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OAK RIDGE National Laboratory

Molten Salt Reactor PROGRAM

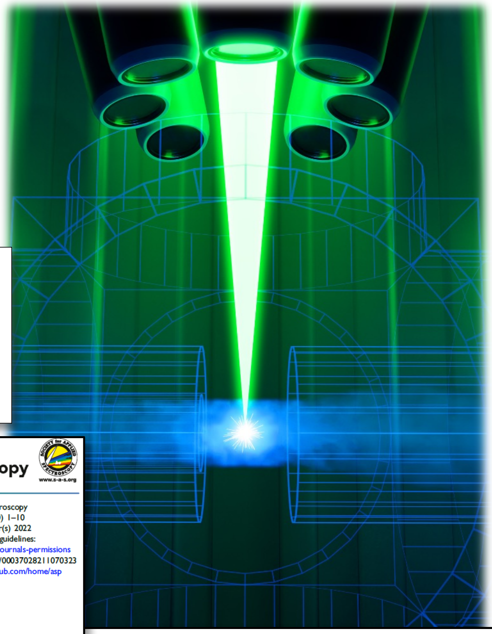
Laser-Induced Breakdown Spectroscopy Isotope Ratio Measurements

Hunter B. Andrews
Oak Ridge National Laboratory

Annual MSR Campaign Review Meeting 2-4 May 2023

LIBS is being used to help progress molten salt reactor research

LIBS off-gas sensor



Open Access | Feature Paper | Editor's Choice | Article

Monitoring Xenon Capture in a Metal Organic Framework Using Laser-Induced Breakdown Spectroscopy

by Hunter B. Andrews [1,*], Praveen K. Thallapally [2] and Alexander J. Robinson [2]

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Applied Spectroscopy

Special Issue

Applied Spectroscopy
2022, Vol. 0(0) 1–10
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Quantification of Lanthanides in a Molten Salt Reactor Surrogate Off-Gas Stream Using Laser-Induced Breakdown Spectroscopy

Hunter B. Andrews and Kristian G. Myhre

frontiers | Frontiers in Energy Research

TYPE Original Research
PUBLISHED 09 January 2023
DOI 10.3389/fenrg.2022.1100536

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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

Applied Spectroscopy

Special Issue: Laser-Induced Breakdown Spectroscopy

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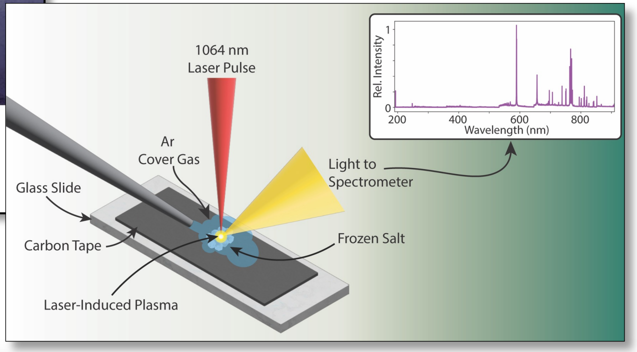
Monitoring Noble Gases (Xe and Kr) and Aerosols (Cs and Rb) in a Molten Salt Reactor Surrogate Off-Gas Stream Using Laser-Induced Breakdown Spectroscopy (LIBS)

Hunter B. Andrews[1], Joanna McFarlane[2] and Kristian G. Myhre[1]

LIBS to probe salt-material interaction



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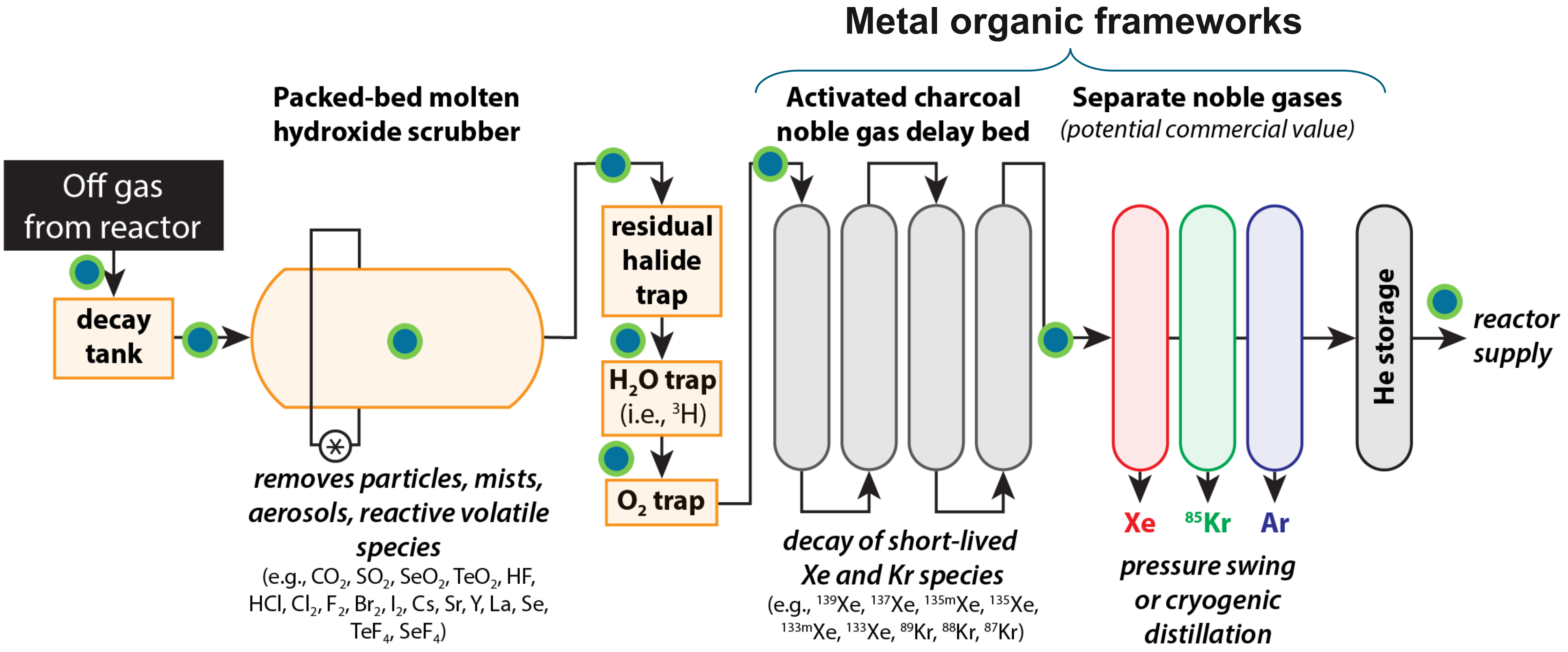
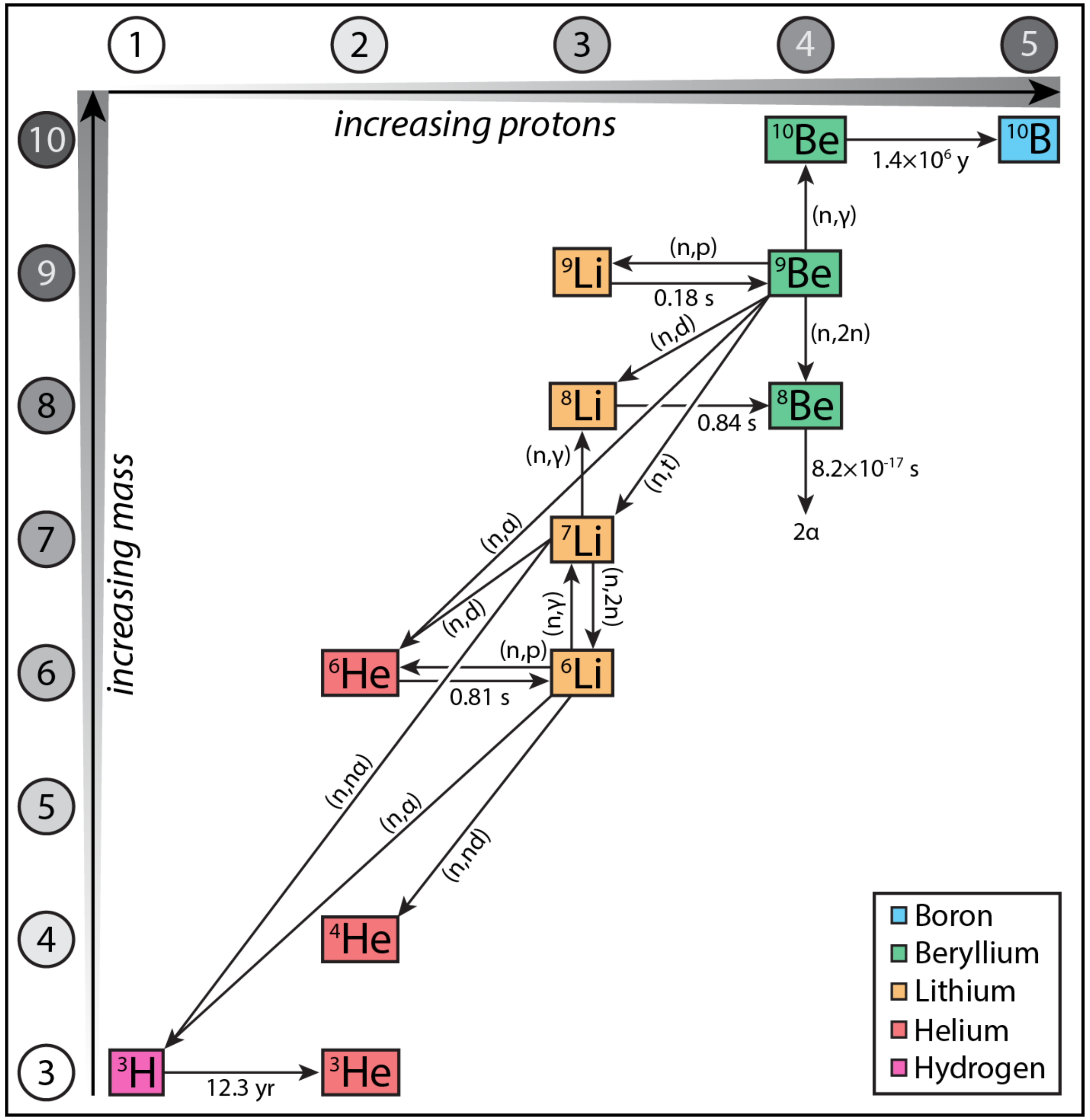
The off-gas treatment system development is critical for continued MSR development



