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OAK RIDGE National Laboratory

Pacific Northwest NATIONAL LABORATORY

Molten Salt Reactor PROGRAM

On-line Monitoring for MSR Off-Gas Treatment: Elemental approaches/MOFs for Xe capture

Hunter B. Andrews[1] and Praveen K. Thallapally[2]

[1]Oak Ridge National Laboratory, [2]Pacific Northwest National Laboratory

Annual MSR Campaign Review Meeting 2-4 May 2023

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Molten Salt Reactor PROGRAM

Metal Organic Frameworks for Noble Gas Management

Praveen K. Thallapally, and Alexander Robinson

Pacific Northwest National Laboratory

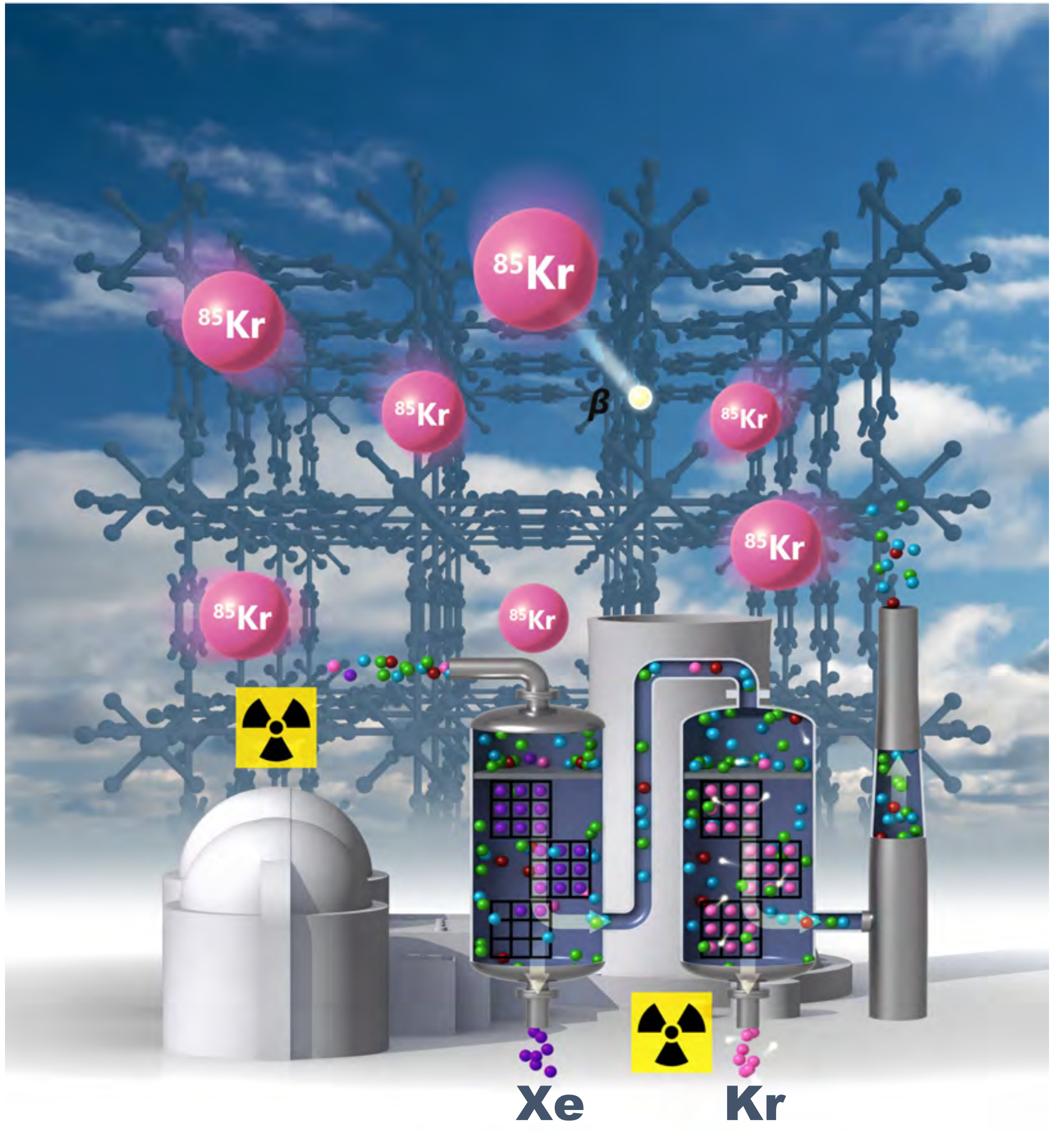
Driving Factors

❑ Why

- U.S. EPA 40 CFR 190 and NRC regulation requires volatile radio nuclides (^{14}C, ^{3}H, ^{131}I, ^{133}Xe and ^{85}Kr) must be captured and sequestered
- Noble gas capture is the most difficult to capture as they are inert by definition
- Potential economic incentive if captured

❑ Major sources of emissions:

- Regular operation of nuclear power plant
- Advanced reactors
- Reprocessing of spend nuclear fuel
- Nuclear accidents
- Medical isotope facilities



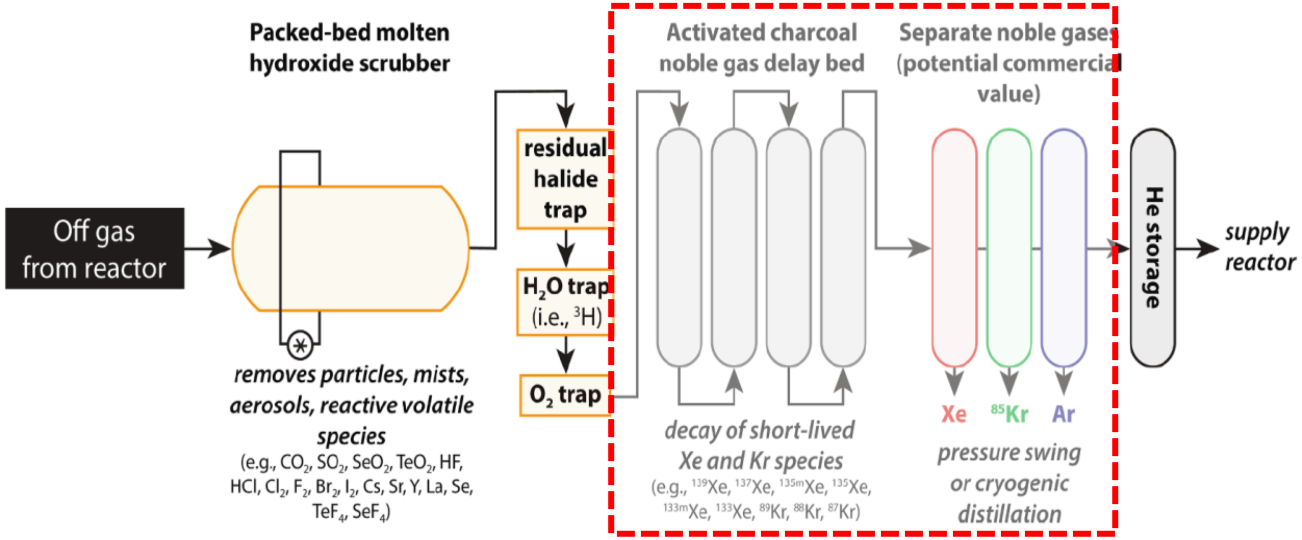
Current Technologies and Alternatives

Current Technology

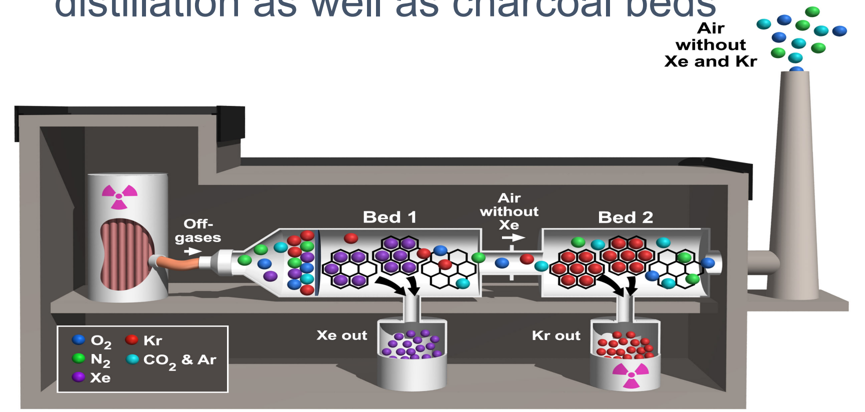
- Cryogenic removal of Xe and Kr
  - Projected to be expensive
  - Potential for O_3 accumulation
  - Hazardous conditions

➢ **Charcoal** delay beds (MSR)

- o Requires 4-5 charcoal tanks with 6 – 9 foot in diameter and 50 foot long
- o Fire hazard: Presence of oxygen and heat production due to radioactive decay
- o Oxygen needs to be removed upfront from cryogenic distillation as well as charcoal beds



Riley, B. J et. al., Nuclear Engineering and Design., 2019, 345, 94.
Nichols J. P., Status of noble gas removal and disposal report, 1971, ORNL-TM-3515



➢ MOFs as Alternate Technology

- o Higher capacity and selectivity represents significant cost reduction compared to cryogenic and charcoal beds
- o Smaller size columns, reduced footprint and no fire hazard
- o Remove Xe (non-radioactive) and Kr in separate steps at near RT
  - o Recover process costs by selling Xe?
- o Remove Kr in single step

Liu *et. al., Ind. Eng. Res. & Chem.*, 53, 12893-12899, 2014
Thallapally, Vienna et. al., USPTOWO/2017/218346A1
Thallapally, Patricia et. al., Compact and Modular Integrated Off-Gas System and Sensors." Invention Disclosure e-IDR 18117

Applications of Noble Gases

❖ Fortune Business Insights reported "The noble gases market size stood at **USD 40.34 billion in 2020** and continue to grow

➢ High purity of Xe

❑ Space Industry – Propellant

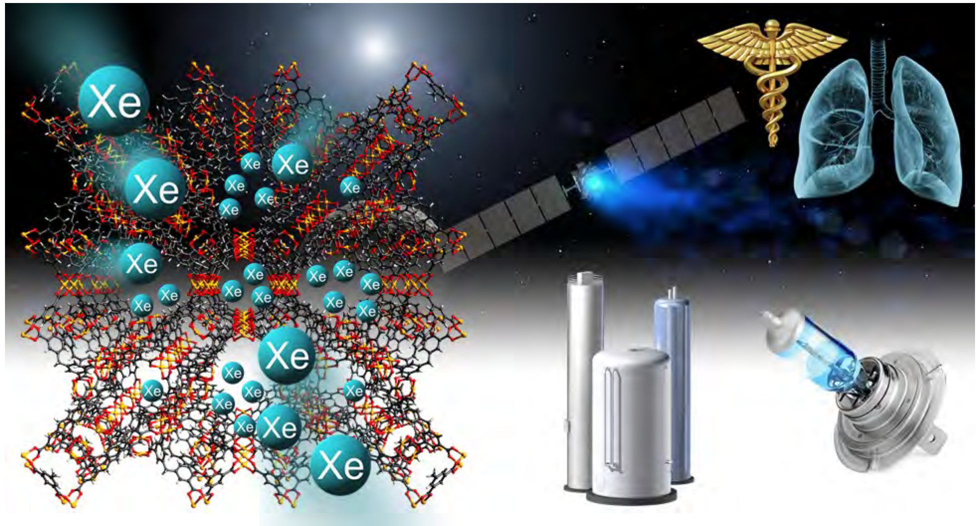
- NASA Xe-ion-thrusters is projected to use approximately 16 metric tones of Xe, for a cost ranging between $81–100 million at today's market price

❑ Medical – Anesthesia, Imaging

- Approximately 313.4 million major surgical procedures were performed around the world in 2012.
- Due to the supply issues and cost of Xe makes it prohibitive to use. Could open-up huge market

