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OAK RIDGE National Laboratory

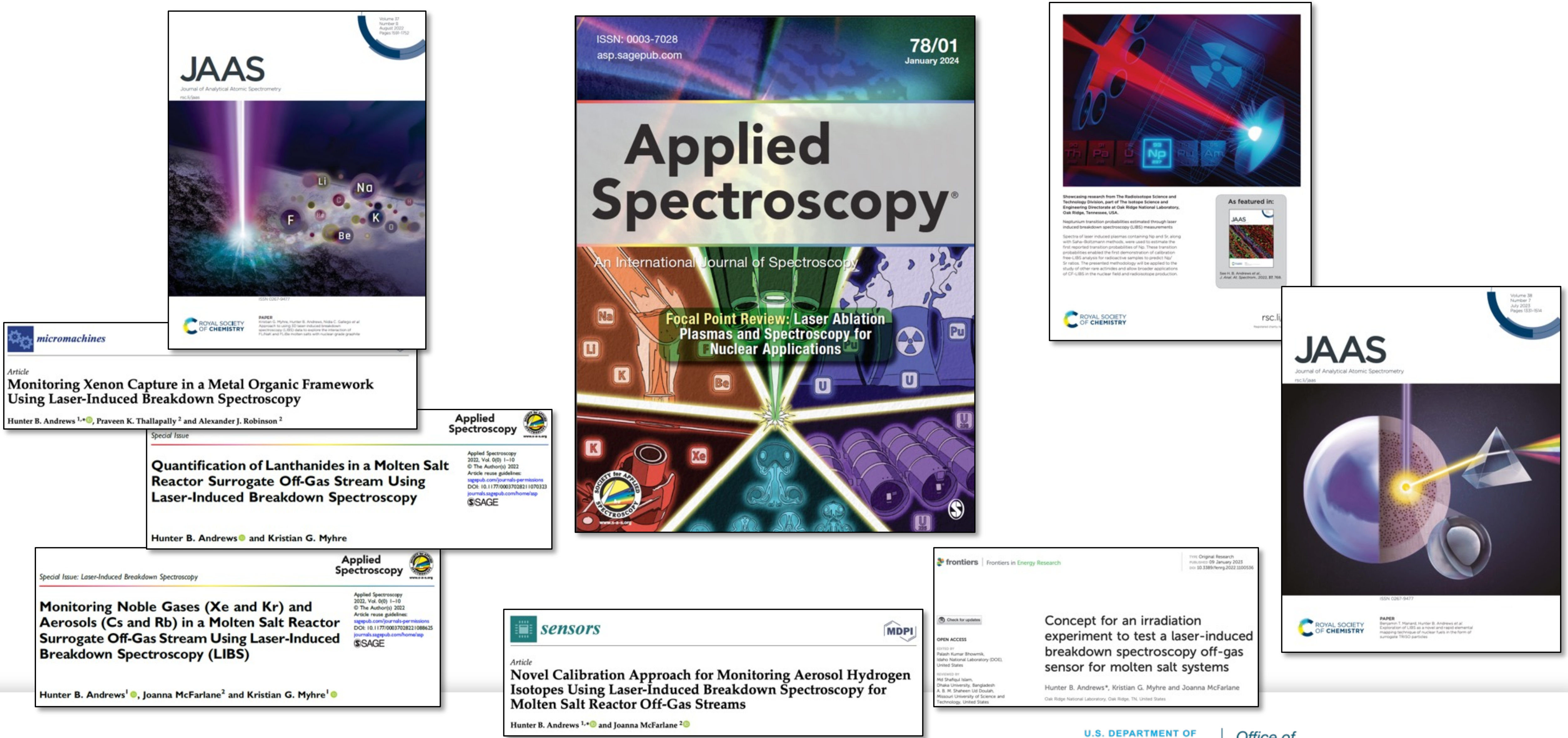
Molten Salt Reactor PROGRAM

Laser-Induced Breakdown Spectroscopy Isotope Ratio Measurements

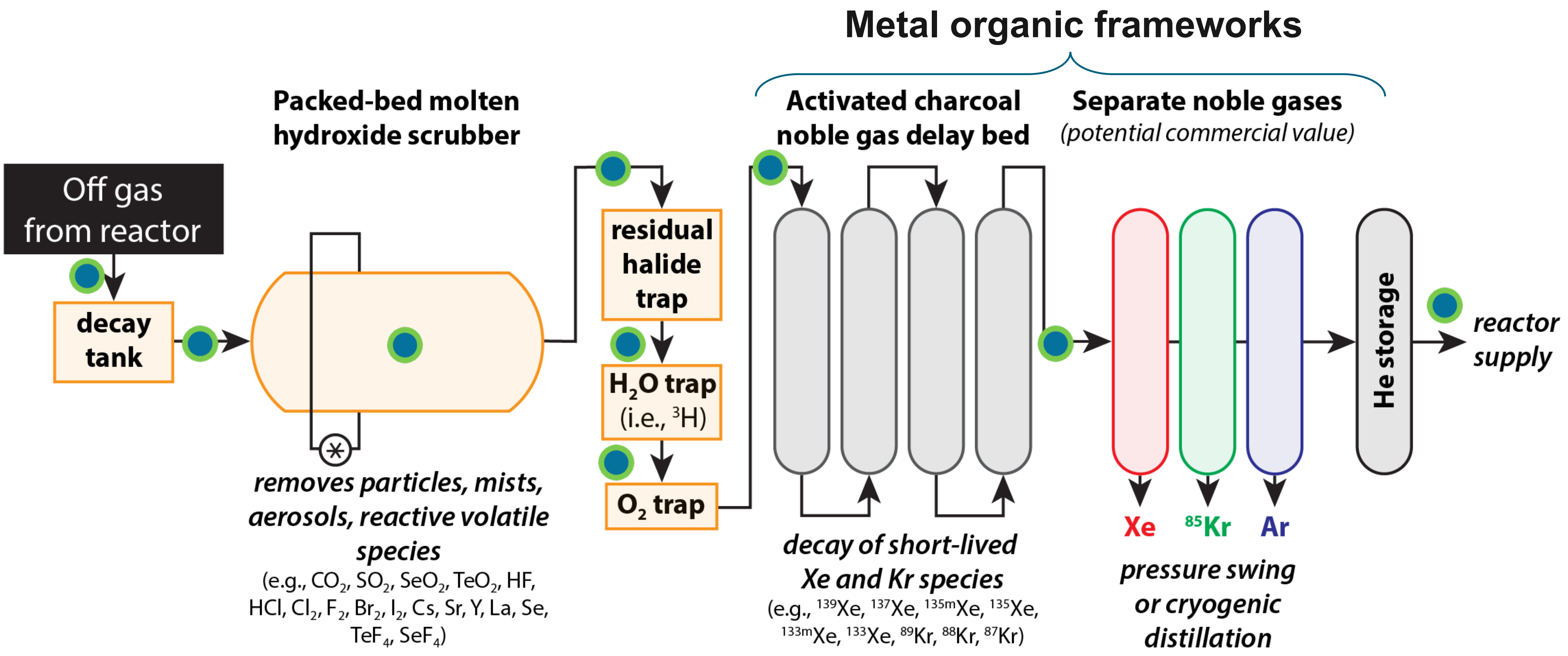
Hunter B. Andrews
Oak Ridge National Laboratory

Annual MSR Campaign Review Meeting April 2024

ORNL is developing LIBS for nuclear technology across the board



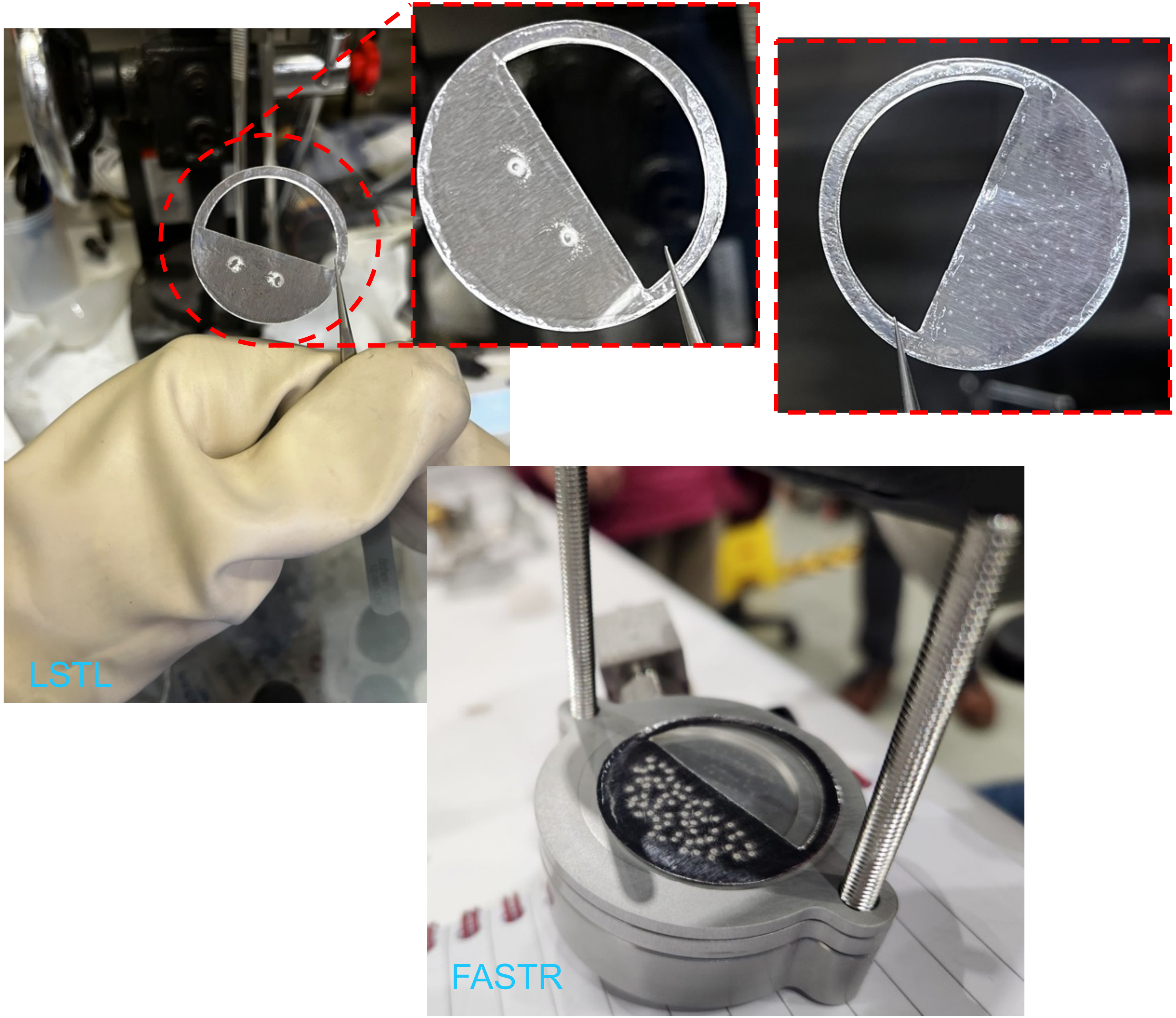
The off-gas treatment system development is critical for continued MSR development



