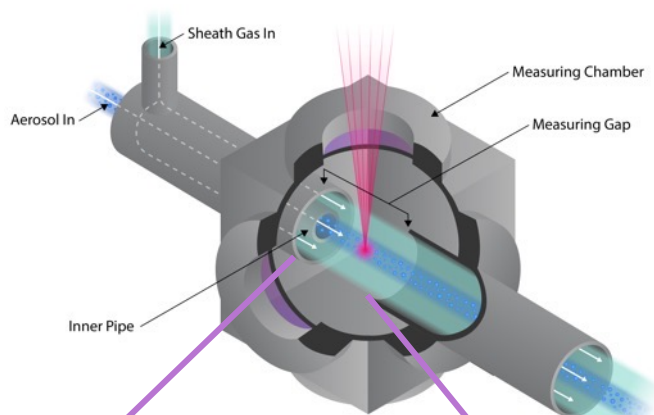
- Liquid fuel
- Inert environment
- Radiation
- Aerosol formation
- Changing chemistry



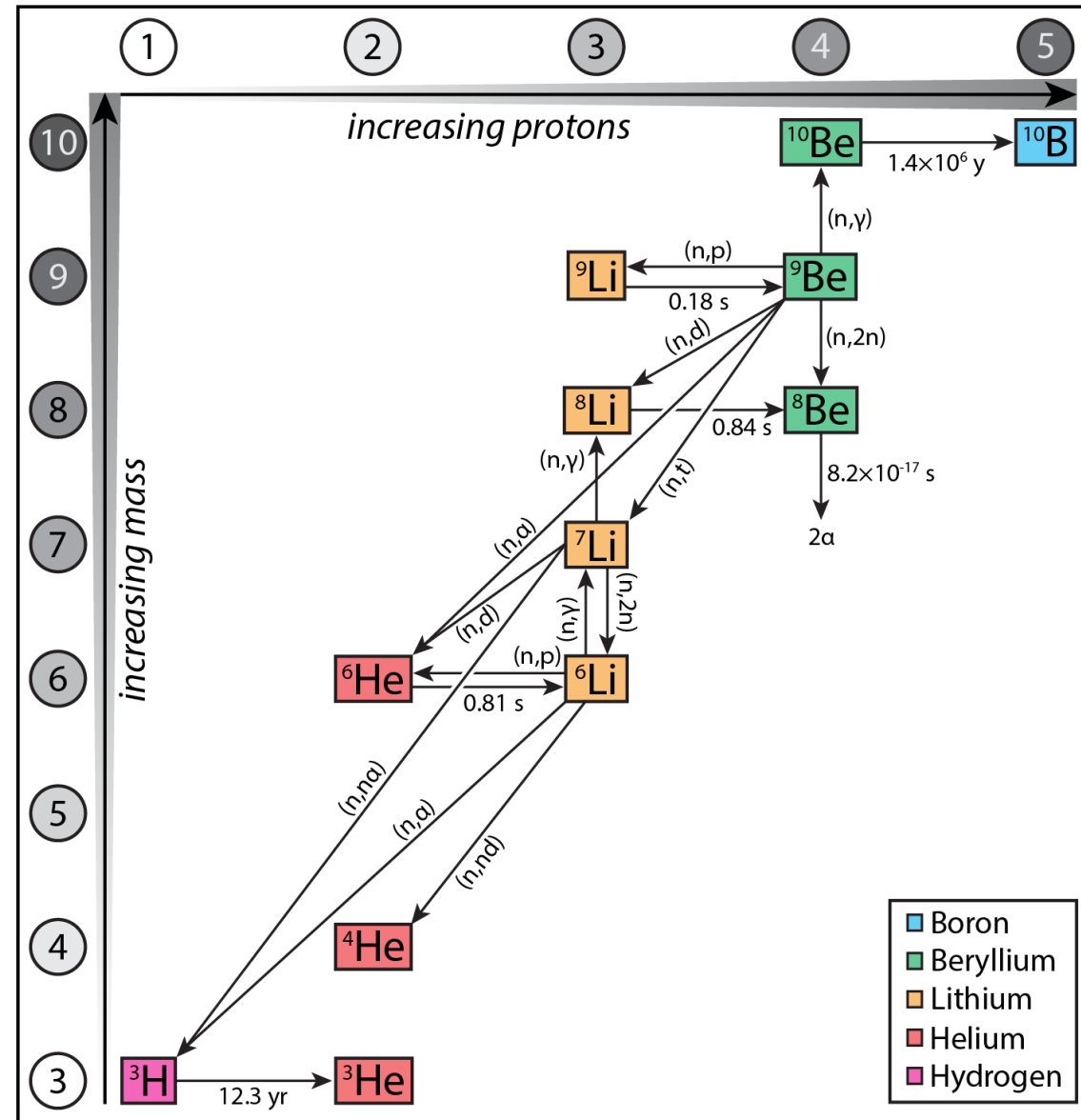
What is LIBS?



MSR Off-gas streams can be monitored using LIBS



Salt isotopes impact a reactor's ^3H generation



How can LIBS measure isotopic signatures?

- **LIBS emissions come from transitions from upper to lower energy states in the excited species**
 - Small changes in these transition frequencies can be generated from minor differences in the nuclear structure of different isotopes
- **The main isotopic effects stem from changes in mass, nuclear spin, and nuclear charge distribution**

$$\delta\nu_i^{AA'} = \delta\nu_{i,MS}^{AA'} + \delta\nu_{i,FS}^{AA'}$$

Frequency shift between isotope A and A' Mass shift contribution Field shift contribution

The main contribution to isotopic shifts changes based on the region of the periodic table

