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Development of Laser Induced Breakdown Spectroscopy Sensor for Molten Salt Reactor Off-Gas Stream

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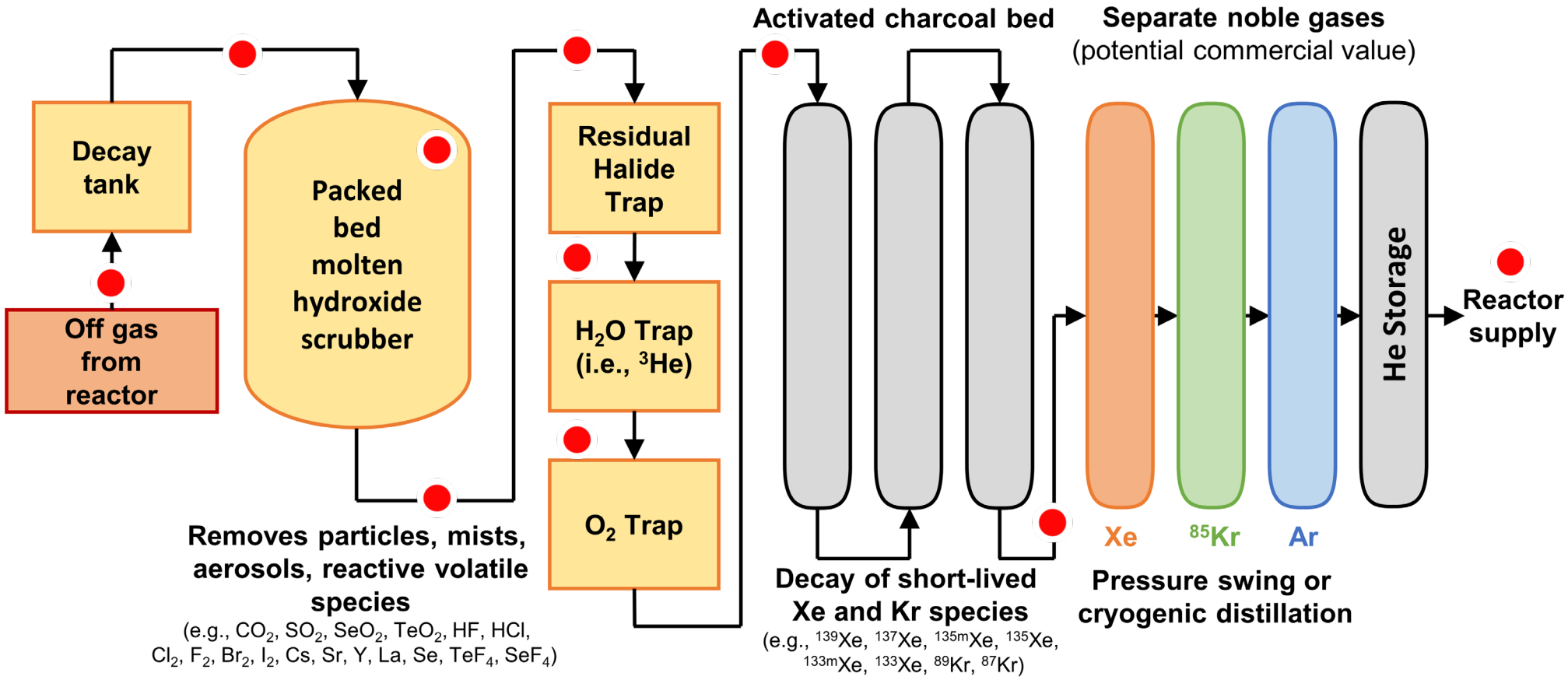
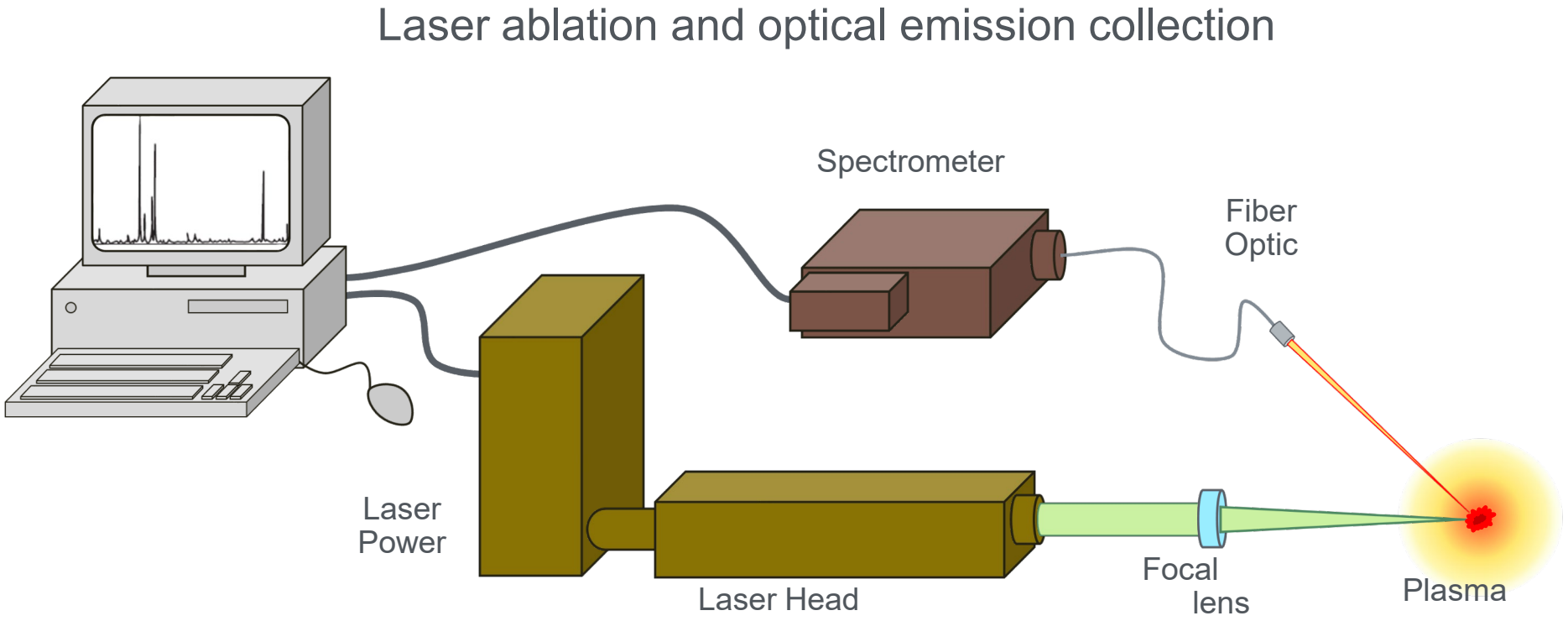
U.S. DEPARTMENT OF ENERGY

We're seeking to enable molten salt reactor (MSR) deployment by developing technology for off-gas analysis



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

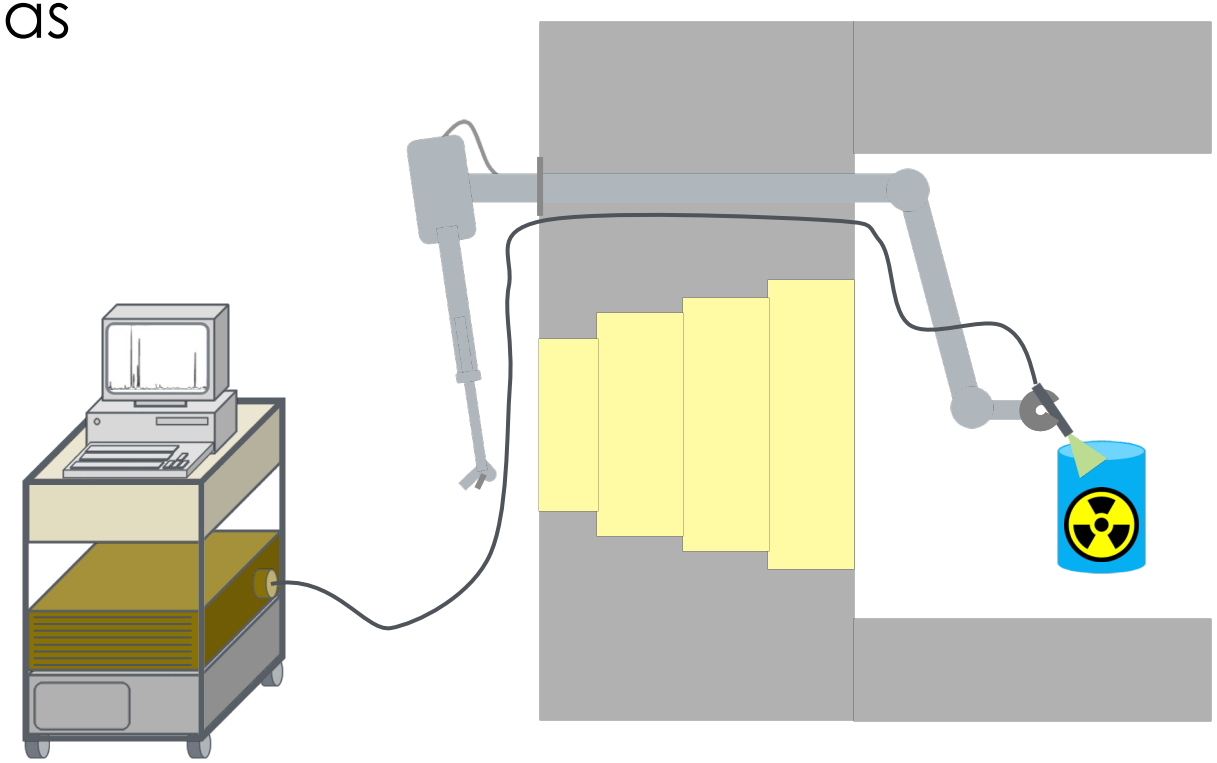
What is laser-induced breakdown spectroscopy (LIBS)?



Why laser induced breakdown spectroscopy (LIBS)?