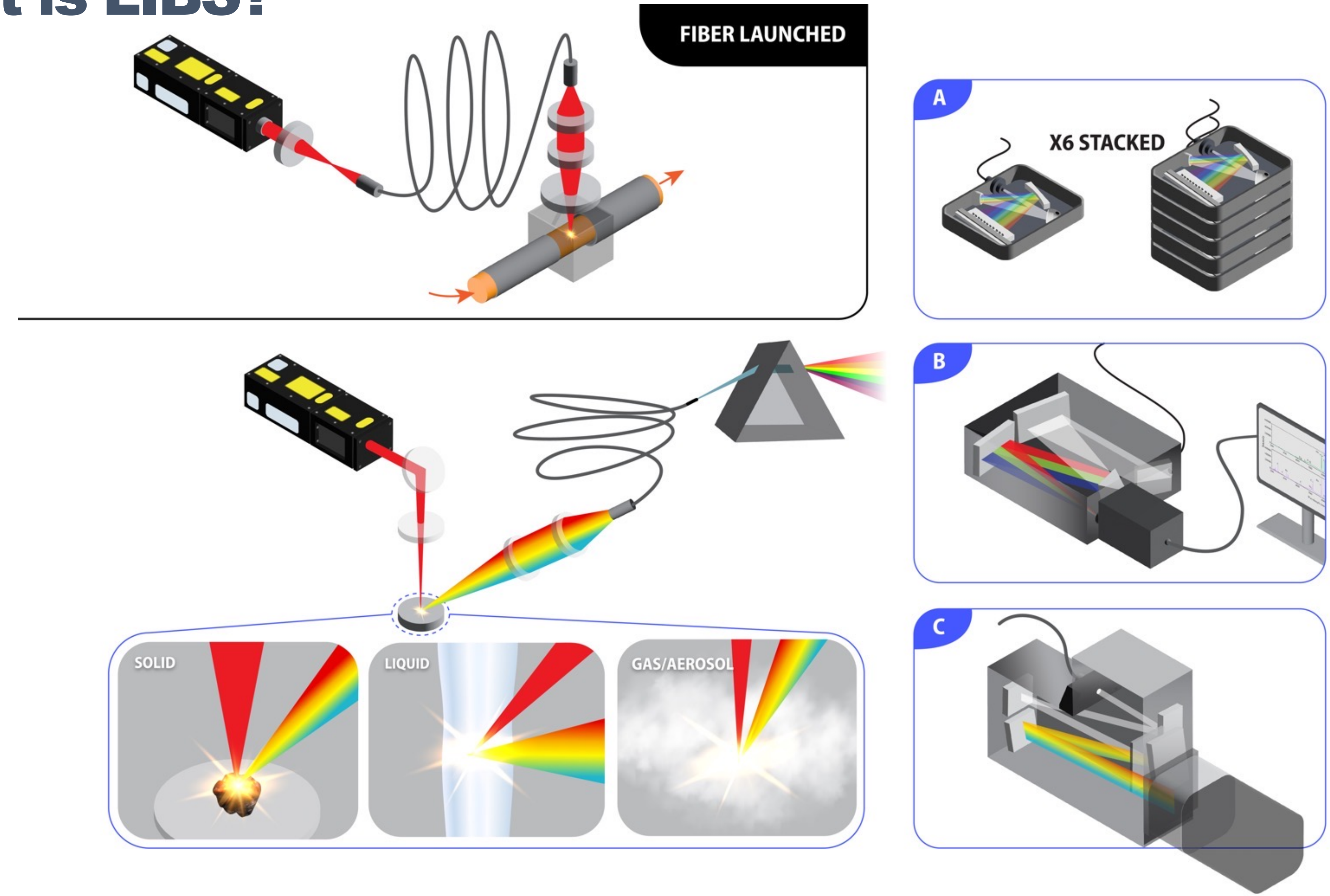
Andrews et. al., Nuclear Engineering and Design., 2021, 385, 111529.

MSR Challenges

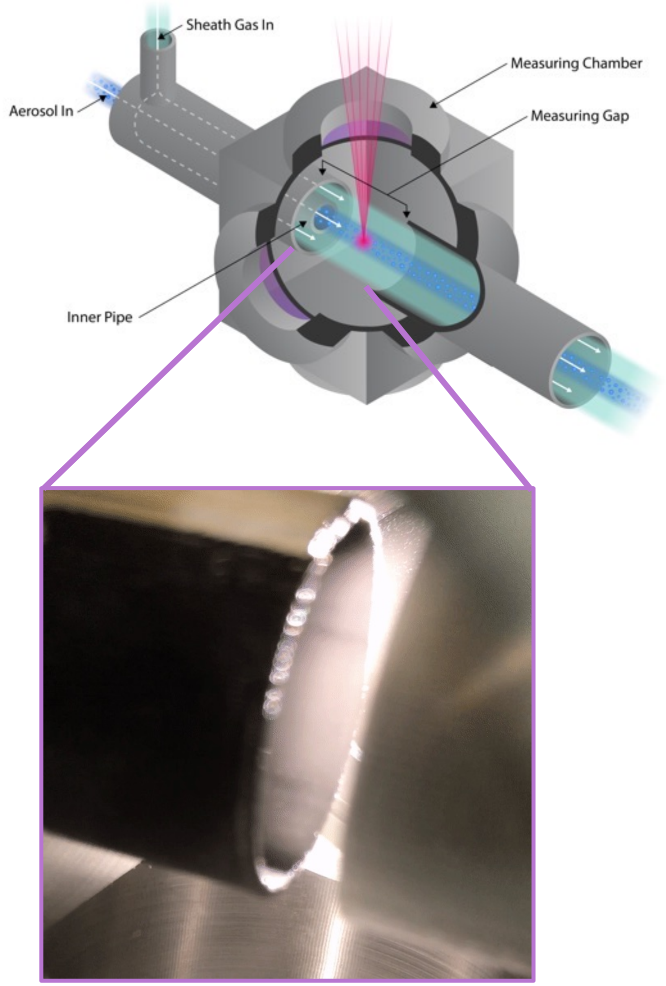
- Liquid fuel
- Inert environment
- Radiation
- Aerosol formation
- Changing chemistry

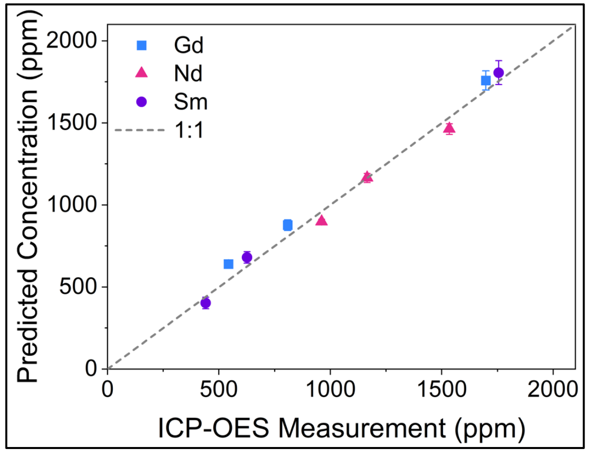


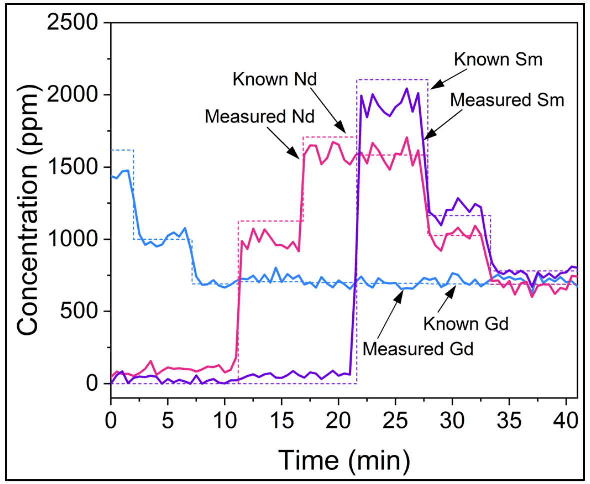
What is LIBS?