❑ Semiconductor – Plasmas in deposition and etch

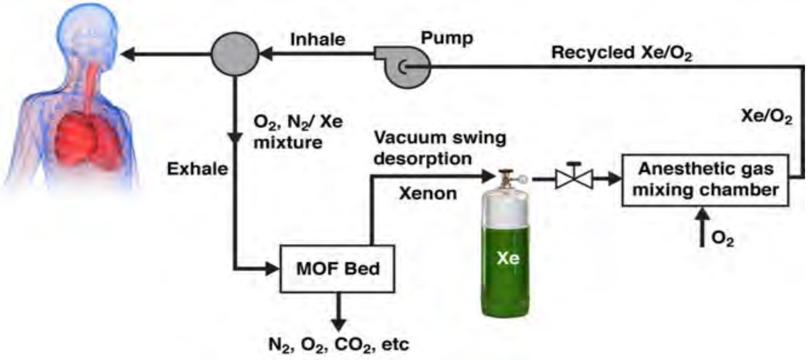
- Demand for chips increase so as noble gases (~multi billion-dollar industry)



Elsaidi, Thallapally et. al., *ACS. Mat. Lett.*, 2020

➢ High purity of Kr

❑ Buildings – Window insulation
❑ Automotive – Head lights, Laser lights
❑ Geoscience – to detect the age of ancient ground water

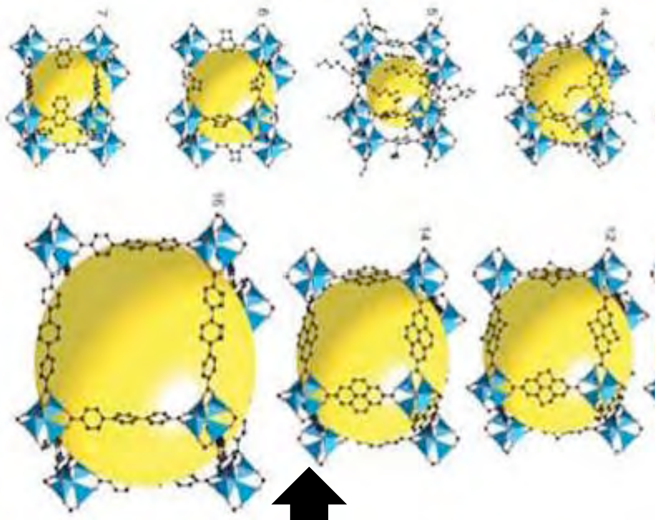


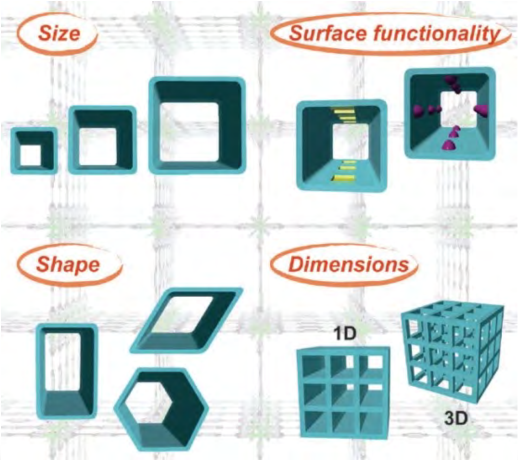
Elsaidi, Thallapally et. al., *Chem. Eur. J.*, 23, 10758 – 10762, 2017

Metal Organic Frameworks

	Zeolites/Charcoal	MOFs
Safety	Potential bed fires (charcoal)	NA
Type	Inorganic/Organic	Hybrid
Diversity	Limited	Infinite
Pore Size	Fixed	Fine-tunable 0.3 to 10 nm
Surface Area	Up to 1000 m^2/g	Up to 8000 m^2/g
Capacity*	Moderate	High
Selectivity	Need to remove CO_2, and Water	Not required (CaSDB) Yes for water (for some MOFs)
Cycle	200	>2000 (PNNL) (water adsorption n desorption)
Stability	Up to 1 x 10^7 RAD	1.75MGy PNNL and SNL Study Recent literature shows even higher stability
Cost	Varies	Varies;

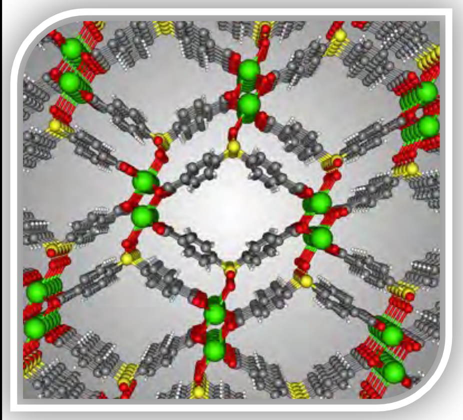
- ► **MOFs with higher adsorption capacity, and selectivity represents significant cost reduction compared to existing technology**
- ► **Smaller-size columns and reduced footprint**





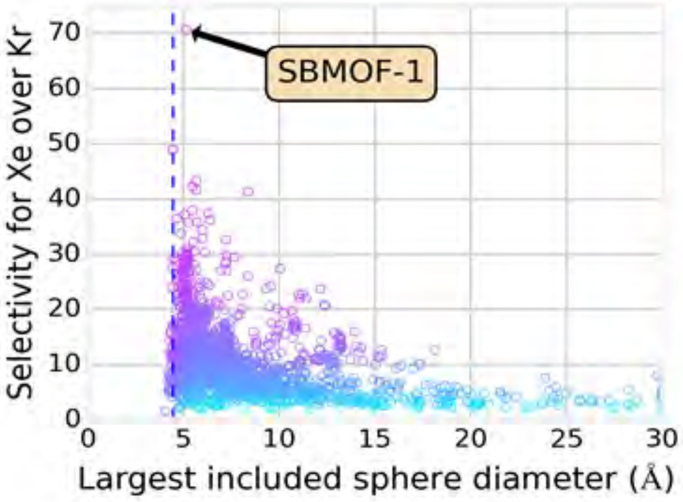
Yaghi *et. al.*, Science 2013, 974; Kitagawa *et. al.*, Angew Chem. 2002; Ferey *et. al.*, Science 2002

Leading MOF Material for Noble Gas Management



- ❑ **Modelling predicts the CaSDB (SBMOF-1) is the best among 5000 experimental and 125,000 hypothetical MOFs.**
- ❑ **3D network structure connected with CaO units**
- ❑ **Small pore diameter (4.1 Å) with surface area of 120 m^2/g**
- ❑ **Very stable in air**

Banerjee *et. al., Nature Communications,* 2016



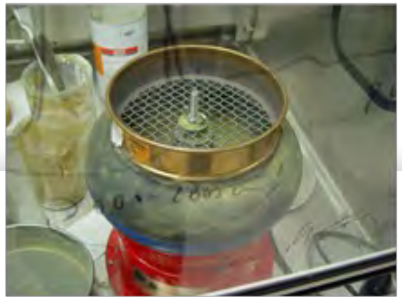
- ❑ **A rare example of computationally inspired material discovery**

Thallapally, Ali Z. Riley, BJ., Paviet, P., Matyas, J., Vienna, J., Compact and Modular Integrated Off-Gas System and Sensors." Invention Disclosure e-IDR 18117

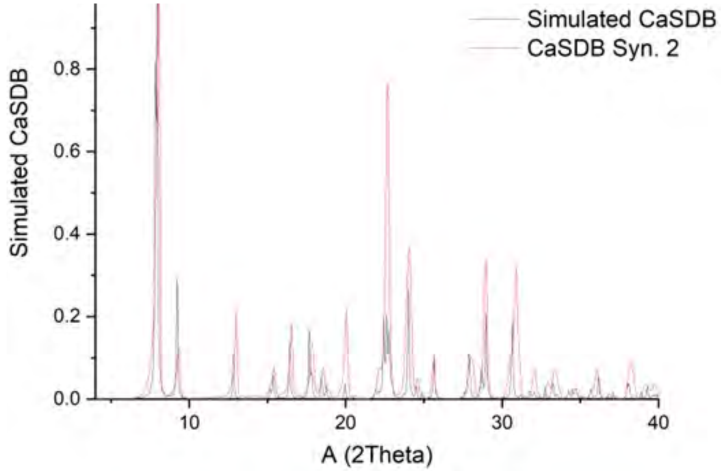
Thallapally, PK., Vienna et. al., USPTO WO/2017/218346A1

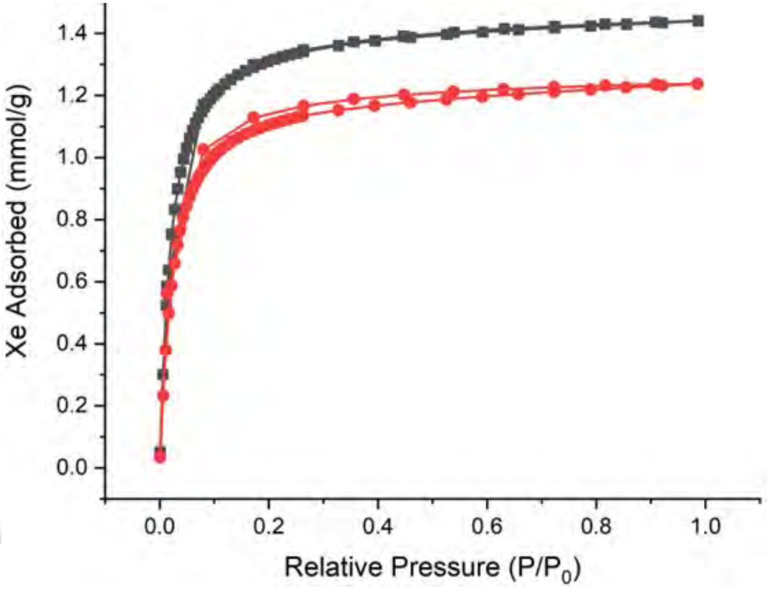
Banerjee, D, Thallapally, PK, Kunapuli R., McGrail, BP, Liu J et al., Surface acoustic wave sensors for refrigerant leak detection., *USPTO WO2021/041359 A1*

MOF Synthesized at PNNL



- Identical PXRD confirmed (powder to pellet)
- No amorphous phase
- Reduced BET surface area



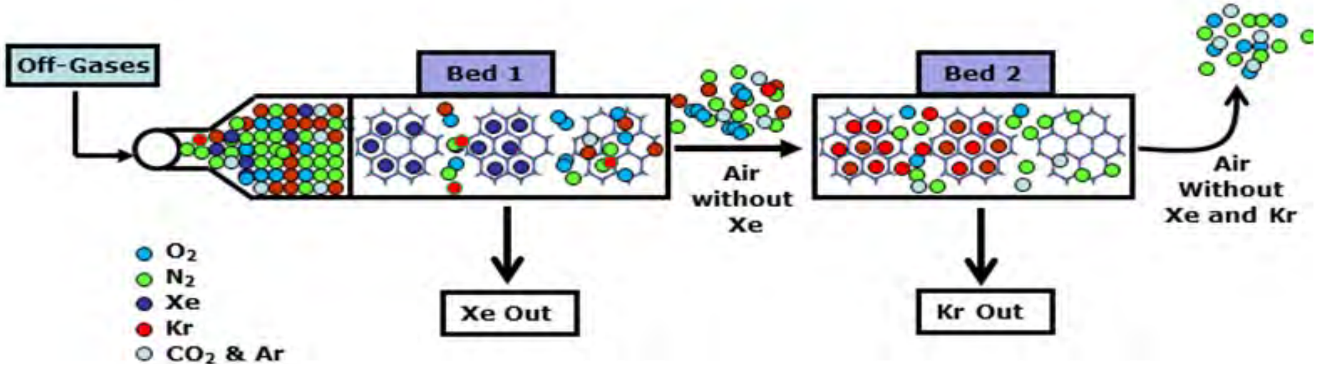


Property	Value
Pressed Pressure	**2000 psi for 3 min**
Size	**600 – 850**
BET Surface area	**15 m^2/g**
BET Surface area, Po	**120 m^2/g**

Breakthrough Measurements Apparatus

Two-Column Breakthrough

- **A two-bed technique to remove and separate**
  - **Bed 1 remove Xe from air**
  - **Bed 2 remove Kr**
    - ✓ **Yields air without Xe and Kr**
    - ✓ **Off-gas can be released**



Results:

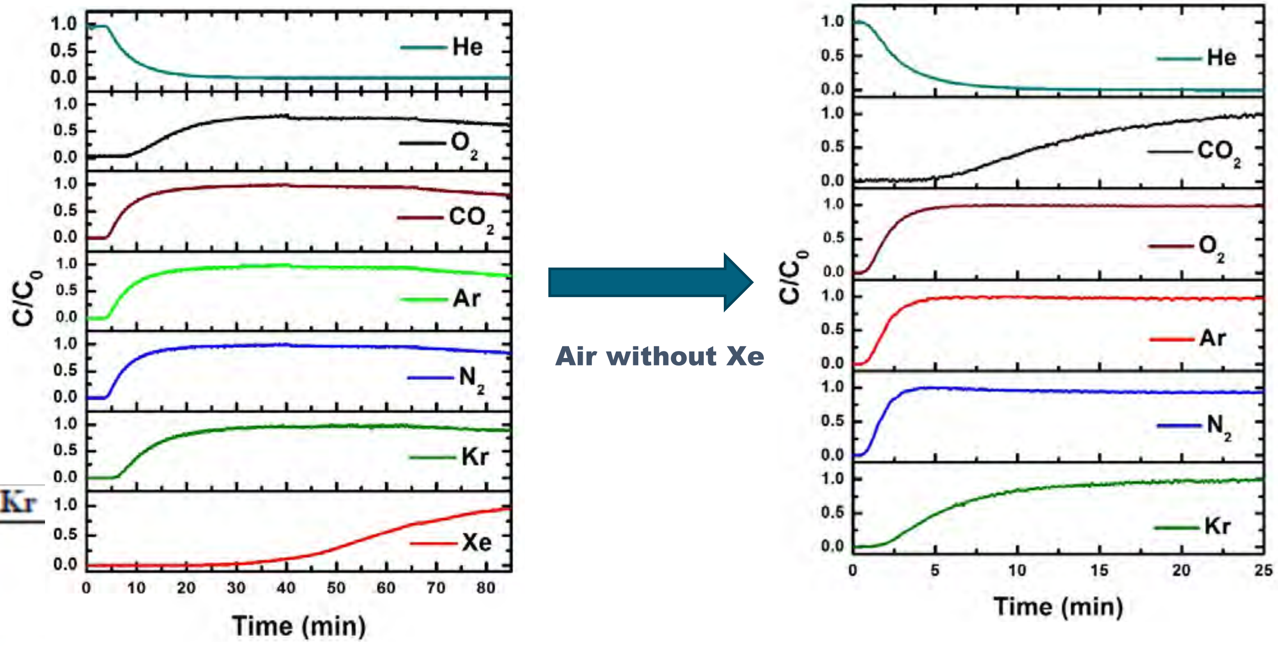
- **Bed - 1**

Gas	Breakthrough Time (min)	Capacity (mmol/kg)	Selectivity of Xe
Xe	18	16 (33.8)[a]	
Kr	1	0.11 (0.75)[a]	14
CO_2	5	1.2	3
N_2	0.08	47	209
Ar	0.08	5.28	210
O_2	0.08	12	206

[a] Capacity at equilibrium

- **Bed - 2**

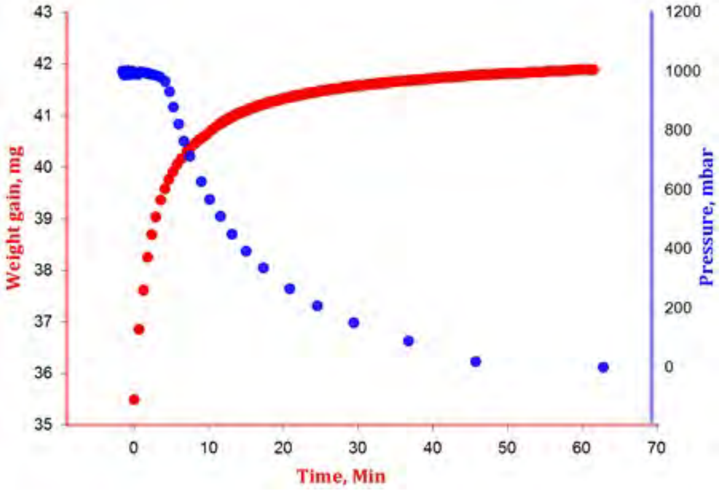
Gas	Breakthrough Time (min)	Capacity (mmol/kg)	Selectivity of Kr
Kr	2.5	0.13	
CO_2	7.5	0.90	0.3
N_2	0.25	80.8	9.9
Ar	0.25	9.09	9.3
O_2	0.25	21.2	9.3

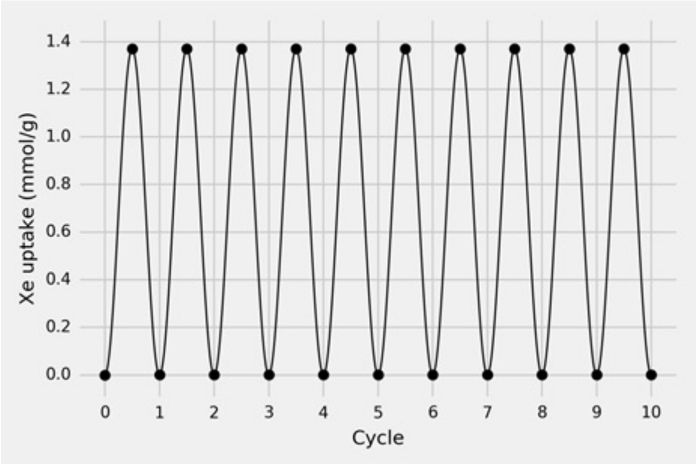


Bed 1 **Bed 2**

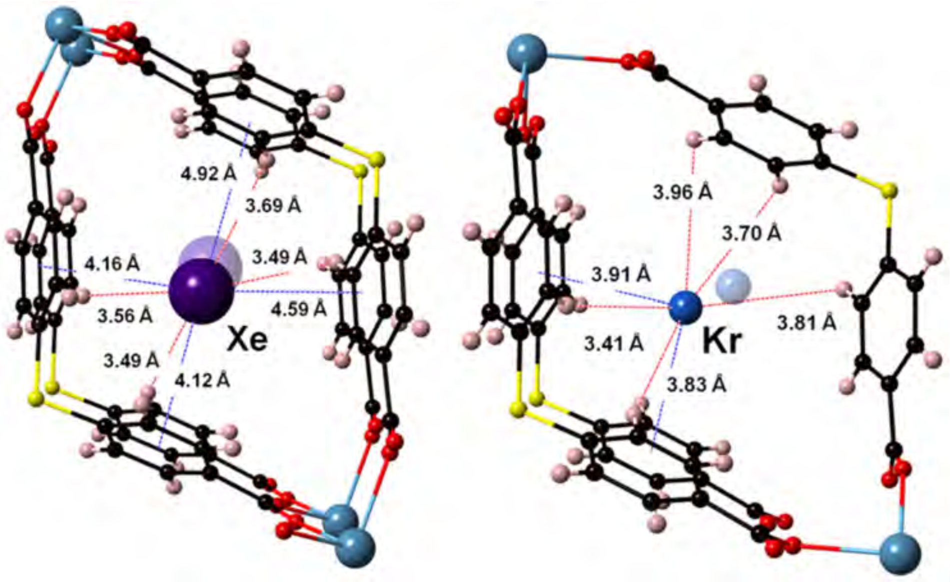
- Thallapally, Ali Z. Riley, BJ., Paviet, P., Matyas, J., Vienna, J., Compact and Modular Integrated Off-Gas System and Sensors." Invention Disclosure e-IDR 18117
- Thallapally, PK., Vienna et. al., USPTO WO/2017/218346A1
- Banerjee, D, Thallapally, PK, Kunapuli R., McGrail, BP, Liu J et al., Surface acoustic wave sensors for refrigerant leak detection., *USPTO WO2021/041359 A1*

Kinetics and Cycle Experiments at Room Temperature

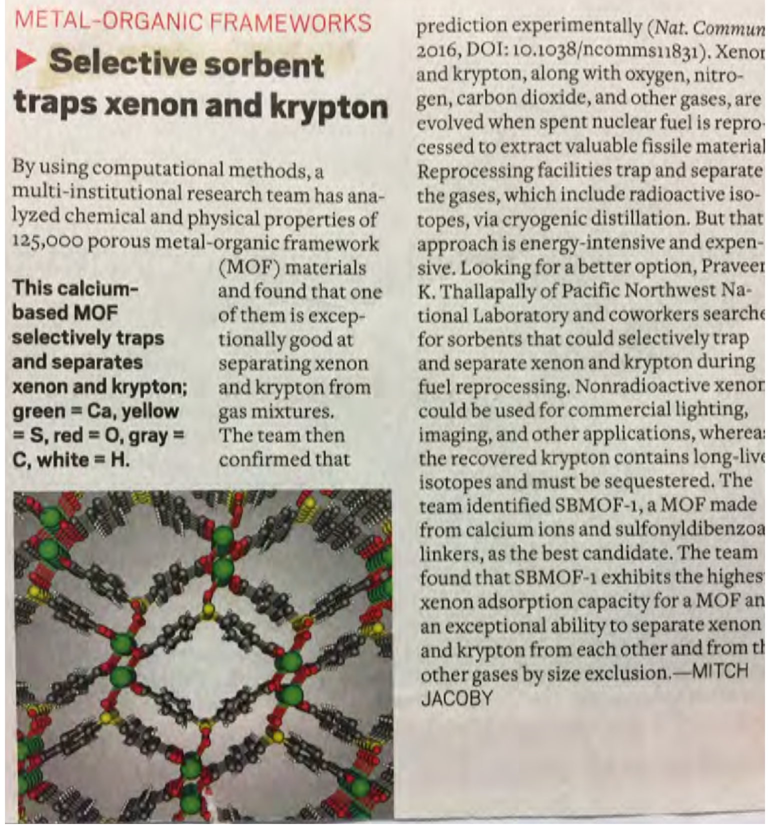




- Faster kinetics, 80% of Xe adsorbed within 10 minutes.
- Cycling study indicate no loss of capacity even after 20 cycles.



Chemical & Engineering News., 94, 26, June 27, 2016


METAL-ORGANIC FRAMEWORKS

Selective sorbent traps xenon and krypton

By using computational methods, a multi-institutional research team has analyzed chemical and physical properties of 125,000 porous metal-organic framework (MOF) materials and found that one of them is exceptionally good at separating xenon and krypton from gas mixtures. The team then confirmed that prediction experimentally (Nat. Commun 2016, DOI: 10.1038/ncomms11831). Xenon and krypton, along with oxygen, nitrogen, carbon dioxide, and other gases, are evolved when spent nuclear fuel is reprocessed to extract valuable fissile material. Reprocessing facilities trap and separate the gases, which include radioactive isotopes, via cryogenic distillation. But that approach is energy-intensive and expensive. Looking for a better option, Praveen K. Thallapally of Pacific Northwest National Laboratory and coworkers searched for sorbents that could selectively trap and separate xenon and krypton during fuel reprocessing. Nonradioactive xenon could be used for commercial lighting, imaging, and other applications, whereas the recovered krypton contains long-lived isotopes and must be sequestered. The team identified SBMOF-1, a MOF made from calcium ions and sulfonyldibenzoa[te] linkers, as the best candidate. The team found that SBMOF-1 exhibits the highest xenon adsorption capacity for a MOF and an exceptional ability to separate xenon and krypton from each other and from th[e] other gases by size exclusion.—MITCH JACOBY

This calcium-based MOF selectively traps and separates xenon and krypton; green = Ca, yellow = S, red = O, gray = C, white = H.

