

Integrated Fuel Cycle Solutions

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Greg Holmbeck	Electrochemical Manipulation and Radiolytic Evaluation of Organic Phase Neptunium
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Steven Herrmann	Impurity Removal from Molten Salt Systems via High-speed Rotating Disc Collection Electrode

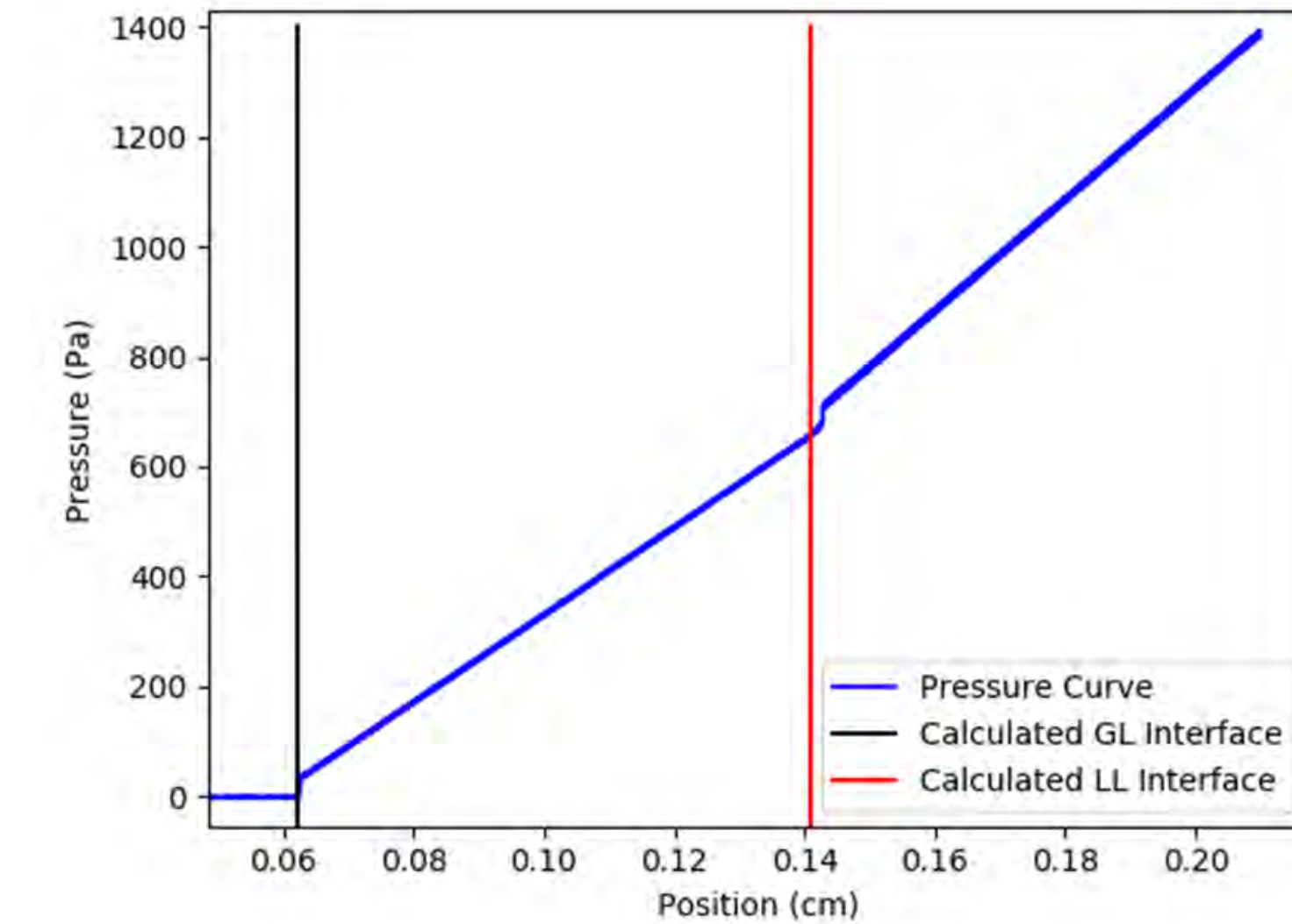
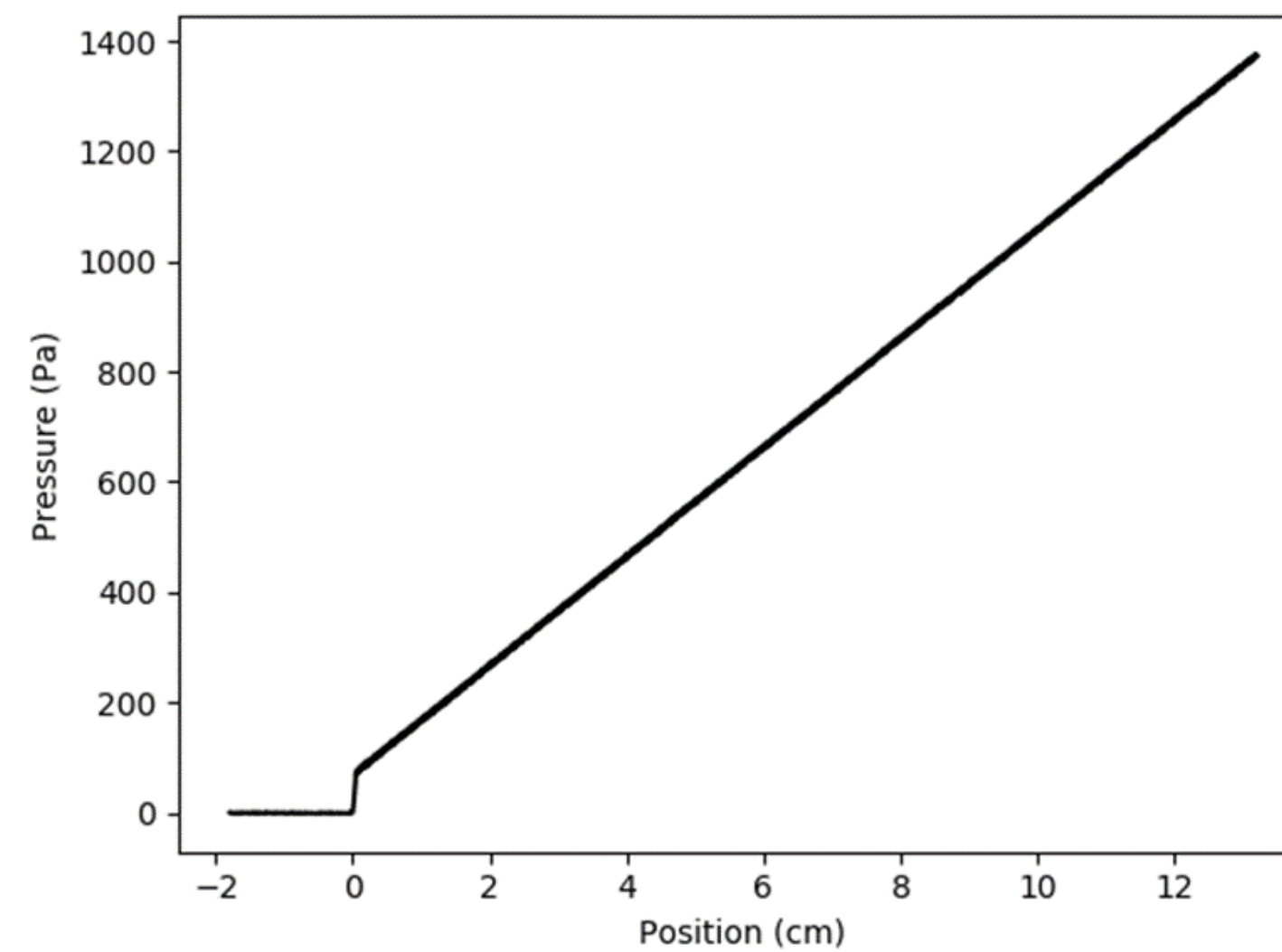
Optimization of a Dynamic Single Bubbler in Immiscible Fluids for Nuclear Safeguards Applications

