

Spectroscopic Evaluation of Iodine Radiolysis with Exposure to a ^{60}Co Source

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Introduction

- The sensitivity of lab-accessible spectroscopies to changes in iodine speciation during irradiation and/or acidification was determined.
- Standard solutions of dissolved I^- , IO_3^- , and IO_4^- were used to calibrate and define detection limits for multiple spectroscopies.
- Spectroscopies included UV-Vis, FTIR, ^{127}I NMR, and Raman spectroscopy.
- Interpretation of spectroscopic results was aided through synchronous autocorrelation spectra from 2D correlations analyses.

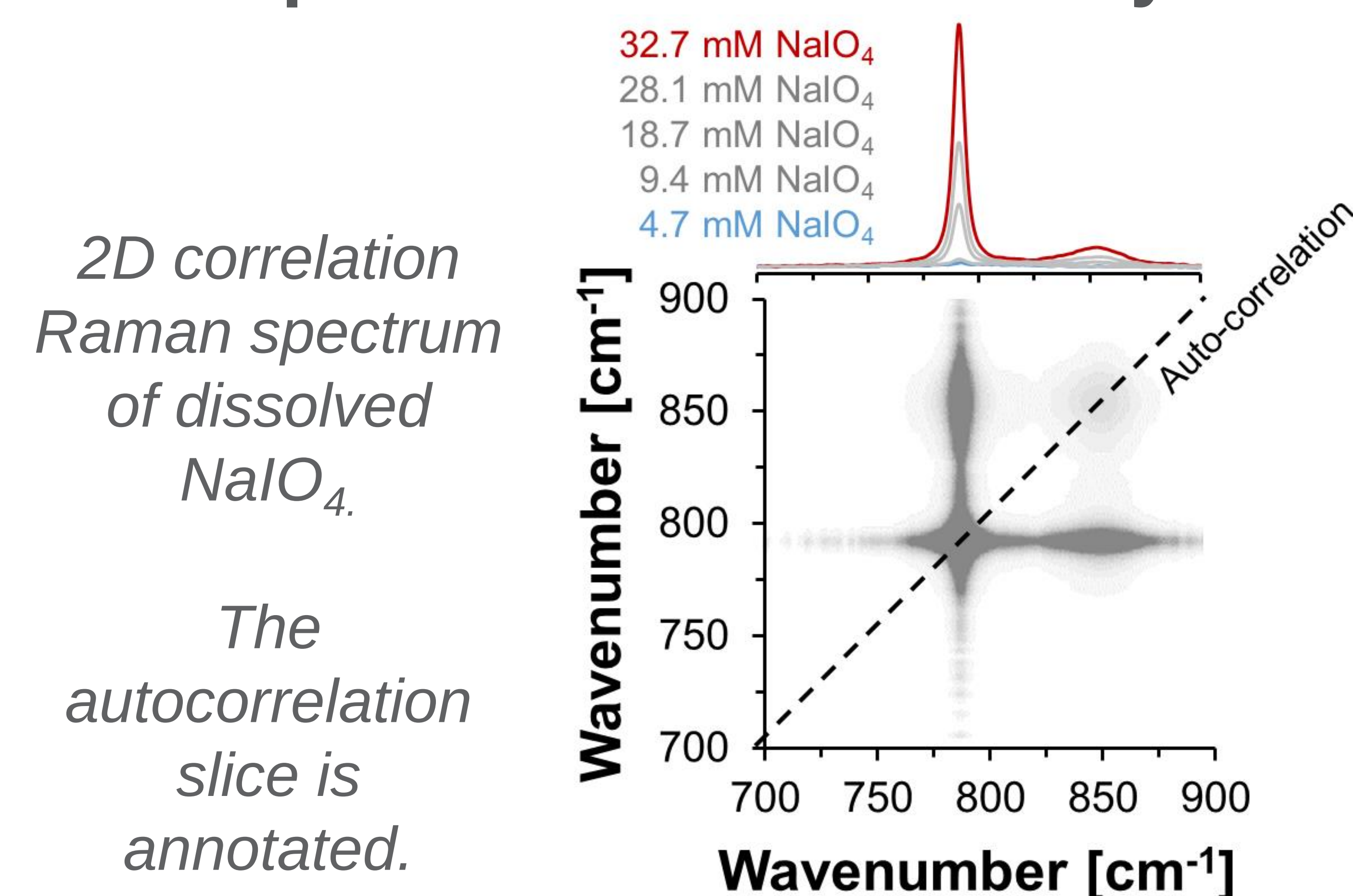
Radiolysis Methodology

- NaI solutions were irradiated using the Radiological Exposures and Metrology (REM) Laboratory at PNNL with an 11000 Ci ^{60}Co source.