Banerjee and co-workers *Nature Communications,* 2016

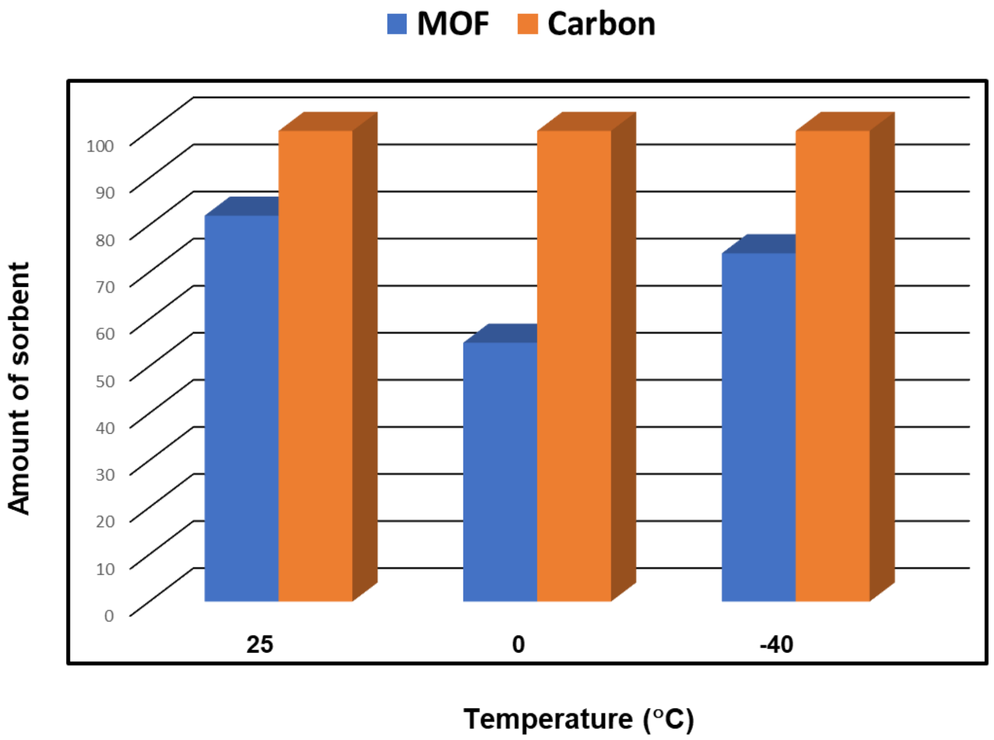
Thallapally, PK., Vienna et. al., USPTO WO/2017/218346A1

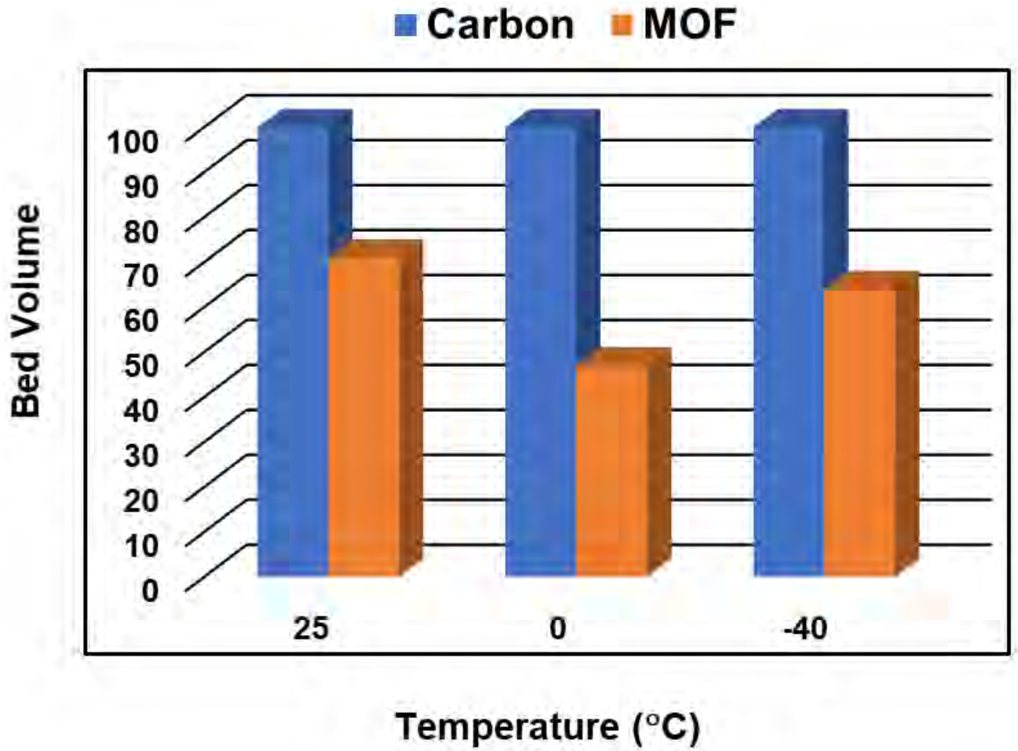
Thallapally, Ali Z. Riley, BJ., Paviet, P., Matyas, J., Vienna, J., Compact and Modular Integrated Off-Gas System and Sensors." Invention Disclosure e-IDR 18117

Banerjee, D, Thallapally, PK, Kunapuli R., McGrail, BP, Liu J et al., Surface acoustic wave sensors for refrigerant leak detection., *USPTO WO2021/041359 A1*

Comparison of MOF vs Nucon Carbon

Bed Size Vs Bed Volume





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- Thallapally, P. K., Robinson, A. J., Zbib, A., Riley, B. J., Chong, S., Liu, J., Murphy, M. K., Okabe, P., Sherrod, R. *Noble Gas Management: SBMOF 1 vs. NUCON Carbon*; PNNL-33314: The U.S. Department of Energy - Office of Nuclear Energy: GAIN VOUCHER, 2022

What next?

- For Nuclear Energy needs, MOFs are being developed and tested with success.
- More research is necessary to evaluate if MOFs are beneficial to collection of Xe from molten salt reactors.
- Integrate MOF capture technology with molten salt test loop
- Build a lab and bench scale system coupled with selective gas sensors

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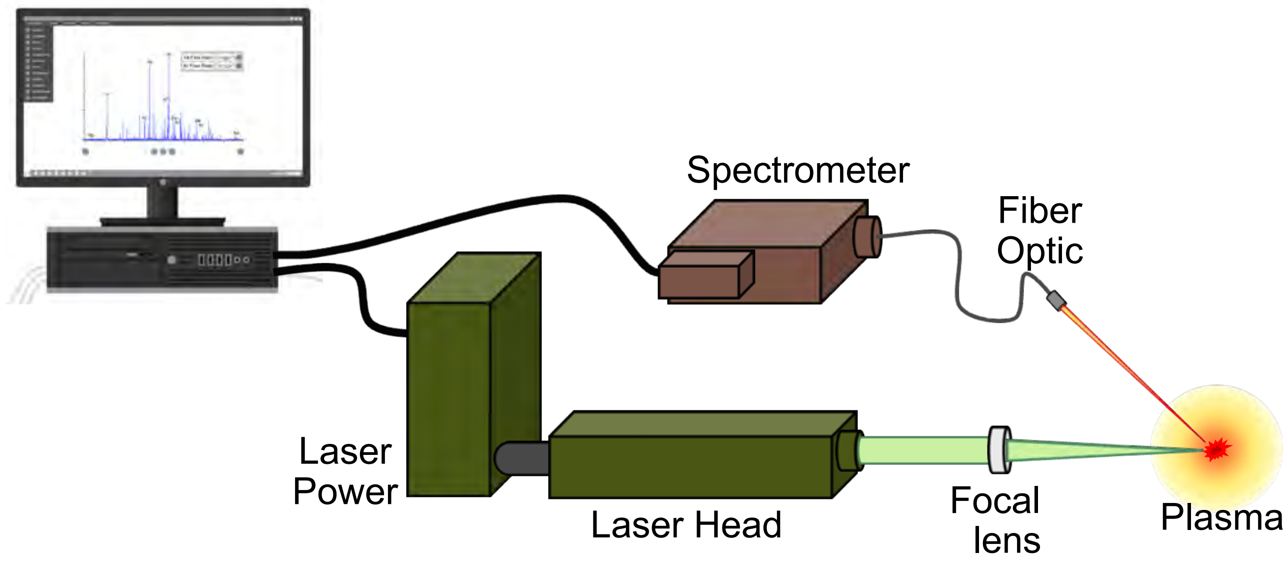
Laser-Induced Breakdown Spectroscopy

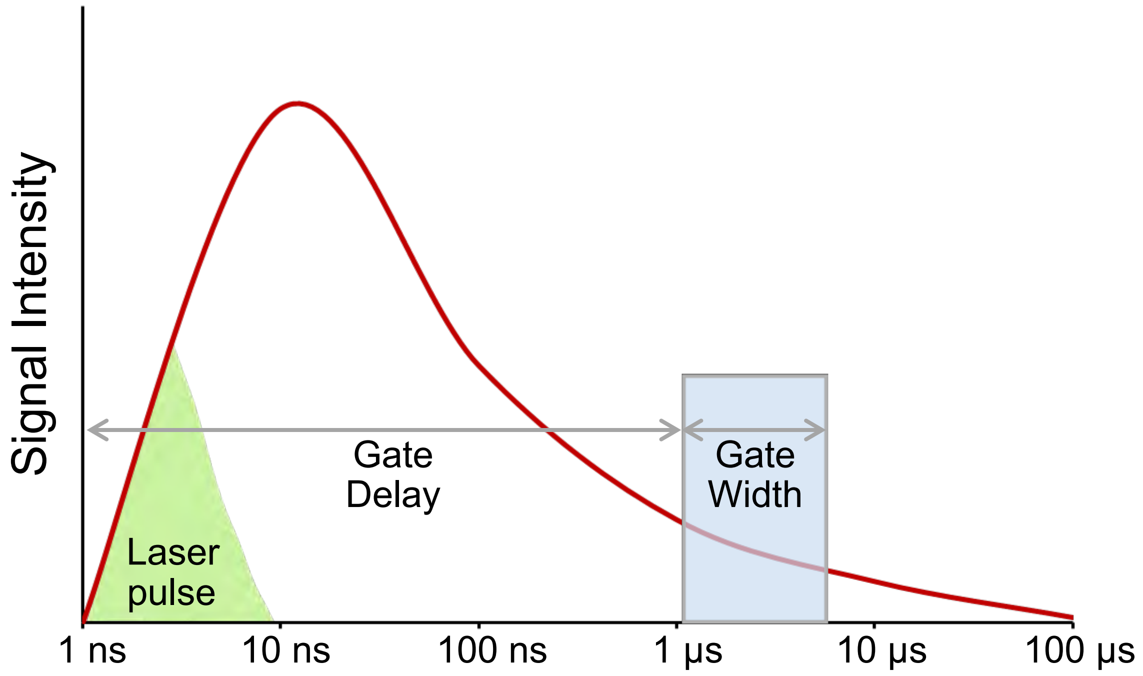
Hunter Andrews
Oak Ridge National Laboratory

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



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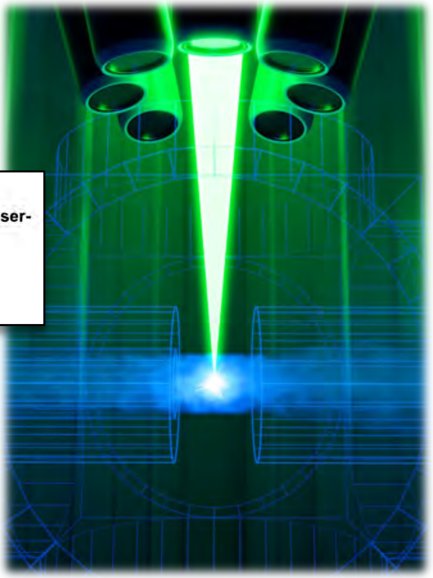
LIBS is being used to help progress molten salt reactor research

LIBS off-gas sensor

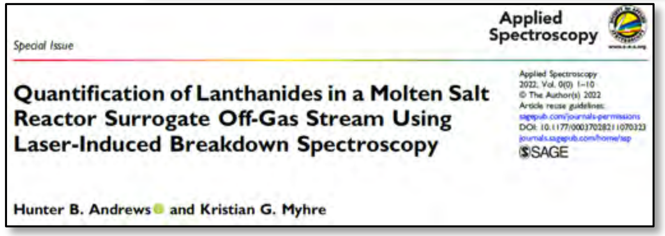


Open Access | Feature Paper | Editor's Choice | Article

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]

[1] Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA
[2] Pacific Northwest National Laboratory, Richland, WA 99352, USA