Elemental analysis via optical emission spectroscopy of laser induced plasmas

- Benefits:
  - Little to no sample prep
  - Useful for solid, liquid, and gas analysis
  - Typical sensitivities of ppm
  - Quasi-nondestructive (nanograms per shot)
  - Can be completely fiber optic based



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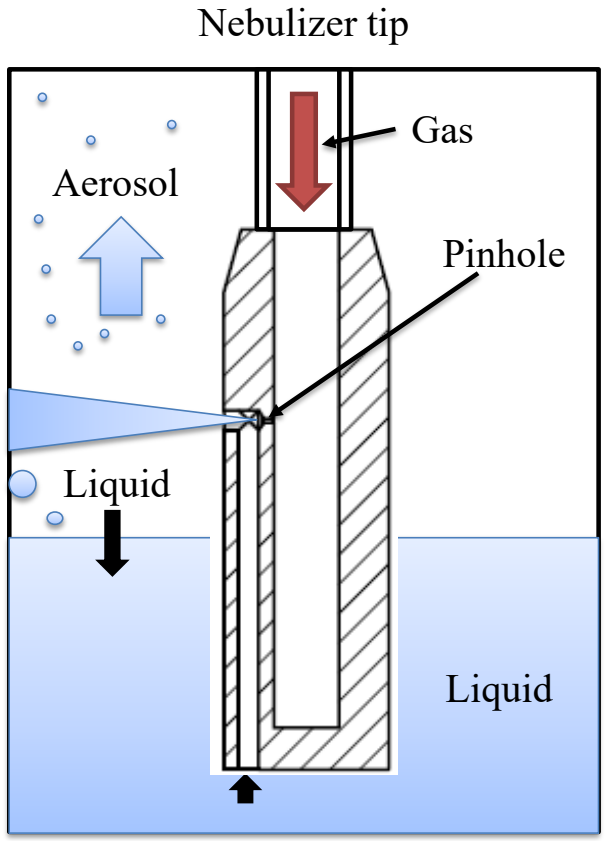
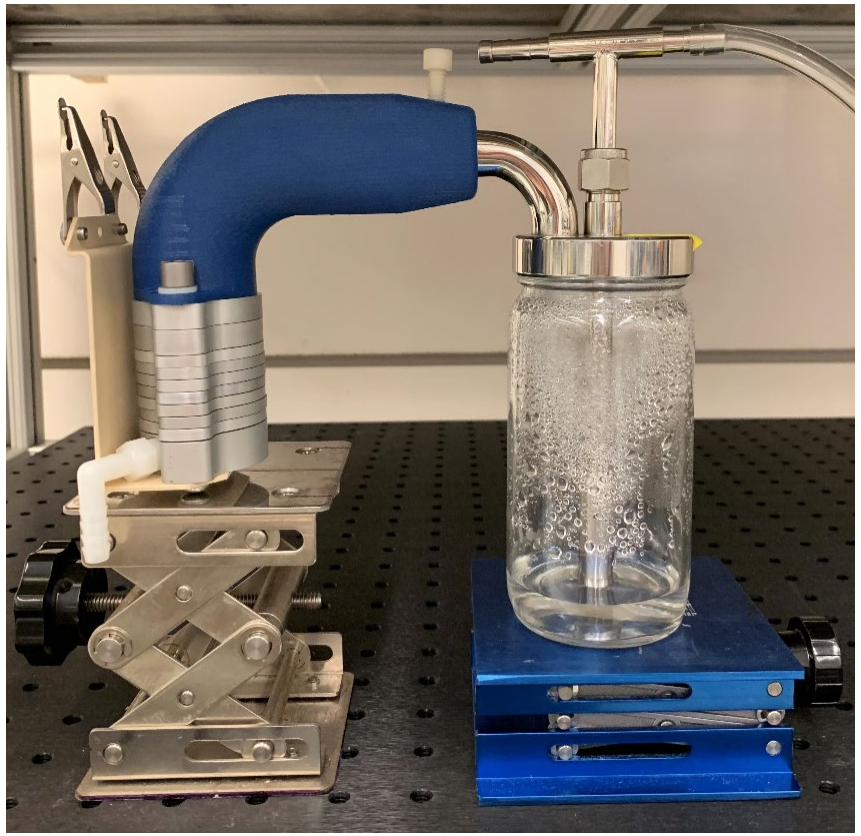
Design Challenges

- Producing a surrogate aerosol stream
- Designing a measurement cell

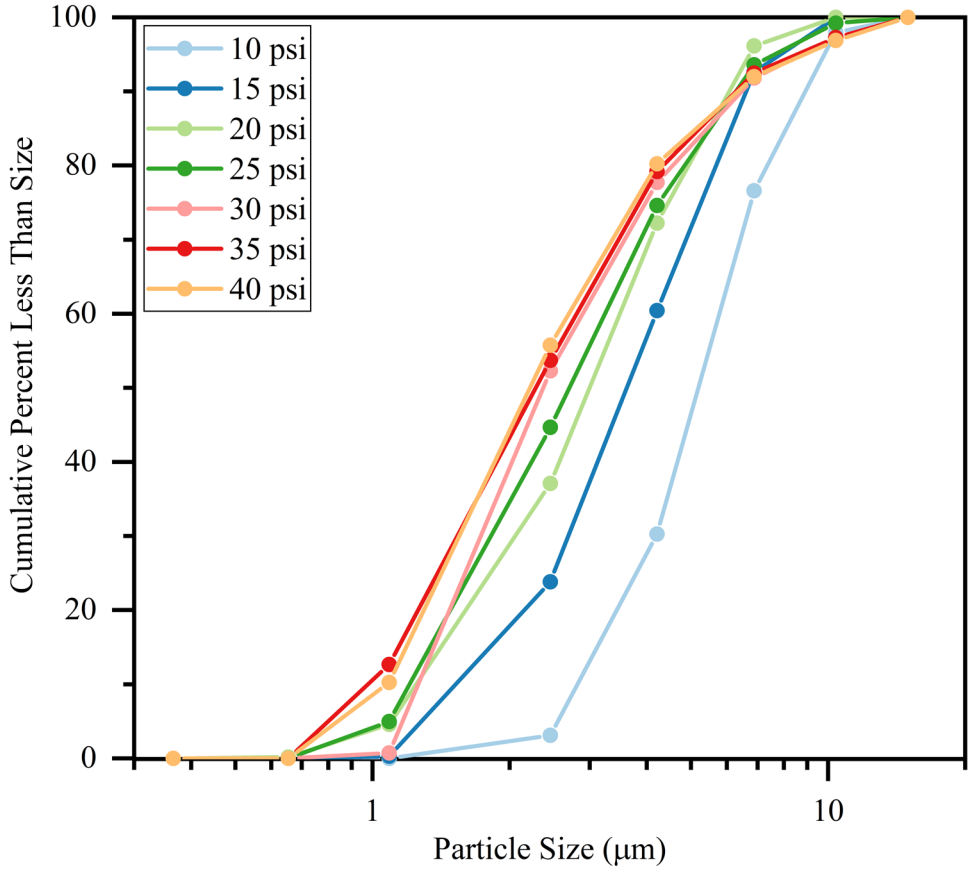
A collision nebulizer was selected to generate aerosol stream for analysis

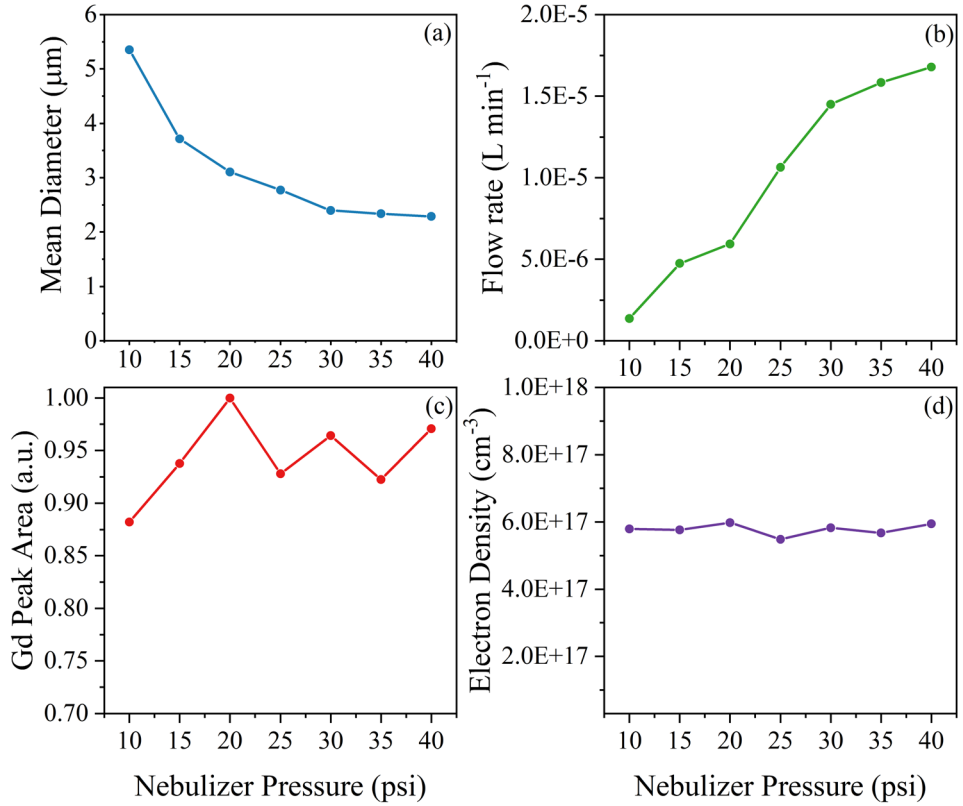


[1] A. Williams, Virginia Commonwealth University, 2016.