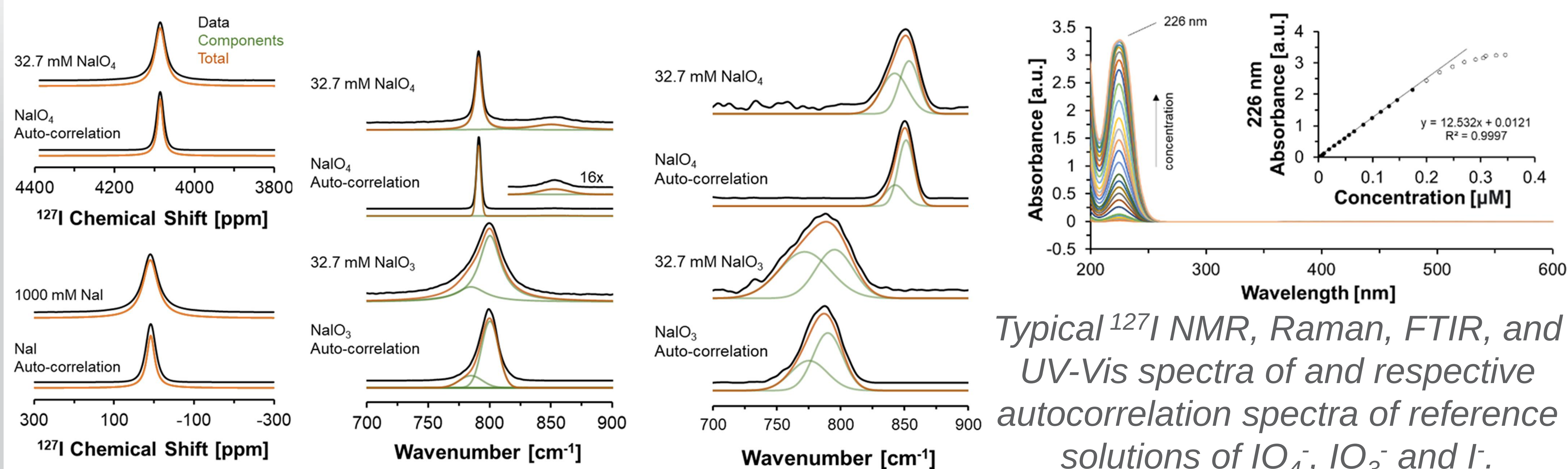


Solutions of dissolved sodium iodide immediately prior to irradiation

Example 2D Correlation Analysis



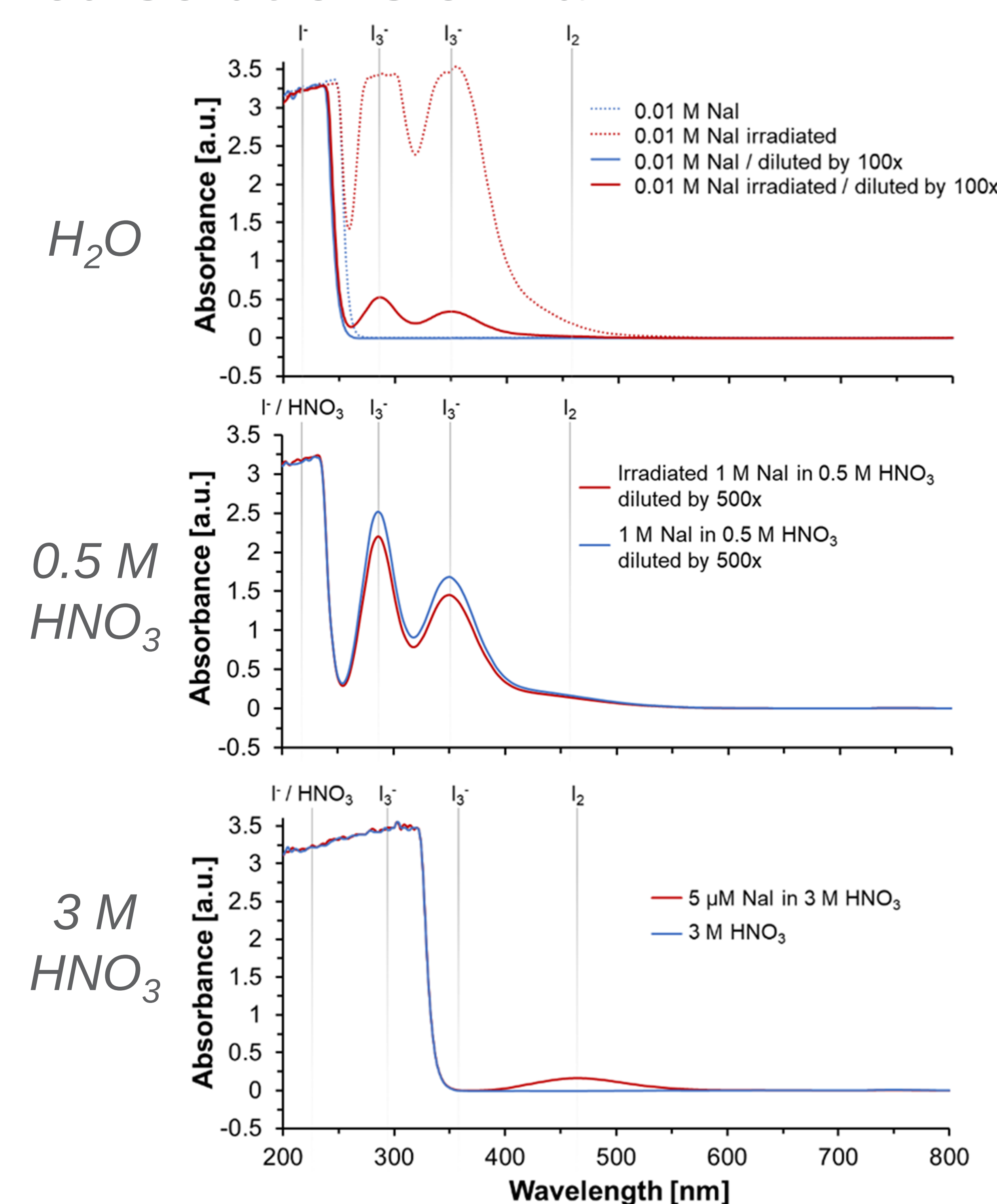
Spectroscopy of standard solutions demonstrate the disparate sensitivities of the spectroscopies to solution forms of iodine



Typical ^{127}I NMR, Raman, FTIR, and UV-Vis spectra of and respective autocorrelation spectra of reference solutions of IO_4^- , IO_3^- and I^- .

UV-Vis spectroscopy probed the formation of I_2 and I_3^- in irradiated and/or acidified solutions of NaI

- In the absence of HNO_3 , irradiation induces a transformation from I^- to I_3^- . Little to no I_2 is apparent.
- At concentrations of 0.5 M HNO_3 , the formation of I_3^- is favored independent of whether the samples are irradiated or not. A small fraction of I_2 is evident.
- At concentrations of 3 M HNO_3 , the formation of I_2 is favored. Work is ongoing to extend the radiolysis studies to 3 M HNO_3 .
- Note that because the formation of I_3^- is three-fold dependent on the concentration of the total iodine.
- Therefore, whether I_3^- or I_2 is the dominant species likely depends on both the concentration of HNO_3 and the initial concentration of I^- .