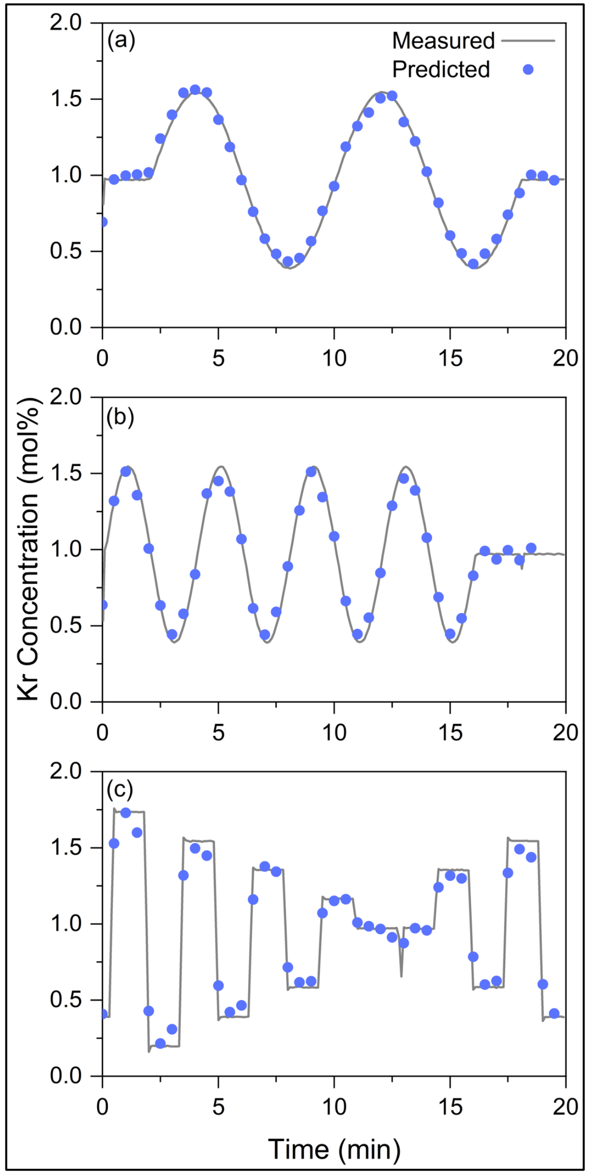


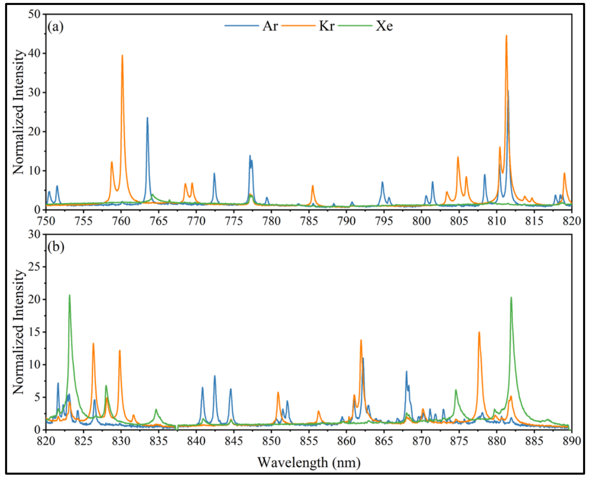
MSR Off-gas streams can be monitored using LIBS

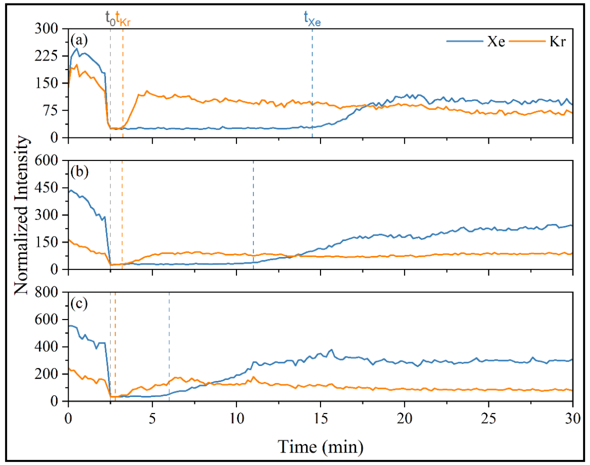




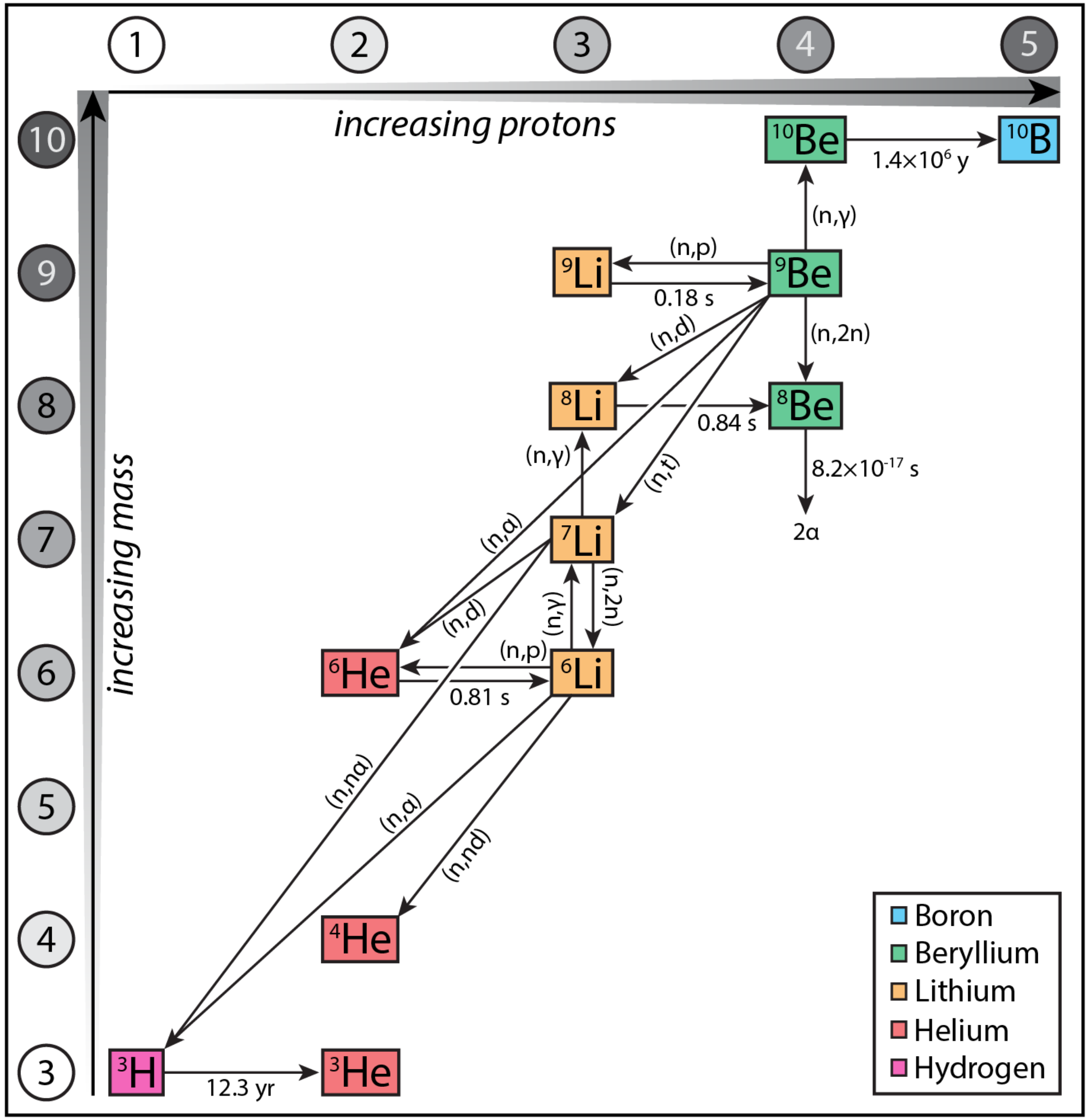








Salt isotopes impact a reactor's ^3H generation



Andrews et. al., Nuclear Engineering and Design., 2021, 385, 111529.