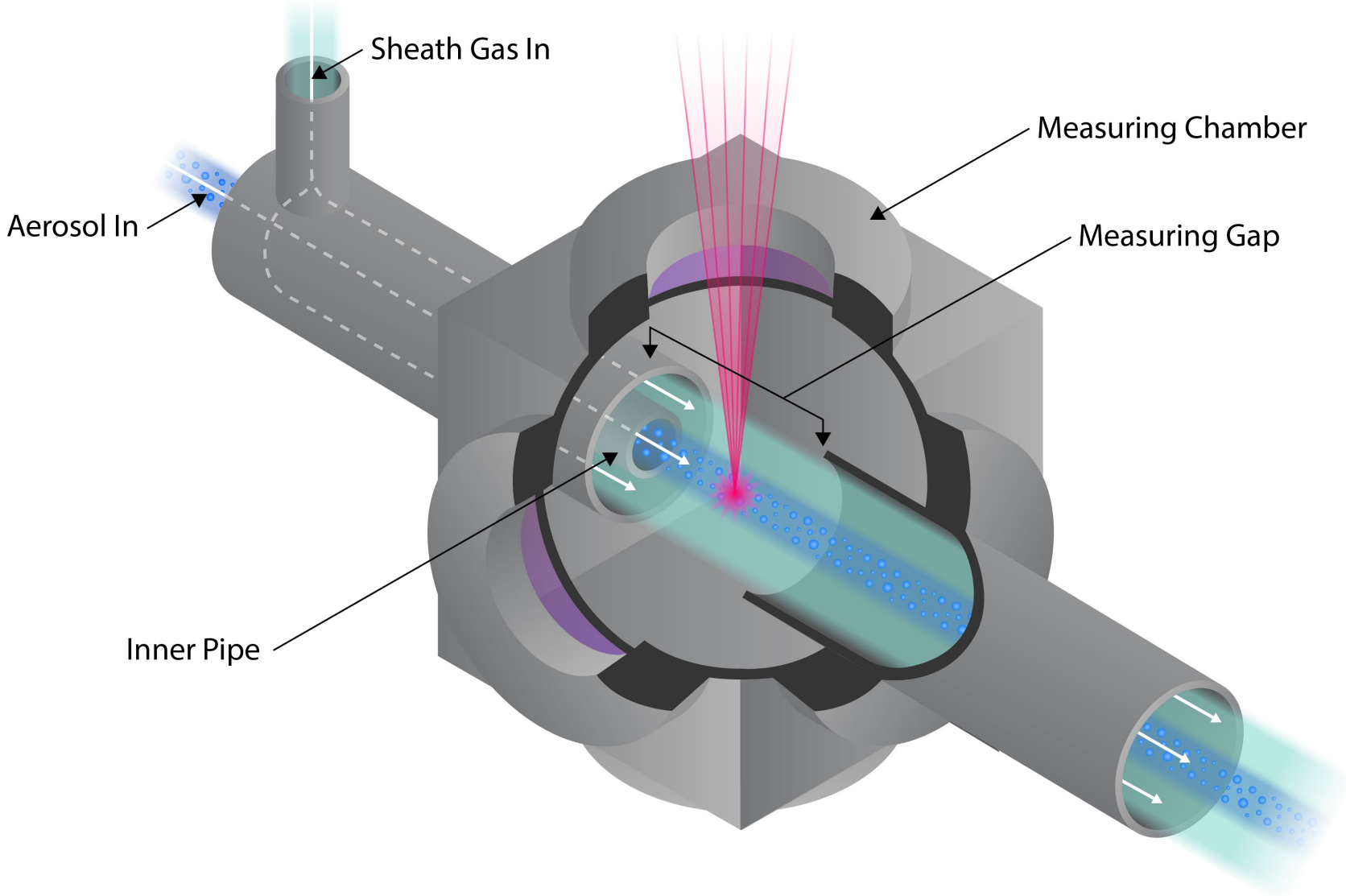


Aerosol particle sizes range from ~1-10 µm in diameter

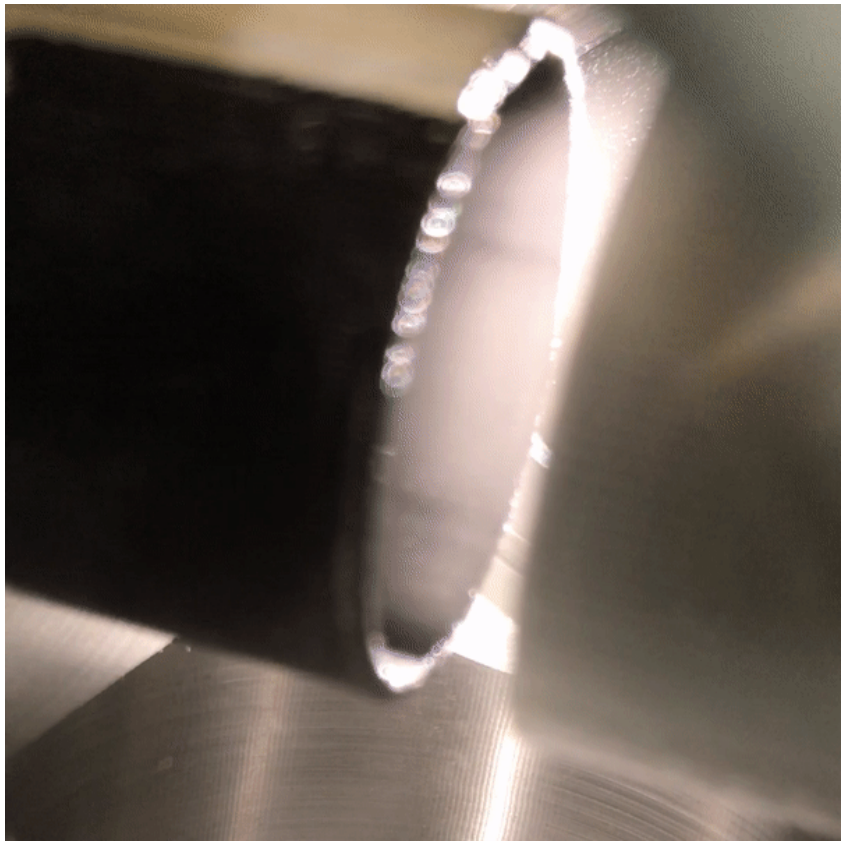




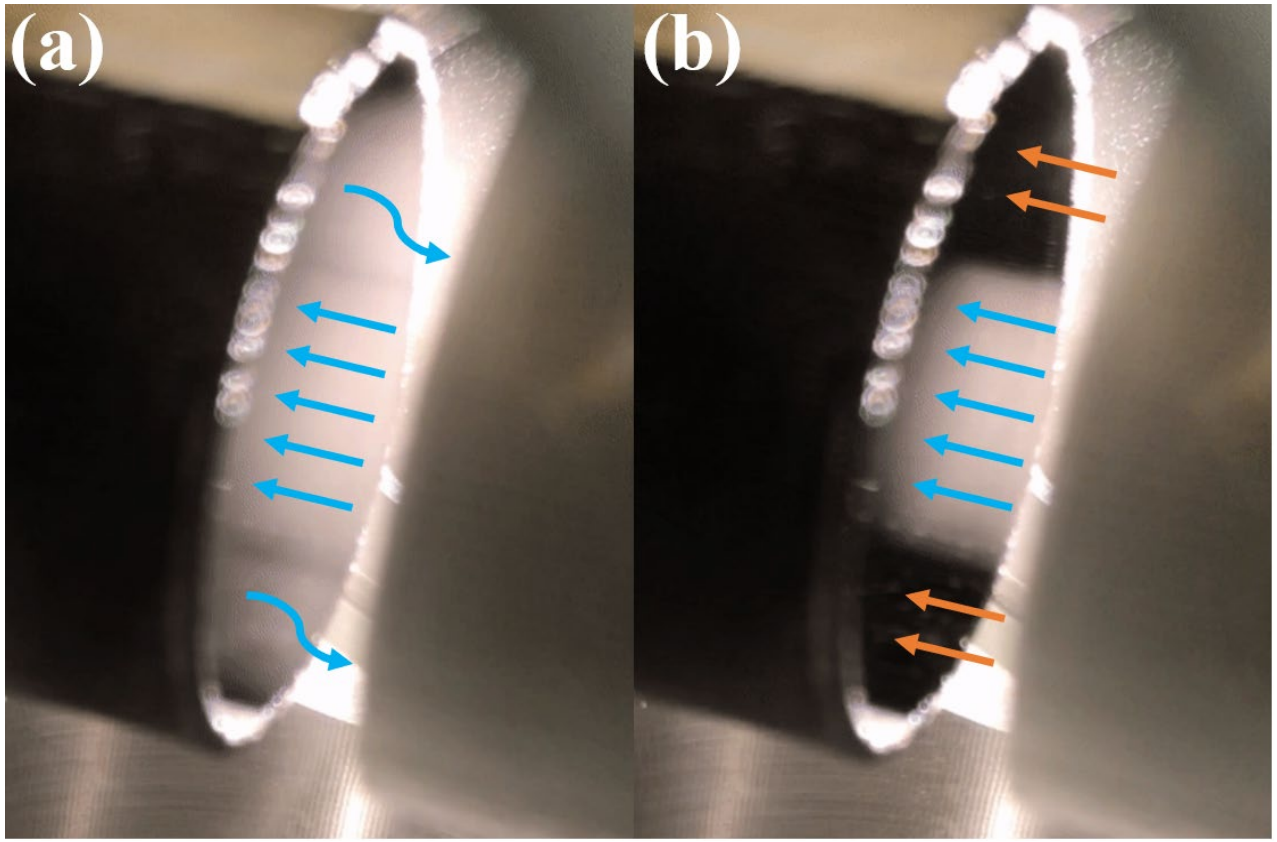
A sheath gas approach was used to contain aerosol stream during measurement



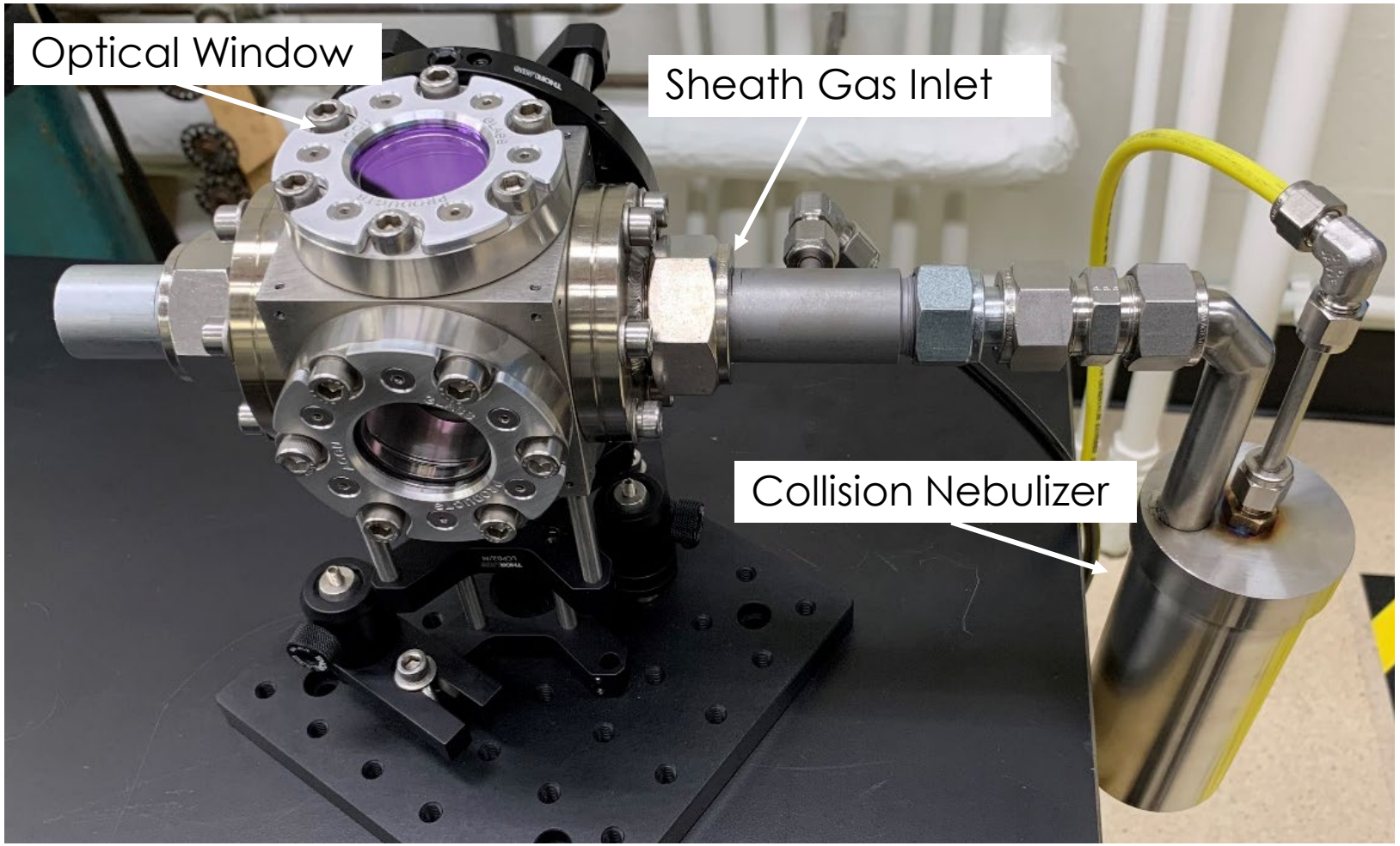
Sheath gas system successfully contained aerosol stream