Conclusions

- Multimodal spectroscopic data on several forms of iodine indicates that the spectroscopies are disparately sensitive to iodine speciation.
- Of the spectroscopies, UV-Vis spectroscopy should be considered the principal method of discriminating irradiation and acidification-induced changes in I^- transformation into I_2 or I_3^- .

Acknowledgements

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- Spectroscopies were performed using facilities at the Environmental Molecular Science Laboratory (EMSL, grid.436923.9), a DOE Office of Science User Facility sponsored by the Office of Biological and Environmental Research at Pacific Northwest National Laboratory (PNNL) operated for DOE by Battelle Memorial Institute operating under Contract No. DE AC05-76RL0-1830.

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Introduction

The National Nuclear Security Administration's (NNSA) Office of Conversion (NA-231) has been aiding, in part through the National Lab System, molybdenum-99 (^{99}Mo) producers to convert their fuel from highly enriched uranium (HEU) to low enriched uranium (LEU) targets and encouraging domestic production. Pacific Northwest National Laboratory (PNNL) has been supporting these efforts through two activities: (1) emissions abatement for radioxenon and (2) iodine chemistry to improve capture of radioiodine. This support includes modeling traditional carbon delay beds, developing prototypes of cooled abatement traps, optimizing iodine capture techniques, characterizing iodine speciation under different radiochemical processing conditions and finally integrating the radioxenon and radioiodine capture efforts to best minimize emissions.