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

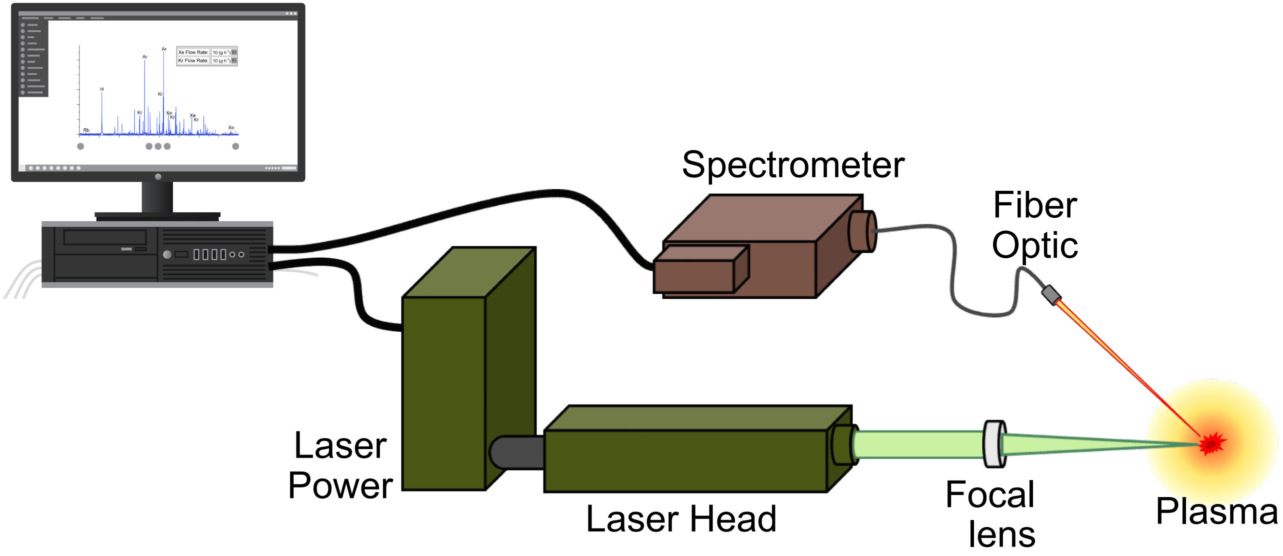
Salt isotopes impact a reactor's ^3H generation



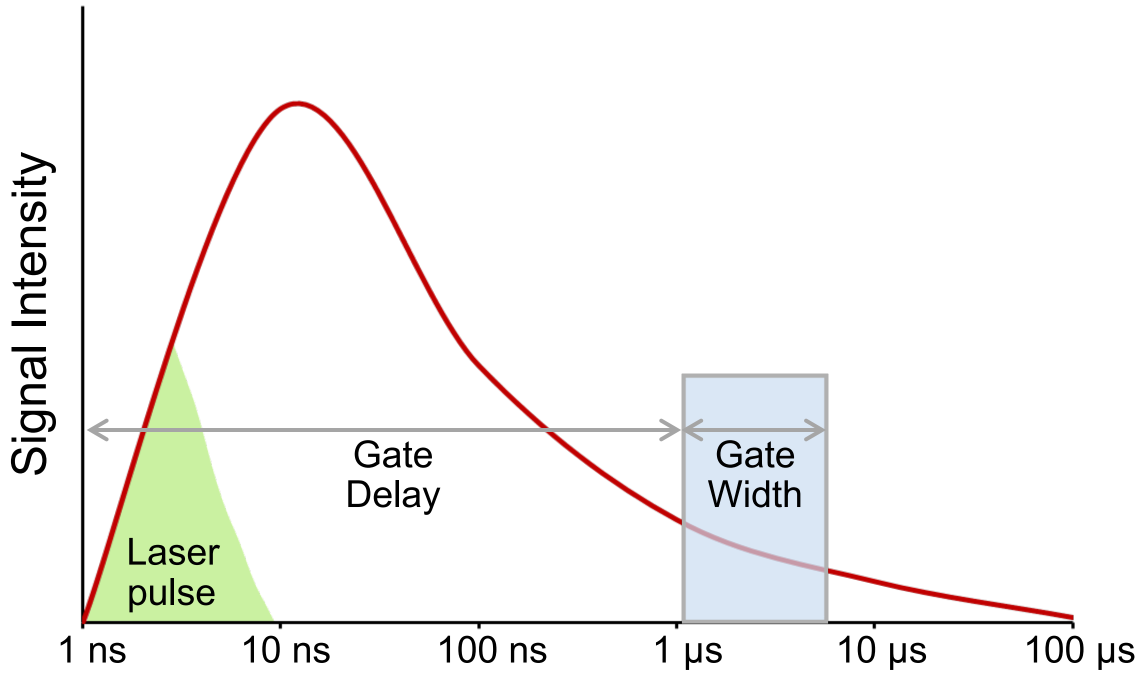
Andrews et. al., Nuclear Engineering and Design., 2021, 385, 111529.

Laser-induced breakdown spectroscopy (LIBS) can provide an elemental fingerprint in real-time

A high energy density laser pulse ablates a sample to form a micro plasma at T~10,000 K



The plasma light is collected with a gated spectrometer to measure an elemental signature



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**

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

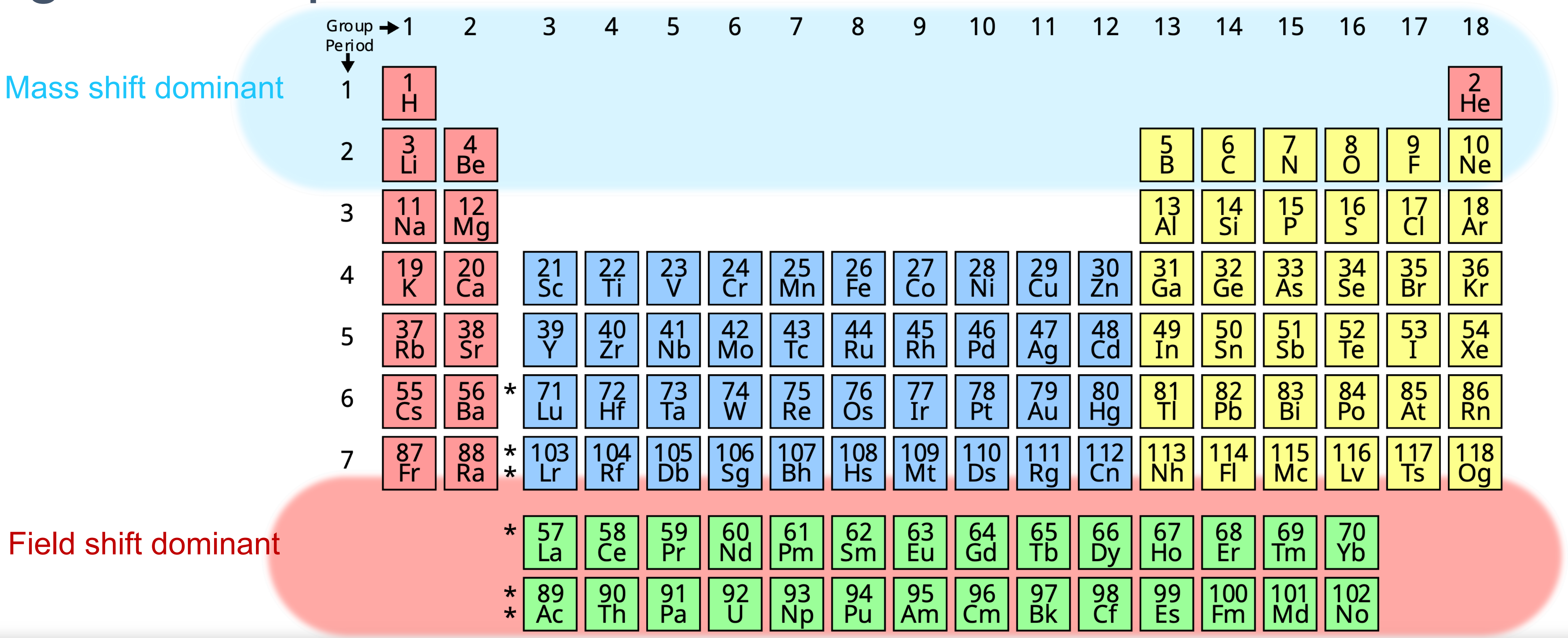
Frequency shift between isotope A and A'