Ammon Williams (N&HS), Tae-Sic Yoo (NS&T), and Anthony Bessler (MFC)

Introduction

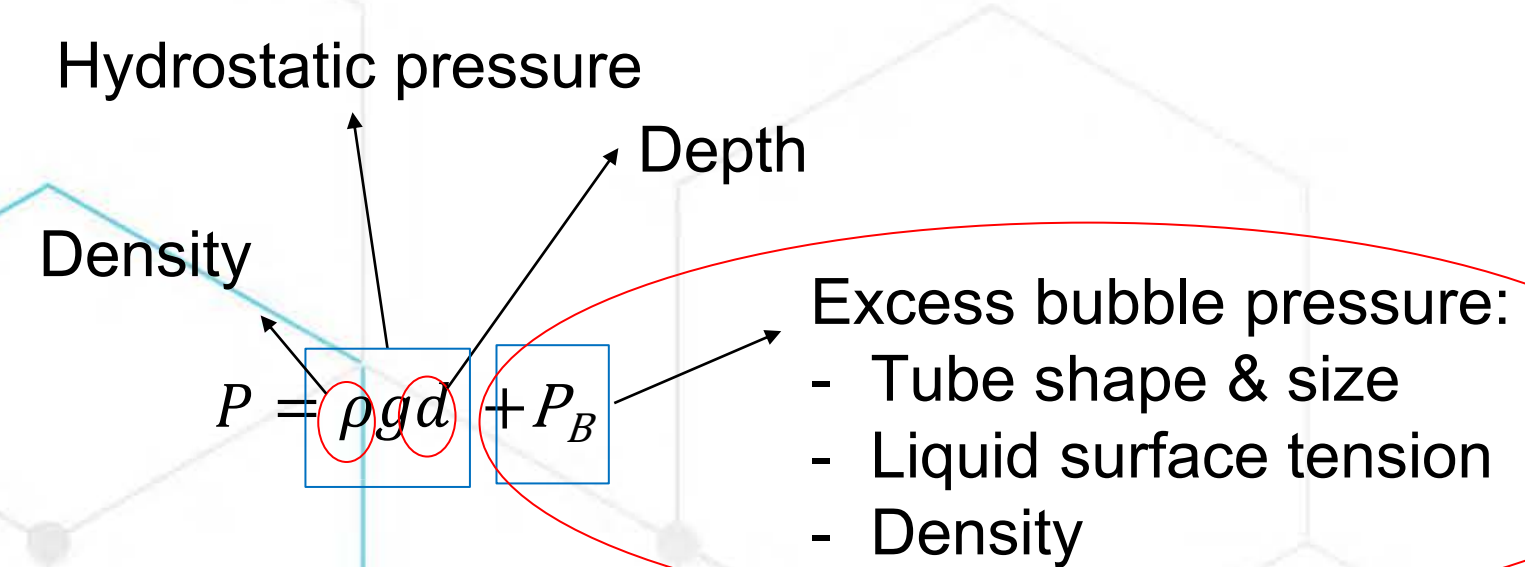
- Special Nuclear Materials (SNM) must be tracked for safeguards (domestic and international)
- SNM is present in bulk liquids in MSRs and Reprocessing
- Standard approach of the IAEA is double bubblers to measure density and level
 - Operation reliance to detailed calibration information
 - Recalibration/maintenance (e.g., corrosion and material buildup)
 - Fluid surface tension assumption
 - Applicable to single-phase homogenous fluids
- Dynamic Single Bubbler (DSB) approach to measure density and level
 - **No calibration and minimal maintenance**
 - **No fluid property assumption**
 - **Operation in immiscible fluids**
 - **Superior statistical estimate quality**

Single Phase and Immiscible Fluids



Equipment and Approach

Overall Governing Bubble Pressure Equation



P_B cancels when using a single bubbler!

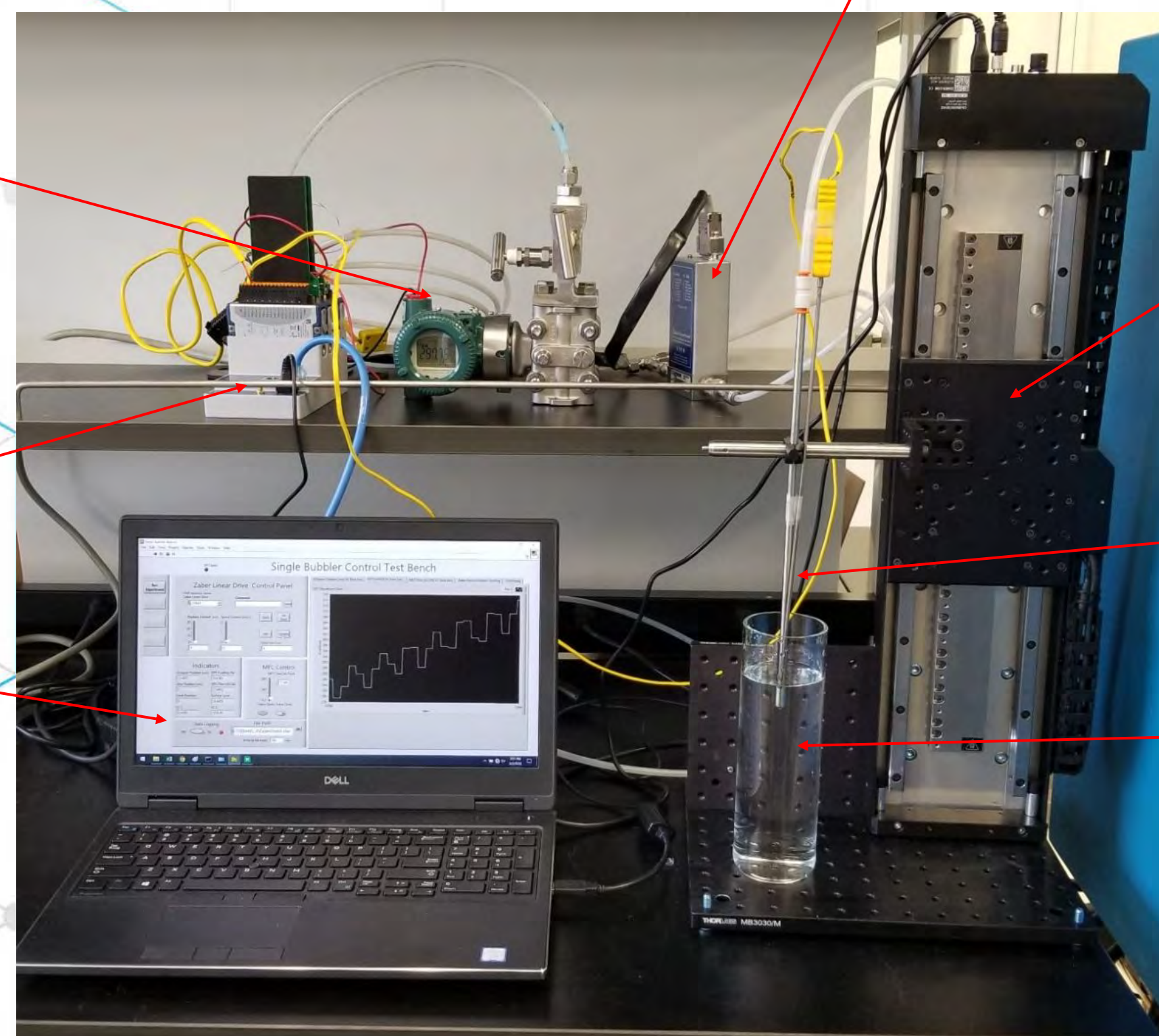
- Excess bubble pressure:
- Tube shape & size
 - Liquid surface tension
 - Density