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

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Harilal et al. Appl. Phys. Rev. 5, 021301 (2018)

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

Mass shift dominant

Field shift dominant

Period ↓ / 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		

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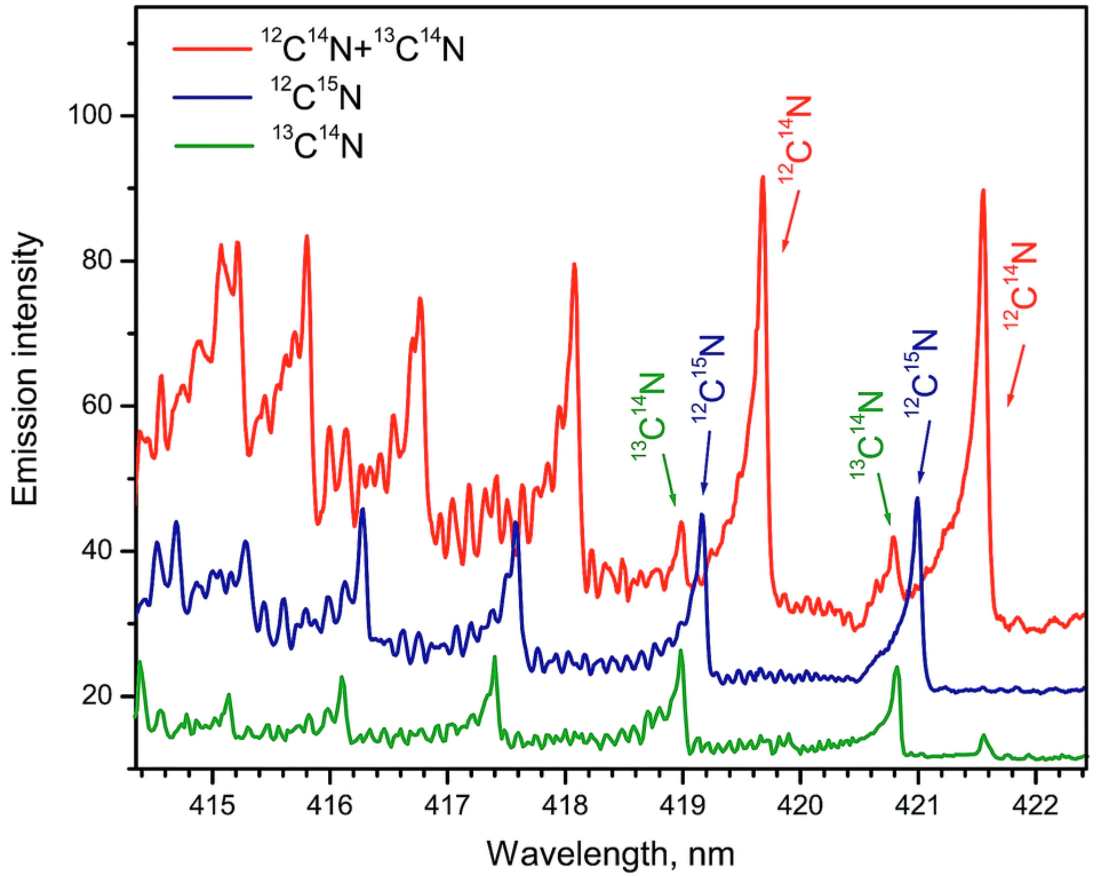
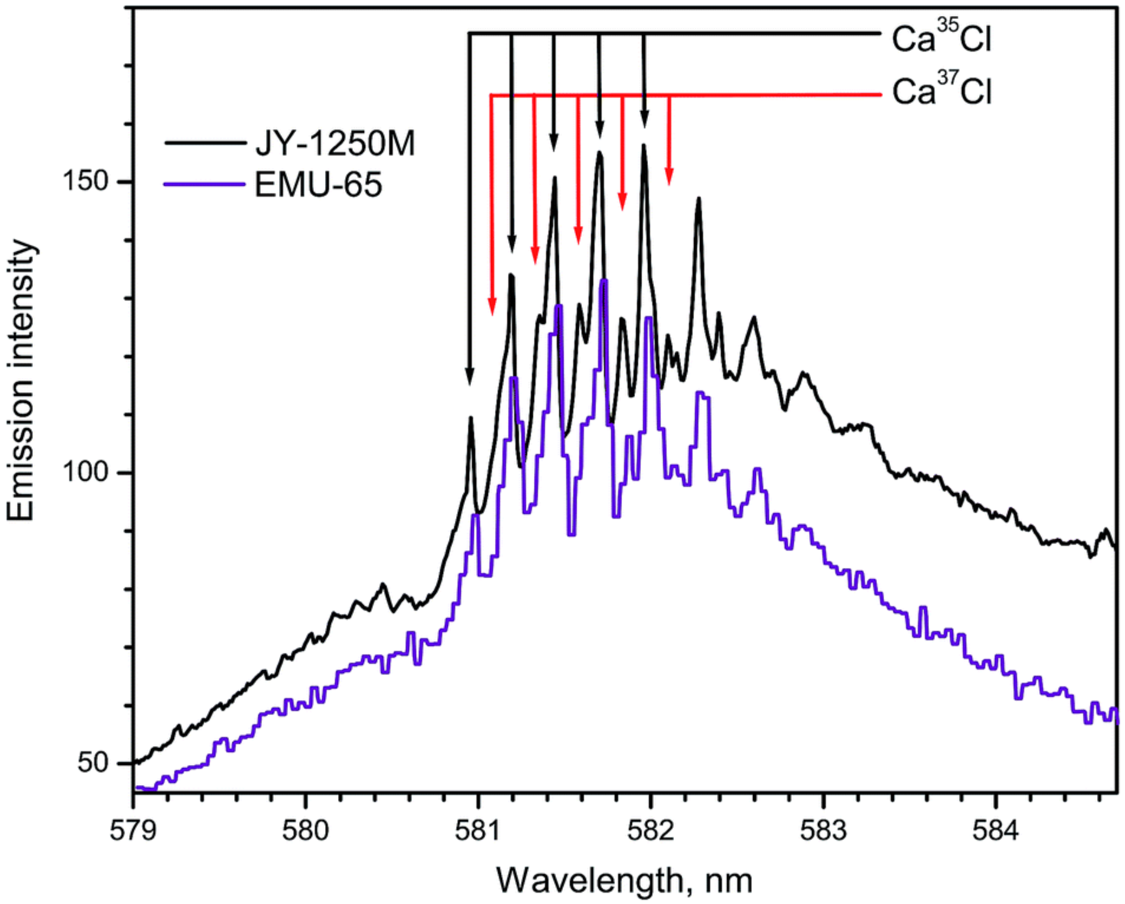
Laser ablation molecular isotopic spectroscopy (LAMIS) extends the isotopic measurement abilities of LIBS

- **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





Bol'shakov et al. *J. Anal. At. Spectrom.*, 2016,31, 119-134

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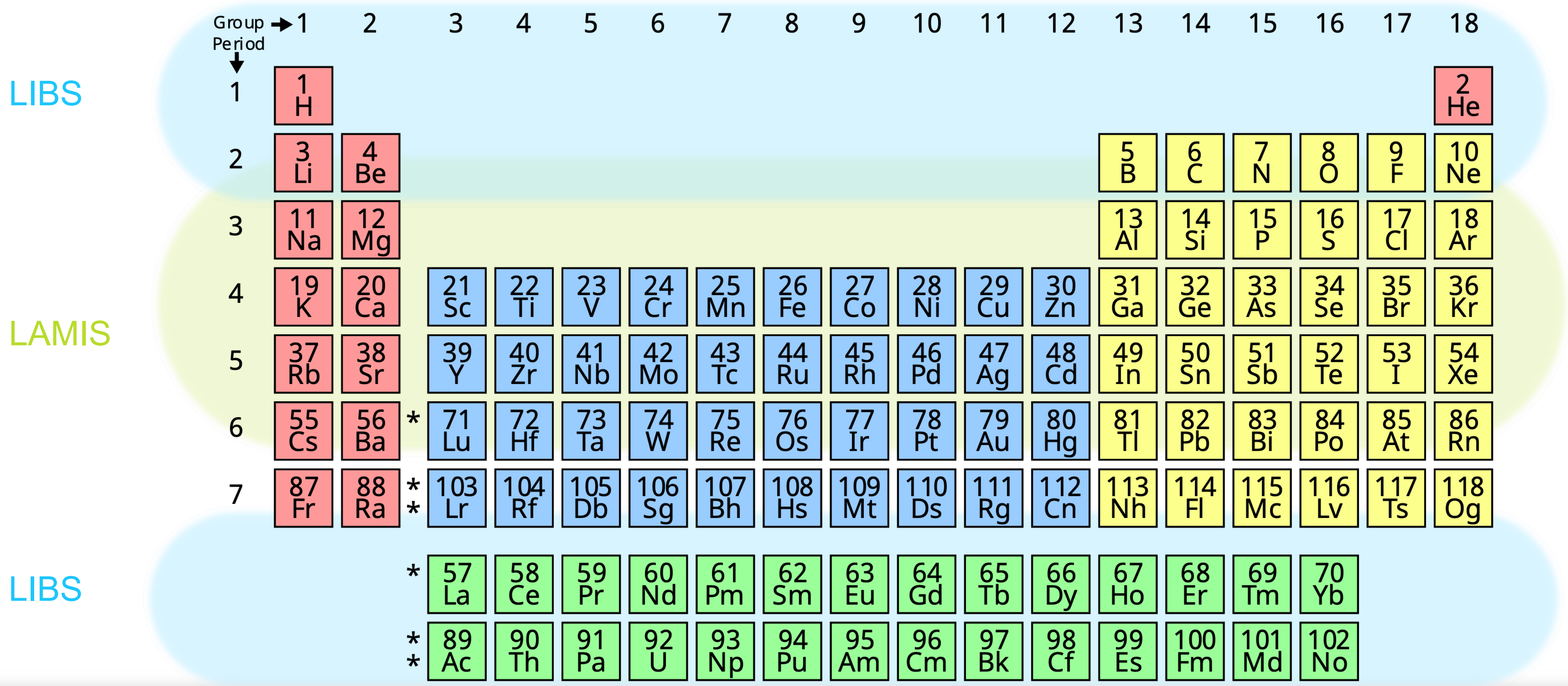
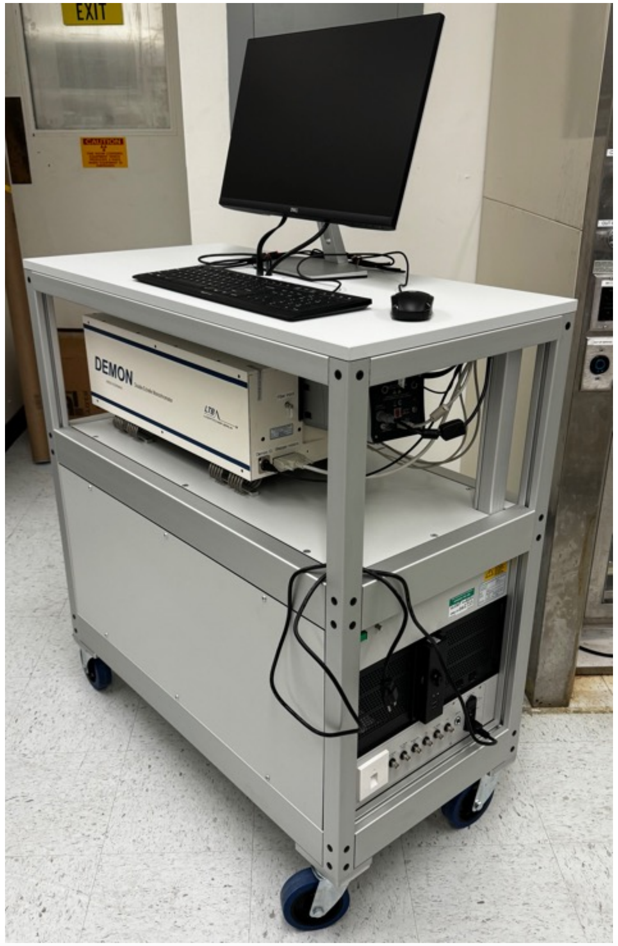
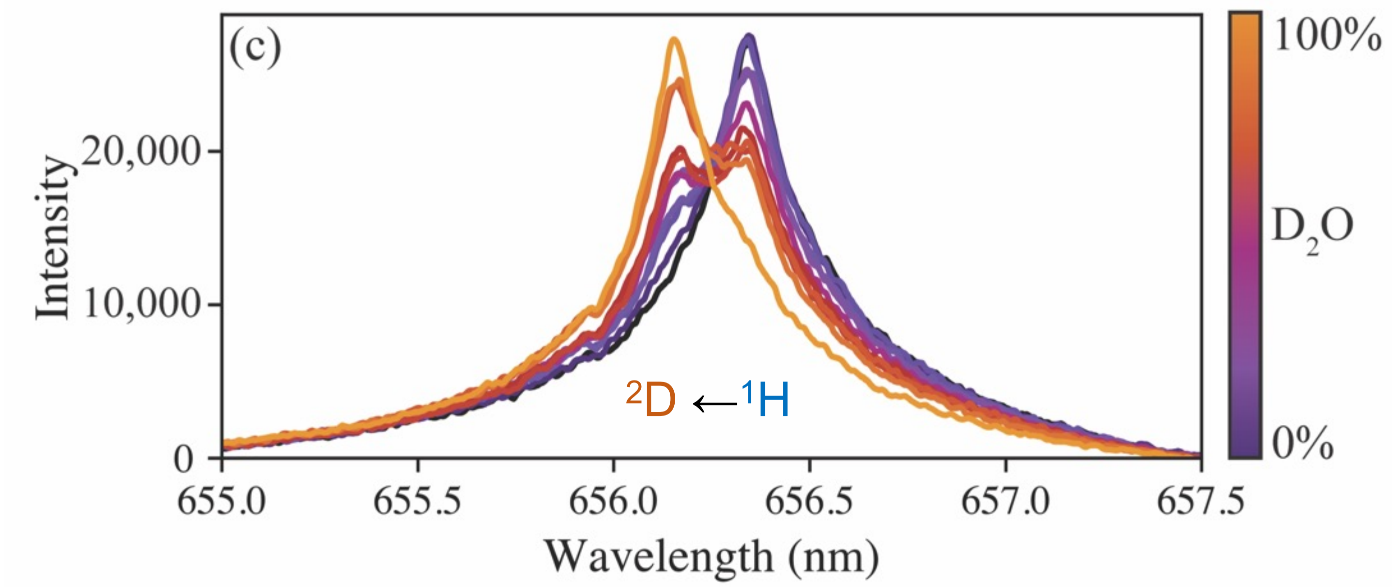
The approach to isotopic measurement varies based on the region of the periodic table