Mass shift dominant

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

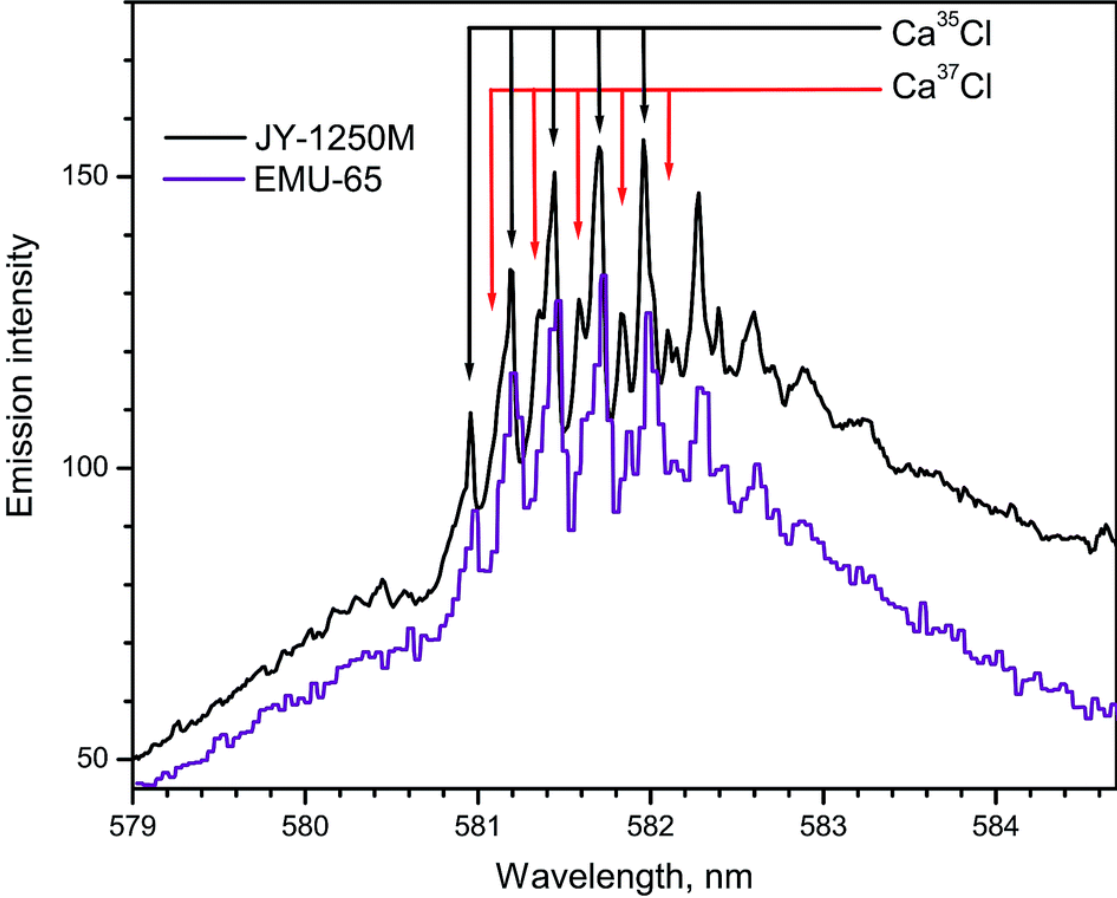
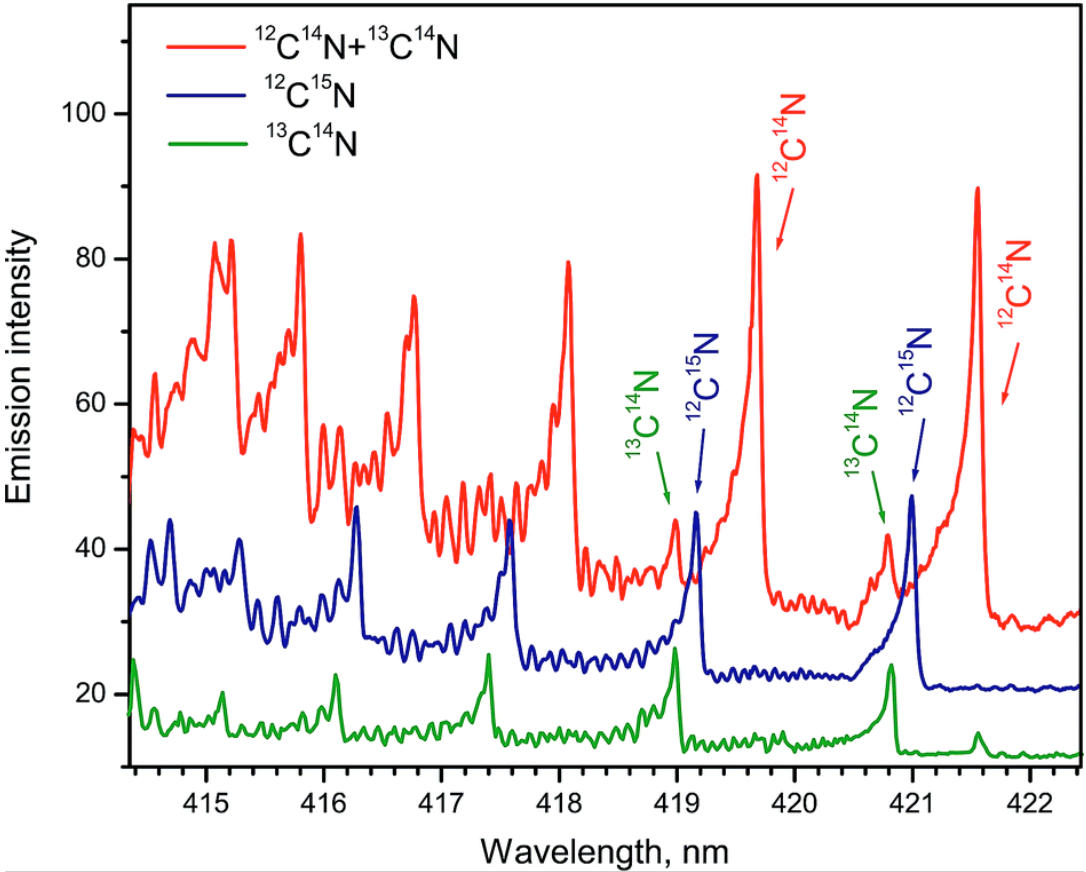
Field shift dominant

* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Laser ablation molecular isotopic spectroscopy (LAMIS) extends the isotopic measurement abilities of LIBS

- **Molecular emissions form later in the plasma lifetime as species in the plasma plume recombine**
- **The formed isotopologues have larger isotopic shifts**
- **The vibrational and rotational contributions to the molecular energy levels are strongly dependent upon the mass difference between isotopes**

Laser ablation molecular isotopic spectroscopy (LAMIS) extends the isotopic measurement abilities of LIBS



The approach to isotopic measurement varies based on the region of the periodic table