Sheath gas is turned on and off repeatedly



A complete prototype aerosol measurement system was manufactured



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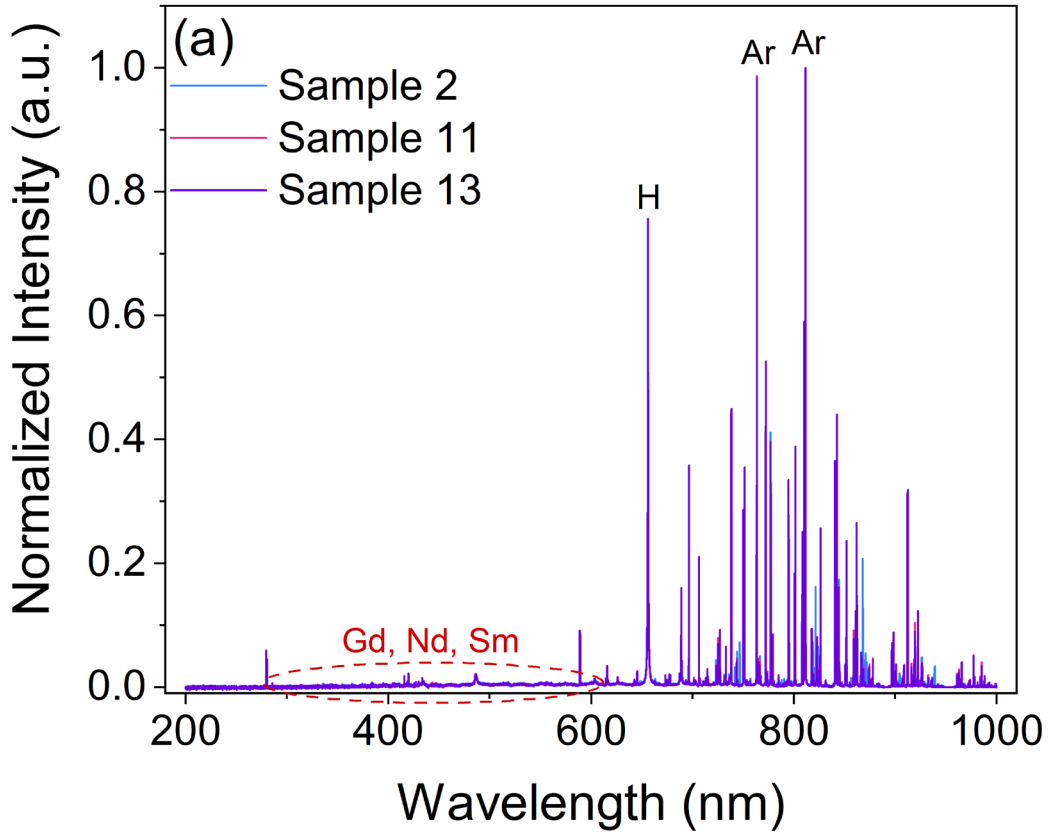
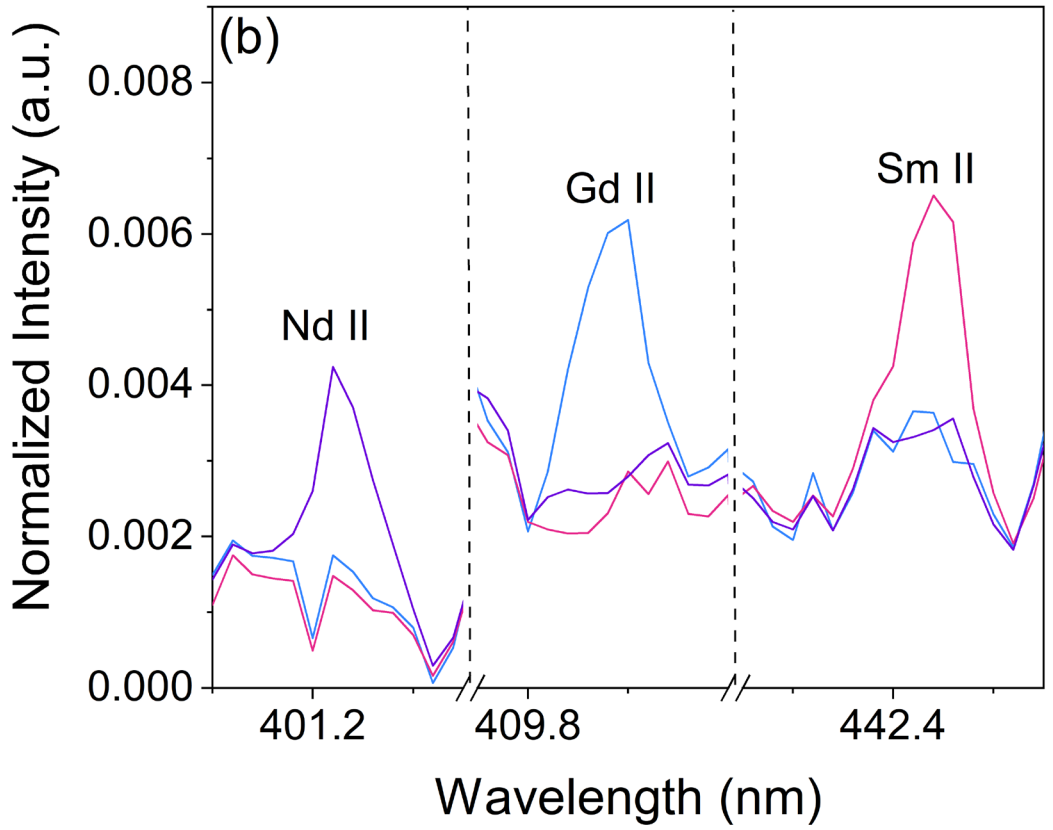
Aqueous aerosol monitoring system

- The three representative elements selected were Gd, Nd, and Sm
  - All act as neutron poisons in a reactor making their concentrations of interest to operators.
  - Concentrations ranging from 0 to 2000 ppm in liquid reservoir
  - 2000 ppm in reservoir ≈5 ppb in aerosol stream

Regression models were developed using a set of calibration samples



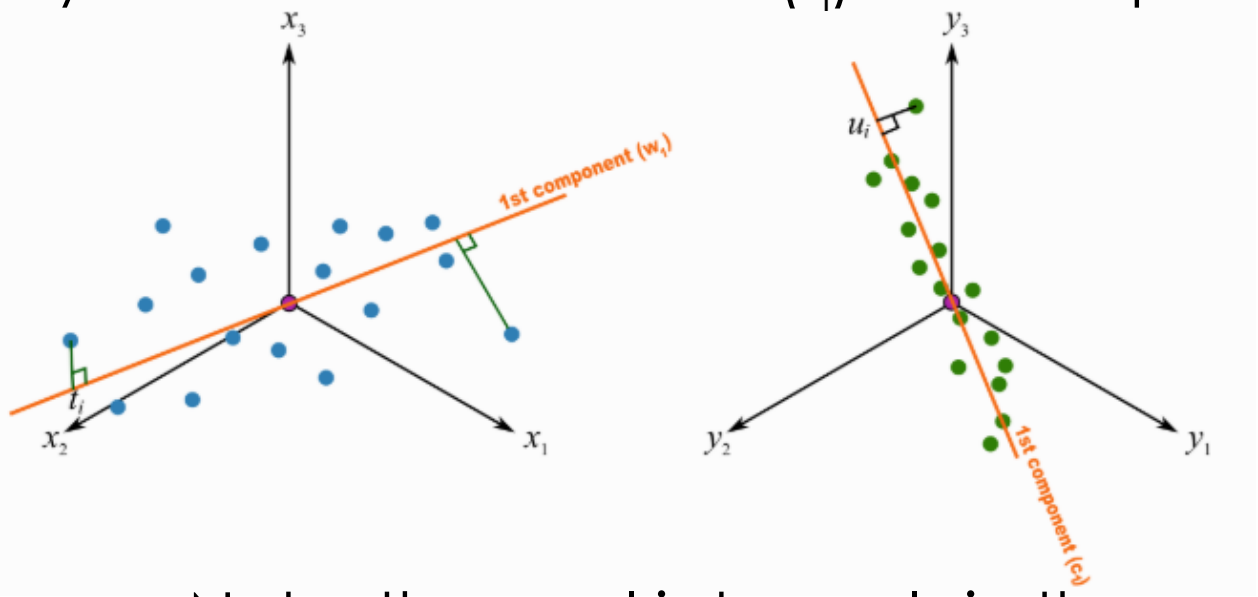


Sample 2 is Gd dominant
Sample 11 is Nd dominant
Sample 13 is Sm dominant

What is PLS regression?

Partial Least Squares Regression (PLS)

1. Matrices X and Y are decomposed into latent structures in an iterative process.
2. The latent structures corresponding to the most variation of Y (u_i) is explained by a latent structure in X (t_i)which explains it the best.



Note: the goal is to explain the most variance in Y, not necessarily X

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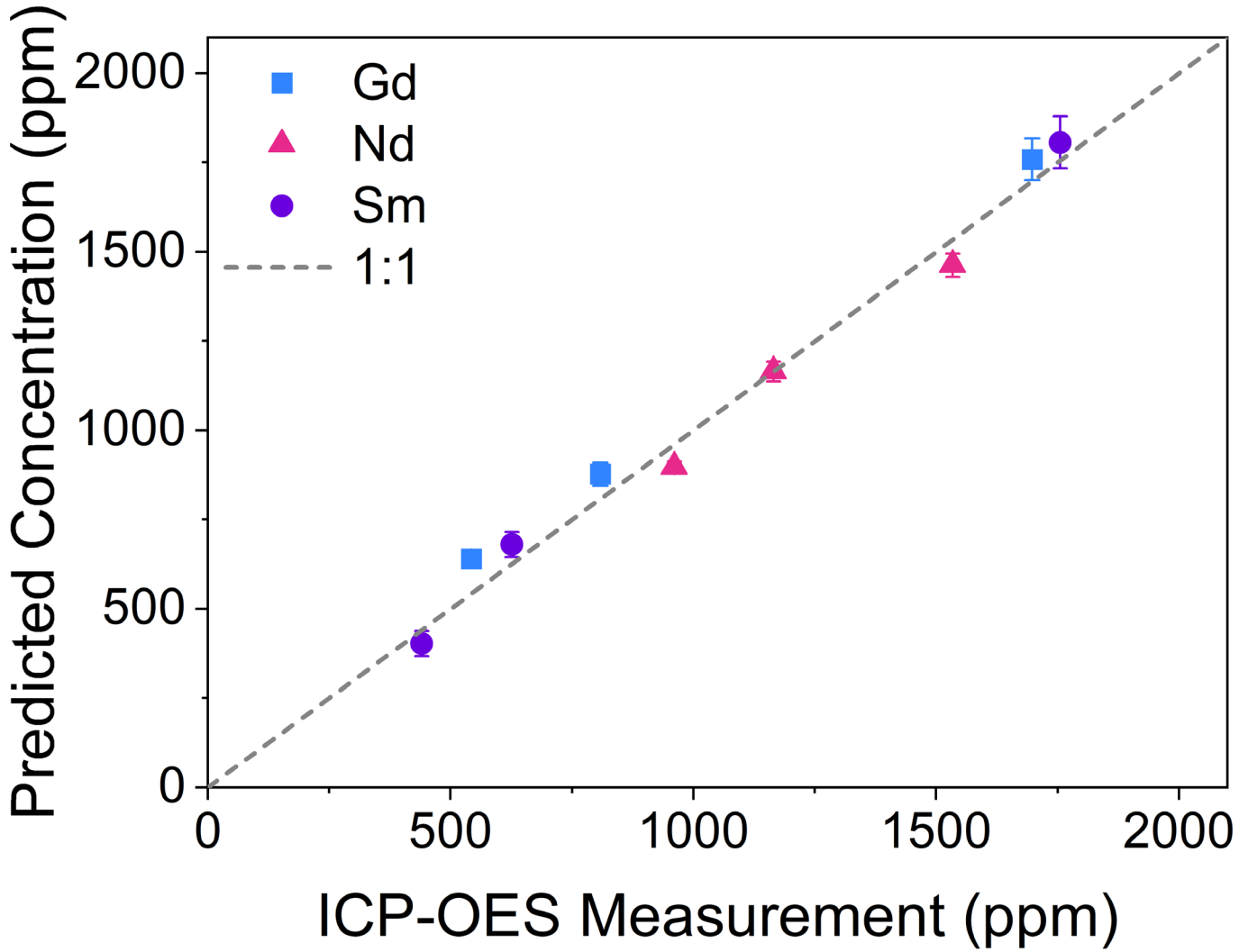
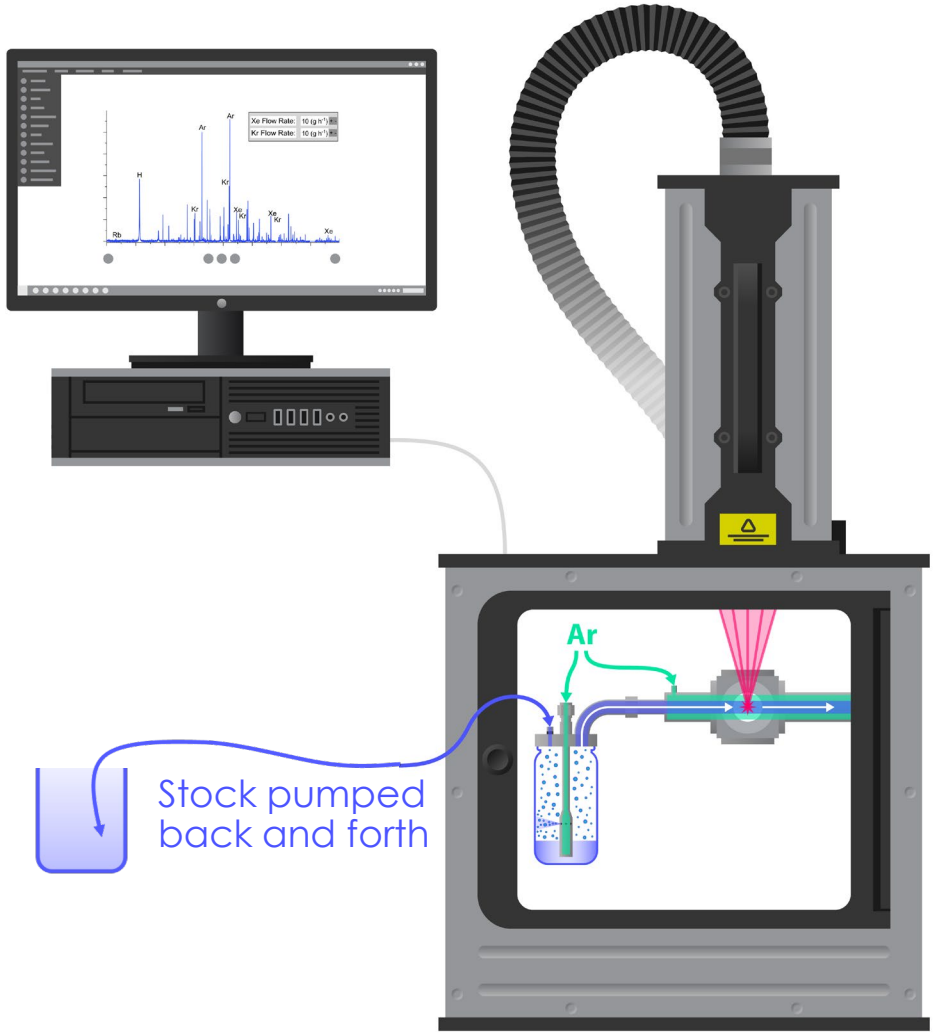
Predicted concentrations of validation samples match ICP-OES measurements