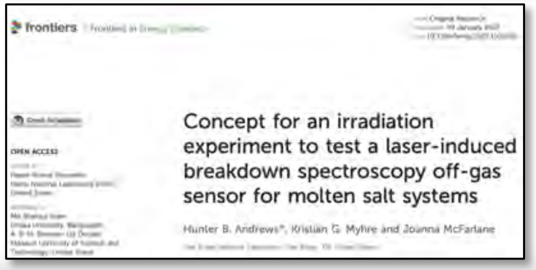
Applied Spectroscopy

Special Issue

Quantification of Lanthanides in a Molten Salt Reactor Surrogate Off-Gas Stream Using Laser-Induced Breakdown Spectroscopy

Applied Spectroscopy 2022, Vol. 0(0) 1–10 © The Author(s) 2022 Article reuse guidelines: sagepub.com/journals-permissions DOI: 10.1177/00037028221070323 journals.sagepub.com/home/asp SAGE

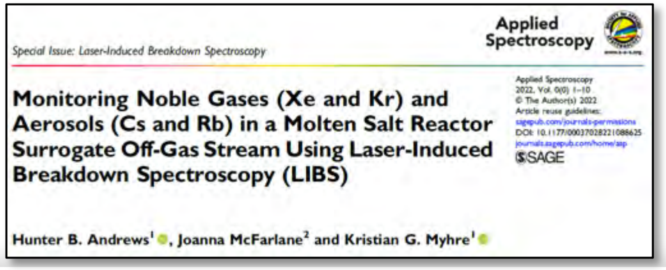
Hunter B. Andrews and Kristian G. Myhre



frontiers

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



Applied Spectroscopy

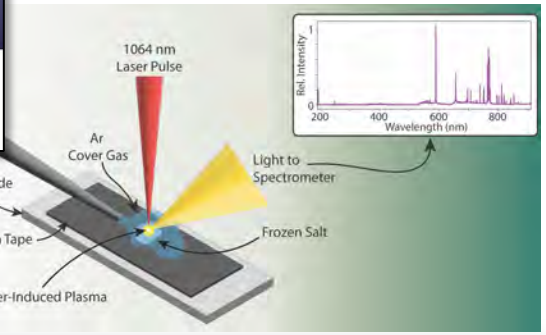
Special Issue: Laser-Induced Breakdown Spectroscopy

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)

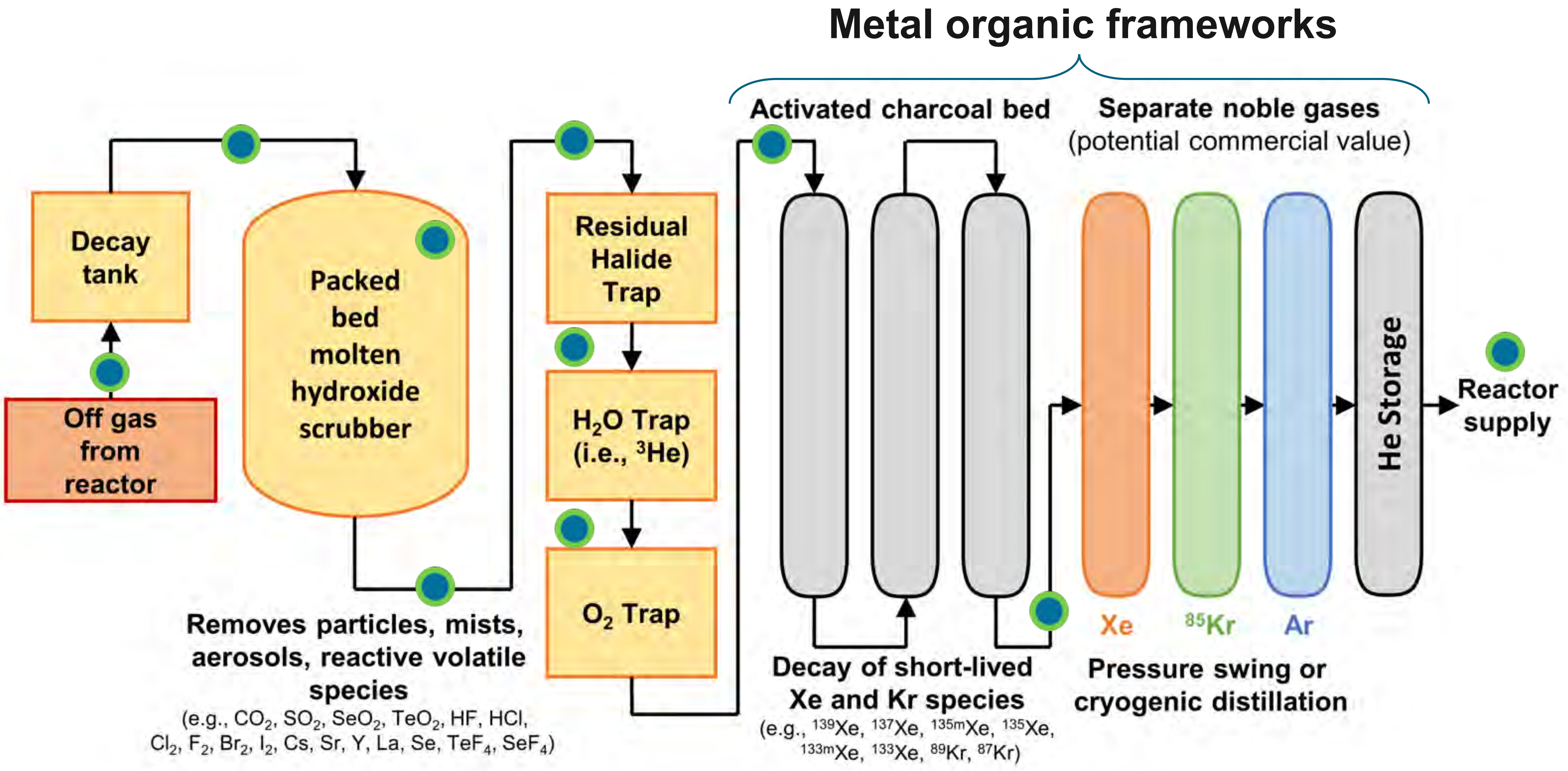
Applied Spectroscopy 2022, Vol. 0(0) 1–10 © The Author(s) 2022 Article reuse guidelines: sagepub.com/journals-permissions DOI: 10.1177/00037028221086625 journals.sagepub.com/home/asp SAGE

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

LIBS to probe salt-material interaction

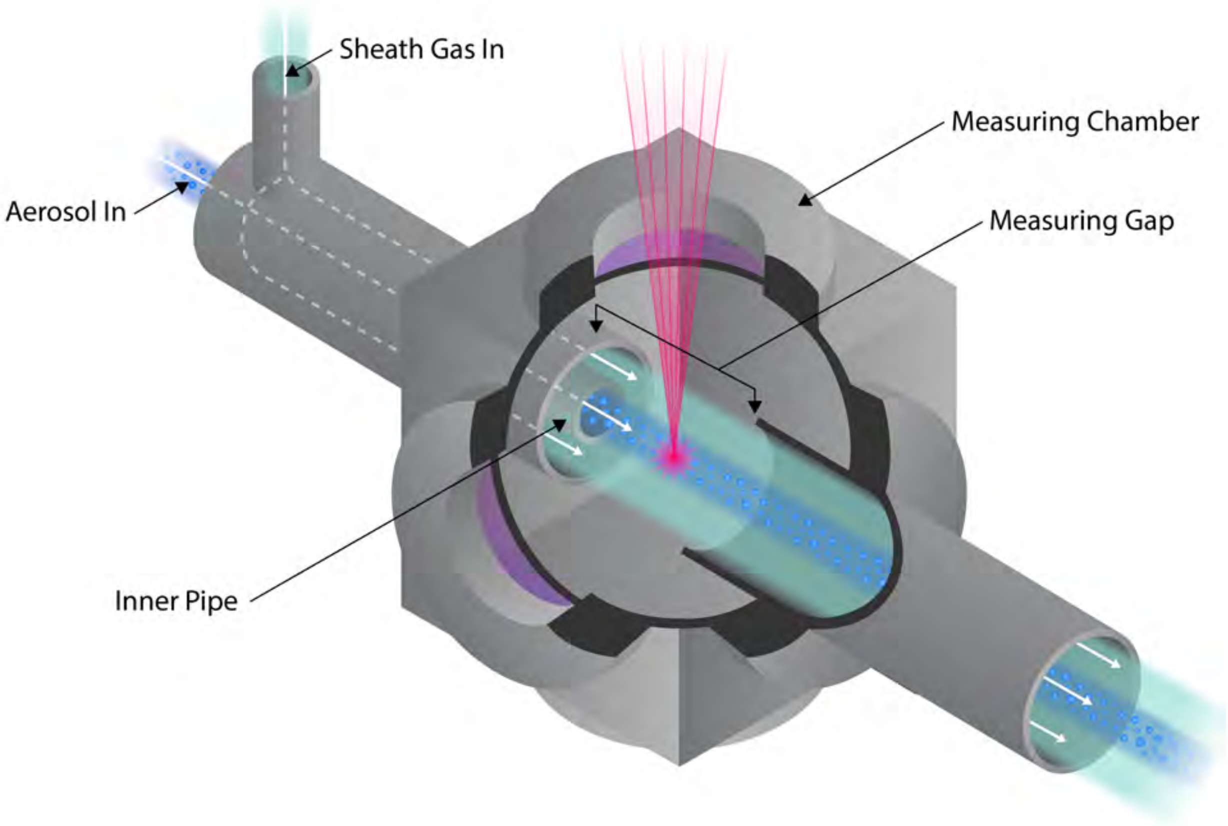


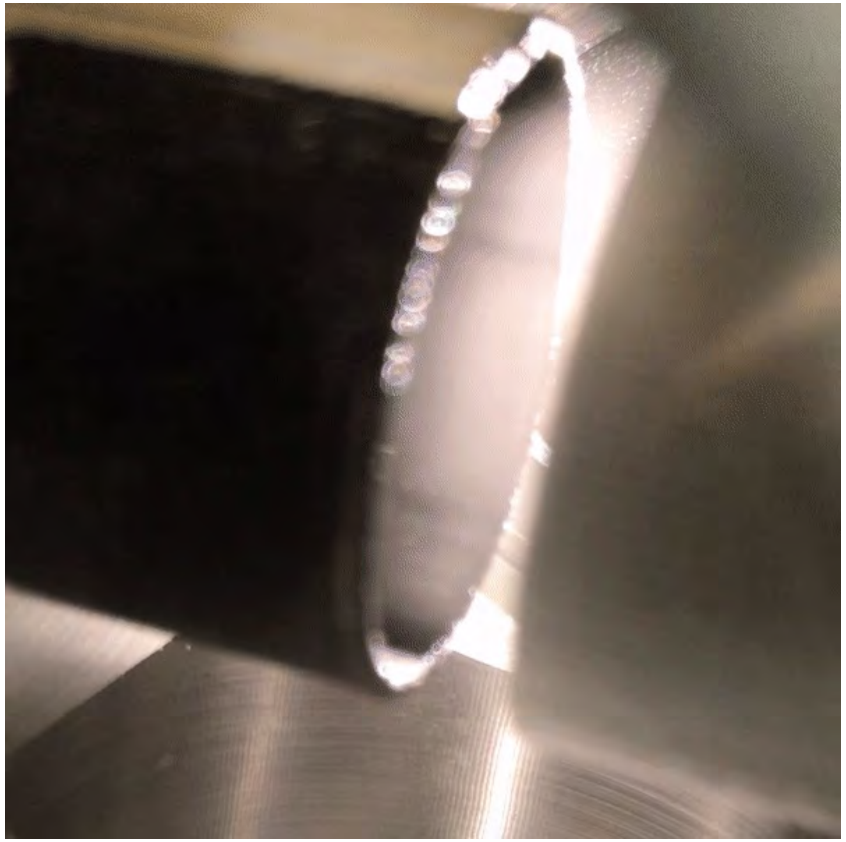
The off-gas treatment system development is critical for continued MSR development