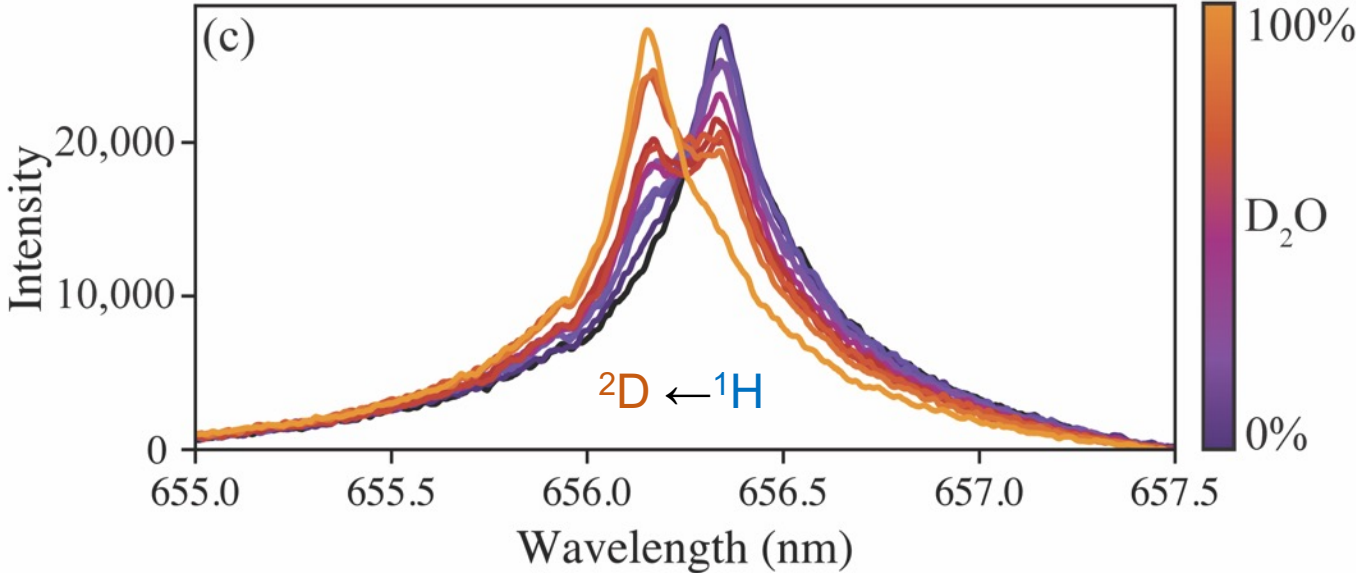
Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1 H																		2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb			
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No			



LIBS

LAMIS

LIBS

FY23 work package targeted establishing these capabilities within the MSR campaign



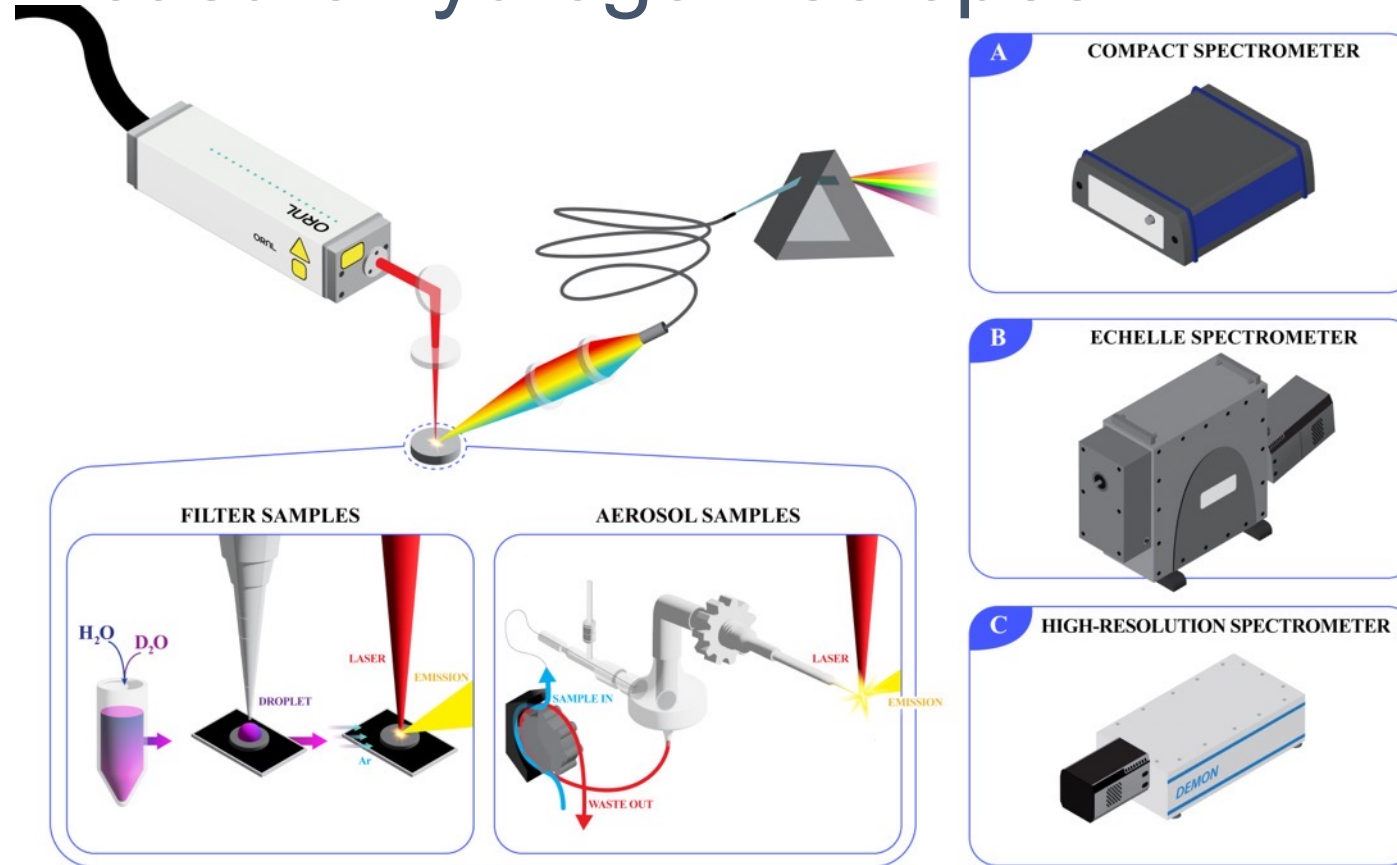
 **sensors** 

Article

Novel Calibration Approach for Monitoring Aerosol Hydrogen Isotopes Using Laser-Induced Breakdown Spectroscopy for Molten Salt Reactor Off-Gas Streams