Modeling Carbon Delay Beds

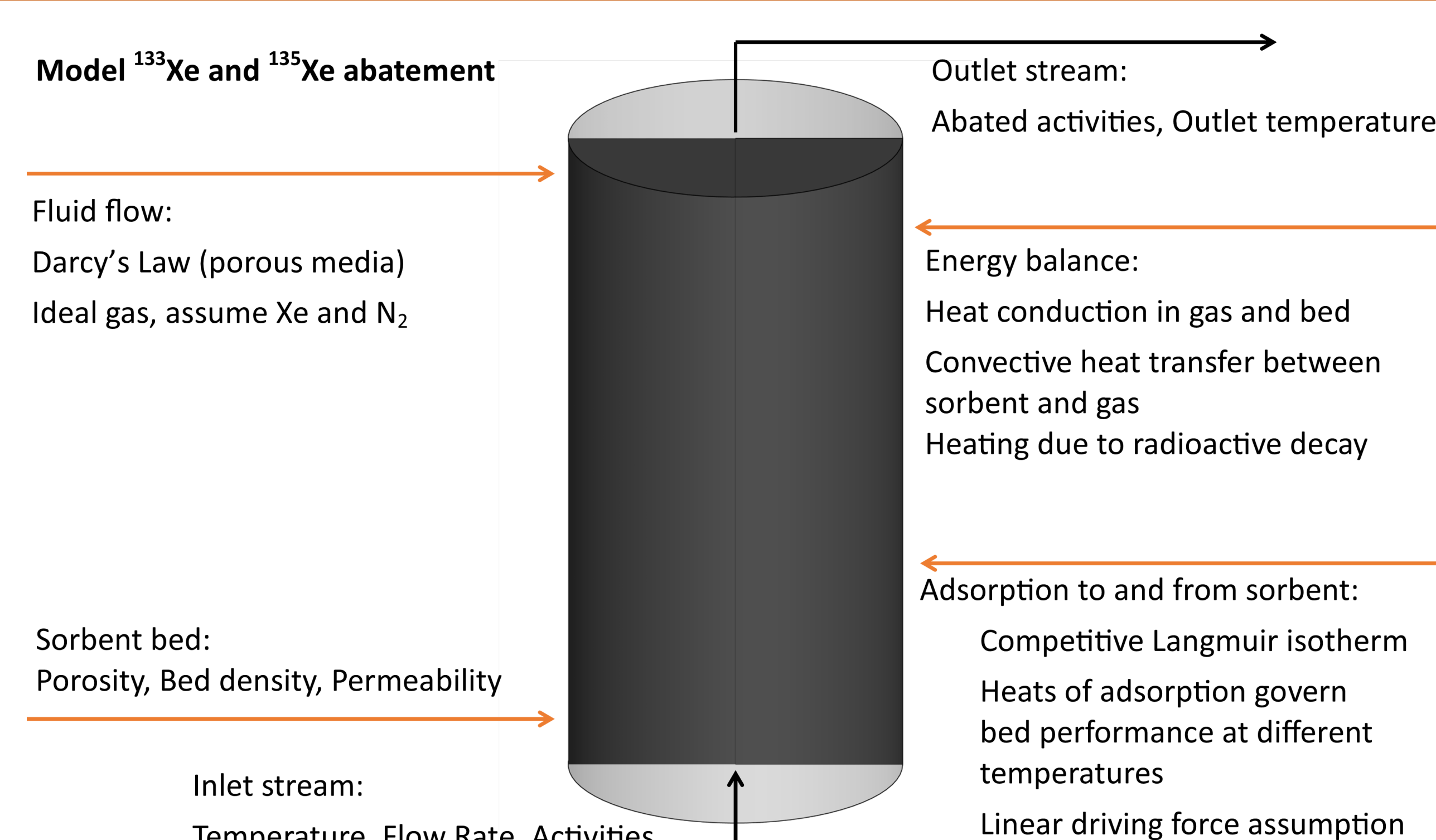


Figure 1. Graphical representation of Xe abatement bed model

Xenon Abatement

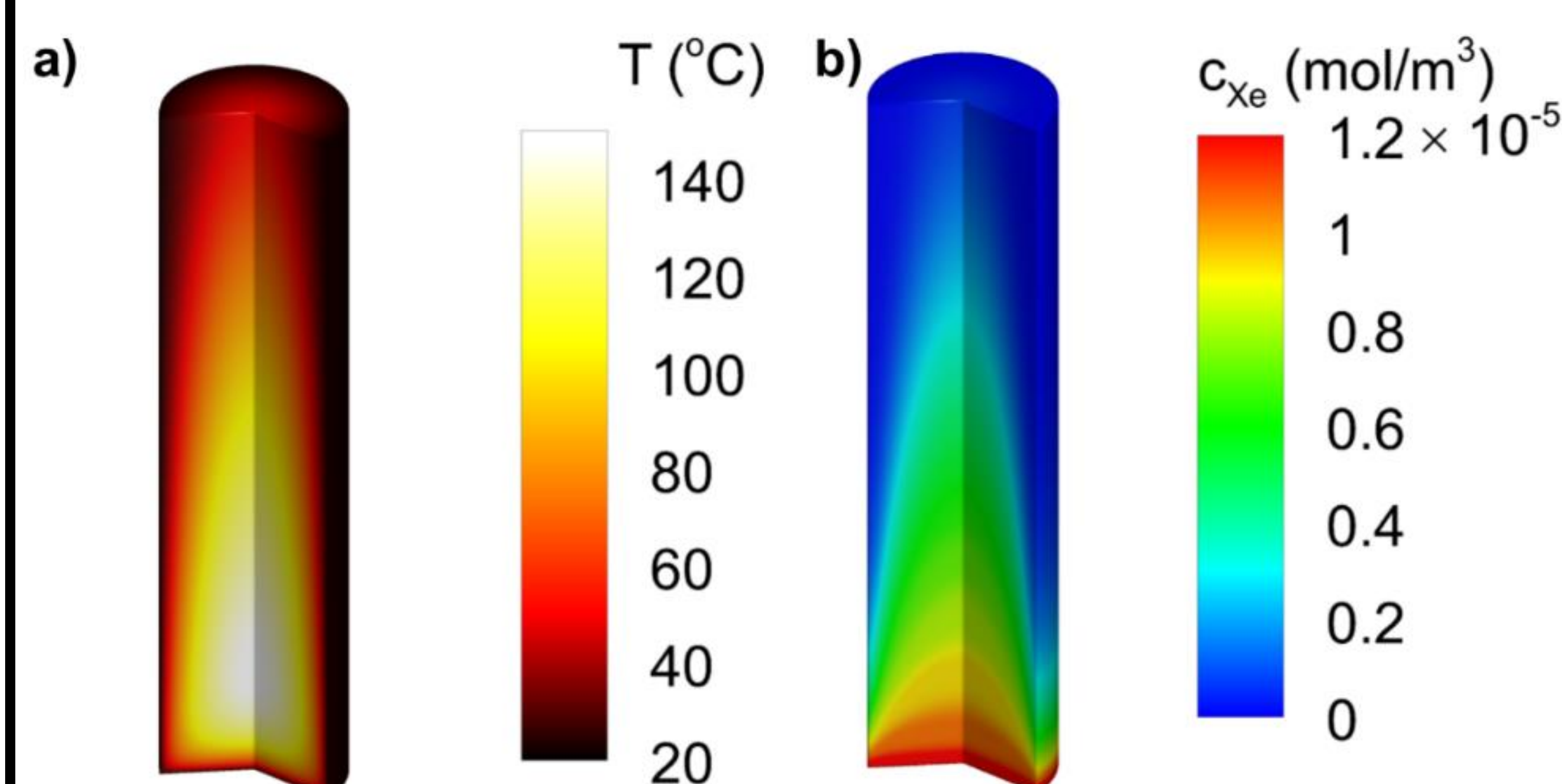


Figure 2. Example of a modeled carbon delay bed showing (a) temperature and (b) xenon concentration