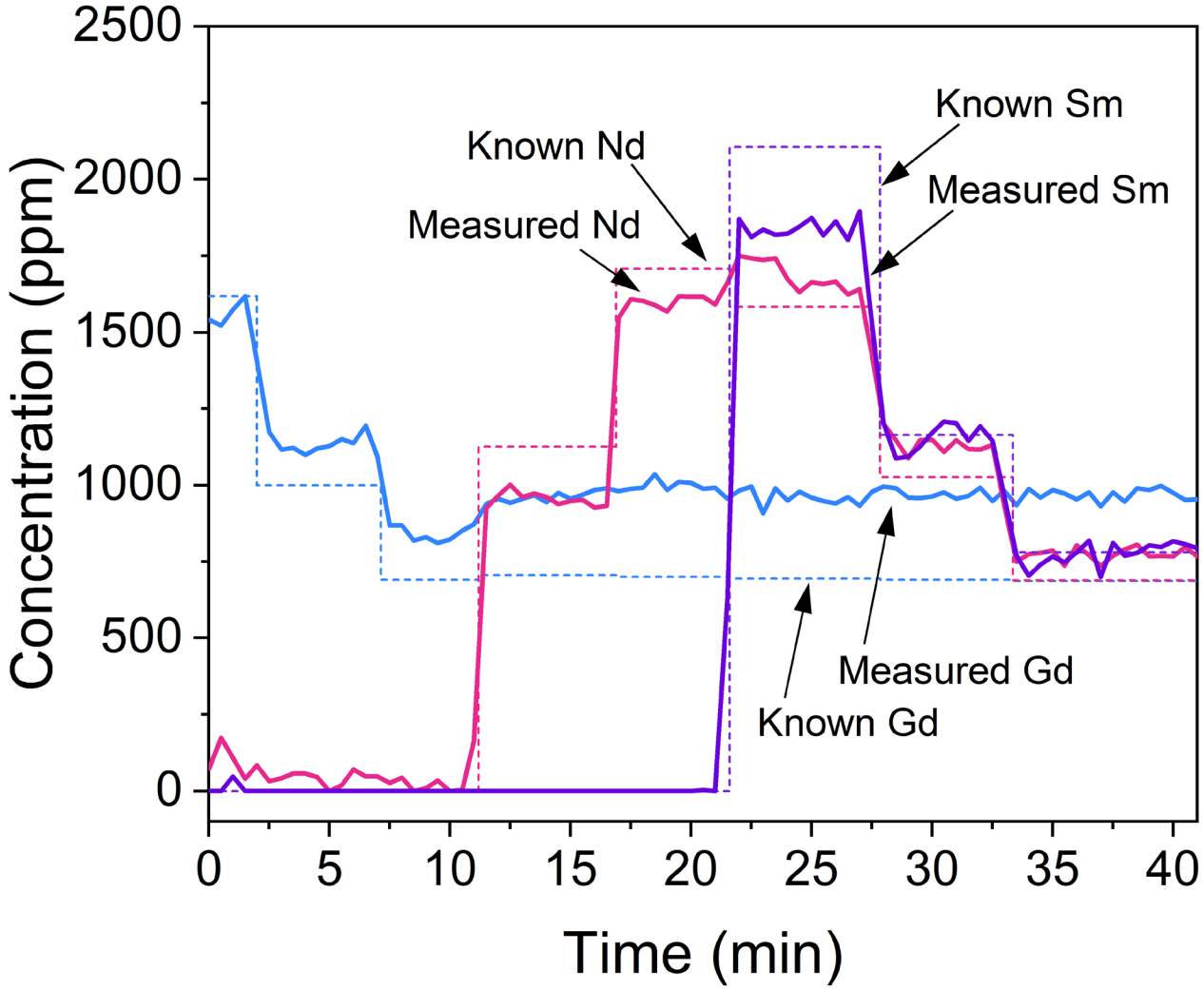


Performing a demonstration to show the measurement system's capability to provide real-time monitoring

- Stock solutions pumped in/out of reservoir to nebulizer to allow real-time changes in concentrations