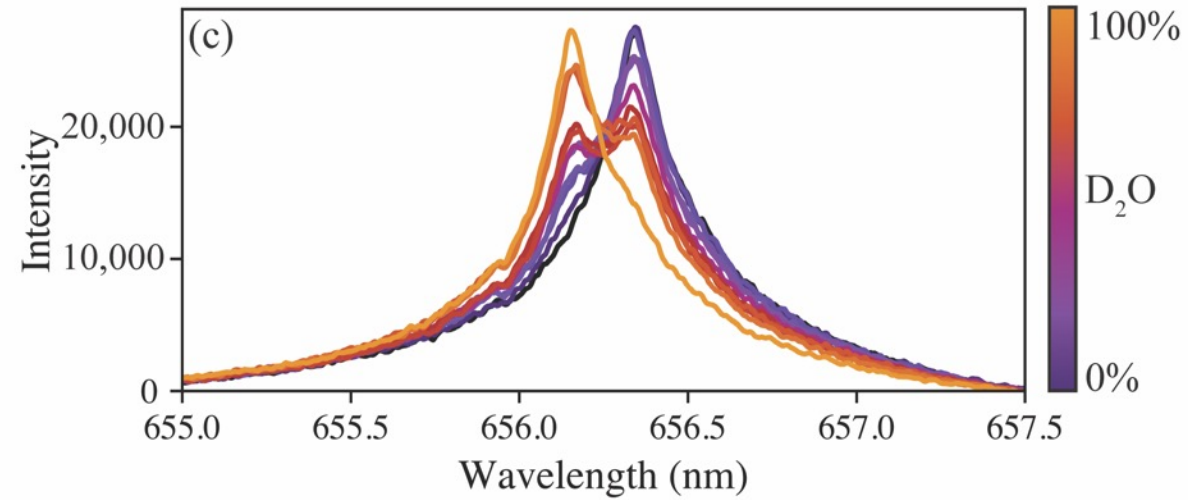
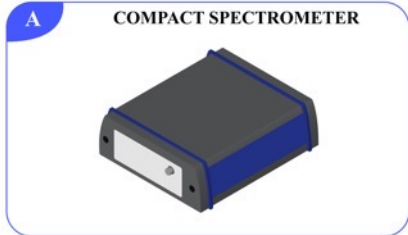
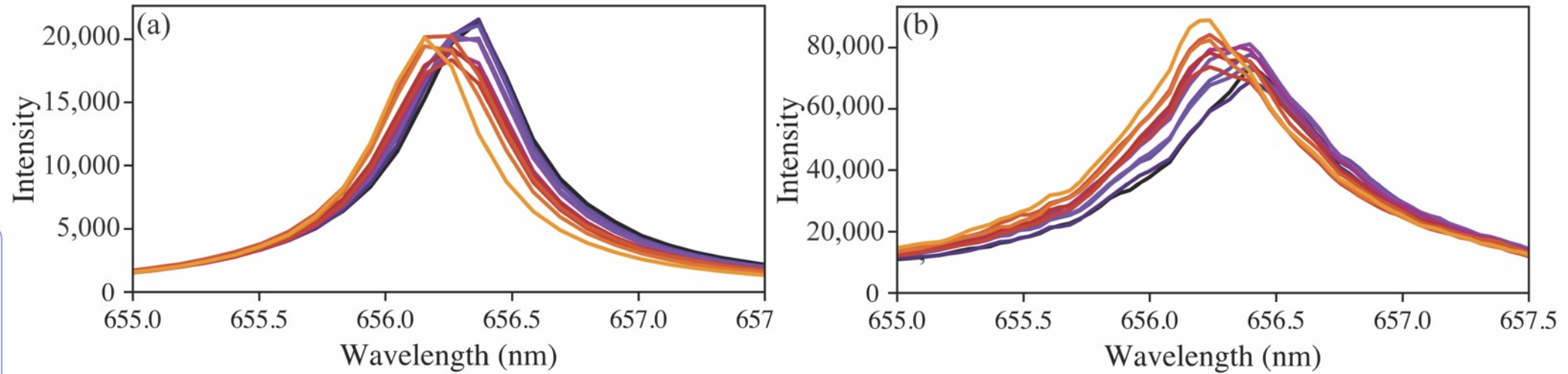
Hunter B. Andrews ^{1,*} and Joanna McFarlane ²

Three spectrometers and two sampling methods were compared to measure hydrogen isotopes