FY23 work package targeted establishing these capabilities within the MSR campaign





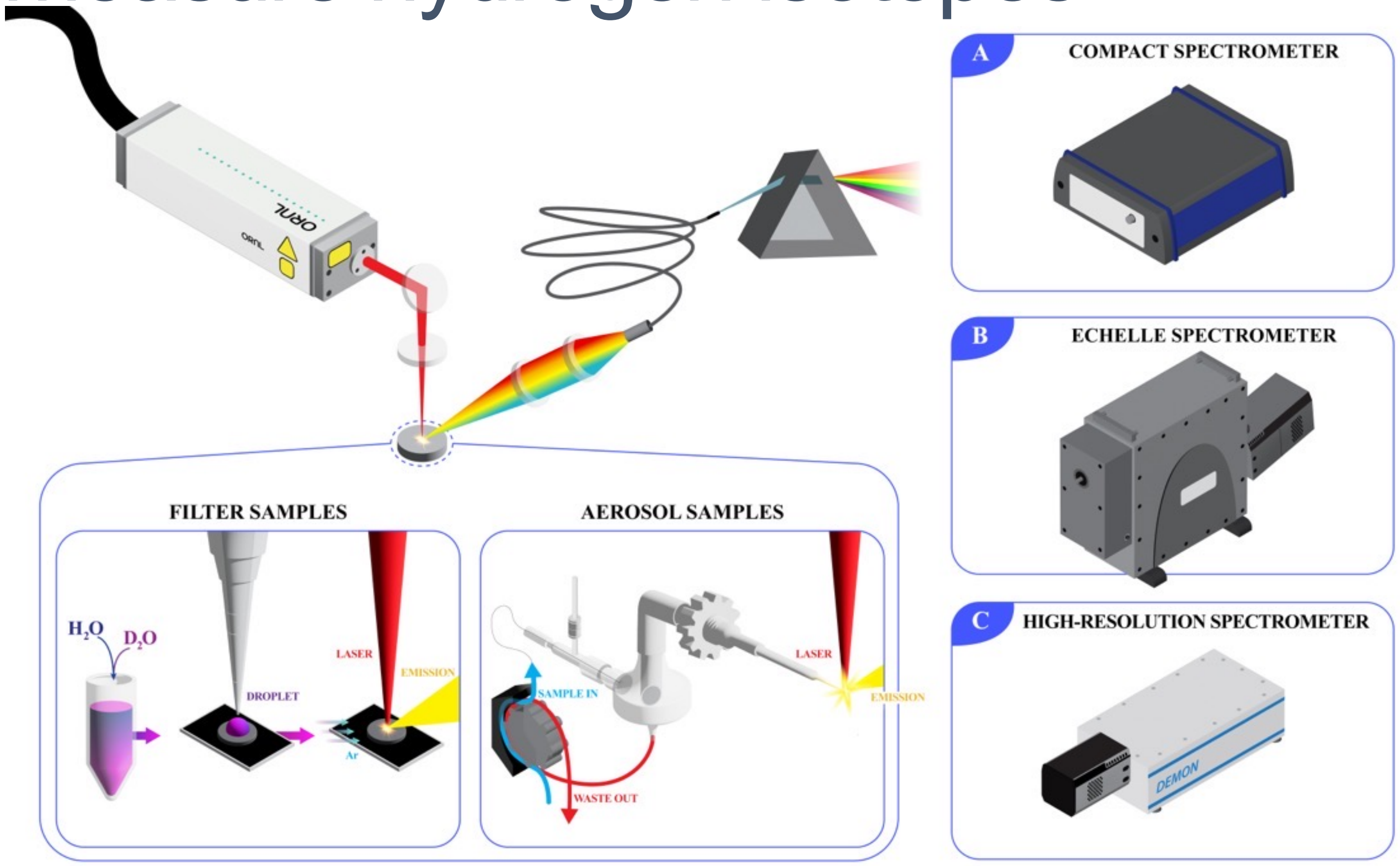
sensors MDPI

Article

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

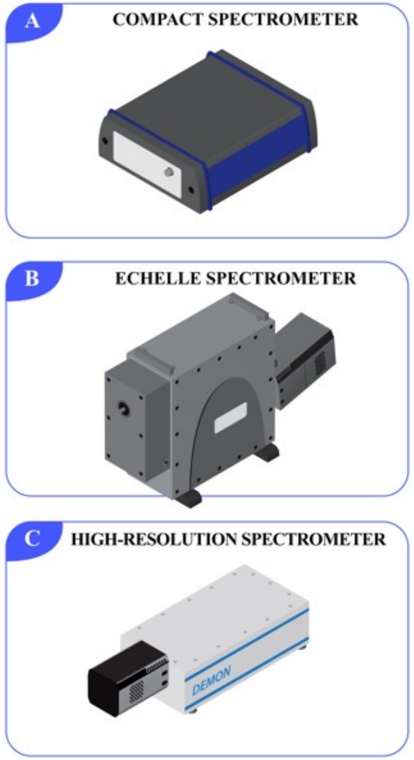
Hunter B. Andrews [1,*] and Joanna McFarlane [2]