Figure 3. Prototype LN cooled abatement trap

Digestion Studies

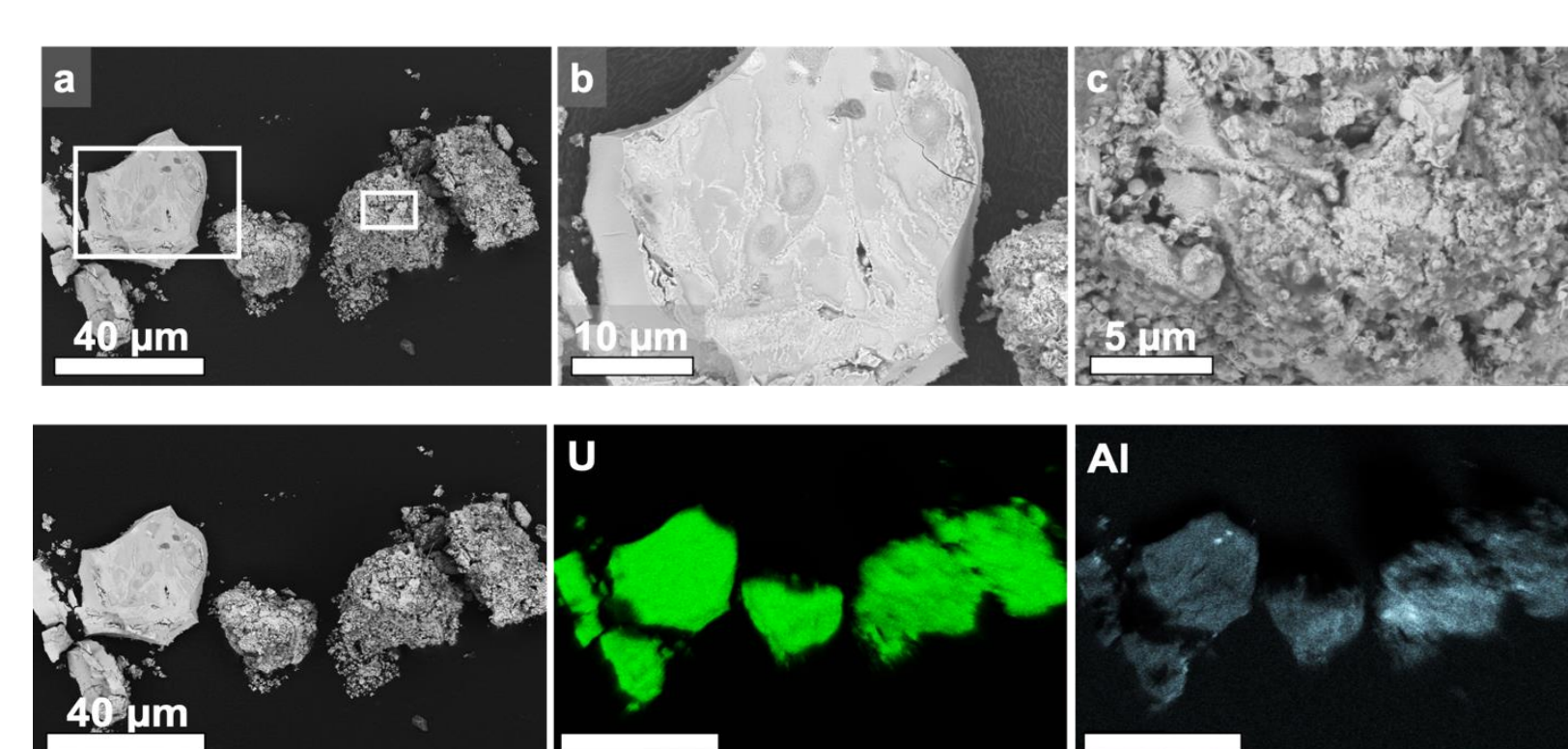


Figure 4. BSE images showing morphological features of an area of a sample (top row). BSE image and elemental X-ray maps for U and Al in an area of the sample (bottom row)

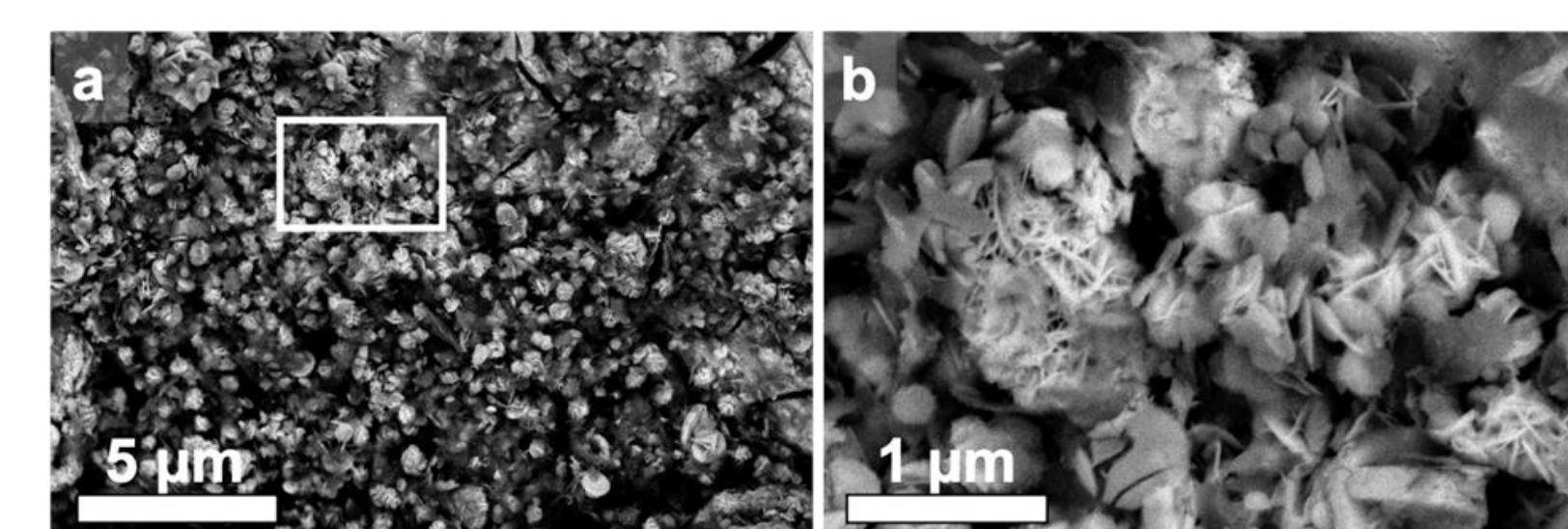


Figure 5. Area showing higher magnification images of areas of a sample. The square in image "a" is shown in further higher magnification in image "b"