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

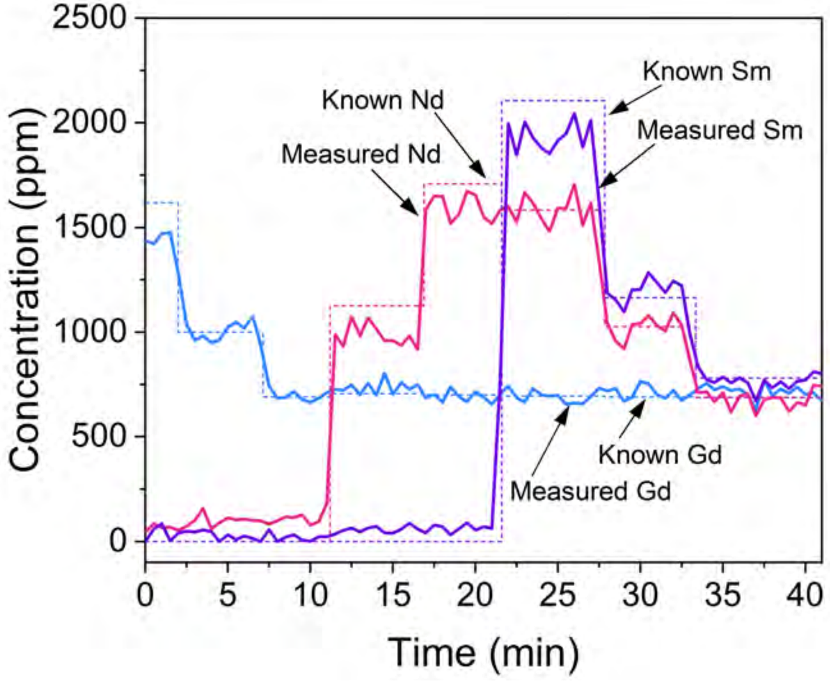
Initial feasibility has been shown on surrogate off-gas streams

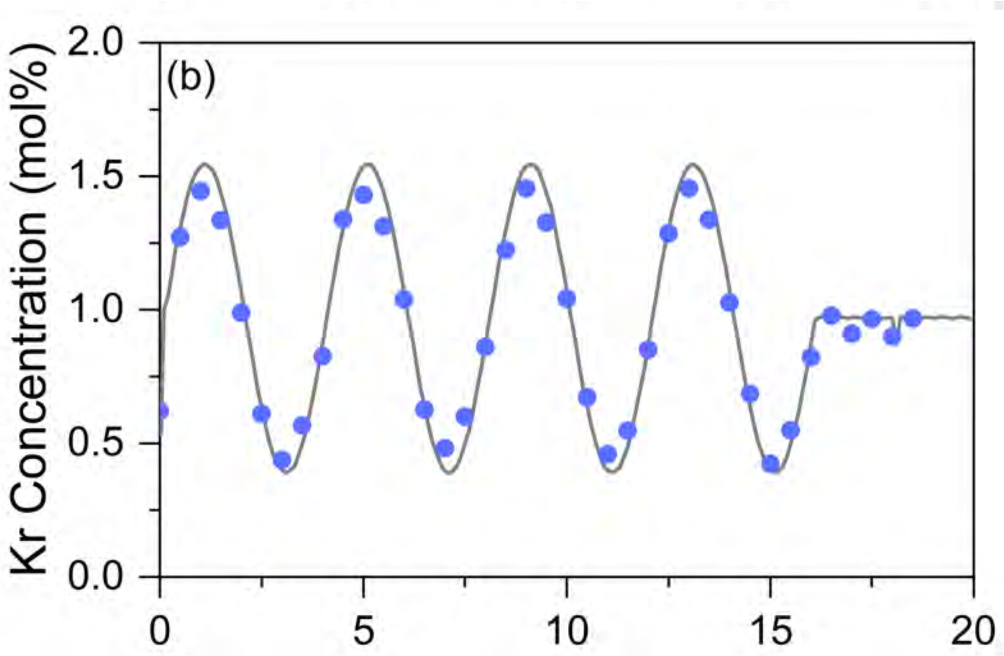




Sheath gas is turned on and off repeatedly

We have successfully used LIBS to monitor aerosolized lanthanides and Kr in real-time





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Coupling LIBS with MOF for Xe breakthrough tests

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

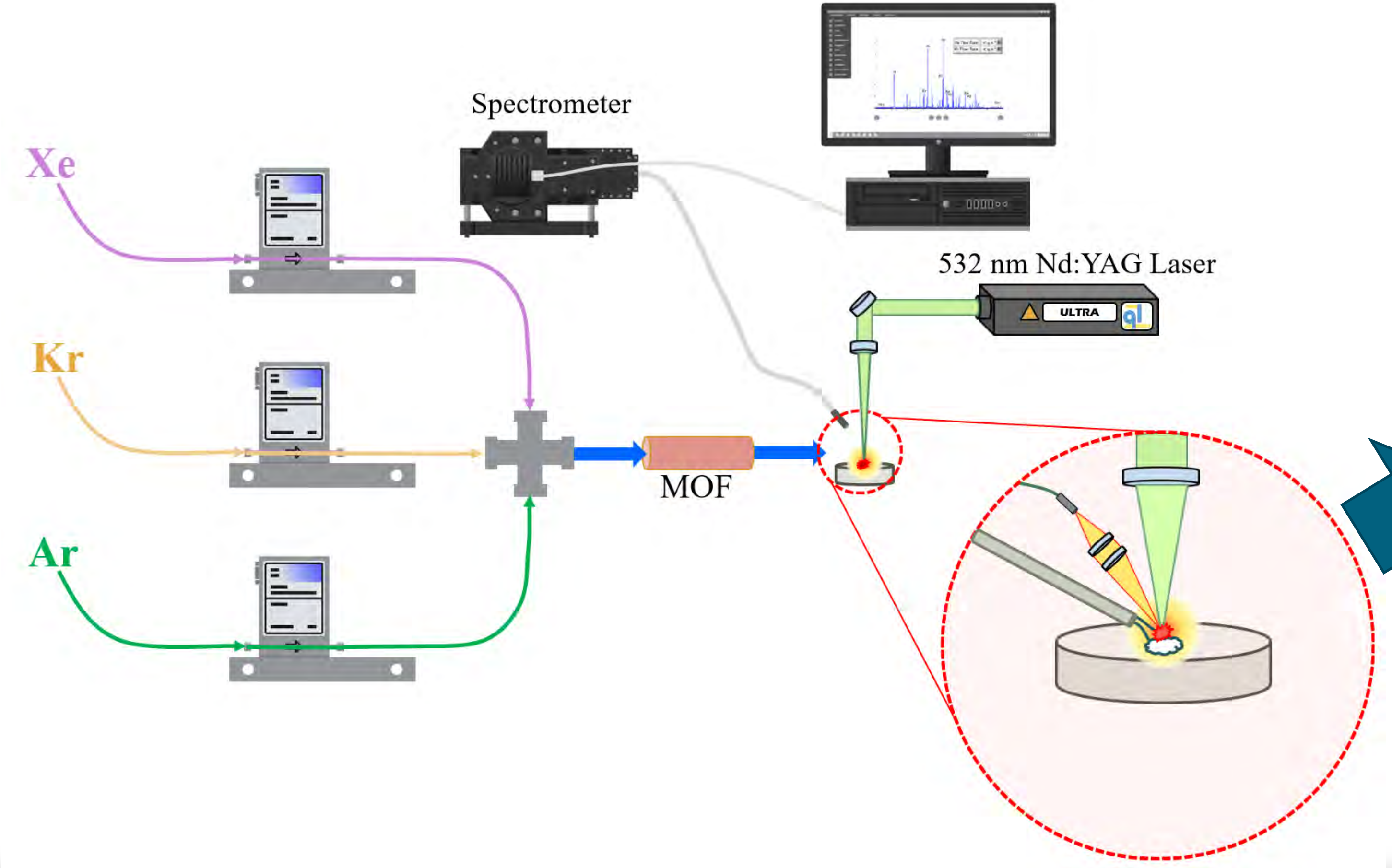
Monitoring Xenon Capture in a Metal Organic Framework Using Laser-Induced Breakdown Spectroscopy

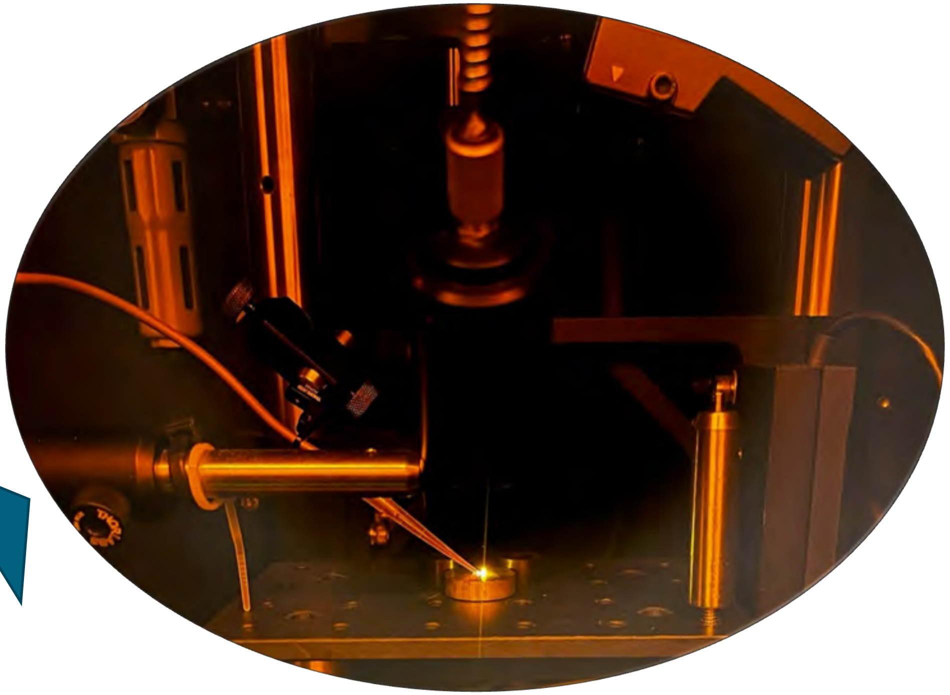
by Hunter B. Andrews [1,*], Praveen K. Thallapally [2] and Alexander J. Robinson [2]

1 Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

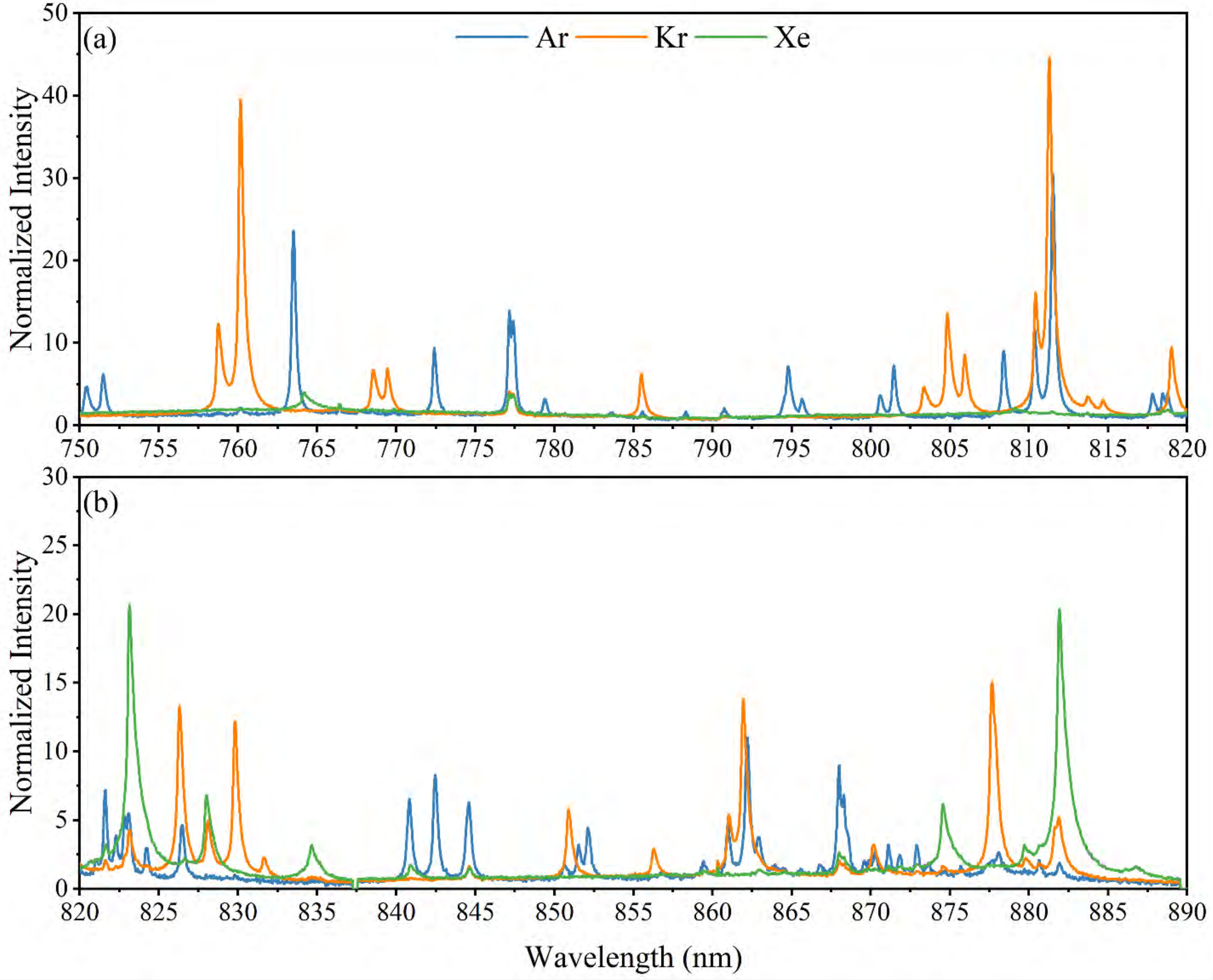
2 Pacific Northwest National Laboratory, Richland, WA 99352, USA