Mass shift contribution

Field shift contribution

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

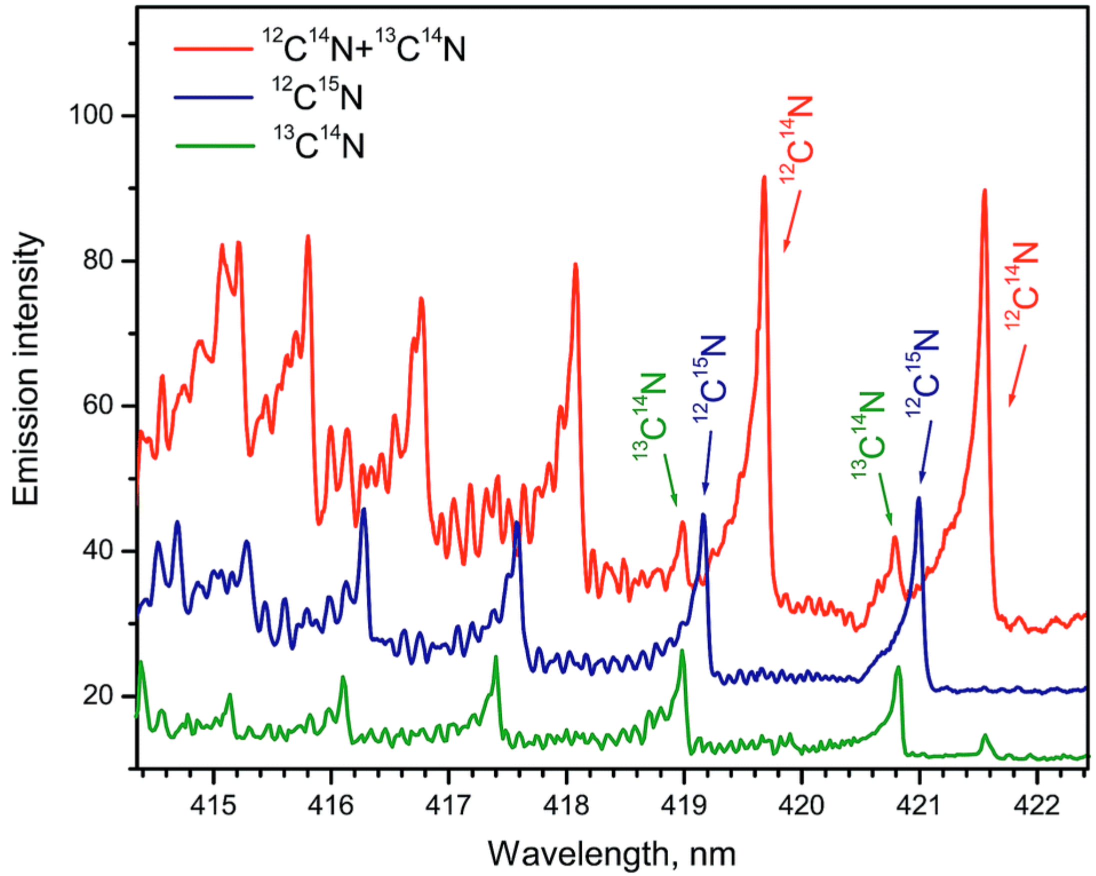
The main contribution to isotopic shifts changes based on the region of the periodic table



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



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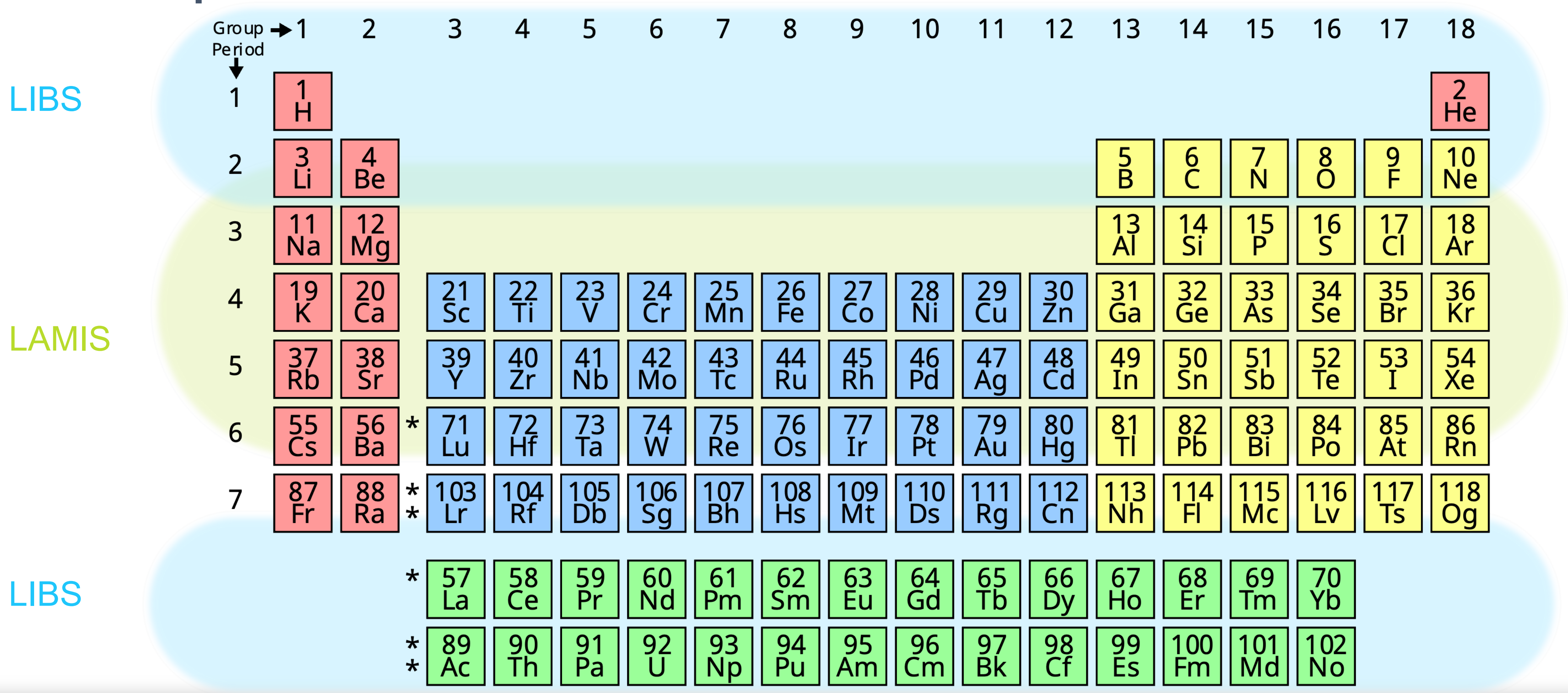
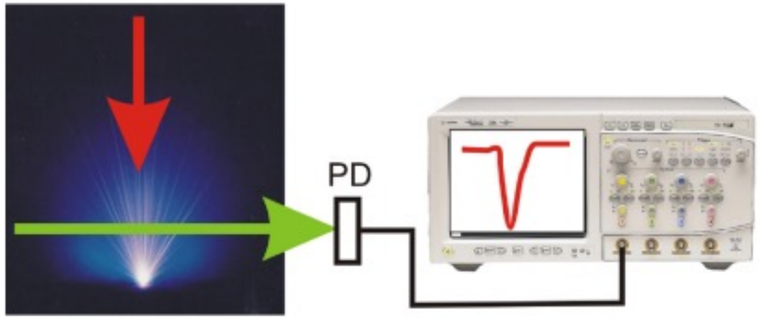
Bol'shakov et al. J. Anal. At. Spectrom., 2016,31, 119-134

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

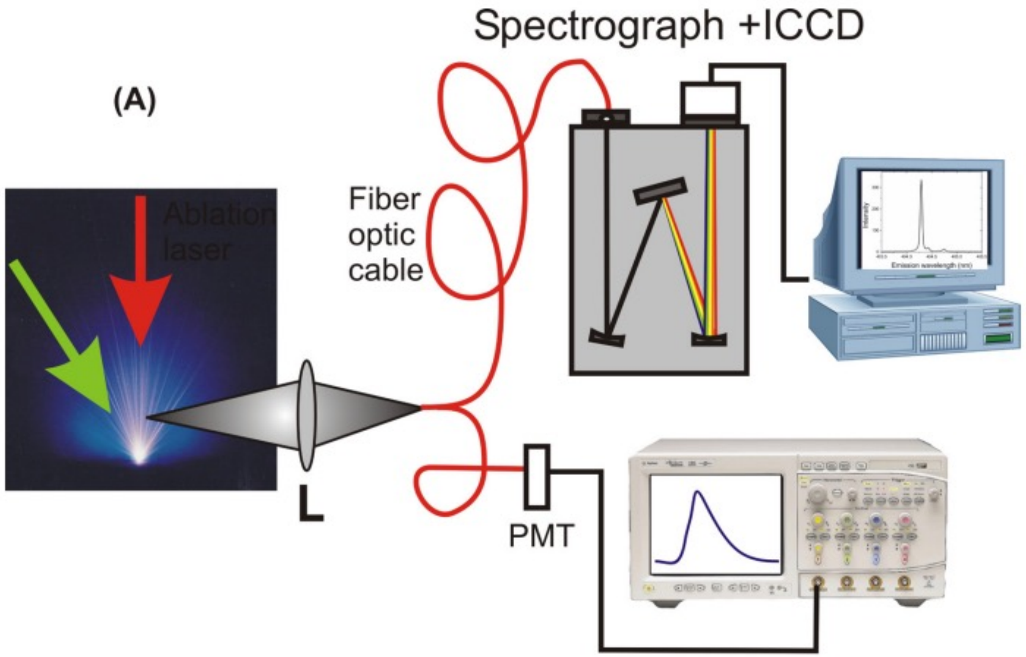


The third way to probe isotopics through laser ablation involves coupling tandem techniques