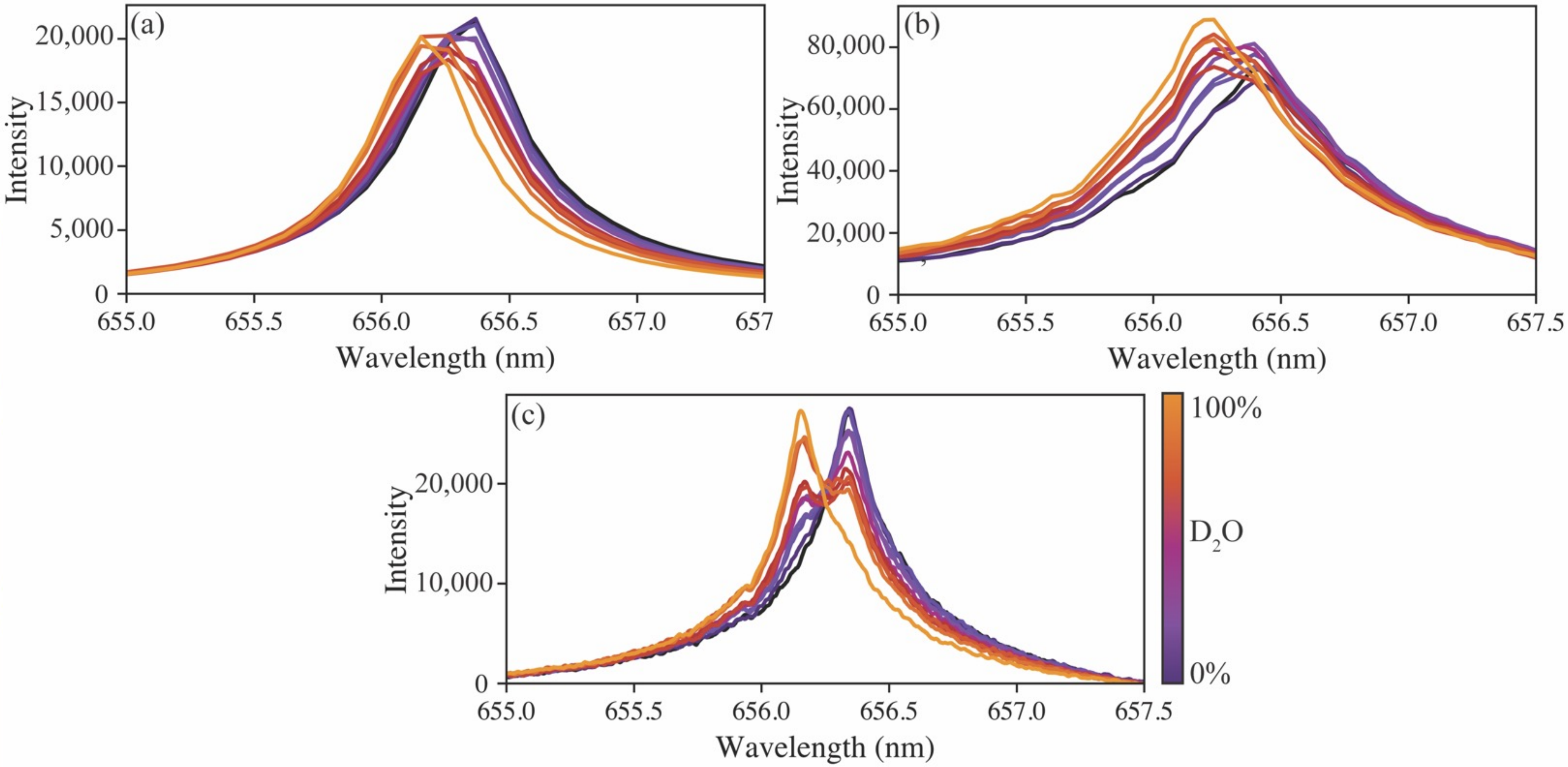
Three spectrometers and two sampling methods were compared to measure hydrogen isotopes



Type	Model *	Resolution (pm)	Wavelength Range (nm)	Delay (µs)	Width (µs)
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

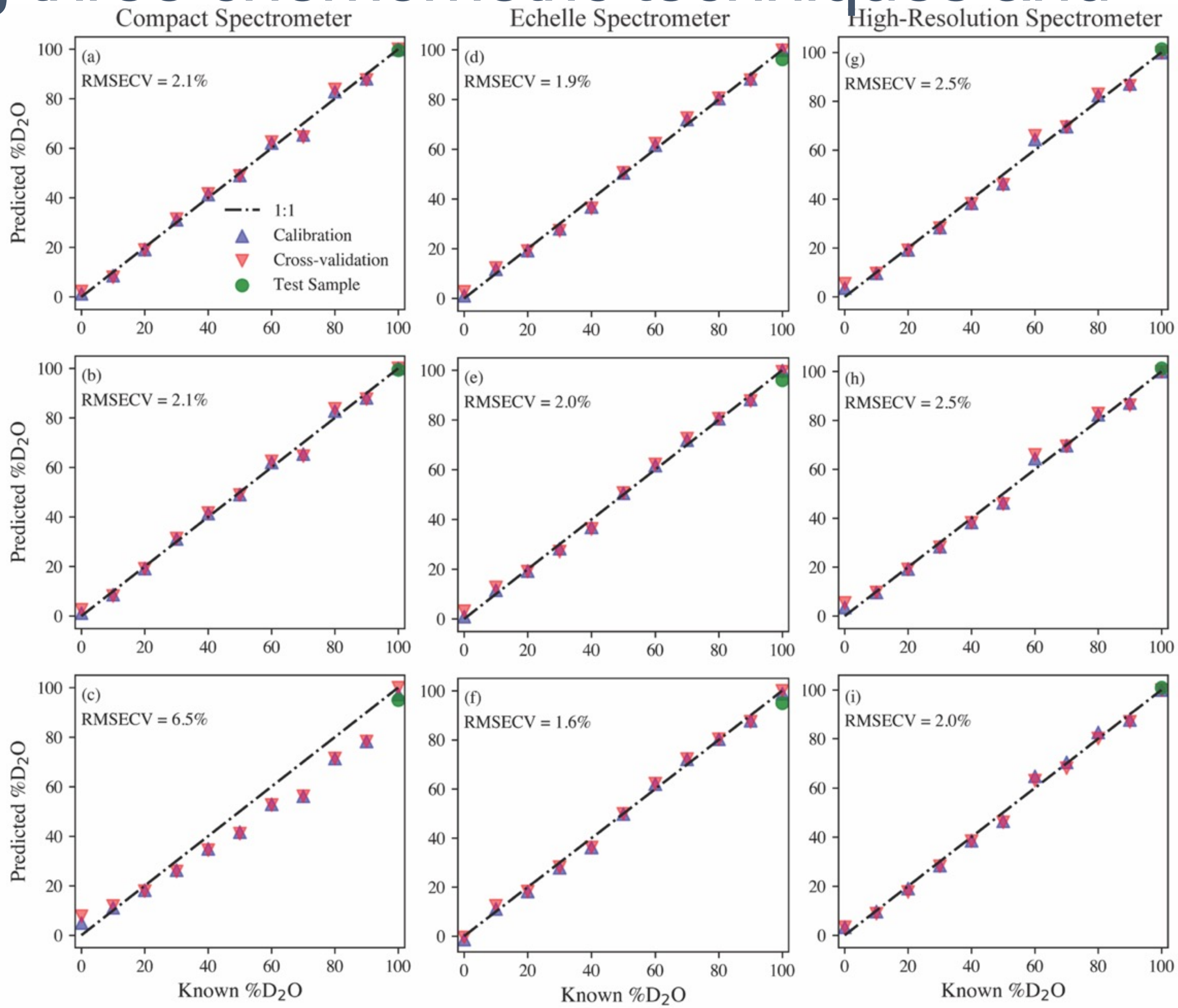
The difference in resolution and sensitivity varied greatly