Mass flow controller (MKS GMA50A)

Differential pressure transducer (Yokogawa EJA110E)

National Instruments cDAQ

LabVIEW



Linear Stage (Zaber X-LDQ0300C)

Dip Tube

Sample

Python Code

- Plots data and calculates:
 - Surface level (change point detection)
 - Liquid-liquid level (change point detection)
 - Density (linear regression of the pressure vs position line)

Parameter Optimizations

- Gas flow rate (5 – 20 cm³/min) did not have a significant effect on density or level
- Dip Rate (0.005 – 0.5 cm/s)
 - Surface level, slower better (005 – 0.1 cm/s)
 - Density, mid range best (0.05 – 0.2 cm/s)
 - Liquid-liquid level, ~0.3 cm/s best

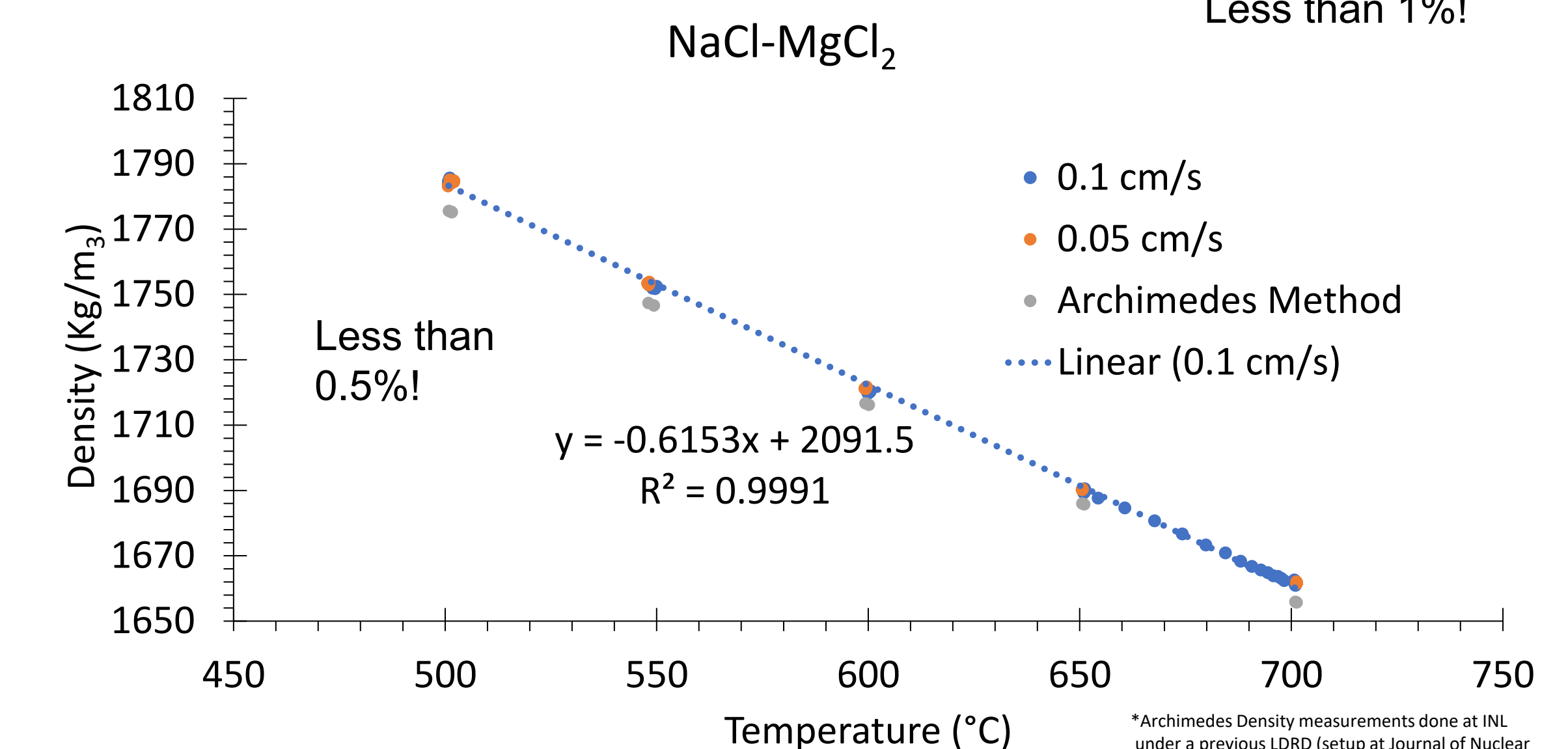
Tube Geometry and Calibration Free Testing