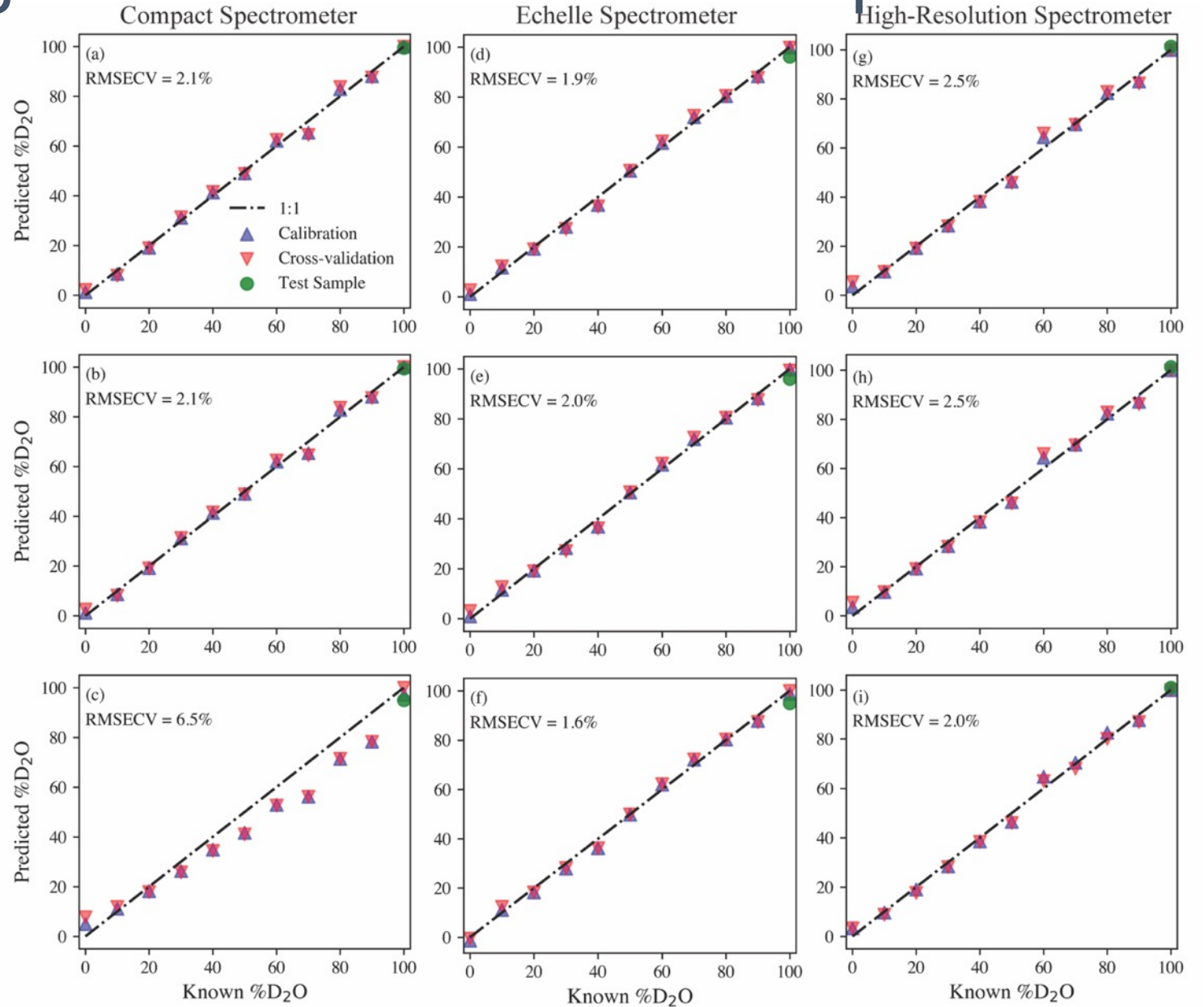
Type	Model *	Resolution (pm)	Wavelength Range (nm)	Delay (μ s)	Width (μ s)
Compact	Avantes, Avaspec 2048	107	501–722	3	1050
Echelle	Andor, Mechelle 5000	39	200–895	2	50
High-resolution	LTB Lasertechnik Berlin, DEMON	3.2	654–658	2	50