Laser ablation – laser absorbance spectroscopy (LA-LAS)



Laser ablation – laser induced fluorescence spectroscopy (LA-LIFS)

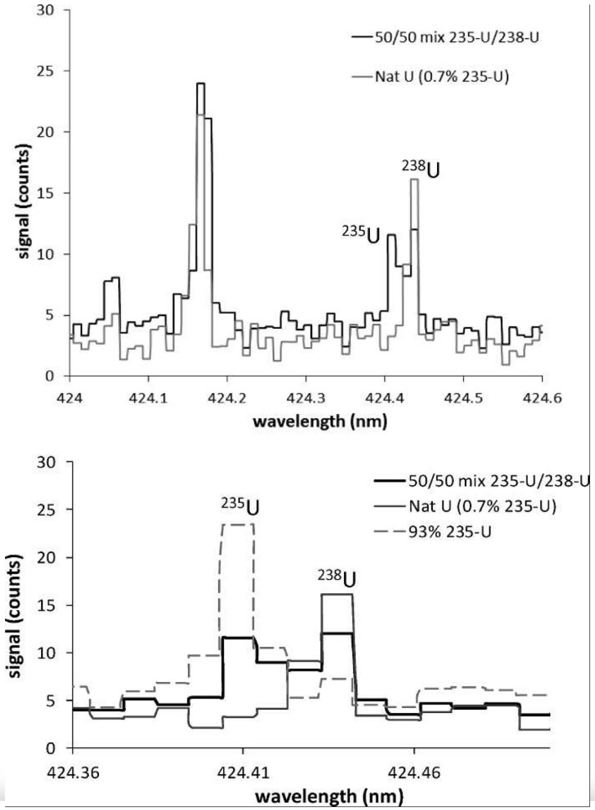


Harilal et al. Appl. Phys. Rev. 5, 021301 (2018)

FY23 work package targets establishing these capabilities within the MSR campaign

- **We are procuring an ultra high-resolution spectrometer for measuring isotope shifts on the scale of picometers**

EMU-65:



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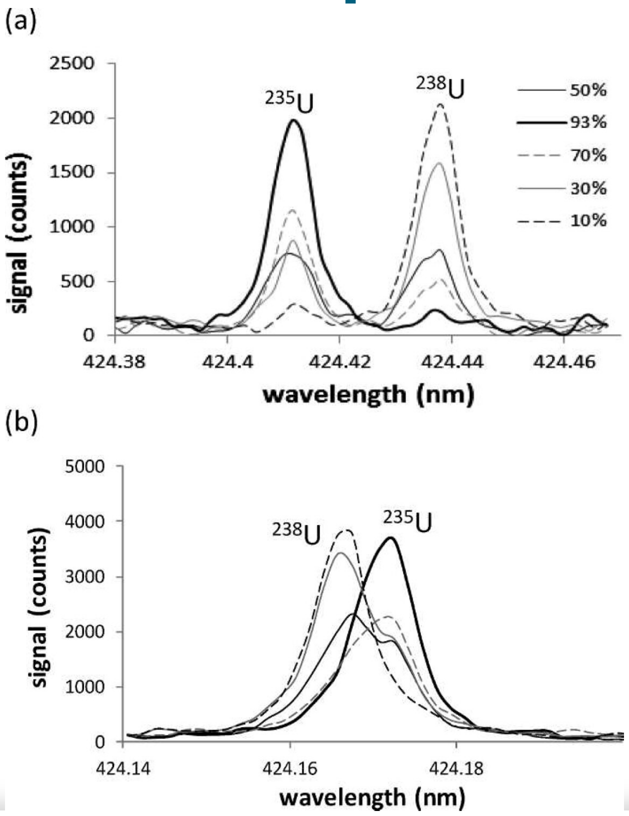
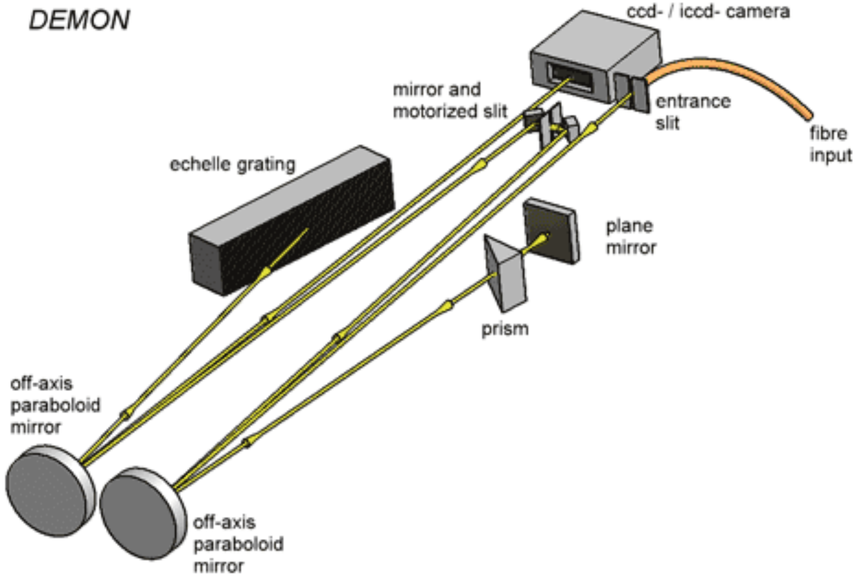


Cremers et al. *Applied Spectroscopy*. 2012,66(3):250-261.

FY23 work package targets establishing these capabilities within the MSR campaign

- **We are procuring an ultra high-resolution spectrometer for measuring isotope shifts on the scale of picometers**

ICCD = nanosecond gating

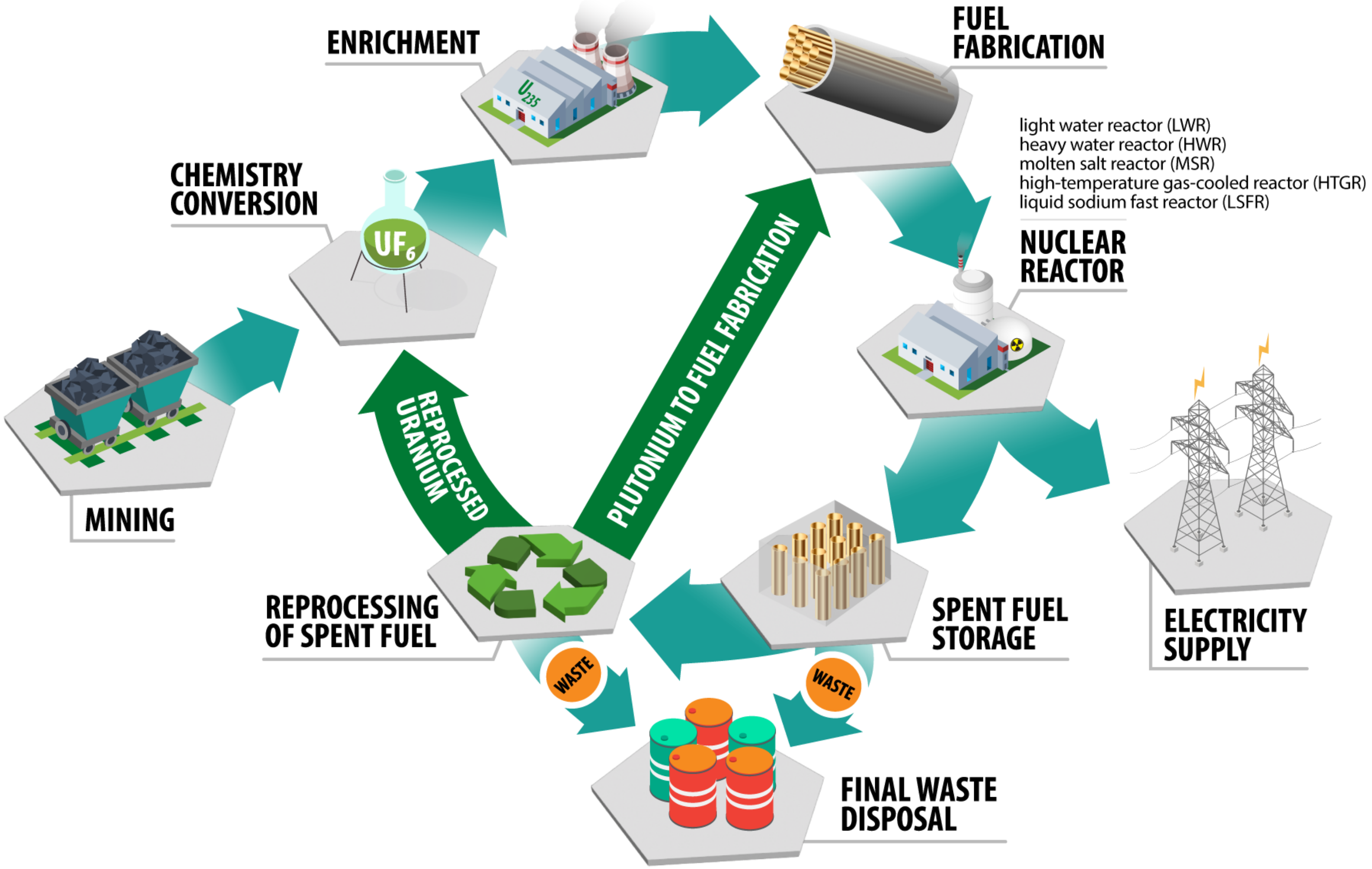


Credit: LTB, Lasertechnik Berlin

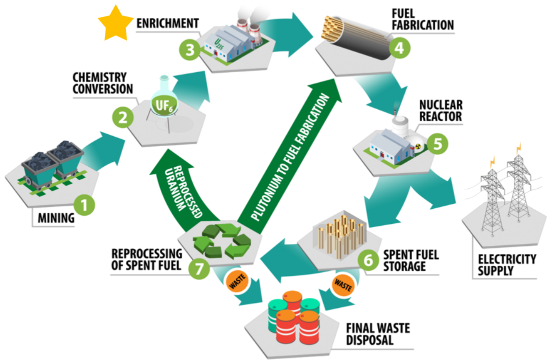
During procuring this new spectrometer, we have been collaborating to put out a comprehensive review of LIBS for nuclear applications