- Calculated density was within 0.03% on average with a max deviation of 0.12% (at 0.083" ID)
- Densities from the literature were typically within the uncertainties of the single bubbler values
- Little to no variation in Level measurements with different dip-tubes
- Indicated this approach is calibration free within the parameters studied!

Fluid Measurements Liquids and Salts

Fluid	Fluid T (°C)	Density (kg/m ³)	Density unc. (kg/m ³)	Lit. Density (kg/m ³)	Level % Difference	Density % Difference
Acetone	20.90	787.86	0.56	789.20	-0.37	0.17
Methanol	21.32	788.74	0.58	790.20	-0.14	0.19
Kerosine	22.14	802.82	0.67	800.00	0.00	-0.35
Water	21.15	998.03	0.71	997.90	0.08	-0.01
5 wt% Nitric acid	23.27	1022.75	0.87	1025.60	-0.16	0.28
10 wt% NaCl	21.56	1069.42	1.05	1070.17	0.15	0.07
22.5 wt% NaCl	20.87	1164.28	1.01	1163.60	0.04	-0.06
21 wt% CaCl	21.34	1186.87	0.76	1181.05	-0.13	-0.49
Glycerol	21.46	1260.40	1.74	1260.10	-0.07	-0.02
35 wt% CaCl	21.49	1332.15	0.96	1337.51	0.83	0.40



Project Number: 22P1065-019FP

LRS Number: INL/EXP-23-742018

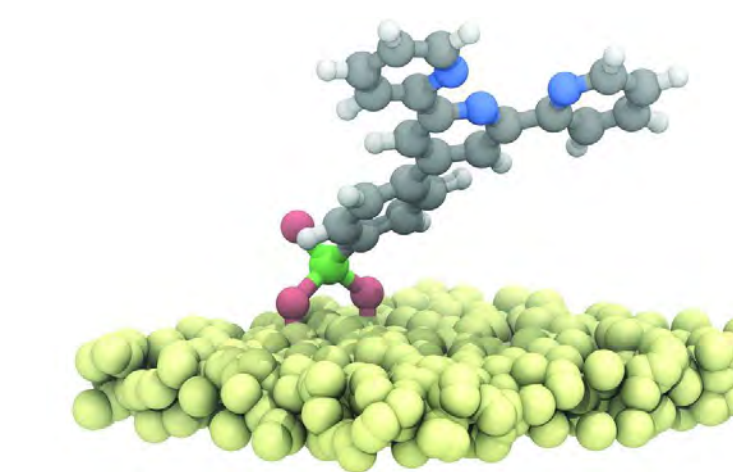
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Electrochemical Manipulation and Radiolytic Evaluation of Organic Phase Neptunium