The difference in resolution and sensitivity varied greatly

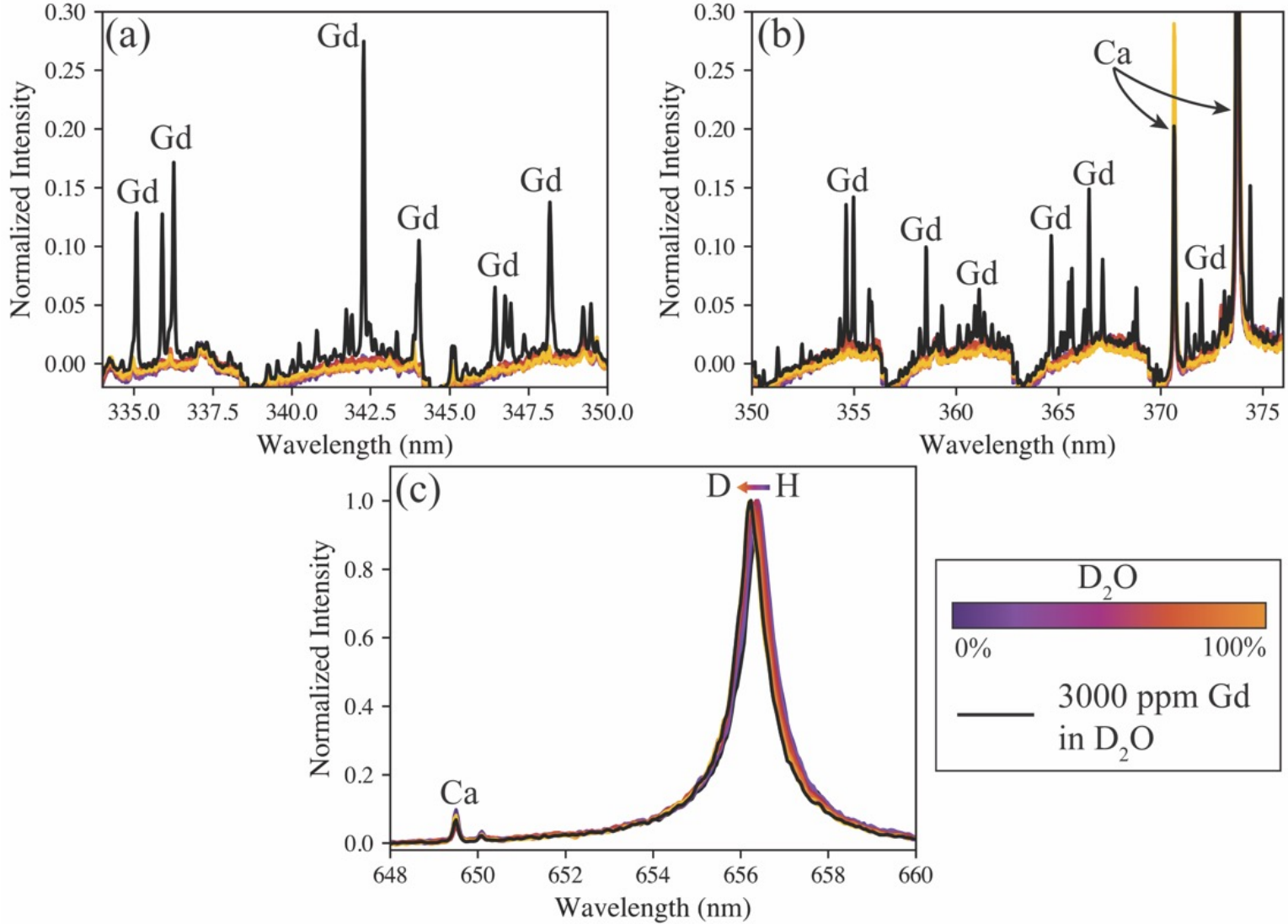


Models were built using three chemometric techniques and each spectrometer

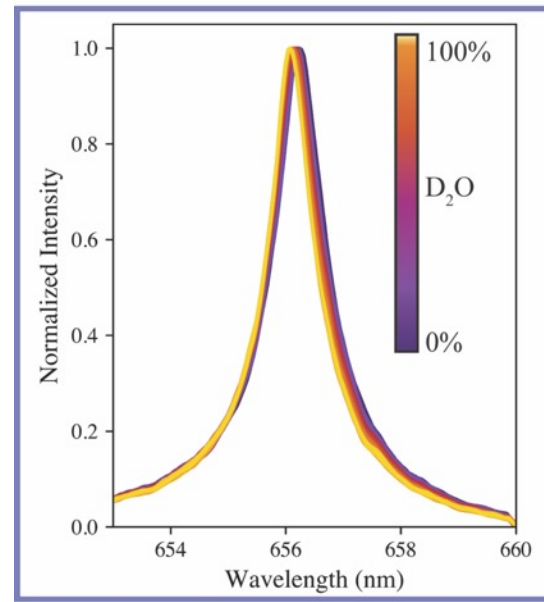
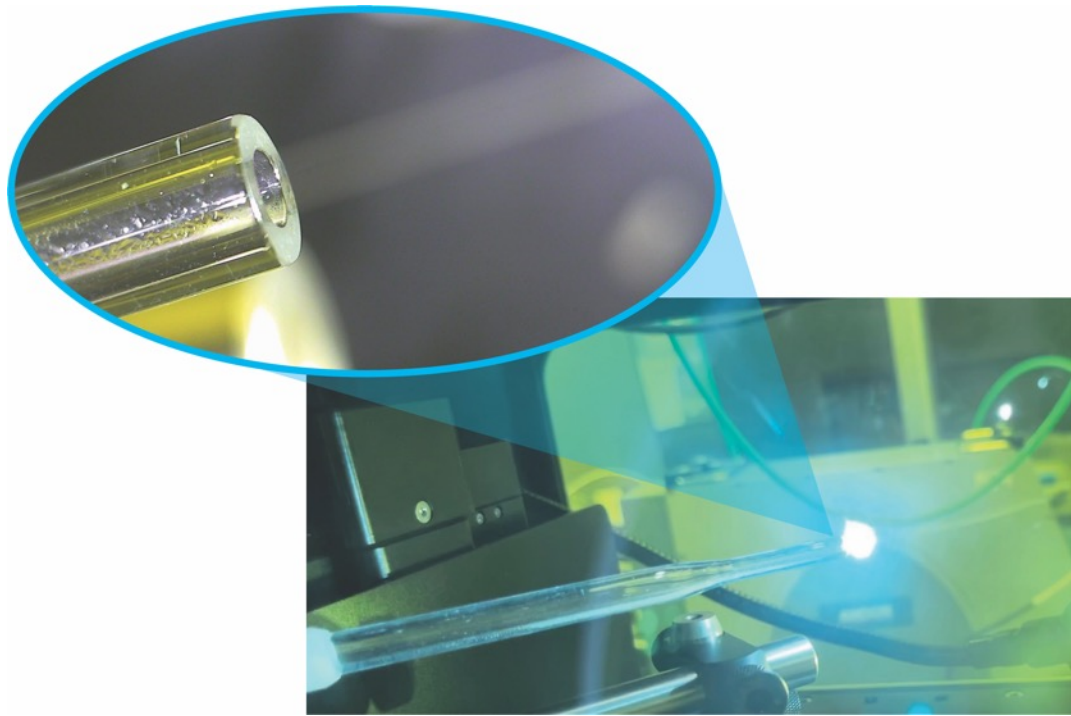
$$RMSECV = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{n}}$$



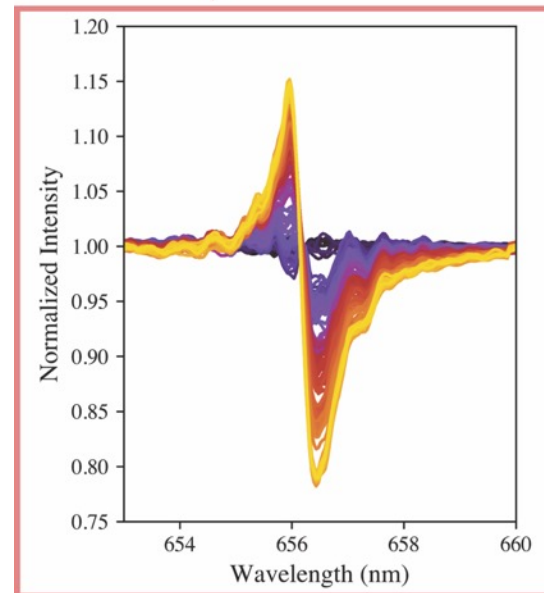
A test sample doped with gadolinium was used to evaluate model and spectrometer versatility



Next, an aerosol system was explored to be more representative of a molten salt off-gas