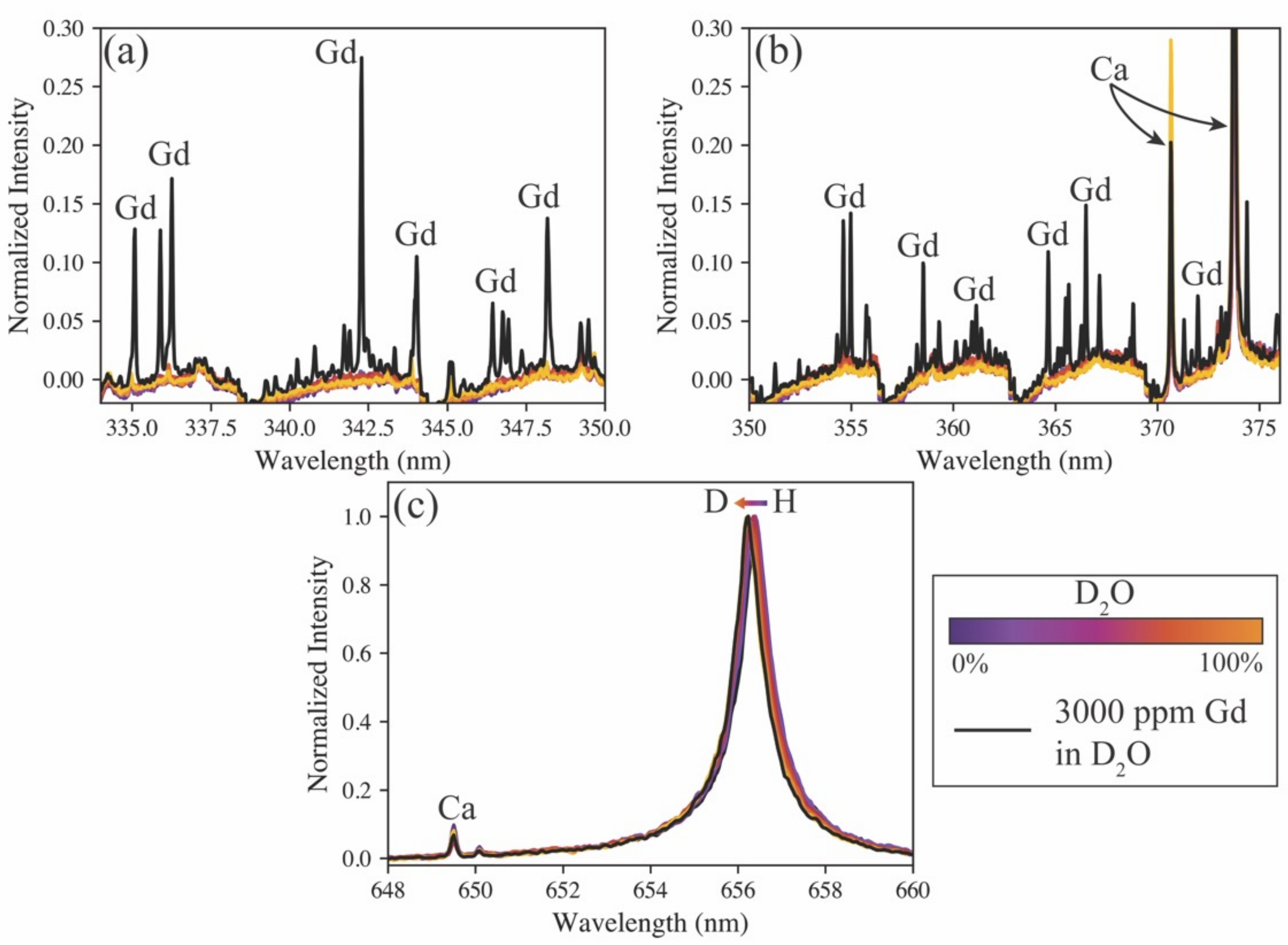


Models were built using three chemometric techniques and each spectrometer

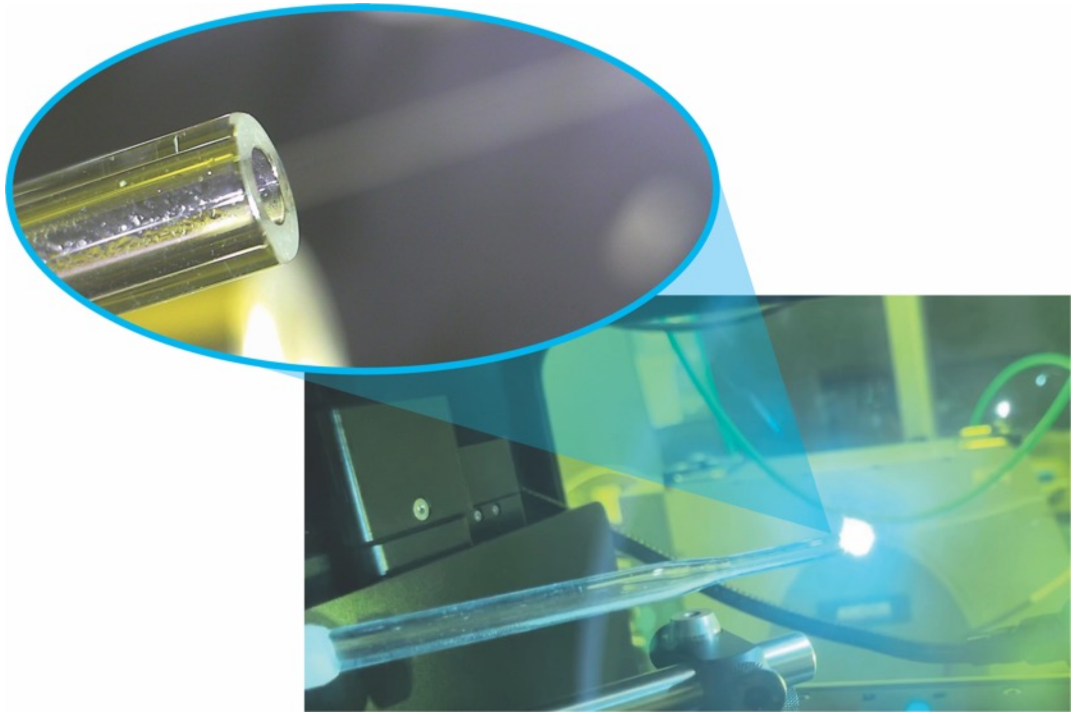
$$RMSECV = \sqrt{\frac{\sum(y_i - \hat{y}_i)^2}{n}}$$

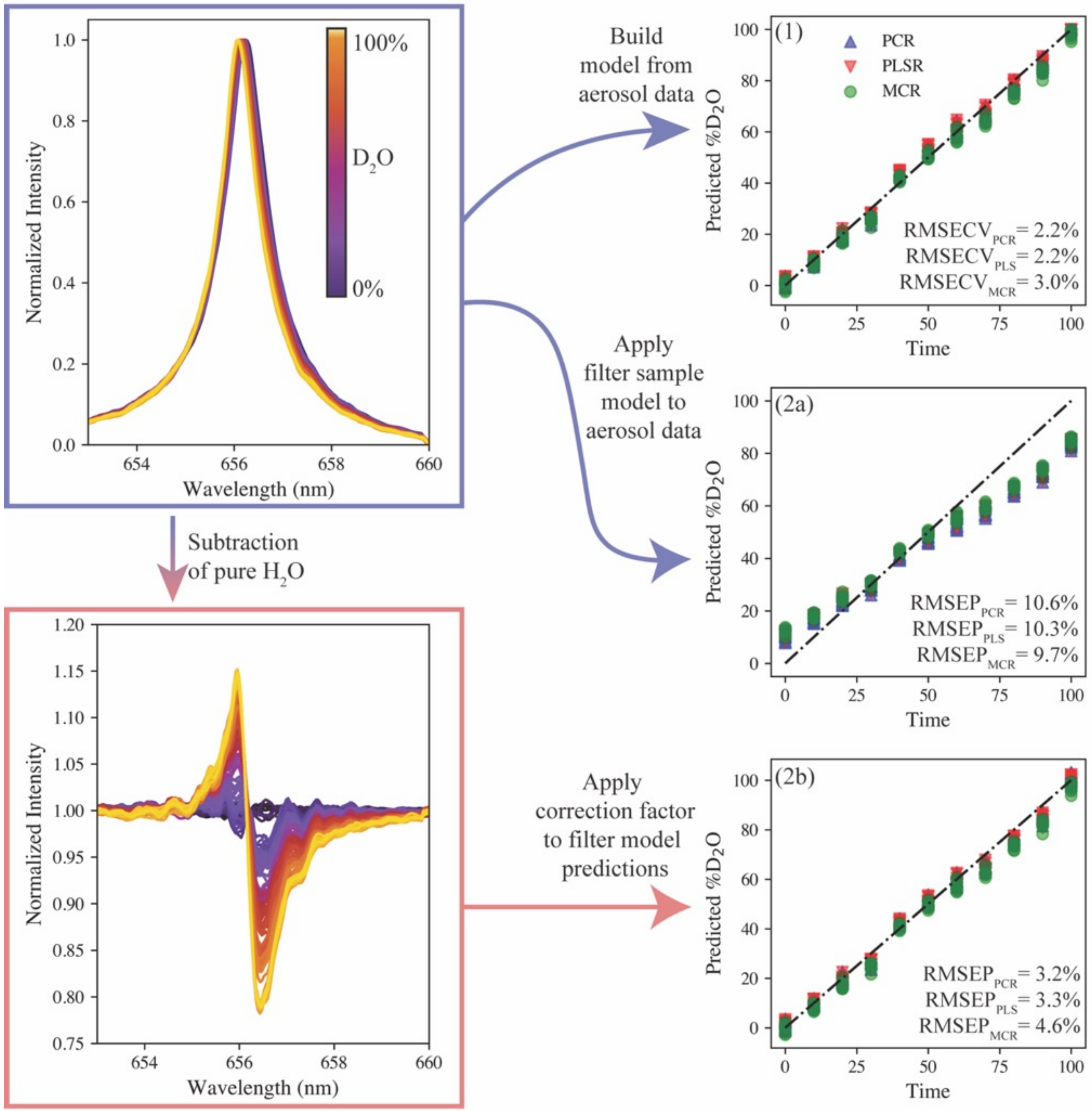


A test sample doped with gadolinium was used to evaluate model and spectrometer versatility