Integrating Iodine Capture and Xenon Abatement

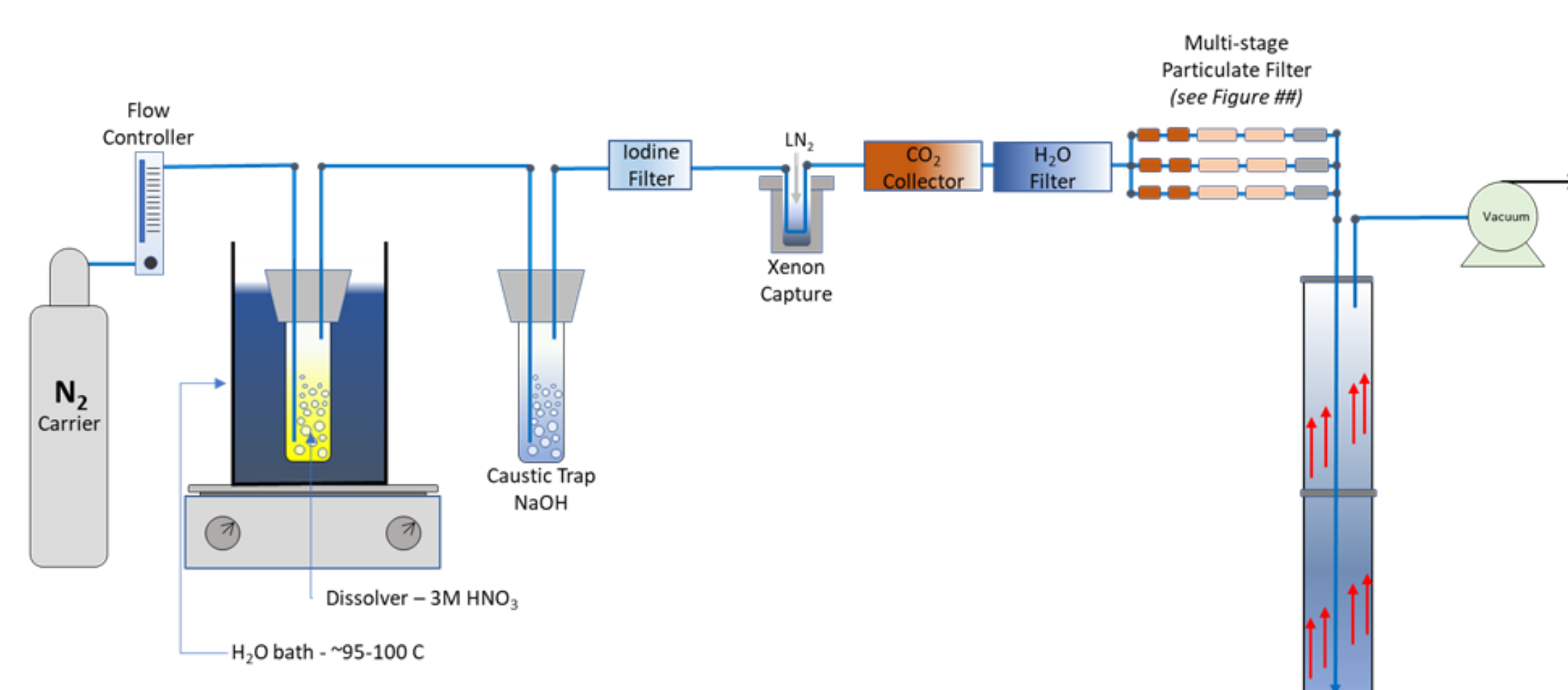


Figure 12. Experimental setup of an integrated iodine capture and xenon abatement system

Iodine Capture Modeling

Staged approach to iodine capture modeling:

- 1. Thermodynamic Equilibrium**
Used PHREEQC¹ to compute multiphase equilibrium (solid-liquid or gas-liquid) where the non-aqueous species (e.g., $\text{I}_2(\text{s})$, $\text{I}_2(\text{g})$, $\text{HI}(\text{g})$) are equilibrated using solubility product (solid-liquid) or Henry's law (gas-liquid) relationships
- 2. Quasi-Transient**
First approximation to a kinetic description using a time-dependent process model, assuming the solution and gas reach equilibrium at each step
- 3. Kinetic Model**
Currently adapting Wren and Ball² model to account for expected conditions

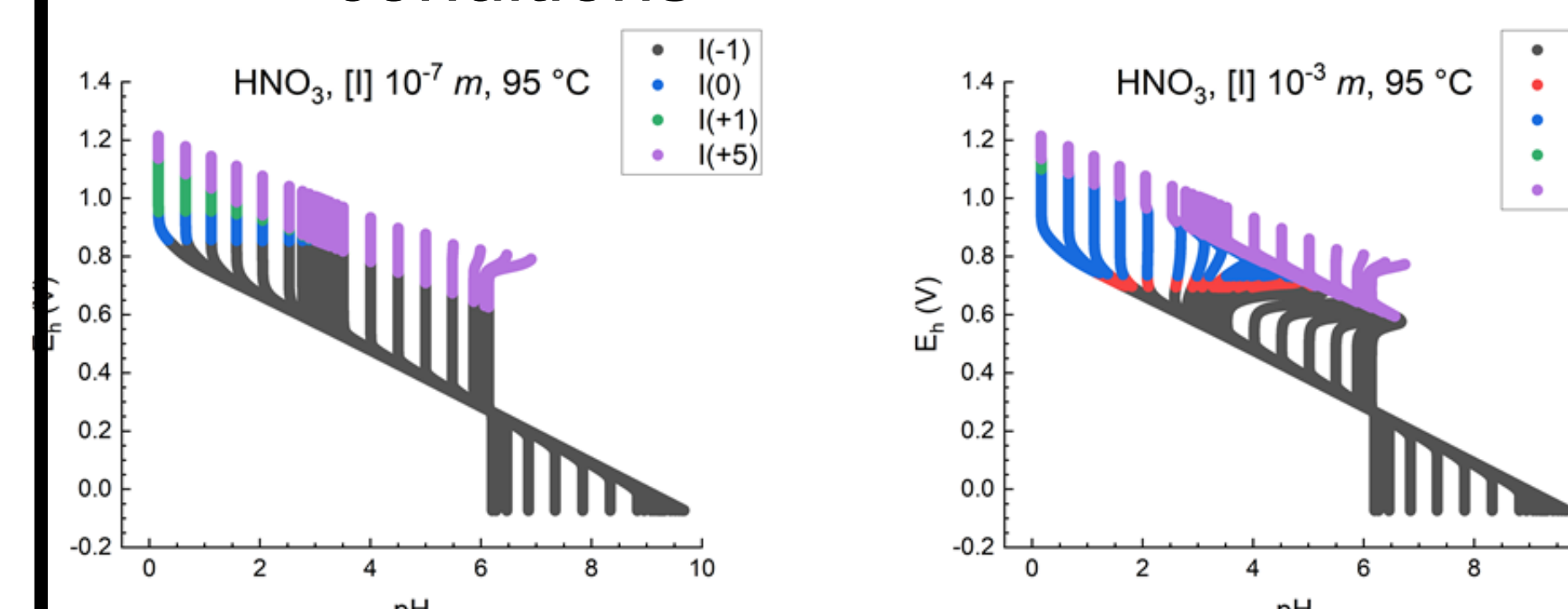


Figure 6. Pourbaix diagrams 95°C for 1×10^{-7} m (left) and 1×10^{-3} m (right) iodide in HNO_3 (Equilibrium Model)