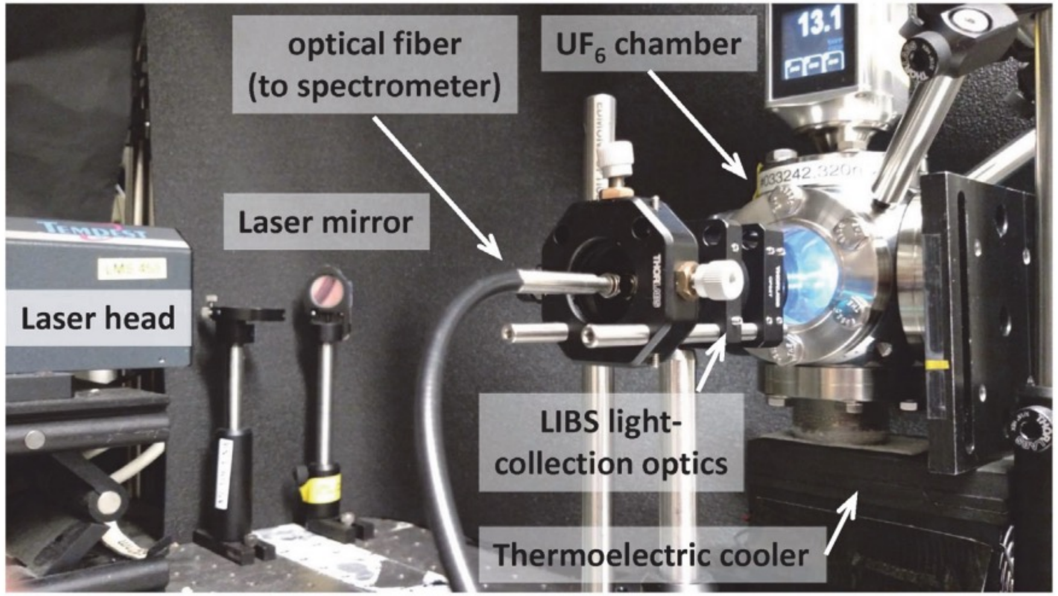
- **Collaboration with University of Florida and Virginia Commonwealth University**
- **To be submitted as a focal point review in *Applied Spectroscopy***

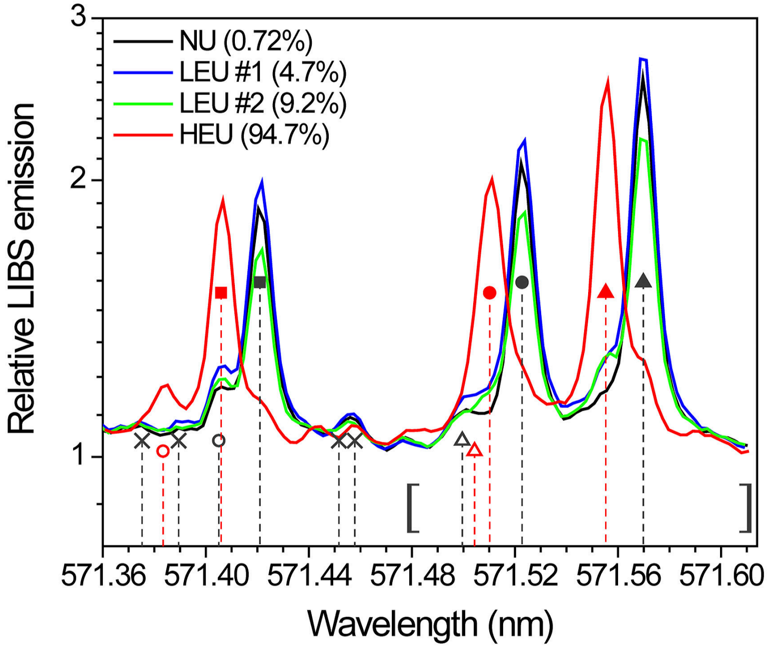
LIBS throughout the nuclear fuel cycle



LIBS used to monitor uranium enrichment







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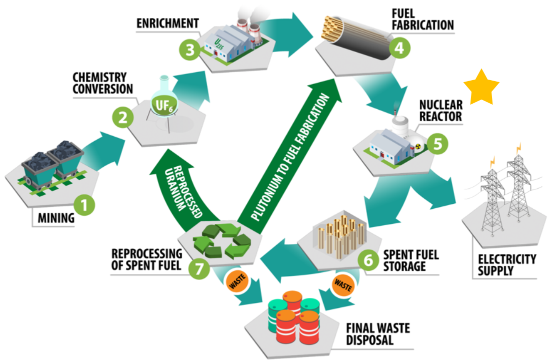
Chan et al. *Applied Spectroscopy*. 2022
Chan et al. *Proceedings of the INMM & ESARDA. 2021.*

LIBS in traditional nuclear reactors



- Fiber optics LIBS focused on impurities in alloys

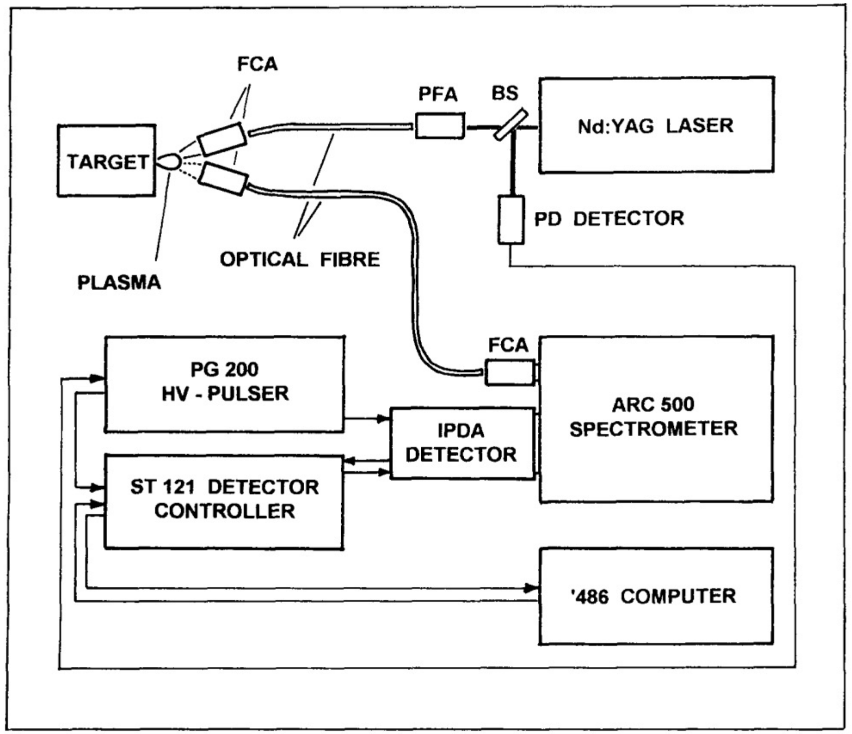


Fig. 1. Schematic diagram of experimental set-up for remote-LIBS analysis system: BS, beam splitter; FCA, fibre coupling assembly; PFA, power focusing assembly; PD, PIN photo diode; IPDA, intensified photo diode array.

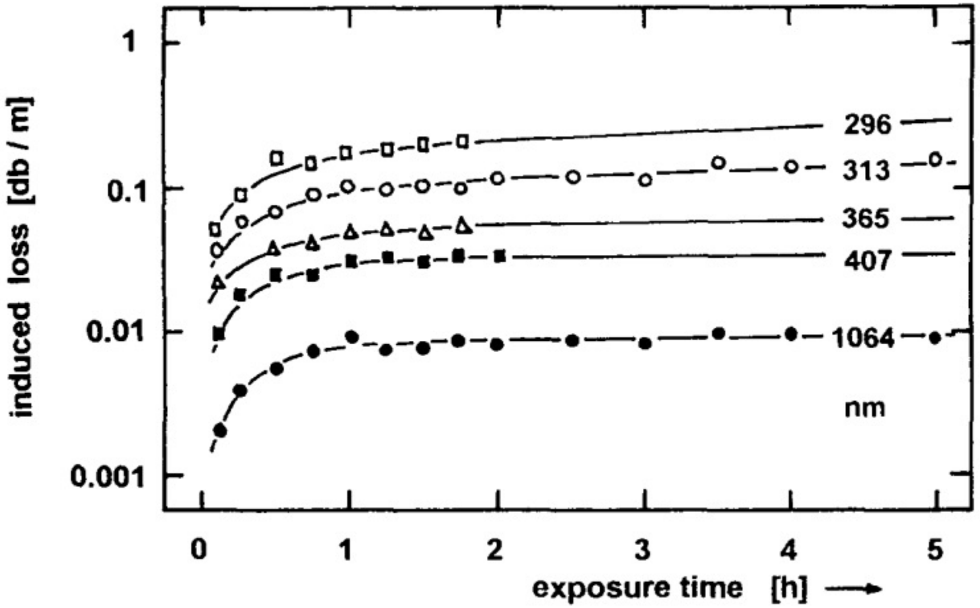


Fig. 3. Radiation-induced attenuation of transmission through HCG fibre at different wavelengths, as a function of exposure to γ-radiation (^{60}Co source, irradiation dose 30 Gray h^{-1}).