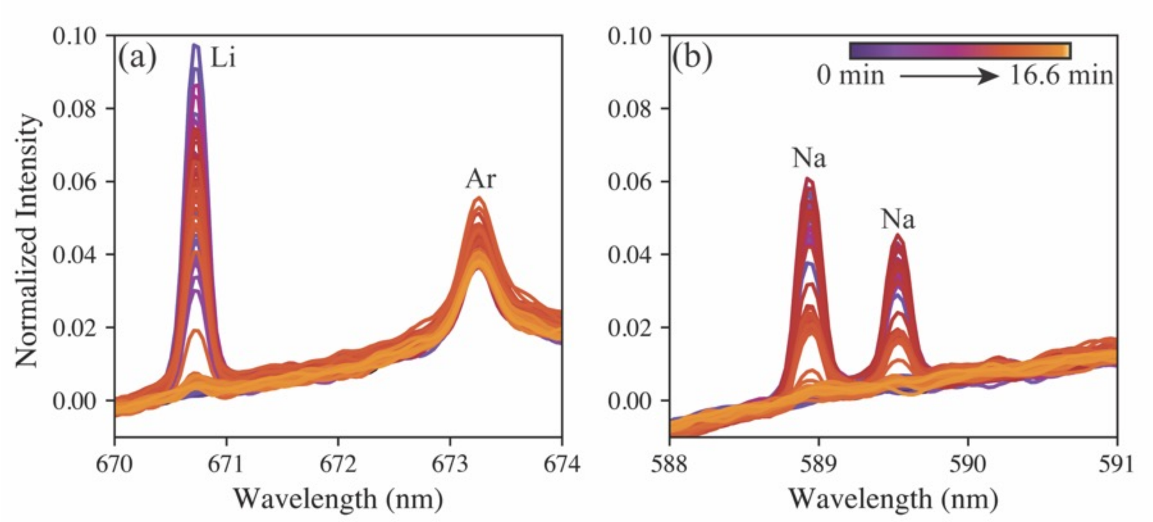


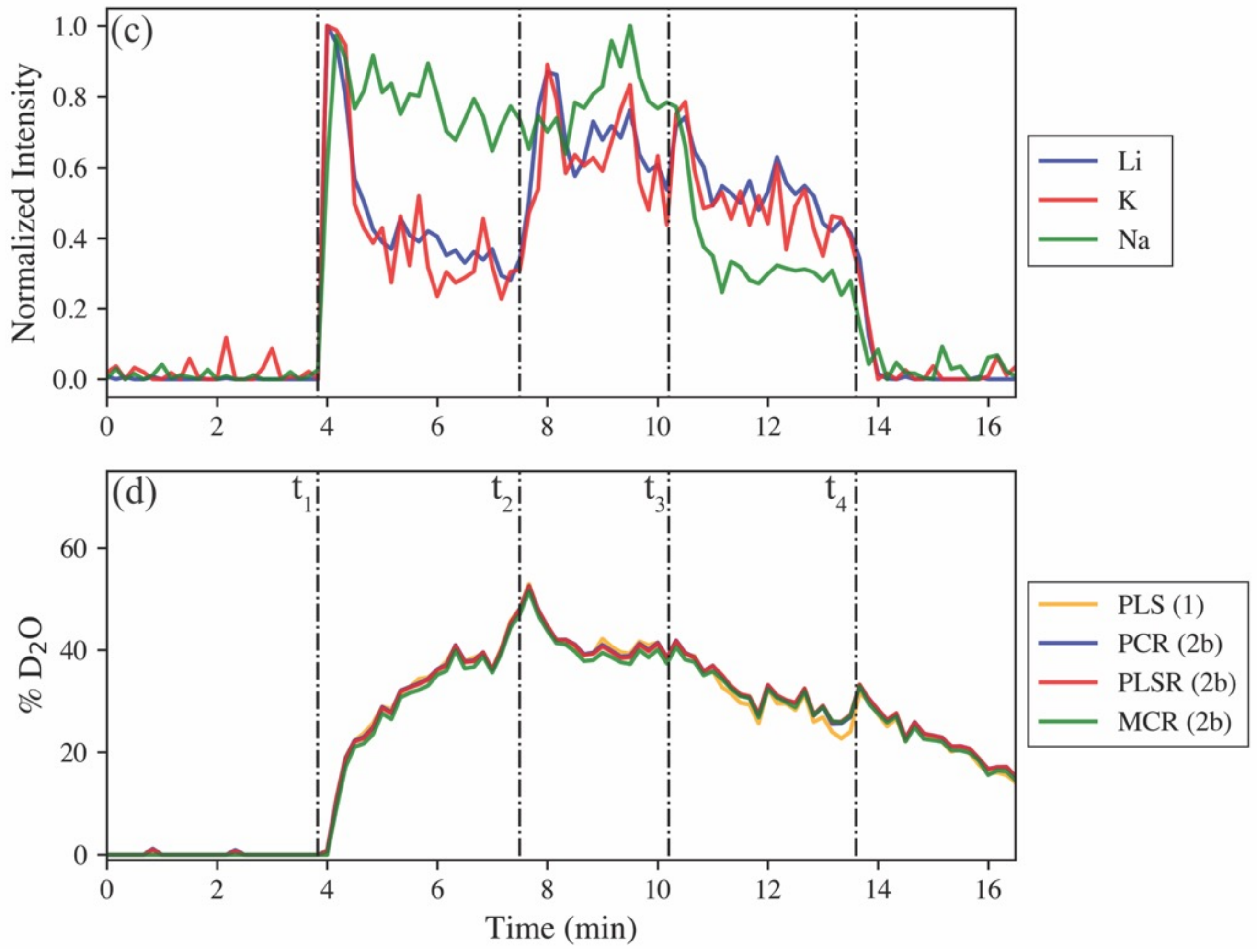
Next, an aerosol system was explored to be more representative of a molten salt off-gas





Overview of real-time test results



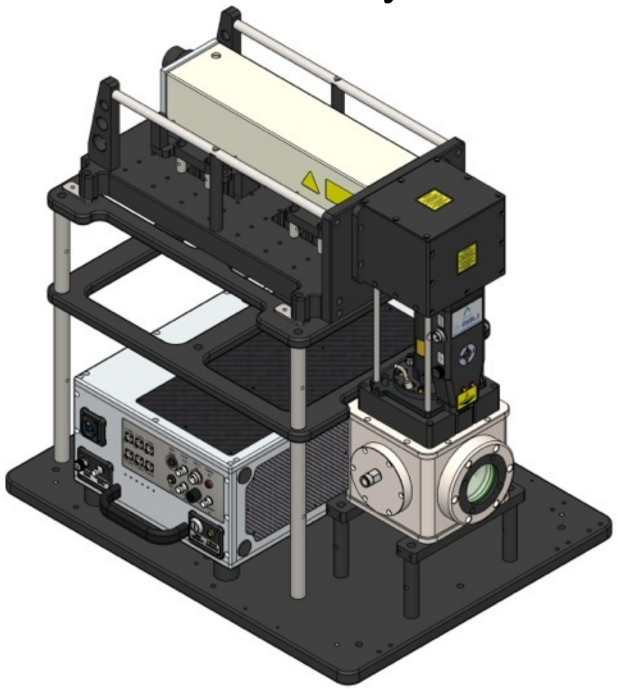


1. Pure H_2O was run to establish a baseline.
2. t_1 (~3.8 min), a spike of FLiNaK in D_2O was added.
3. t_2 (~7.5 min), a spike of FLiNaK in H_2O was added.
4. t_3 (~10.2 min), a spike of pure H_2O was added.
5. t_4 (~13.6 min), the entire reservoir was replaced with pure H_2O to return to the baseline.

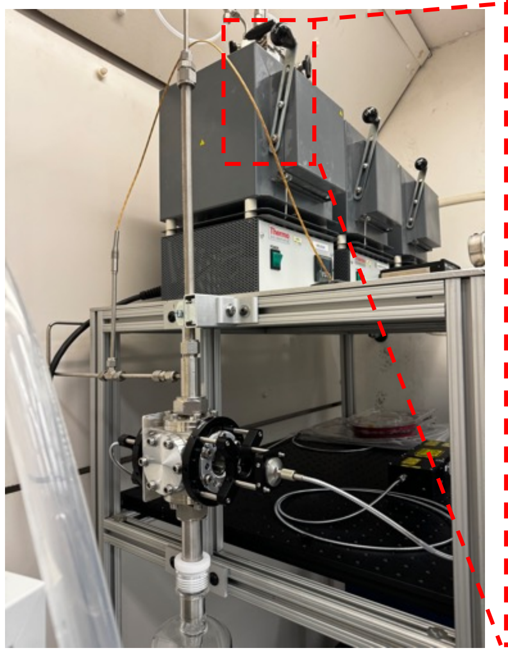
LIBS spectra were recorded in 100 shot accumulates at 10 Hz, providing 100 spectra over the 16.6 min.

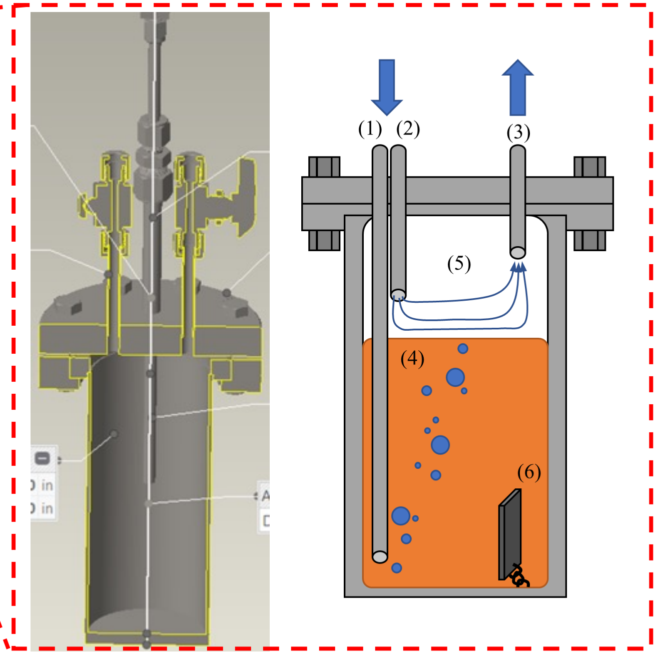
Moving forward we now have the ability to test isotopic measurements within our ongoing LIBS monitoring efforts

Gas LIBS analysis

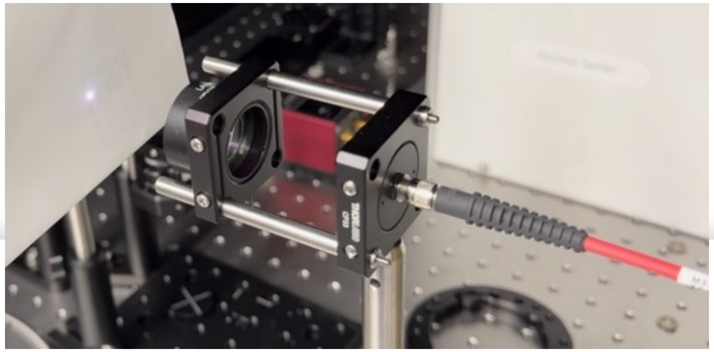


Small-scale aerosol LIBS





Fiber delivered LIBS



Large-scale aerosol LIBS using mobile platform

Thank you

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