New LIBS setup was needed to facilitate MOF size and flowrates

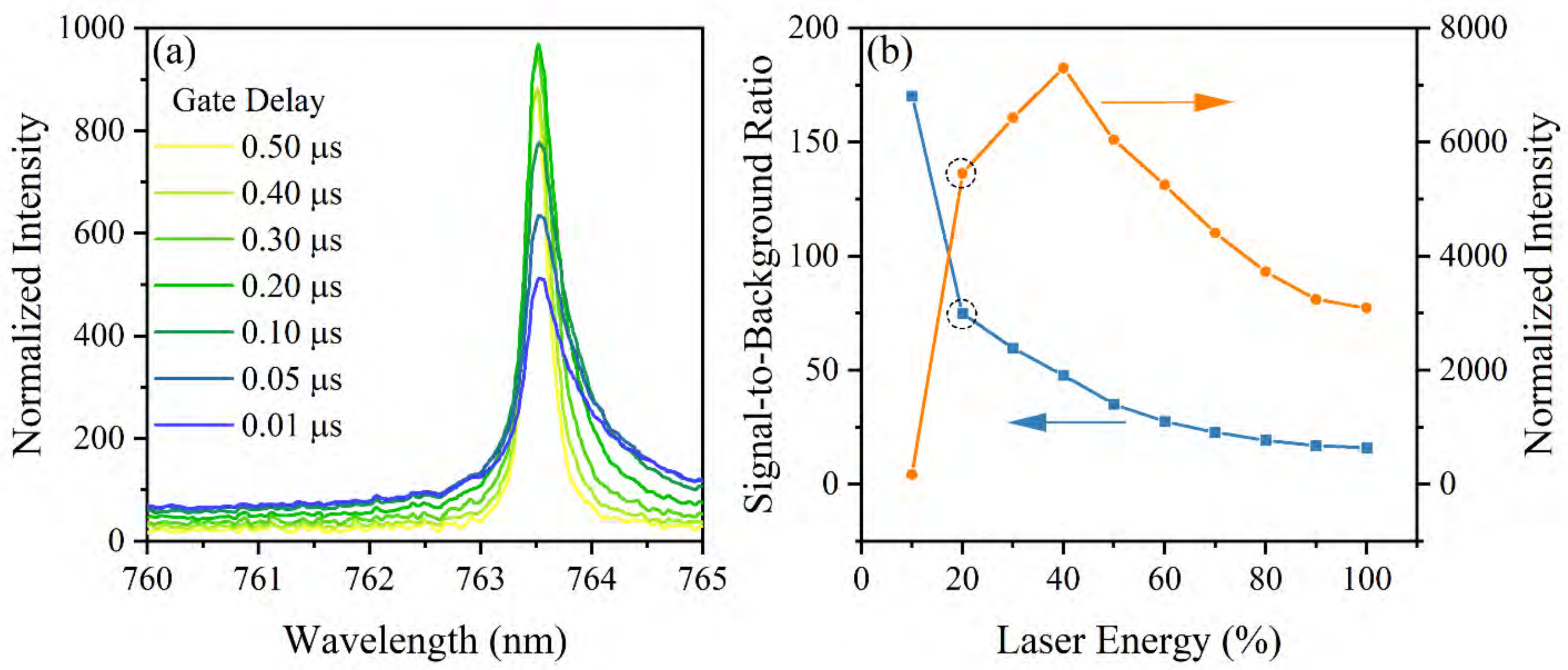




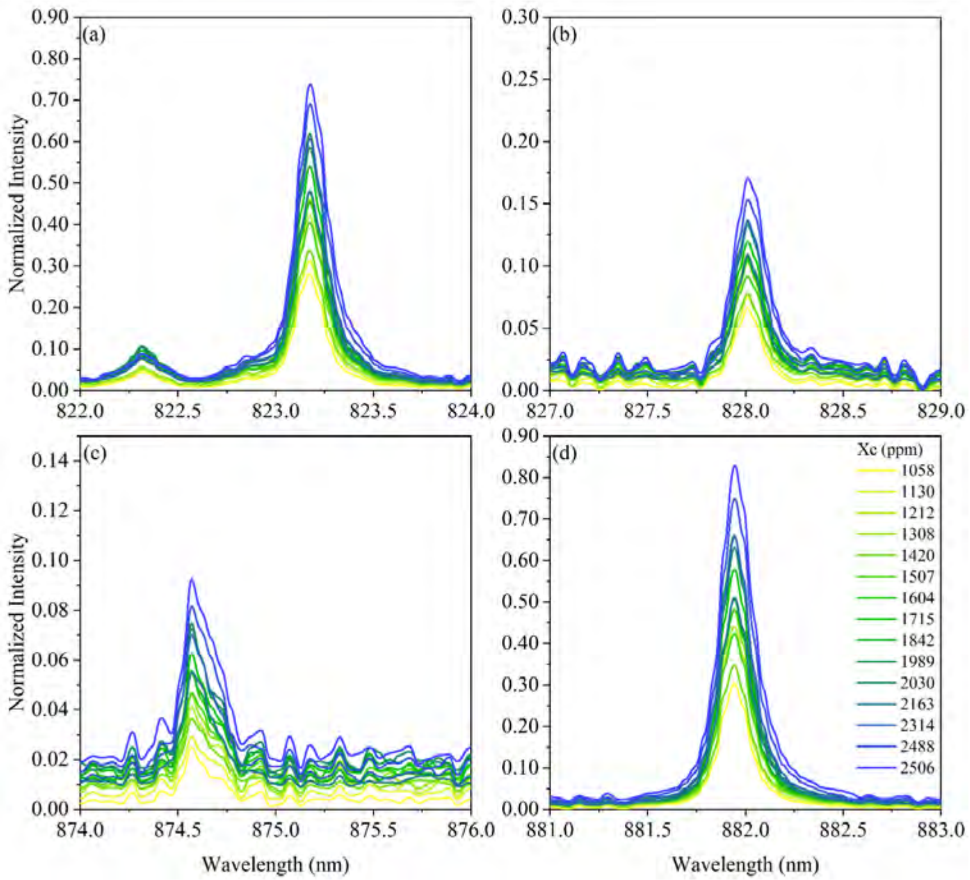
Pure gases were run to facilitate peak identification

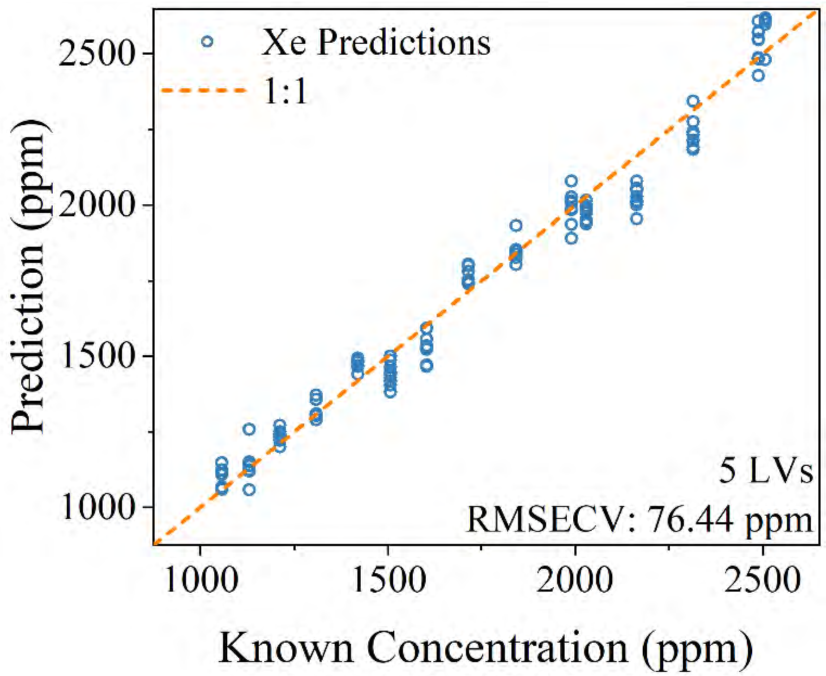


Spectrometer gating and laser energy were optimized prior to data collection



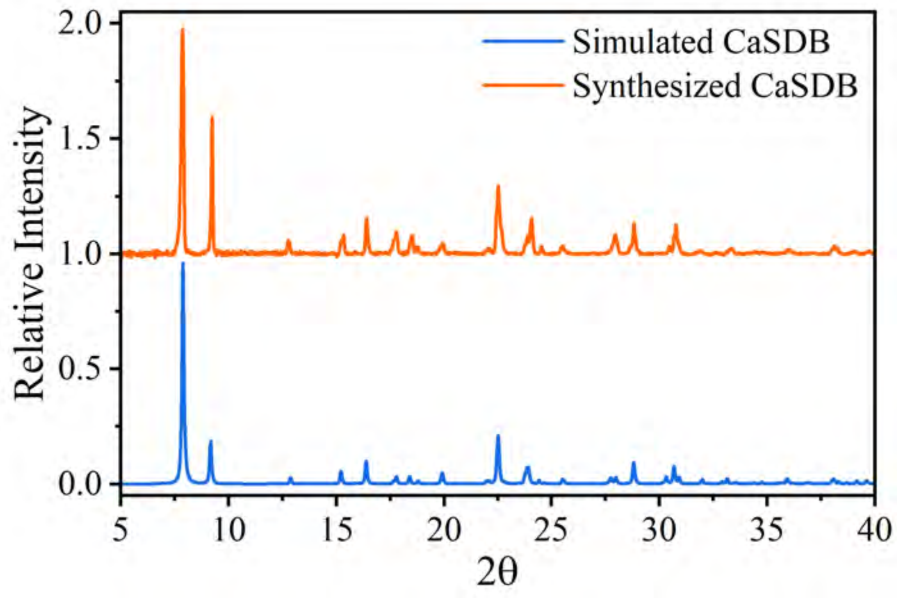
A multivariate model was built for Xe ranging from 1000 – 2500 ppm to estimate limits of detection for the given setup