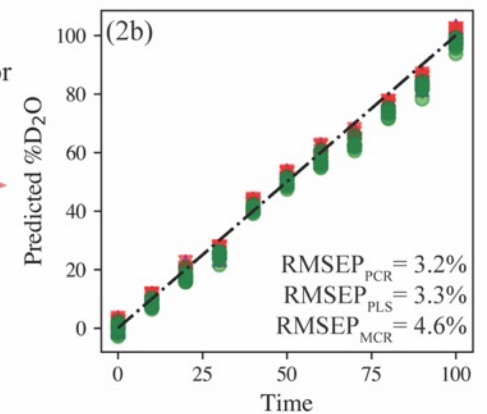
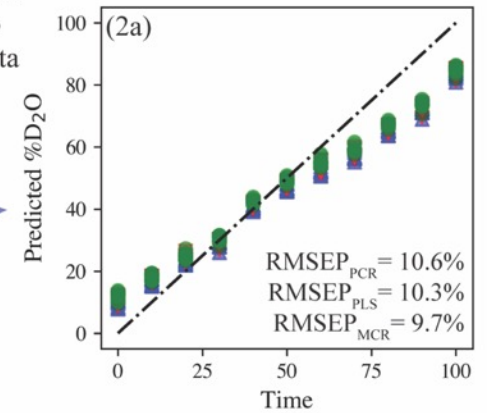
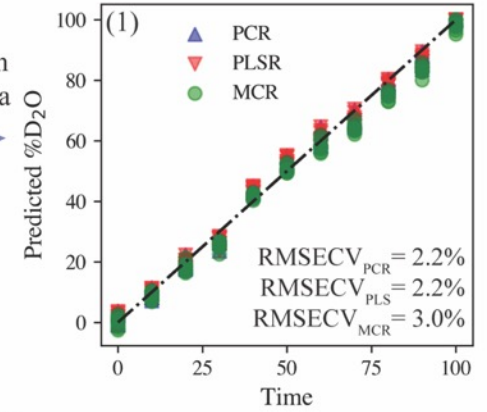
Subtraction of pure H₂O



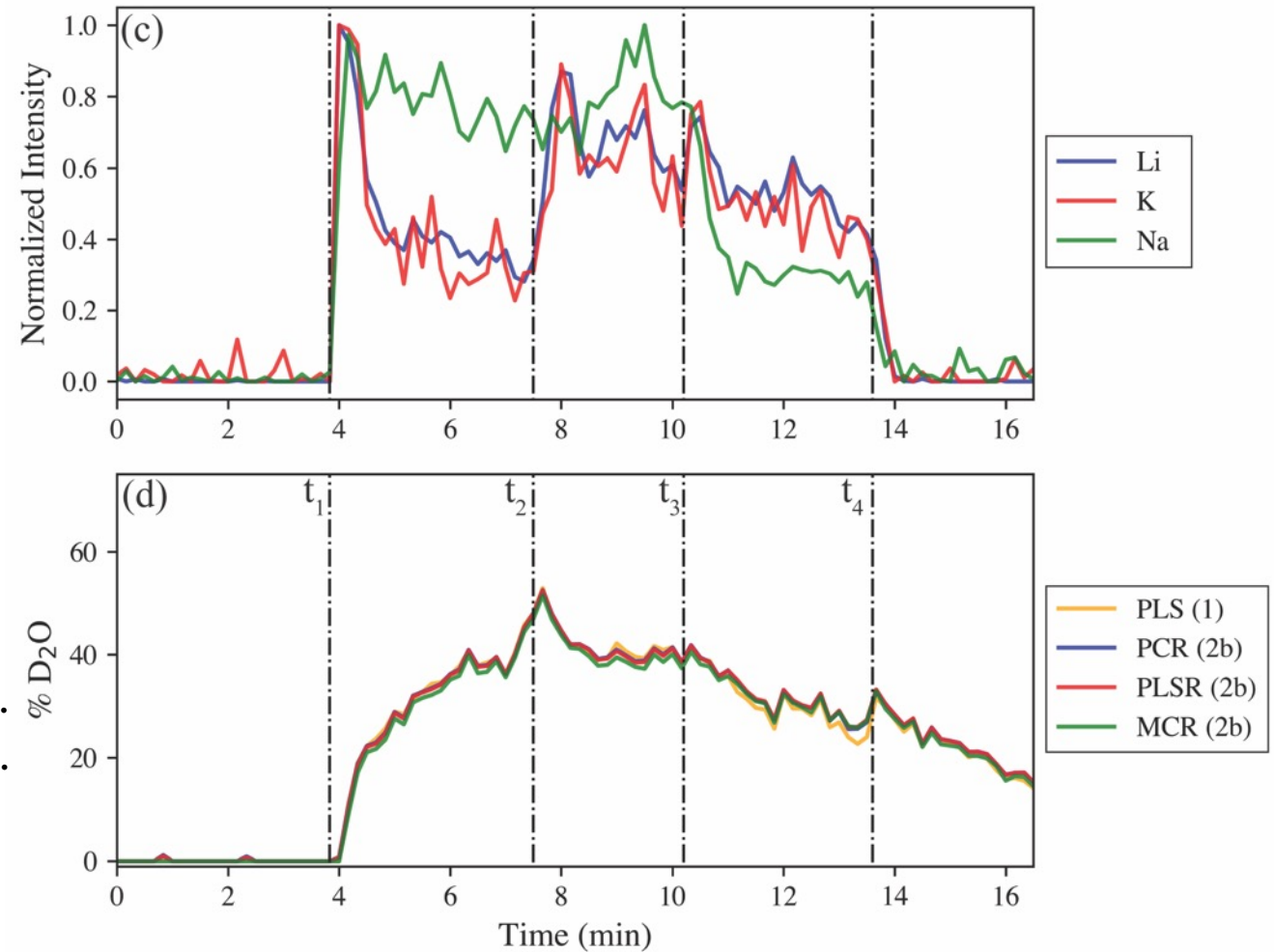
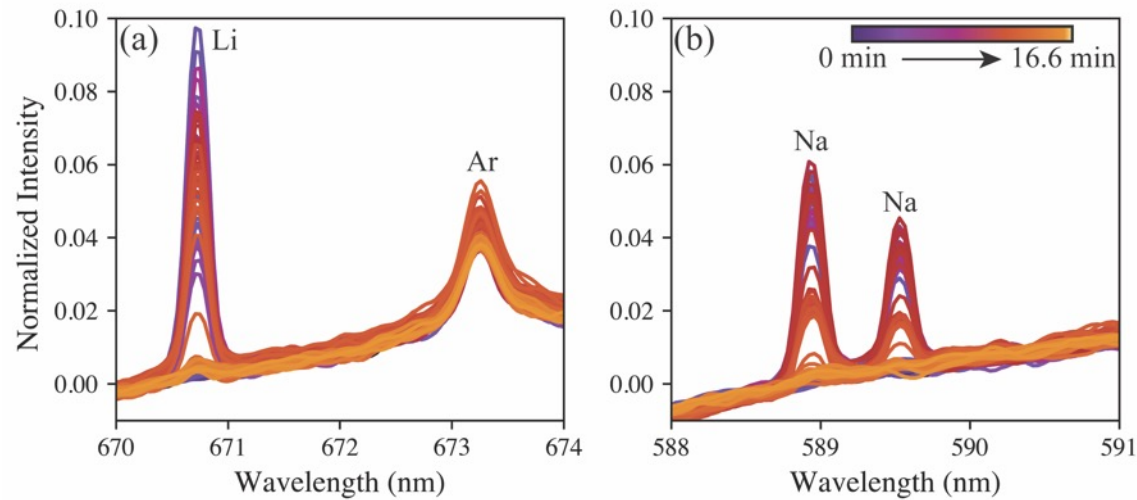
Build model from aerosol data