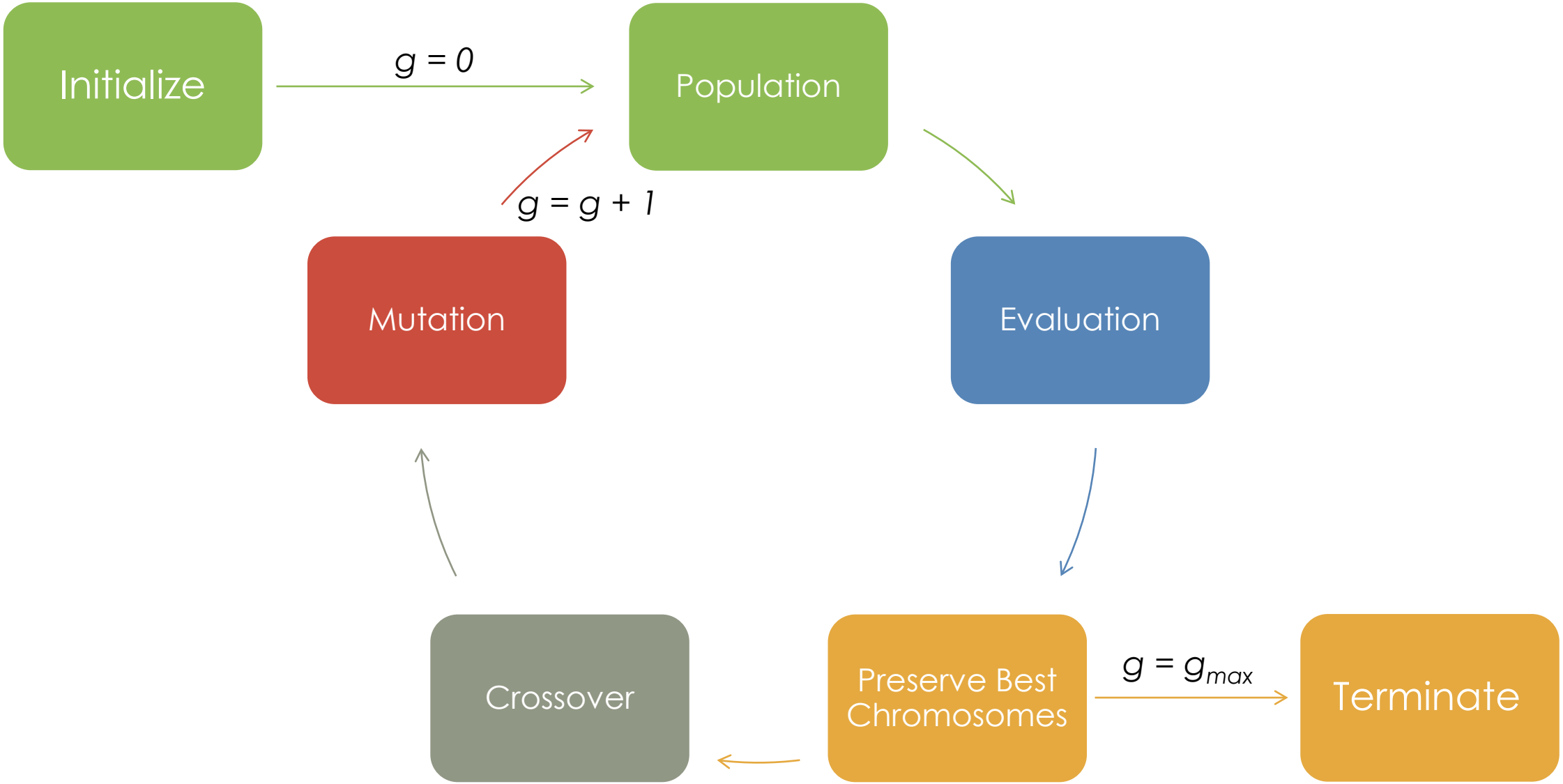


Initial concentration predictions leave room for improvement

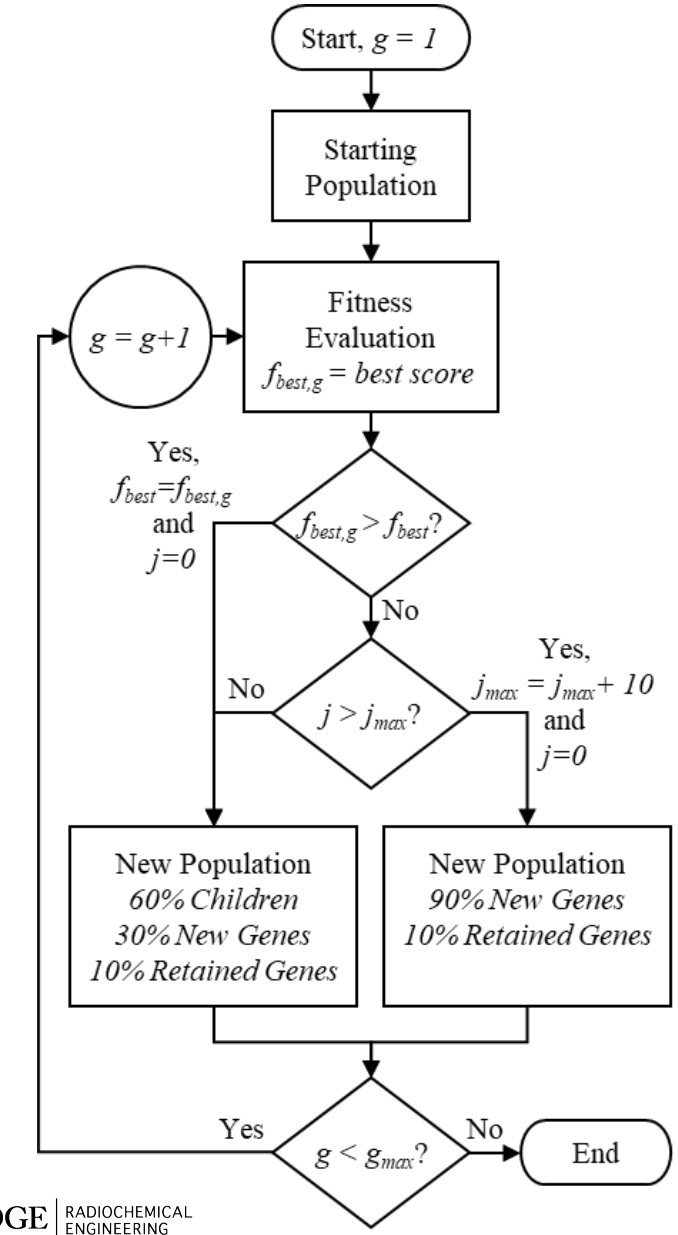


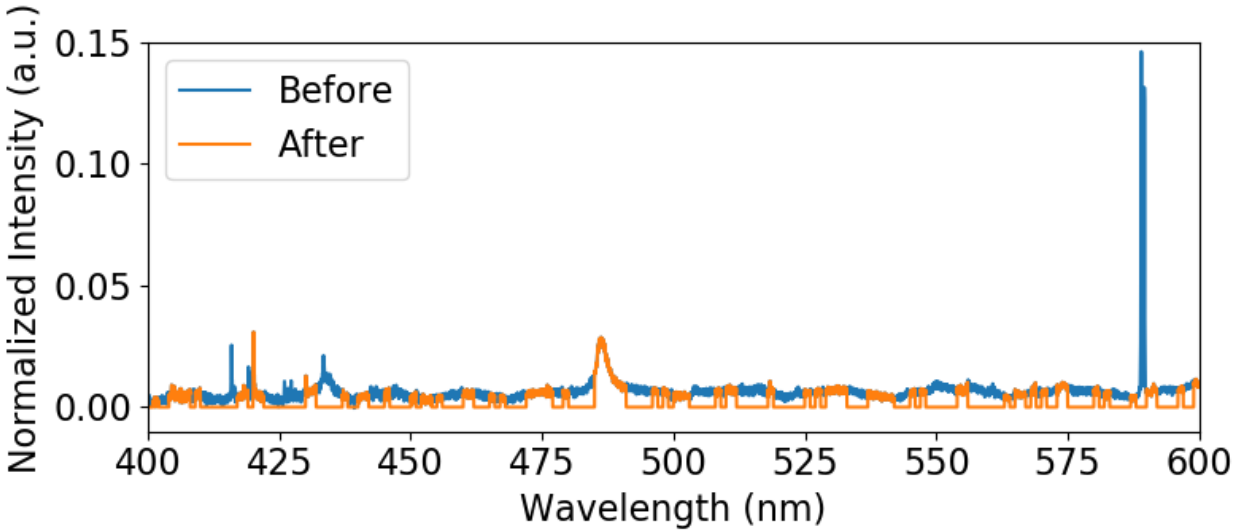
The RMSE values were calculated to be 249, 108, and 99.8 ppm for Gd, Nd, and Sm, respectively.

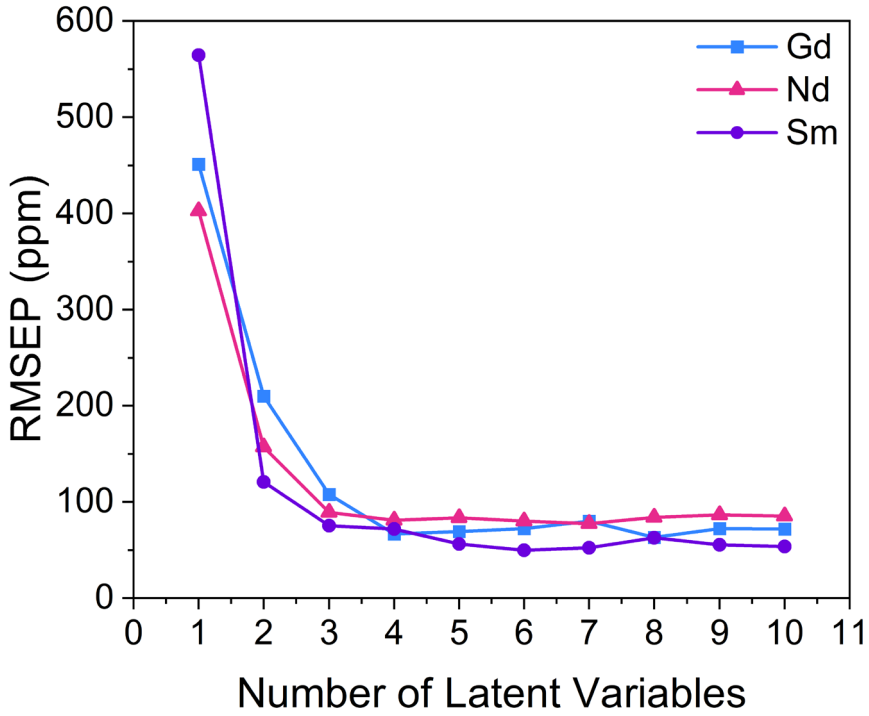
A genetic algorithm is an optimization approach based on Darwin's theory of evolution



A genetic algorithm was used to refine PLS feature selection



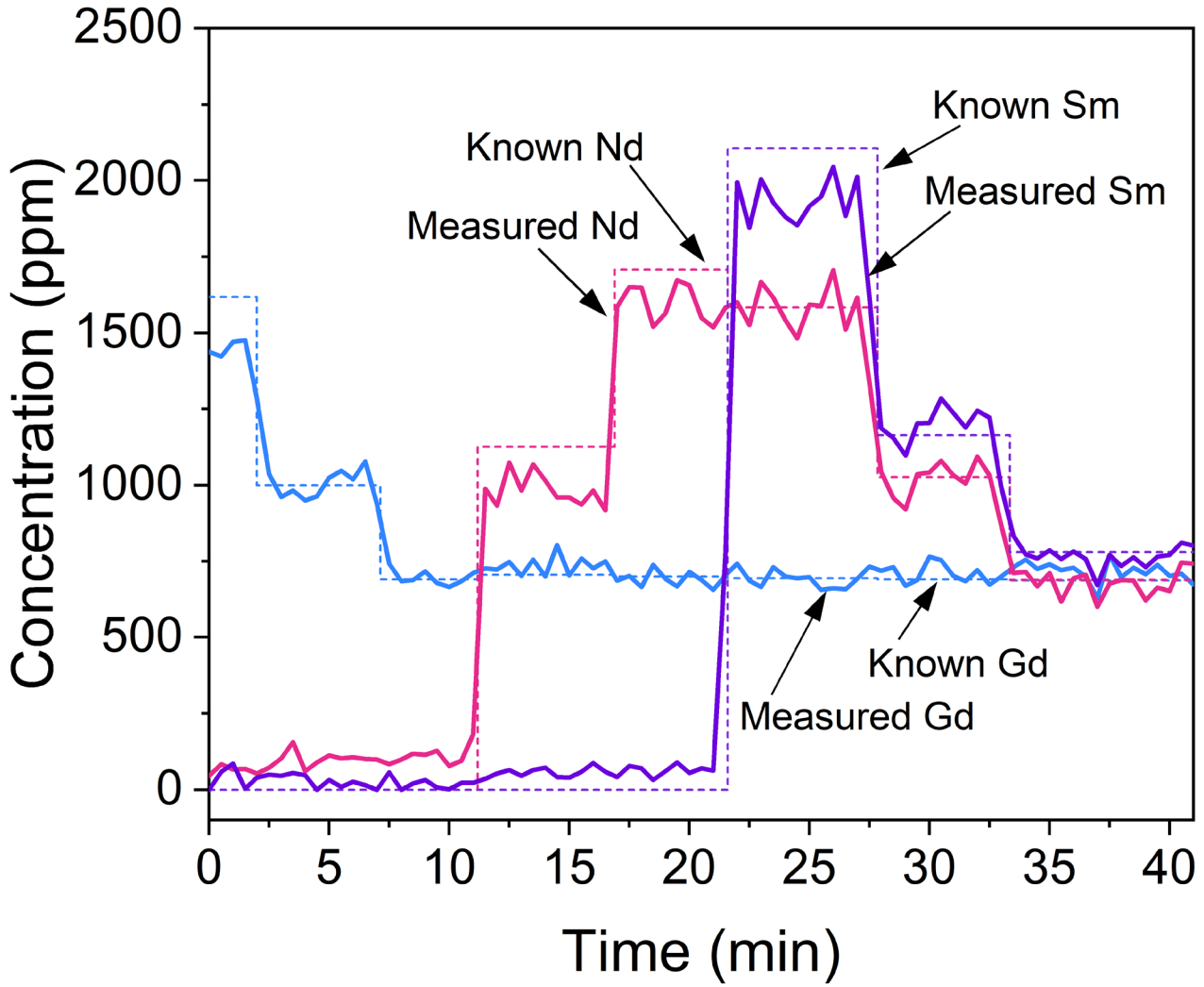




Number of LVs

Gd:	5 →	4
Nd:	6 →	3
Sm:	9 →	3

Genetic algorithm filtered models showed dramatically improved results



This corresponds to a 73, 18, and 25% decrease in RMSE value from the previous model predictions.

The RMSE values were calculated to be 66.5, 89.2, and 75.3 ppm for Gd, Nd, and Sm, respectively.