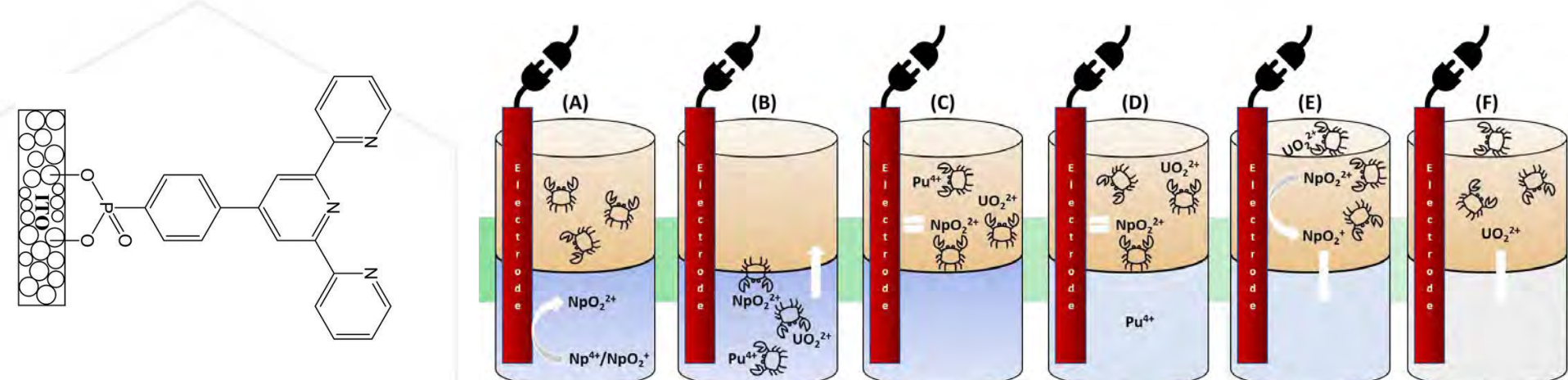


Jeffrey R. McLachlan^{1,2}, Christopher J. Dares², Travis S. Grimes³, Hanna Wineigner^{4,5}, Stephen P. Mezyk⁶, and Gregory P. Holmbeck³

¹Lawrence Berkeley National Laboratory, Berkeley, CA 94720, U.S.; ²Florida International University, Miami, FL 33199, U.S.; ³Center for Radiation Chemistry Research, Idaho National Laboratory, Idaho Falls, ID 83415, U.S.; ⁴Florida State University, Tallahassee, FL 32306, U.S.; ⁵Colorado School of Mines, Golden, CO 80401, U.S.; ⁶California State University Long Beach, Long Beach, CA 90840-9507, U.S.

Background

- Under envisioned used nuclear fuel reprocessing conditions, neptunium (Np) is present in a mixture of extractable Np(IV)/Np(VI) and inextractable Np(V) species, the distribution of which is dependent on several factors that lead to the unintentional partitioning of Np into various phases and product streams, reducing process and cost efficiency.
- With this in mind, we tested an innovative approach to precisely control the oxidation state distribution of Np using novel, high surface area, optically transparent, ligand modified tin-doped indium oxide electrodes (LMEs).



- These proof-of-concept experiments employed a variety of radiation and electrochemistry (echem) techniques to determine: electrode radiation stability; aqueous echem behavior of Np at nITO|P3 electrode surfaces; radiation-induced Np-extractant reaction kinetics; and non-aqueous echem of Np in diethylhexyl butyramide (DEHBA) solutions.

Irradiation Studies

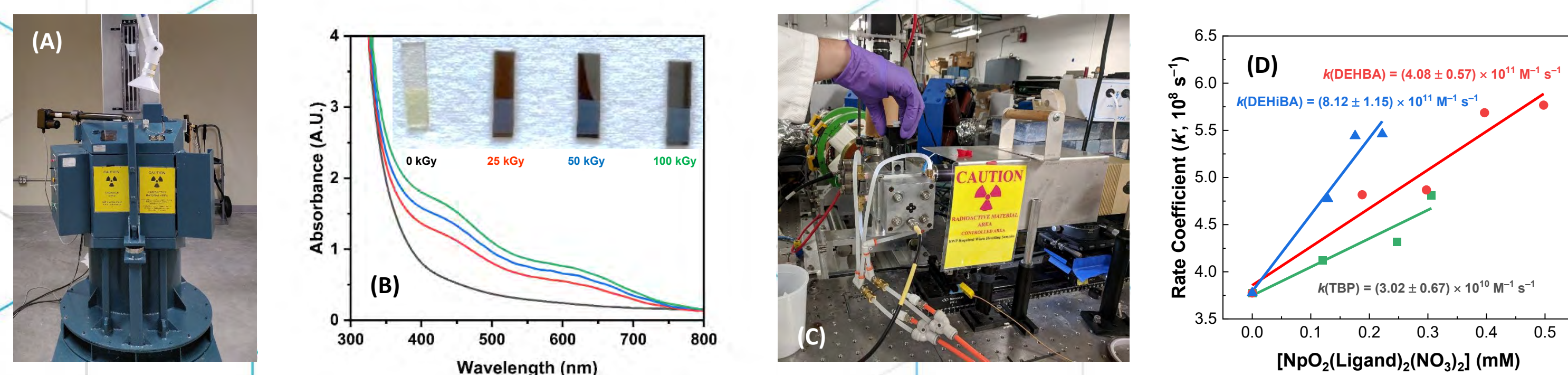


Fig. 1. (A) The INL Center for Radiation Chemistry Research high dose rate Foss Therapy Services Model 812 cobalt-60 gamma irradiator; (B) UV-Visible spectra of nITO electrodes in 0.1 M HNO₃ solution after exposure to 0 (black), 25 (red), 50 (blue), and 100 (green) kGy of gamma radiation; (C) the Brookhaven National Laboratory (BNL) Laser Electron Accelerator Facility (LEAF) actinide pulse radiolysis setup; and (D) the second-order determination of the rate coefficients (*k*) for the reaction of the dodecane radical cation (RH⁺) with Np(VI) complexed tributyl phosphate (TBP), diethylhexyl butyramide (DEHBA), and diethylhexyl isobutyramide (DEHBA) in 0.5 M dichloromethane/dodecane solution at 800 nm.