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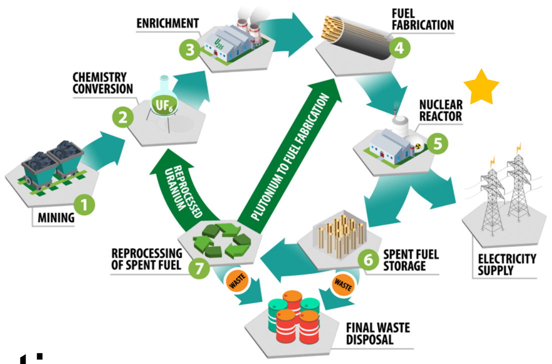
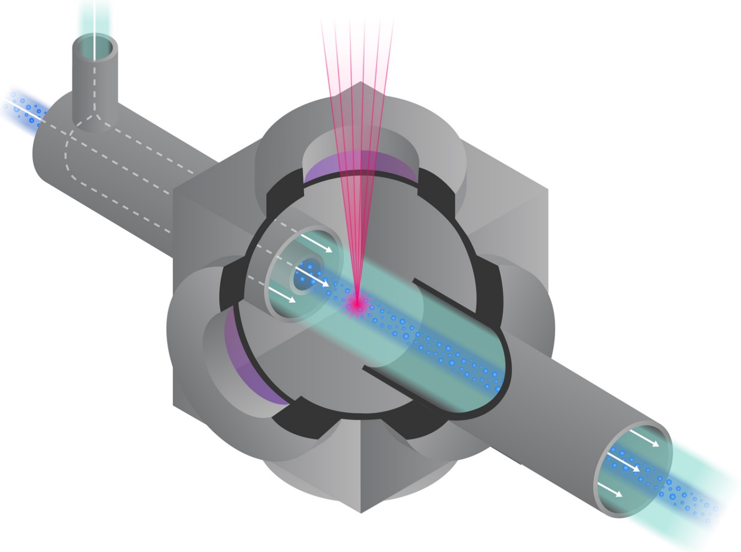
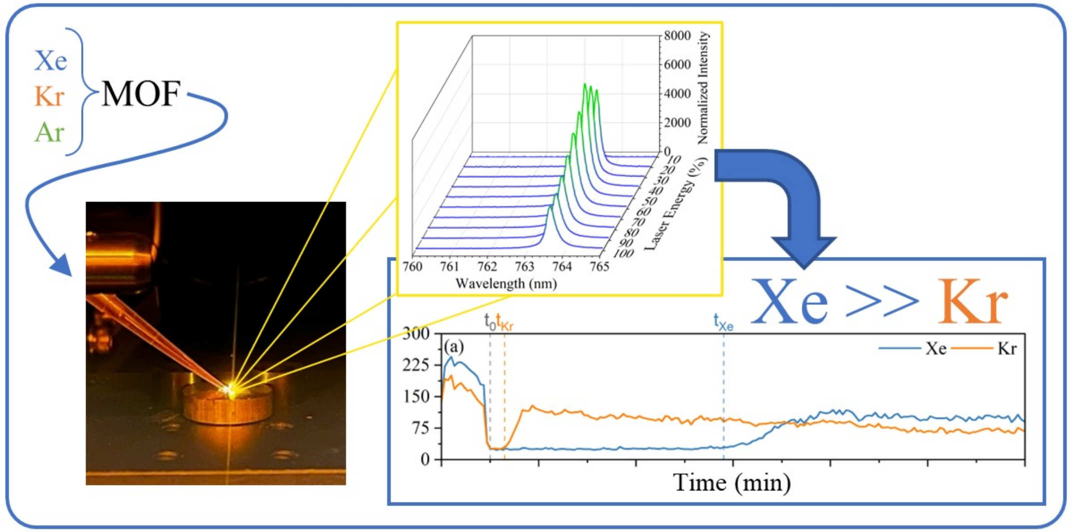
Davies et al. Spectrochimica Acta Part B: Atomic Spectroscopy. 1995 Aug 1;50(9):1059-75.



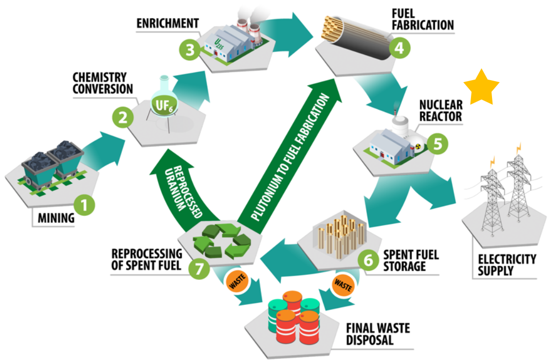
LIBS in advanced reactors

- **LIBS being used to monitor gases in reactors**
  - C particles in gas-cooled reactors to detect graphite degradation
  - Xe/Kr in LSFRs to detect fuel pin failure
  - Xe/Kr + aerosols to monitor off-gas system

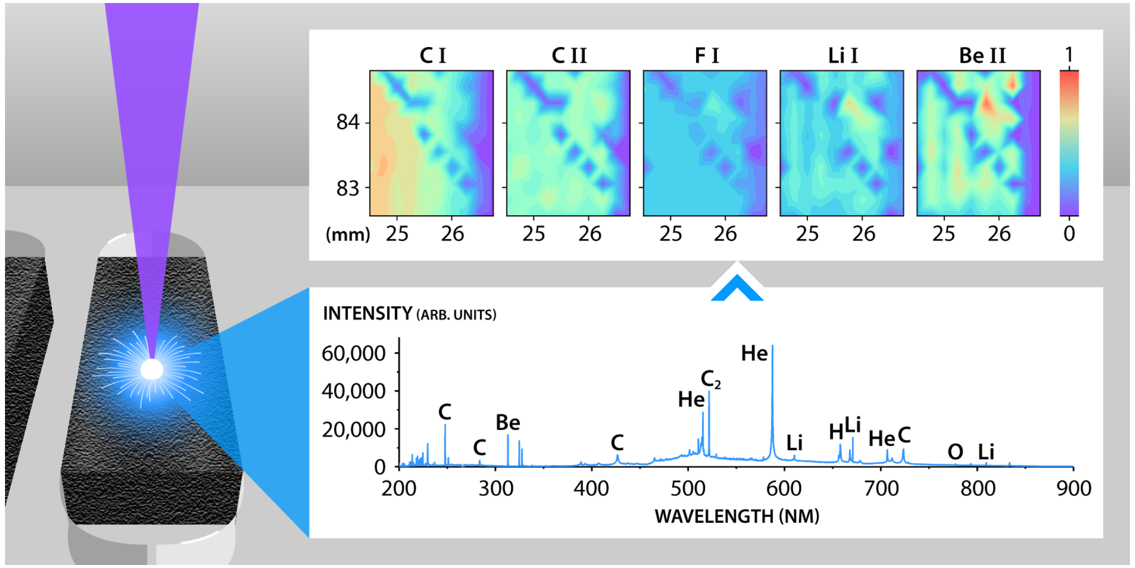


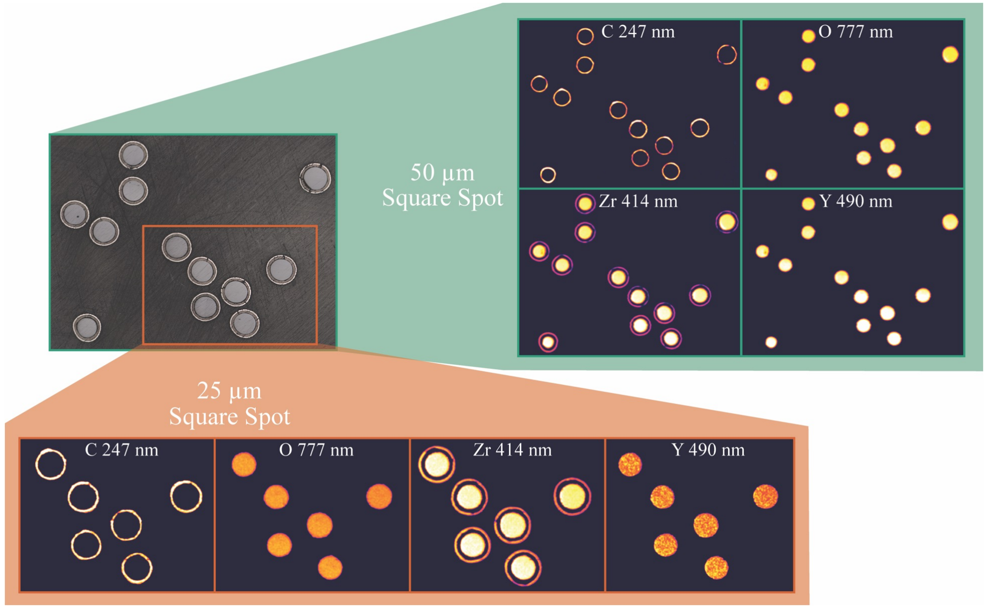


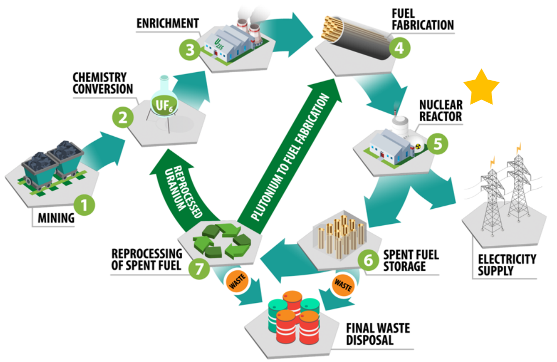
LIBS in advanced reactors



- **LIBS being used to evaluate nuclear reactor mater**
  - Penetration of salts into graphite
  - Elemental mapping of TRISO particles