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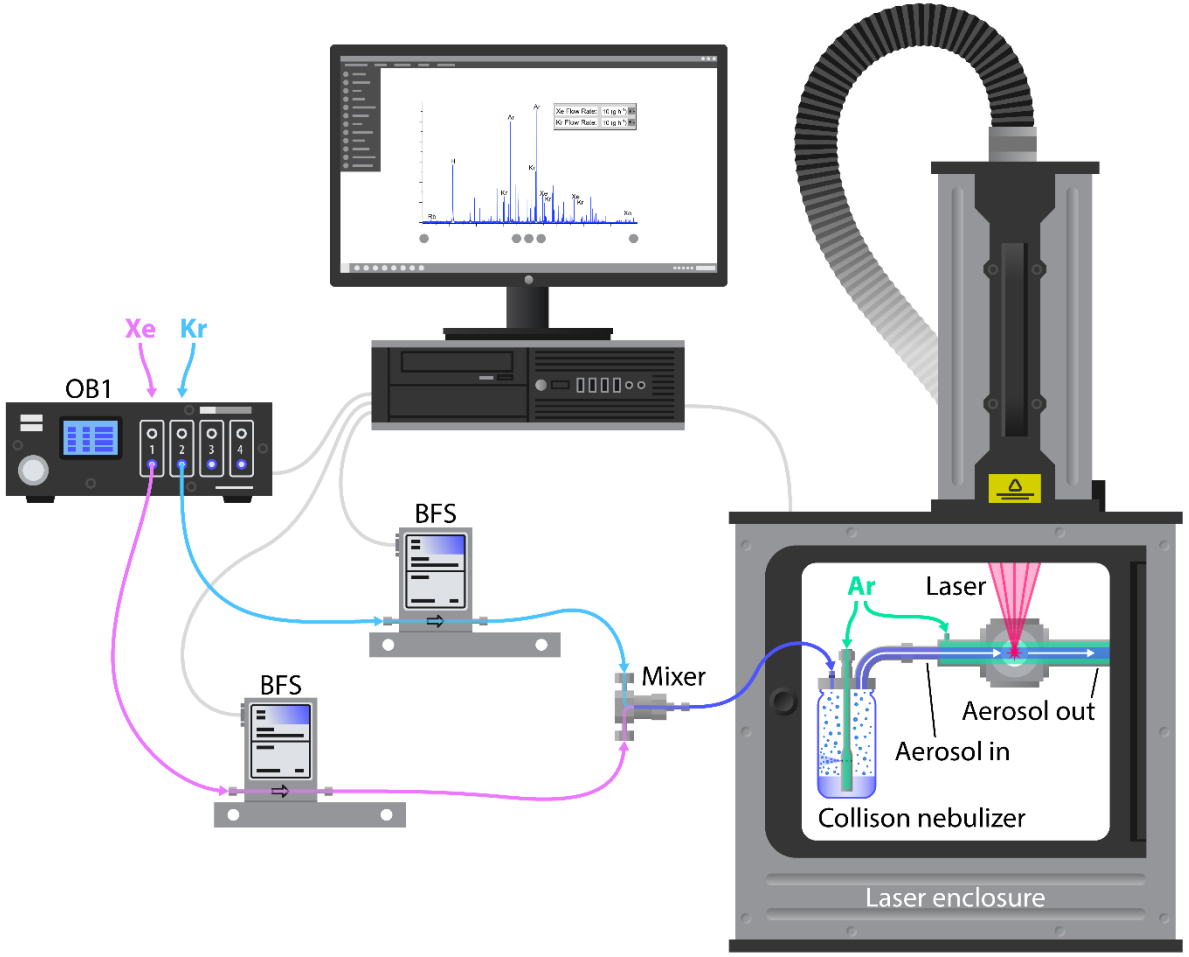
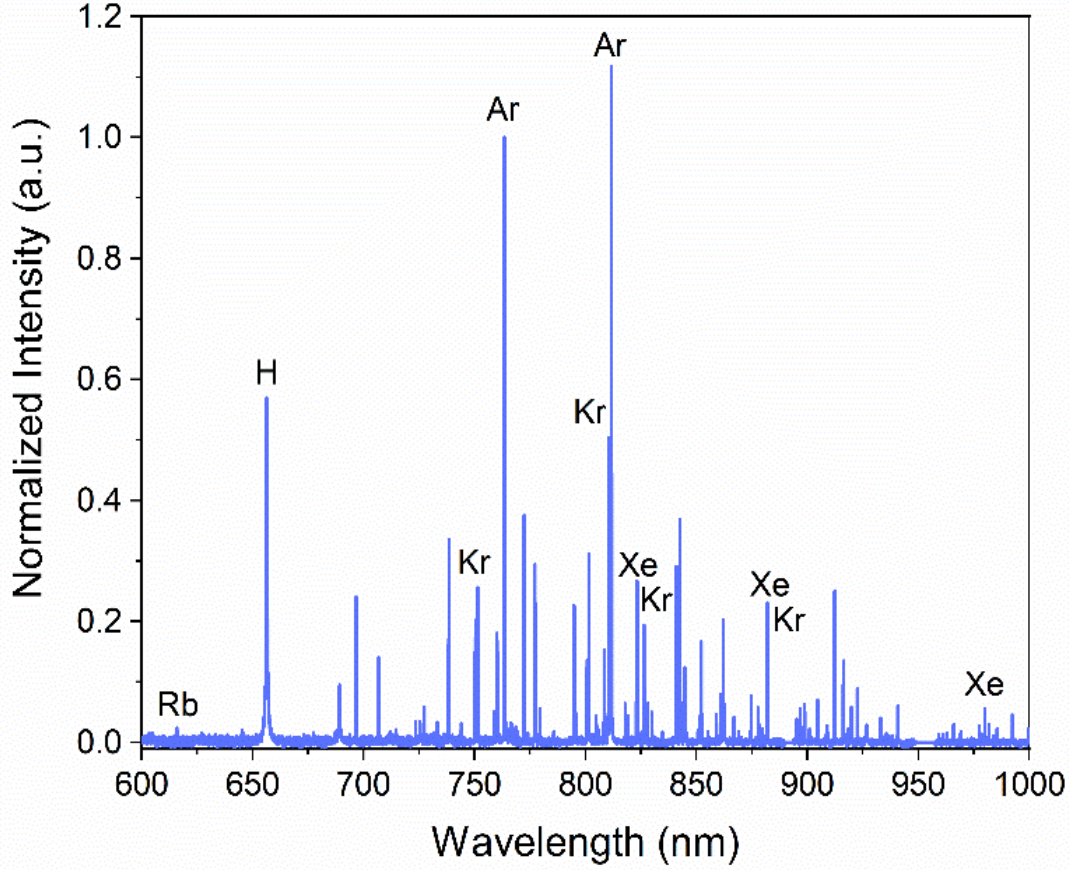
Gaseous monitoring system

- The four representative elements selected were Xe, Kr, Cs, and Rb
  - Xe and Kr are expected to be large contributors to the off-gas loading
    - 0 to 10 g/h
  - Cs and Rb are the corresponding daughters of these gases
    - 0 to 2000 ppm

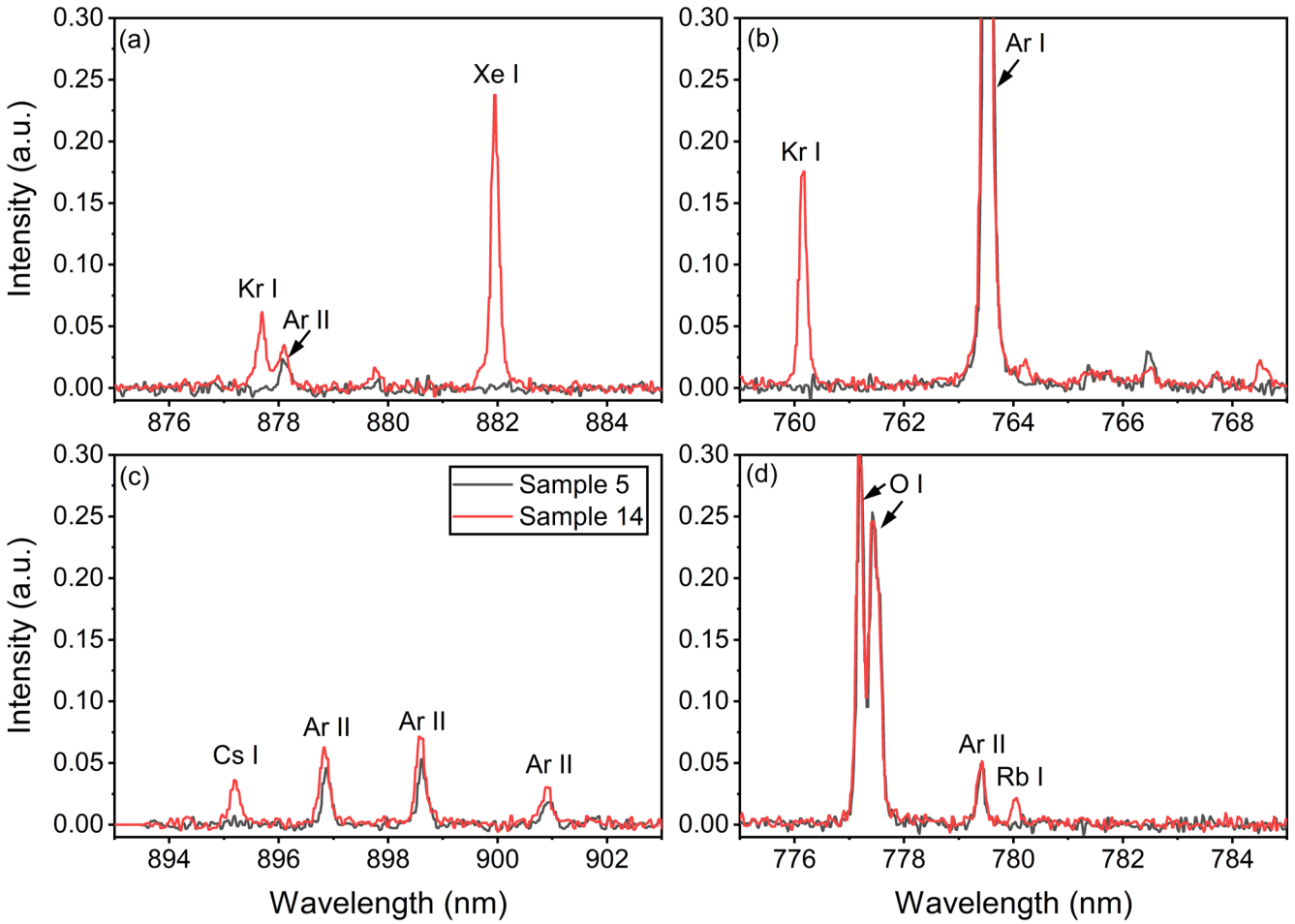
Krypton and xenon showed strong spectral responses





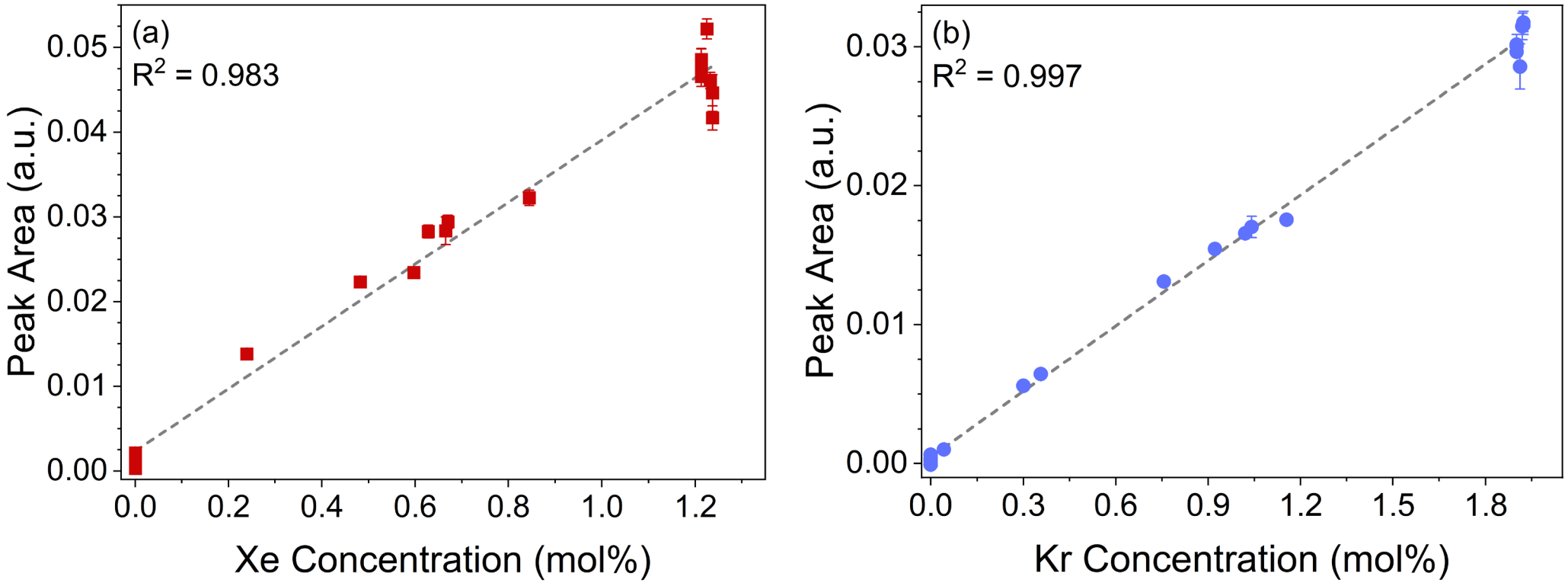
Collected LIBS spectrum of sample 7 containing 1.21 and 1.90 mol% of Xe and Kr and 2000 ppm Rb.