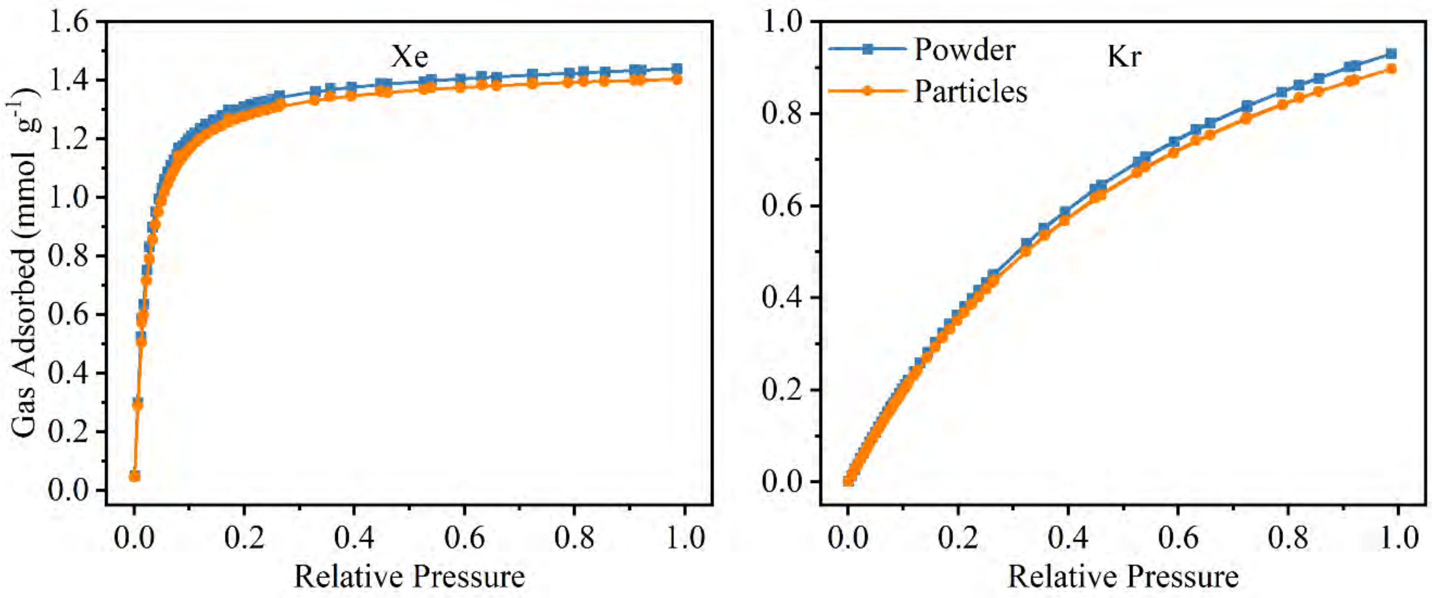




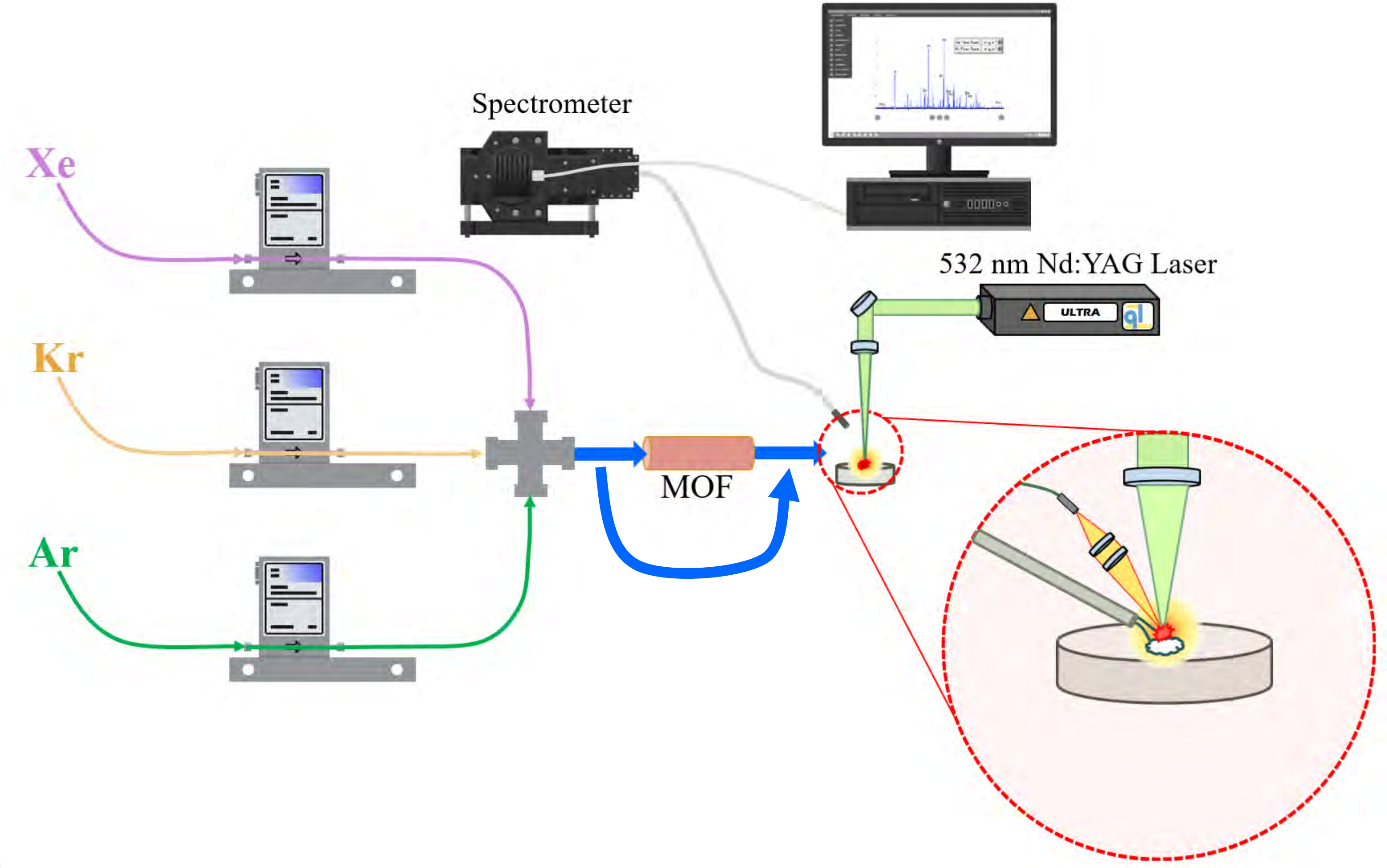
LOD_{Xe}= 167 ppm

MOF column was synthesized at PNNL and shipped to ORNL for testing





MOF column was activated and loaded into testing system

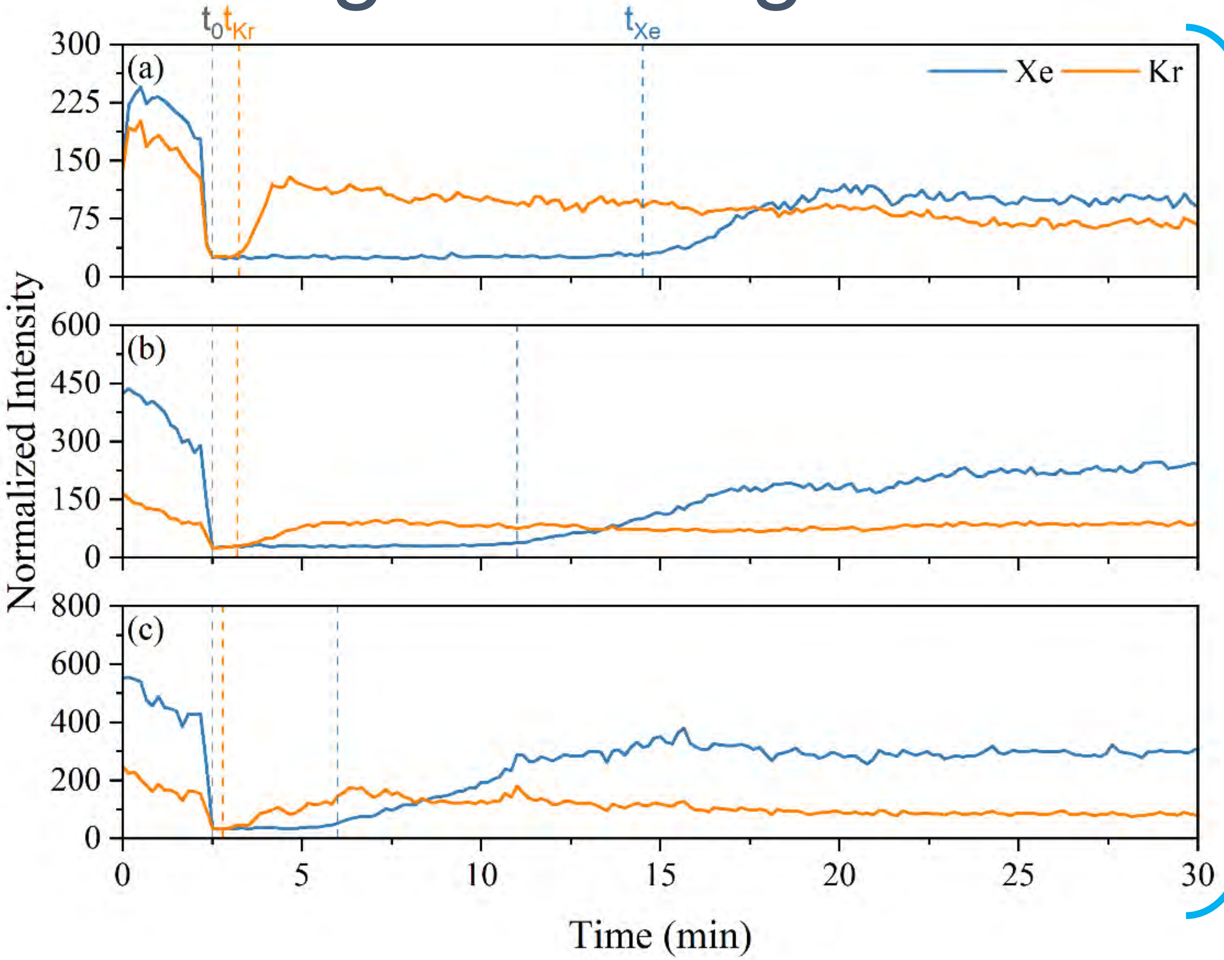


Breakthrough tests were completed on the activated MOF with the LIBS inline for noble gas tracking

(a) 1000 ppm Xe, 1000 ppm Kr

(b) 2000 ppm Xe, 1000 ppm Kr

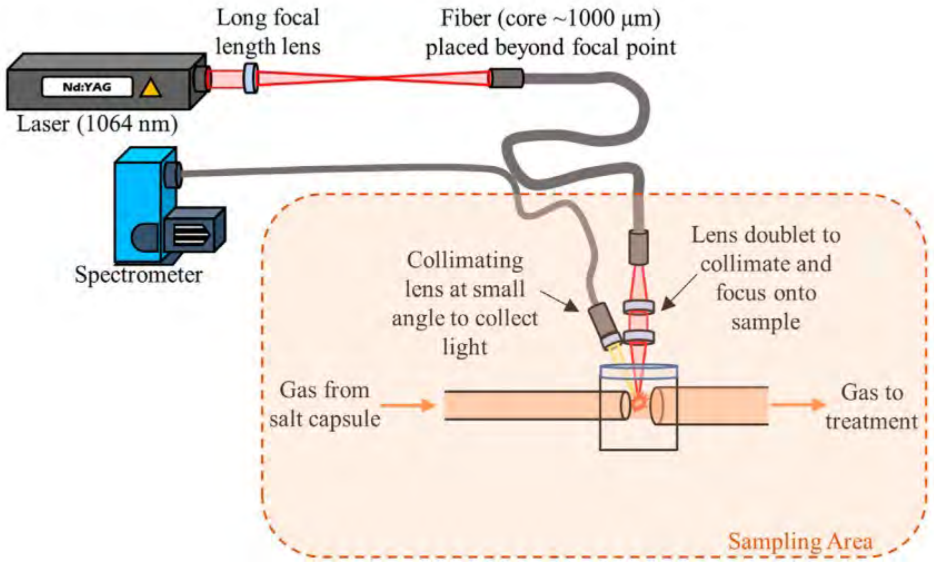
(c) 3000 ppm Xe, 1000 ppm Kr



$$S_{Xe/Kr} = \frac{x_{Xe}/y_{Xe}}{x_{Kr}/y_{Kr}}$$ = ~12-16

FY23 will focus on enhancing the LIBS noble gas sensitivity

- **Driving down detection limits will increase the usefulness for such a technique**
- **Conversations for deploying LIBS gas sensor on molten salt loops are ongoing**



Thank you

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