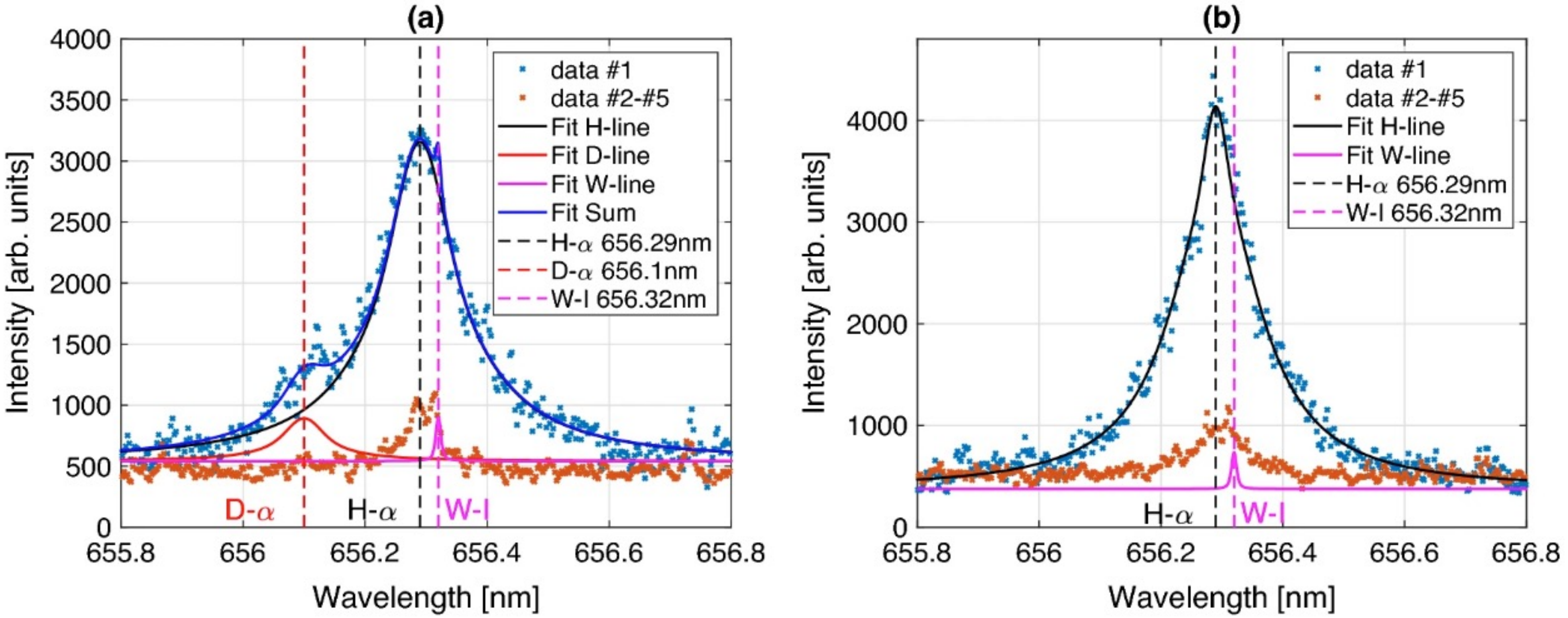






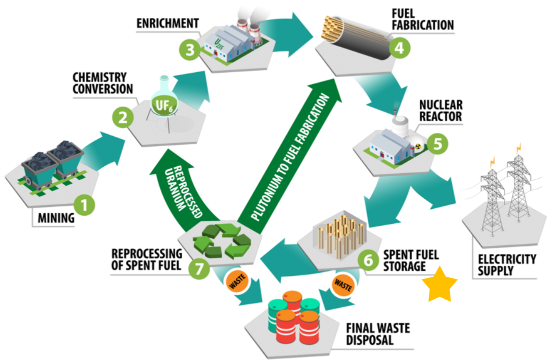
LIBS for fusion reactor research

- Evaluating D intrusion into plasma facing components

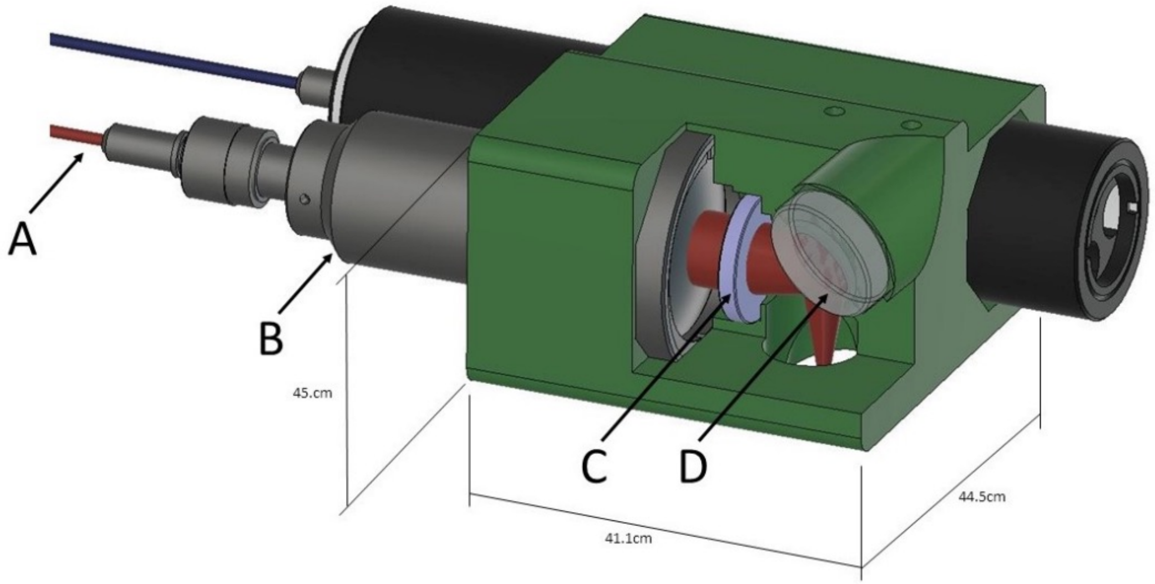


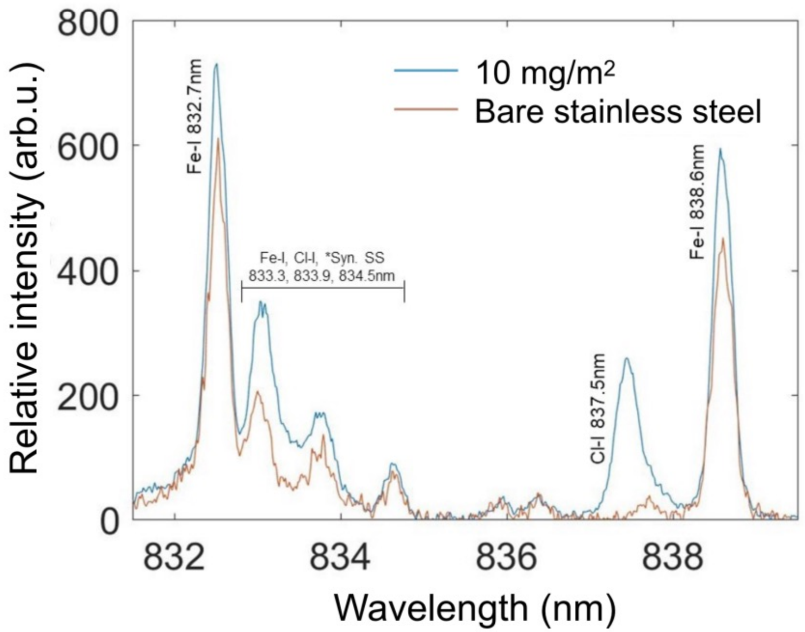
Mittelmann, Steffen, et al. *Scientific Reports* 13.1 (2023): 2285.