Electrochemical Manipulations

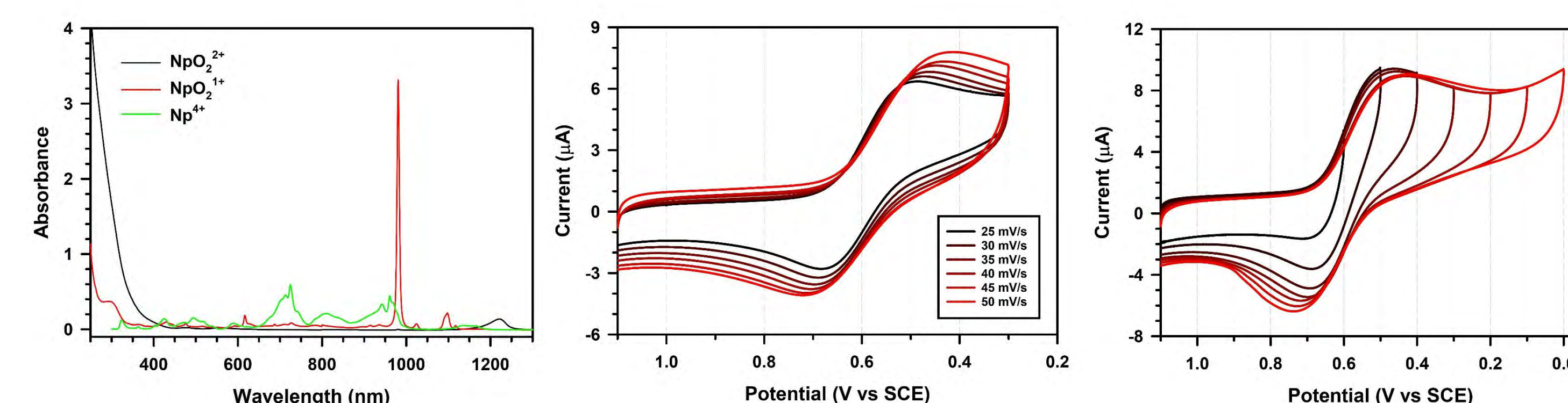


Fig. 3. (A) UV-Visible spectra of an aqueous 1.0 M HNO₃ solution containing ~10 mM Np(VI) after bulk electrolysis at 1.6 V vs. SCE (Black); Np(V) after bulk electrolysis at 0.4 V vs. SCE (Red); and Np(IV) after bulk electrolysis at -0.3 V vs. SCE (Green) at a nITO|Triphosphosphate electrode. (B) Cyclic voltammograms at GCE of the Np(VI/IV) couple in DEHBA with an $E_{1/2} = -0.55$ V vs. SCE. The linear trend through the plot's origin confirms the Np(VI/IV) couple is diffusion limited, with $D_0\text{Np(VI)} = 1.24 \times 10^{-8}$ cm² s⁻¹. (C) Cyclic voltammograms at GCE of the Np(VI/IV) couple in DEHBA at various cathodic limits. As the cathodic limit is extended, the wave corresponding to the reoxidation of Np(V) to Np(VI) shifts, possibly due to a change in coordination environment or some other chemical phenomena.

Research Outputs

Peer-Reviewed Publications

- McLachlan, Jones, Hou, Horne, and Dares, The Interaction of Solvent Radiolysis Products with a Transparent Conductive Oxide. *ChemPhysChem* (Impact Factor = 3.520), **2023**, [Submitted](#).
- Culbertson, Celis-Barros, Pilgrim, McLachlan, Cook, Mezyk, and Horne, Elucidating the Impact of Neptunium and Plutonium Complexation on TBP, DEHBA, and DEHIBA Radiation-Induced Reaction Kinetics. *Inorganic Chemistry* (Impact Factor = 5.436), **2023**, [In Preparation](#).
- McLachlan, Wineigner, Sperling, Albrecht-Schönzart, Dares, and Horne, The Electrochemical Behavior of Neptunium at Phosphate Modified Metal Oxide Electrodes. *ChemComm* (Impact Factor = 4.9), **2024**, [In Preparation](#).
- McLachlan, Wineigner, Sperling, Albrecht-Schönzart, Dares, and Horne, The Electrochemical Behavior of Neptunium in DEHBA and DEHIBA Solvent Systems. *Dalton Transactions* (Impact Factor = 4.569), **2024**, [In Preparation](#).