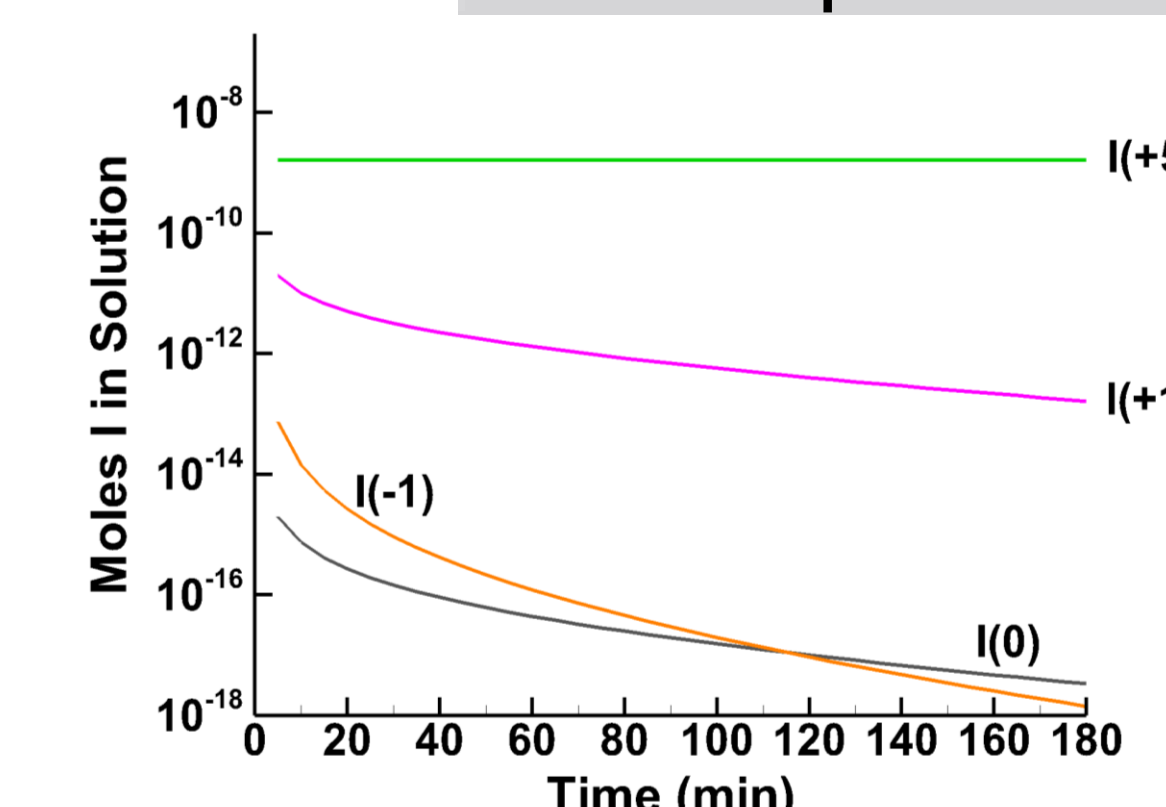


Figure 7. Moles of iodine by oxidation state as a function of time in the quasi-transient simulation. Solution starts with 1×10^{-9} moles of iodine (1×10^{-7} m concentration)

Speciation of Iodine under Irradiation



Figure 8. PNNL ^{60}Co gamma irradiation system.