LIBS for monitoring spent fuel storage



- **Robotic delivered FO-LIBS probe to monitor dry cask storage**





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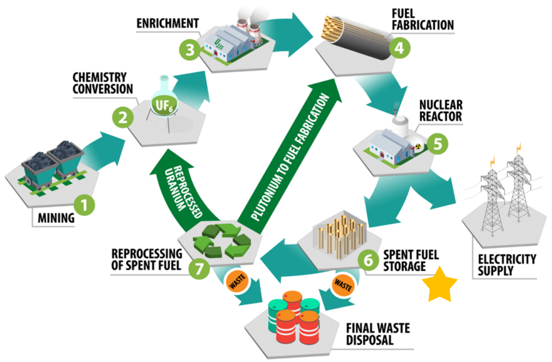
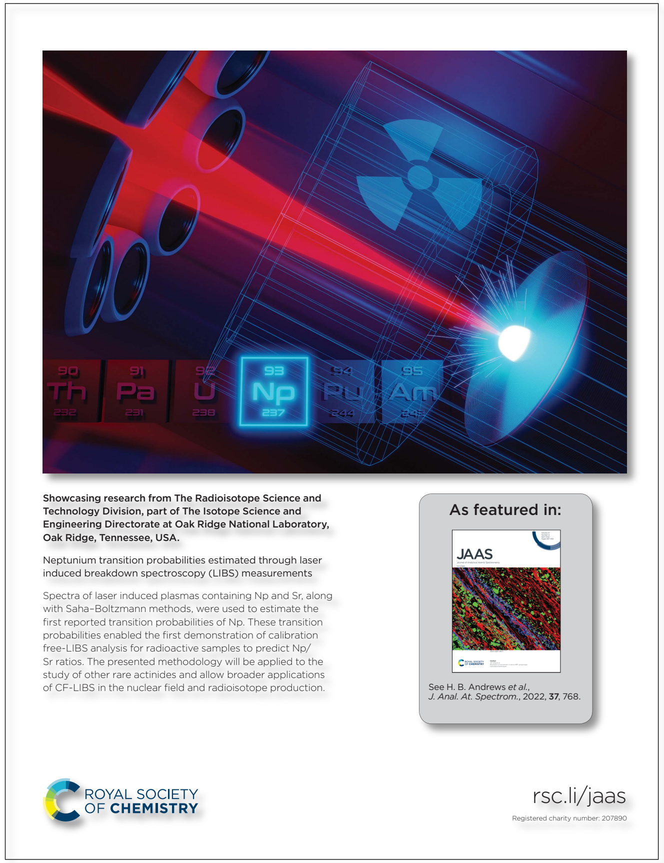
Fobar et al. *Progress in Nuclear Energy* 109 (2018): 188-194.

LIBS for monitoring reprocessing/chemical separations





Showcasing research from The Radioisotope Science and Technology Division, part of The Isotope Science and Engineering Directorate at Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

Neptunium transition probabilities estimated through laser induced breakdown spectroscopy (LIBS) measurements

Spectra of laser induced plasmas containing Np and Sr, along with Saha–Boltzmann methods, were used to estimate the first reported transition probabilities of Np. These transition probabilities enabled the first demonstration of calibration free-LIBS analysis for radioactive samples to predict Np/Sr ratios. The presented methodology will be applied to the study of other rare actinides and allow broader applications of CF-LIBS in the nuclear field and radioisotope production.

As featured in:

JAAS

See H. B. Andrews *et al.*, *J. Anal. At. Spectrom.*, 2022, **37**, 768.

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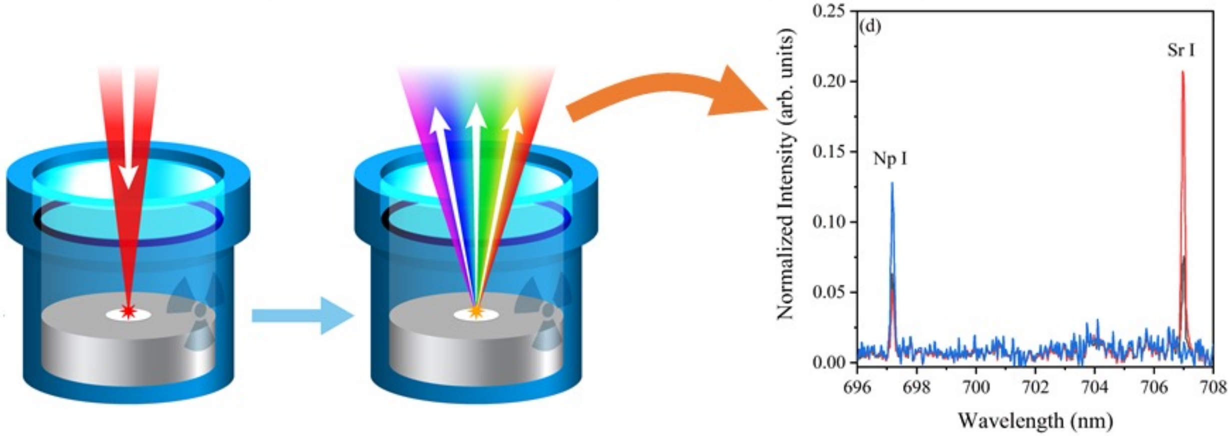
- LIBS is being used for impurity analysis in radioactive samples
- FO-LIBS is pursued here to facilitate remote work in hot cells
- Handheld LIBS is used here as well



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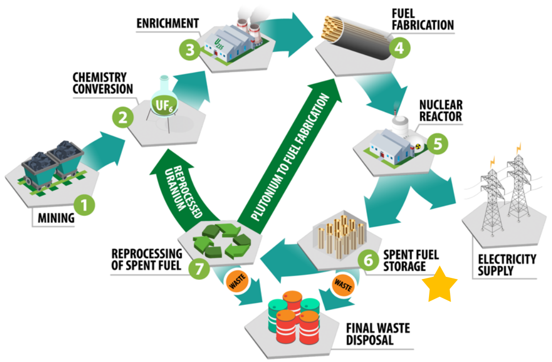
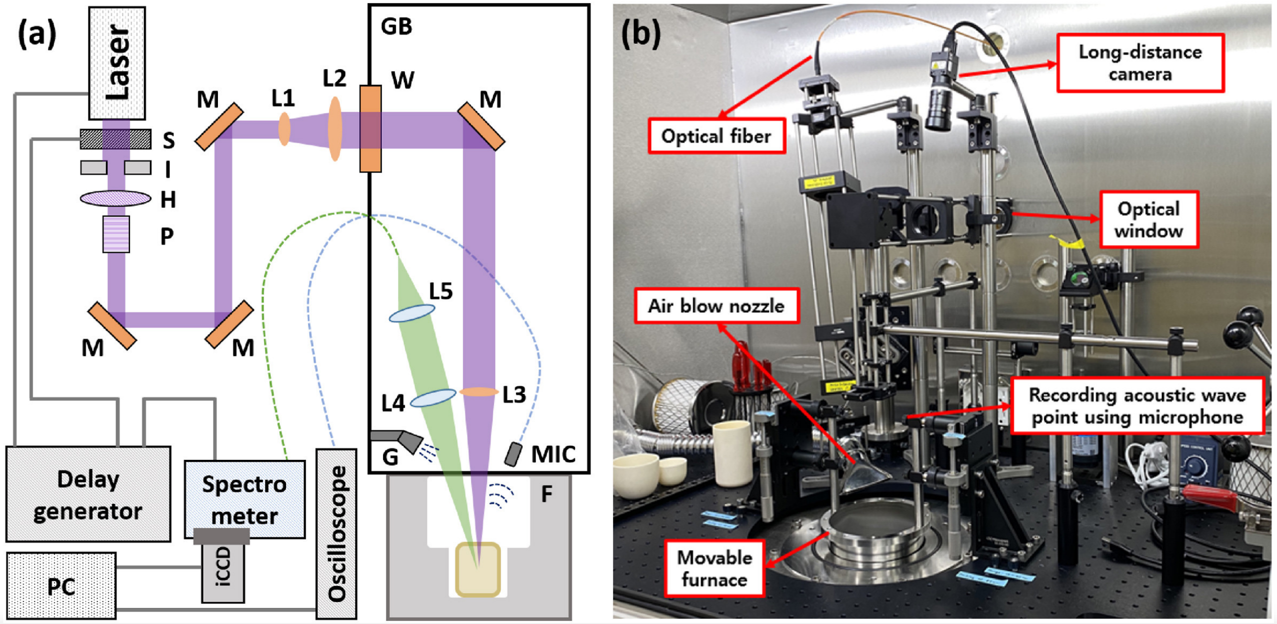
Andrews et al. *Journal of Analytical Atomic Spectrometry* 37.4 (2022): 768-774.

LIBS for pyroprocessing monitoring

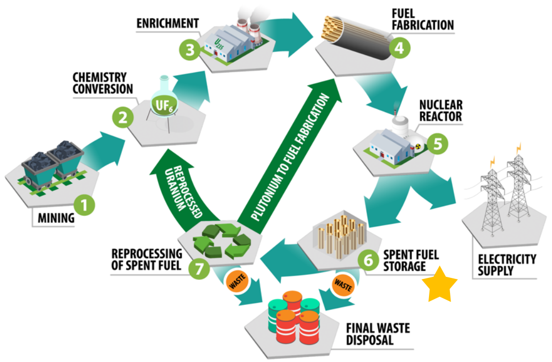


- **LIBS for compositional information on electrorefiner salts**
  - Frozen, liquid, and aerosolized salts
  - Combined techniques such as
    - Acoustic signal + LIBS
    - Electrochemistry + LIBS



Lee et al. Nuclear Engineering and Technology. 2022.

The robust applicability of LIBS is highlighted in this review



- **There are a plethora of lessons learned in the LIBS literature**
- **This review provides a baseline of isotopic signatures that can be probed via LIBS**
- **Upon arrival of new spectrometer proof of principal measurements will be performed and summarized in end of year report**

Oak Ridge National Laboratory

Molten Salt Reactor Program

Thank you

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