A closer look at collected spectra reveal strong gas peaks



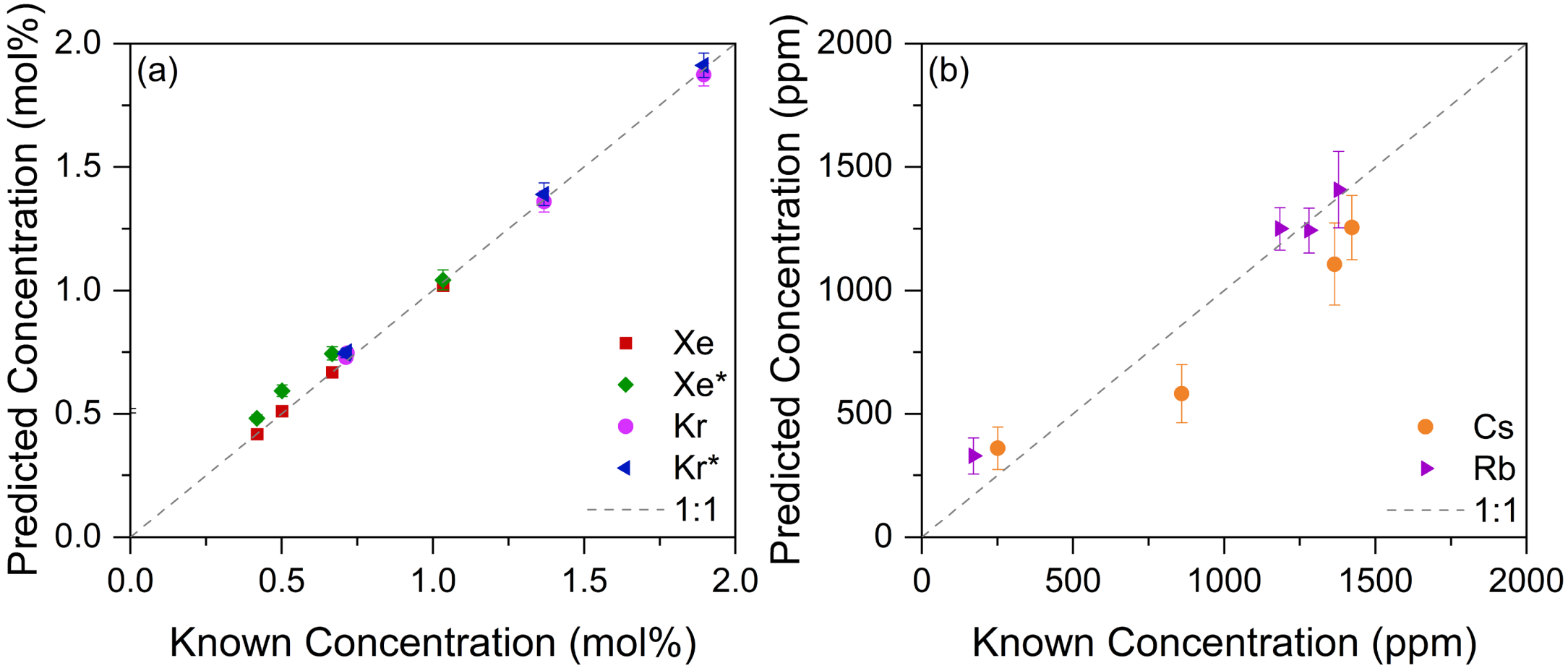
Collected LIBS spectrum of a blank sample (sample 5) and sample 14 containing 1.21 and 1.90 mol% of Xe and Kr and 2000 and 1800.9 ppm of Cs and Rb.

Xe and Kr univariate models were developed



Univariate calibration models, dashed lines, comparing (a) 881.94 nm Xe I peak area and (b) 760.15 nm Kr I peak area response to changes to Xe and Kr mass flow rates, respectively.

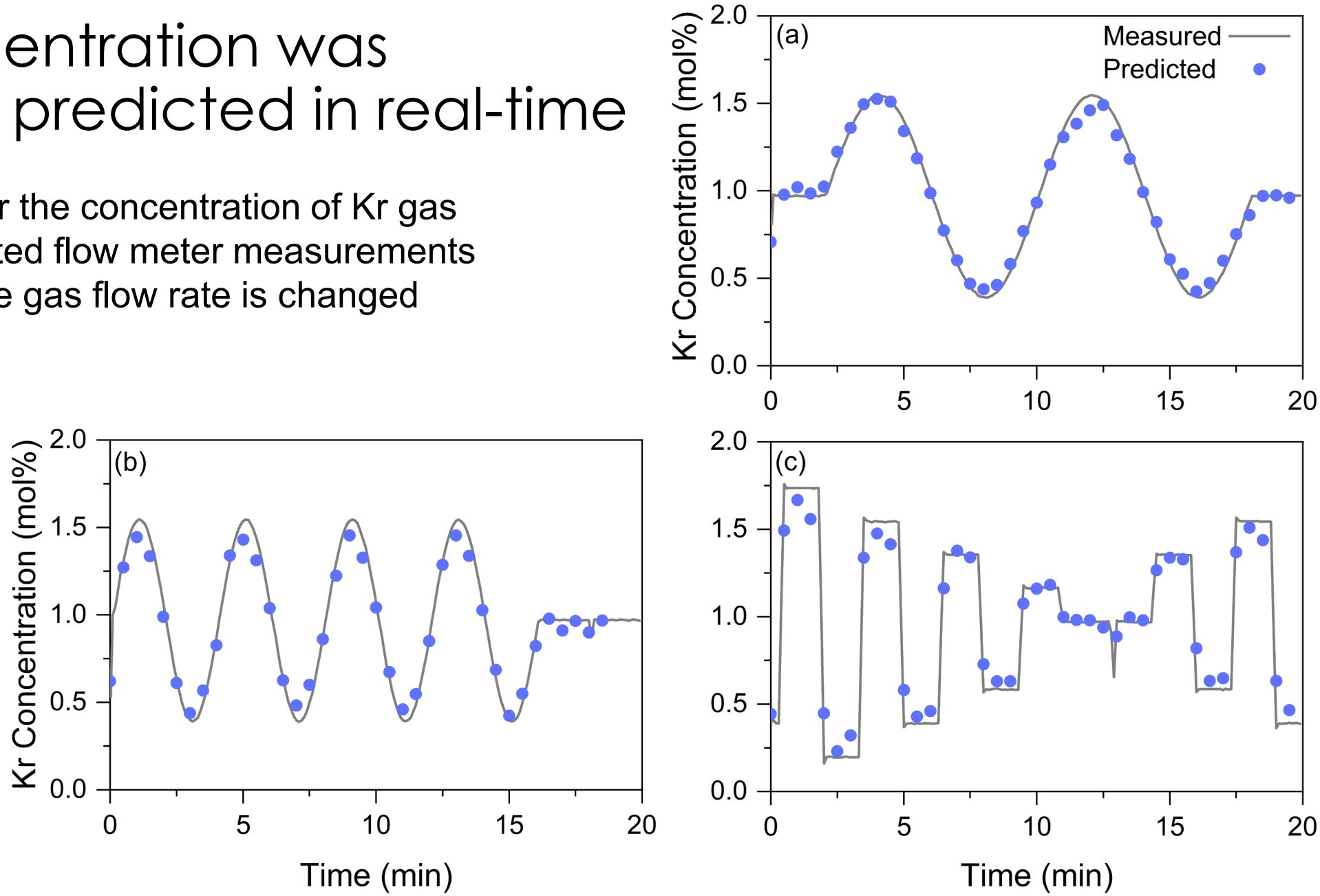
Analytes in test samples were predicted using constructed models



*signifies a univariate regression model

The Kr concentration was successfully predicted in real-time

Model predictions for the concentration of Kr gas compared to converted flow meter measurements in systems where the gas flow rate is changed

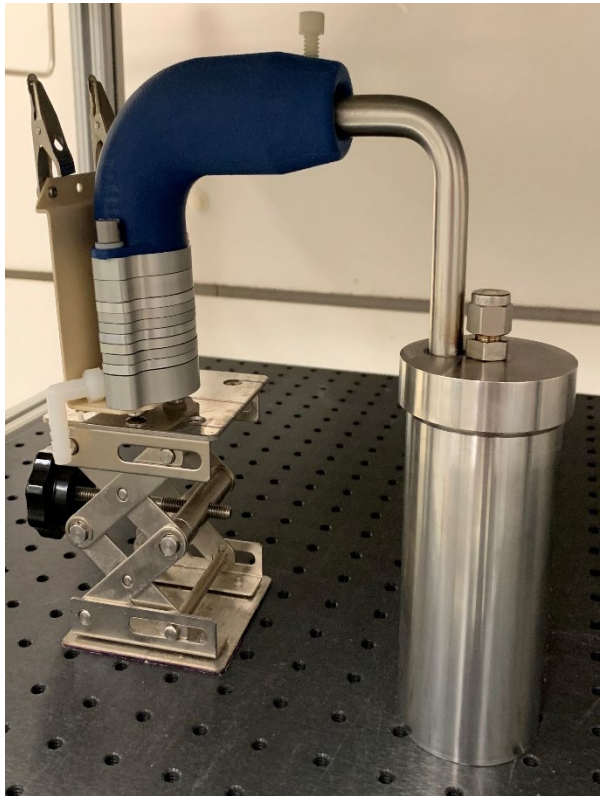


In summary, we have demonstrated a LIBS capability for monitoring aerosols and gases.

- Our sheathed gas measuring system allows effective measurement of the sample stream while protecting optical components
- Multiple elements were simultaneously quantified in the two studies discussed
- A genetic algorithm was used to refine a quantitative model
- Both gases and aerosols were able to be monitored in real-time

Where is this project headed next?

- Future work involves completion of a molten salt aerosol test stand and integrating LIBS sensors with off-gas treatment systems.



Acknowledgments

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Structural Materials	Bruce Pint, Jim Keiser
Graphite	Nidia Gallego
Advanced Material Development	Sam Sham
Waste forms	Brian Riley
Salt Spill	Sara Thomas, Bill Ebert

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Questions?

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