Apply filter sample model to aerosol data

Apply correction factor to filter model predictions



Overview of real-time test results

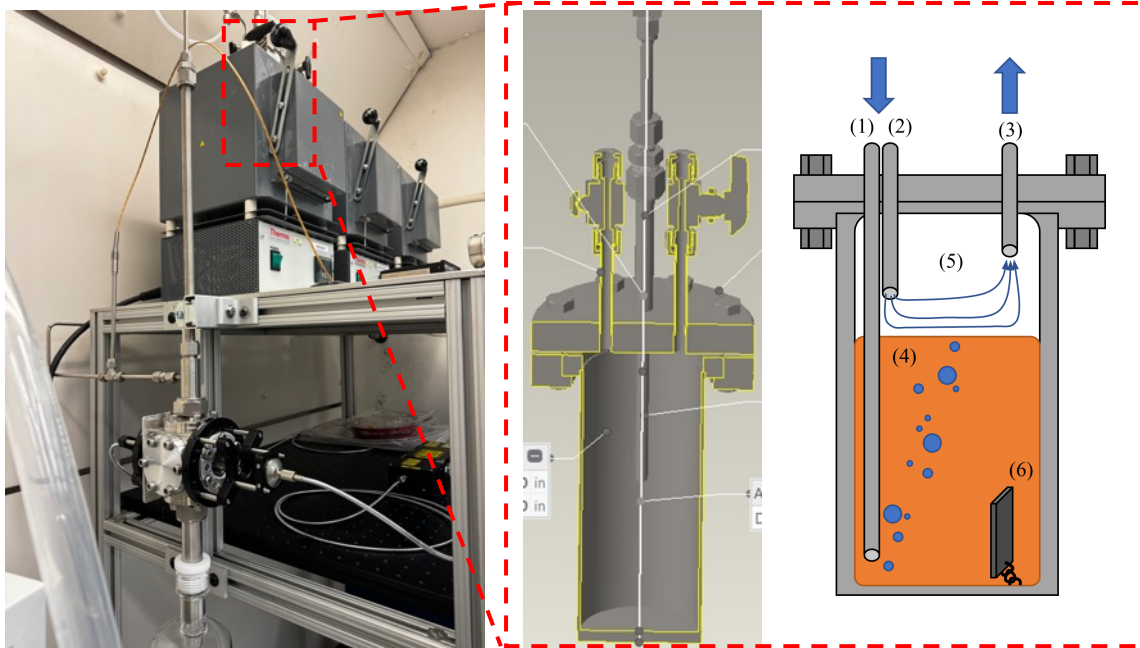


1. Pure H₂O was run to establish a baseline.
2. t_1 (~3.8 min), a spike of FLiNaK in D₂O was added.
3. t_2 (~7.5 min), a spike of FLiNaK in H₂O was added.
4. t_3 (~10.2 min), a spike of pure H₂O was added.
5. t_4 (~13.6 min), the entire reservoir was replaced with pure H₂O to return to the baseline.

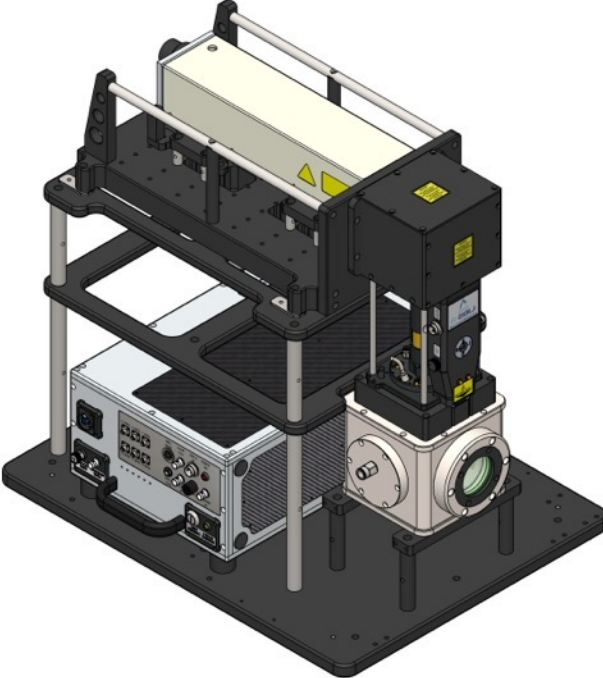
LIBS spectra were recorded in 100 shot accumulates at 10 Hz, providing 100 spectra over the 16.6 min.

Moving forward we now have the ability to test isotopic measurements within our ongoing LIBS monitoring efforts

Small-scale aerosol LIBS



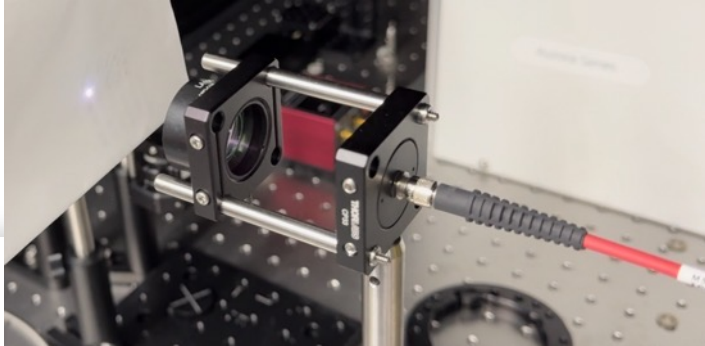
Gas LIBS analysis



Large-scale aerosol LIBS using mobile platform



Fiber delivered LIBS





Thank you

Hunter Andrews, andrewshb@ornl.gov

U.S. DEPARTMENT OF
ENERGY

Office of
NUCLEAR ENERGY