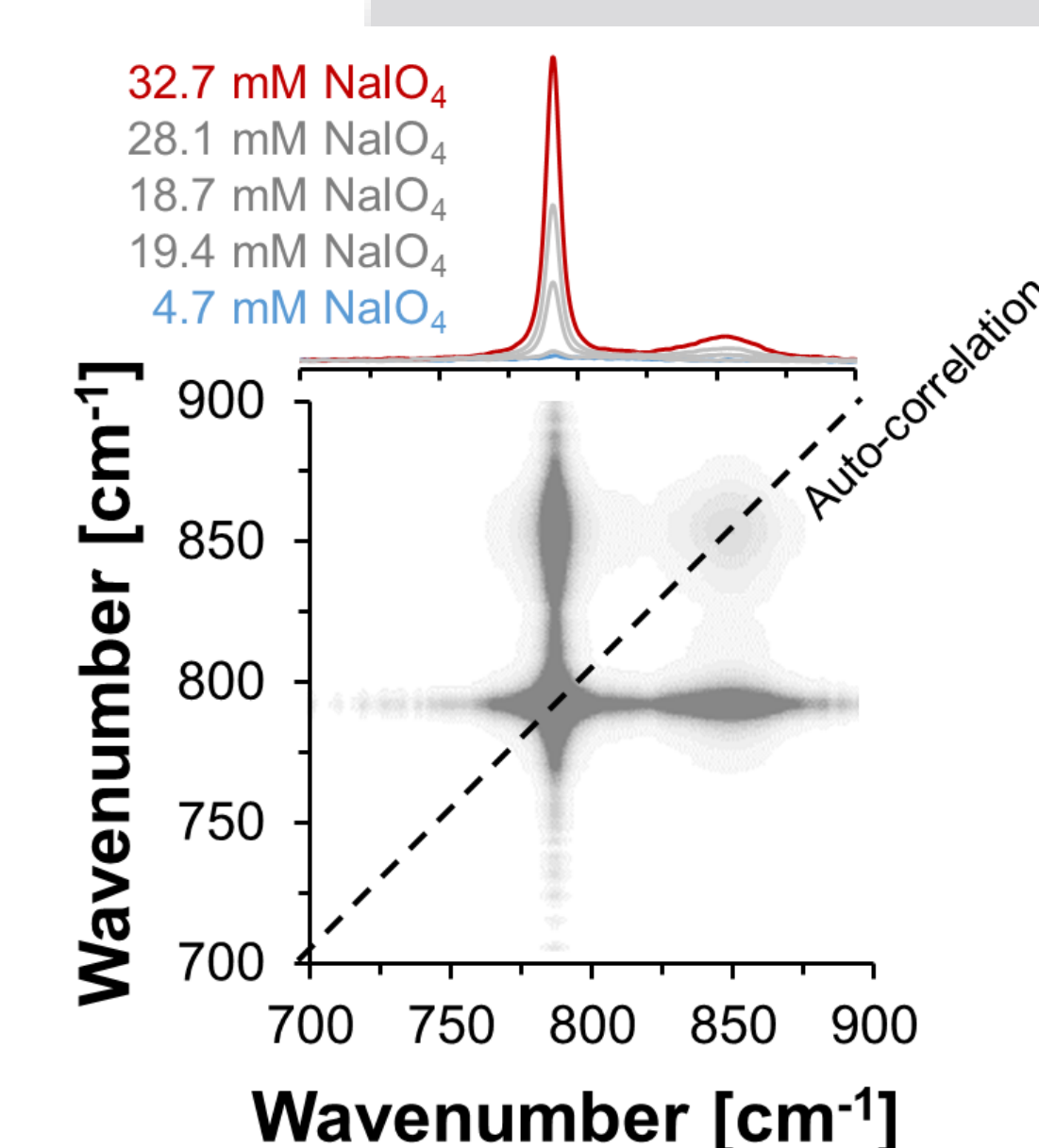


Figure 9. Spectroscopic measurements of iodine species 2D correlation Raman spectrum of dissolved NaIO_4 .

Improving Iodine Capture Models

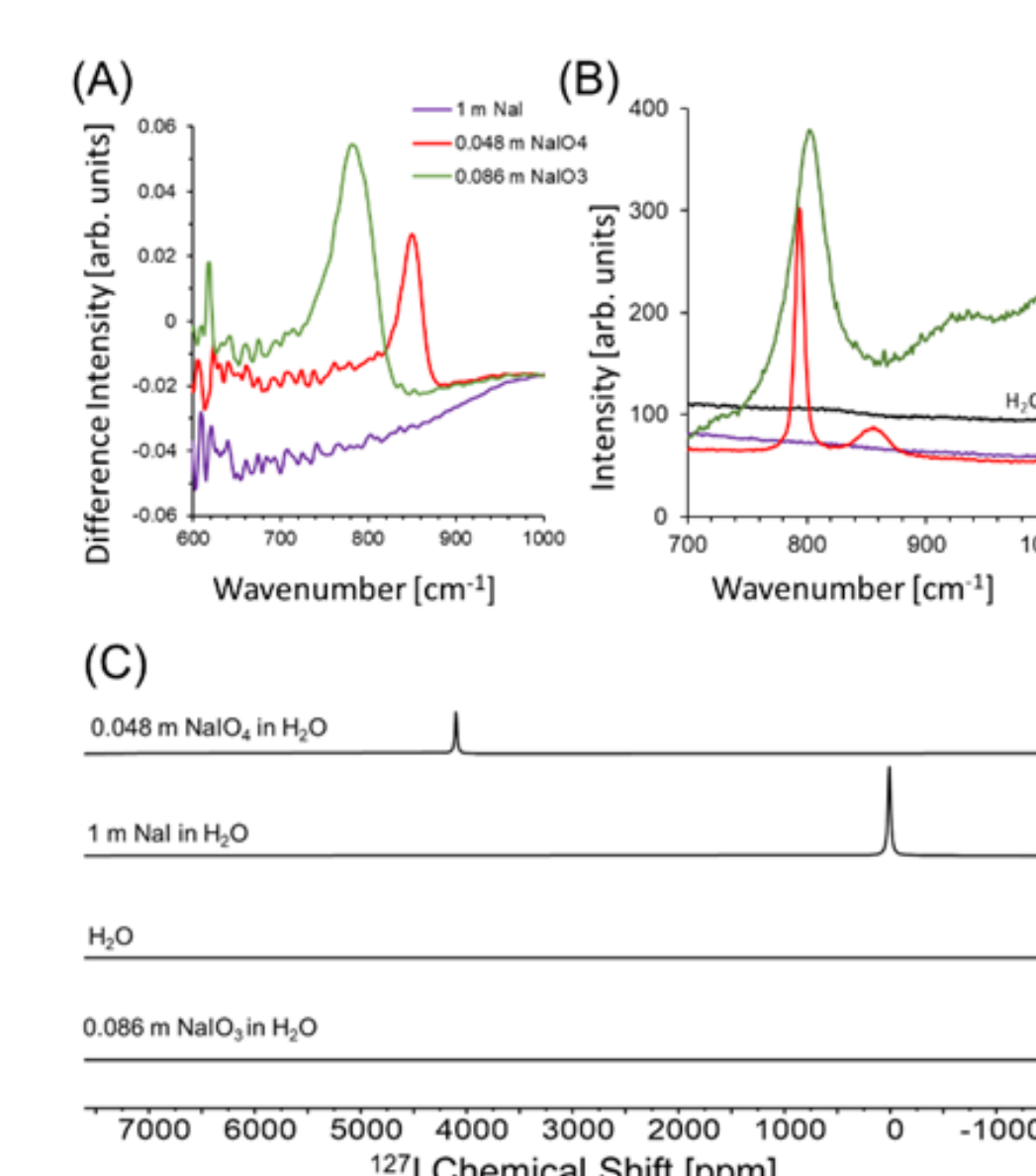


Figure 10. (A) Difference-FTIR spectra (B) Raman spectra, and (C) ^{127}I NMR spectra of the references



Figure 11. Apparatus to collect thermodynamic data at elevated temperatures

Additional staff contributed to this work: Allen, C.J.; Burnett, R.; Graham, T.R.; Munley, W.O.; RisenHuber, M.A.; Soderquist, C.Z.; Thallapally, P.K.; Wittman, R.S

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