Conference Poster Presentation

- 3rd International Conference on Ionizing Processes, Idaho Falls, ID, U.S., July 2022.

Additional Acknowledgements

- McLachlan was supported by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program. The SCGSR program is administered by the Oak Ridge Institute for Science and Education for the DOE under contract number DE-SC0014664.
- BNL LEAF irradiation experiments were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under contract DE-SC0012704.
- We would like to thank Professor Thomas E. Albrecht-Schönzart for making the Florida State University radiochemistry laboratories available to this project, without which the presented electrochemical manipulations of Np would not have been possible.

Project Number: 22P1065-033FP

LRS Number: INL/MIS-23-73877

Radiation-Induced High Temperature Aqueous Chromium Redox Chemistry

PRESENTER : Jacy K. Conrad



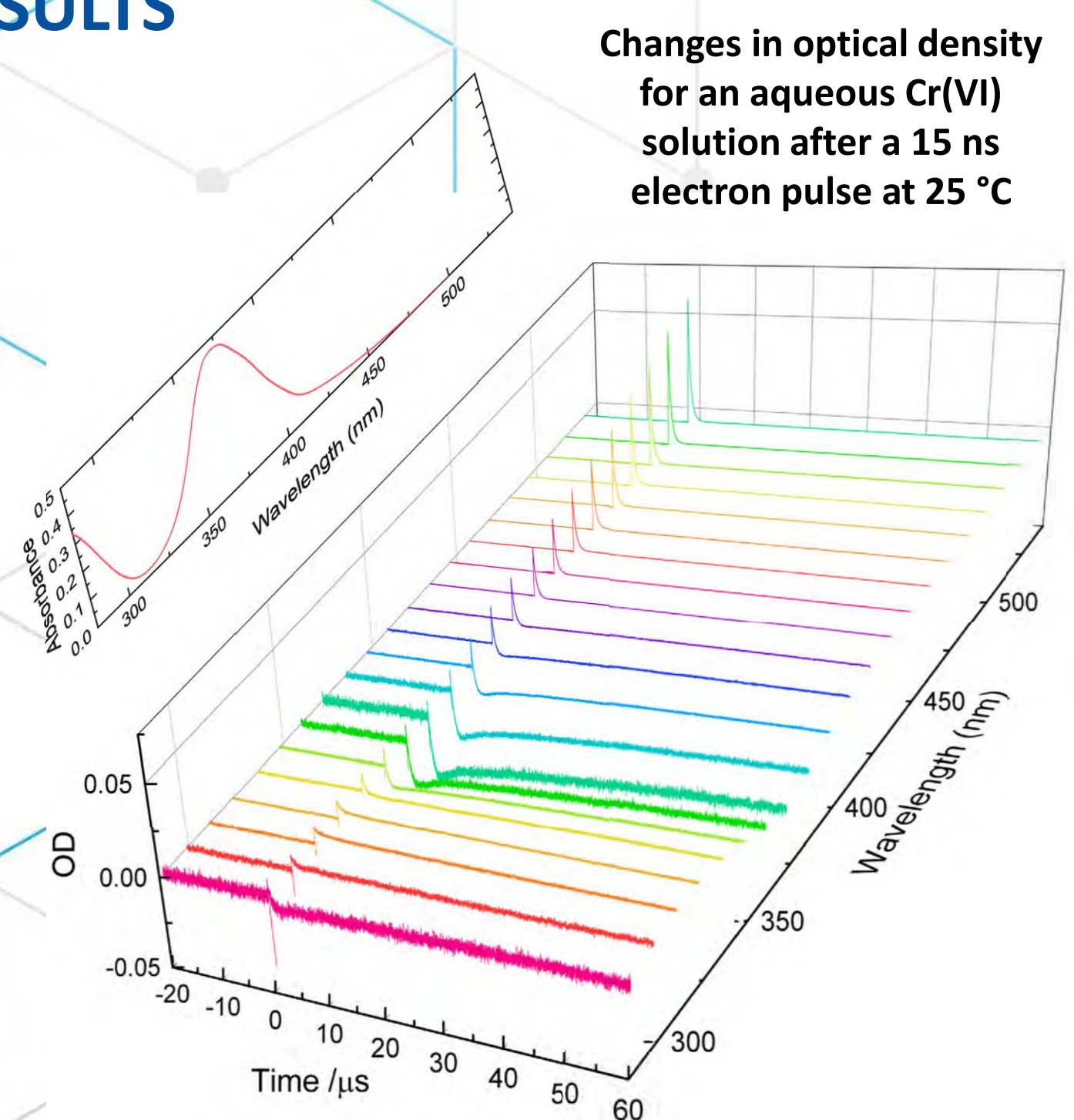
BACKGROUND

Radiolysis of a dilute aqueous solution yields redox-active products capable of changing the metal ion oxidation states, which determine the metal reactivity, solubility, and speciation.

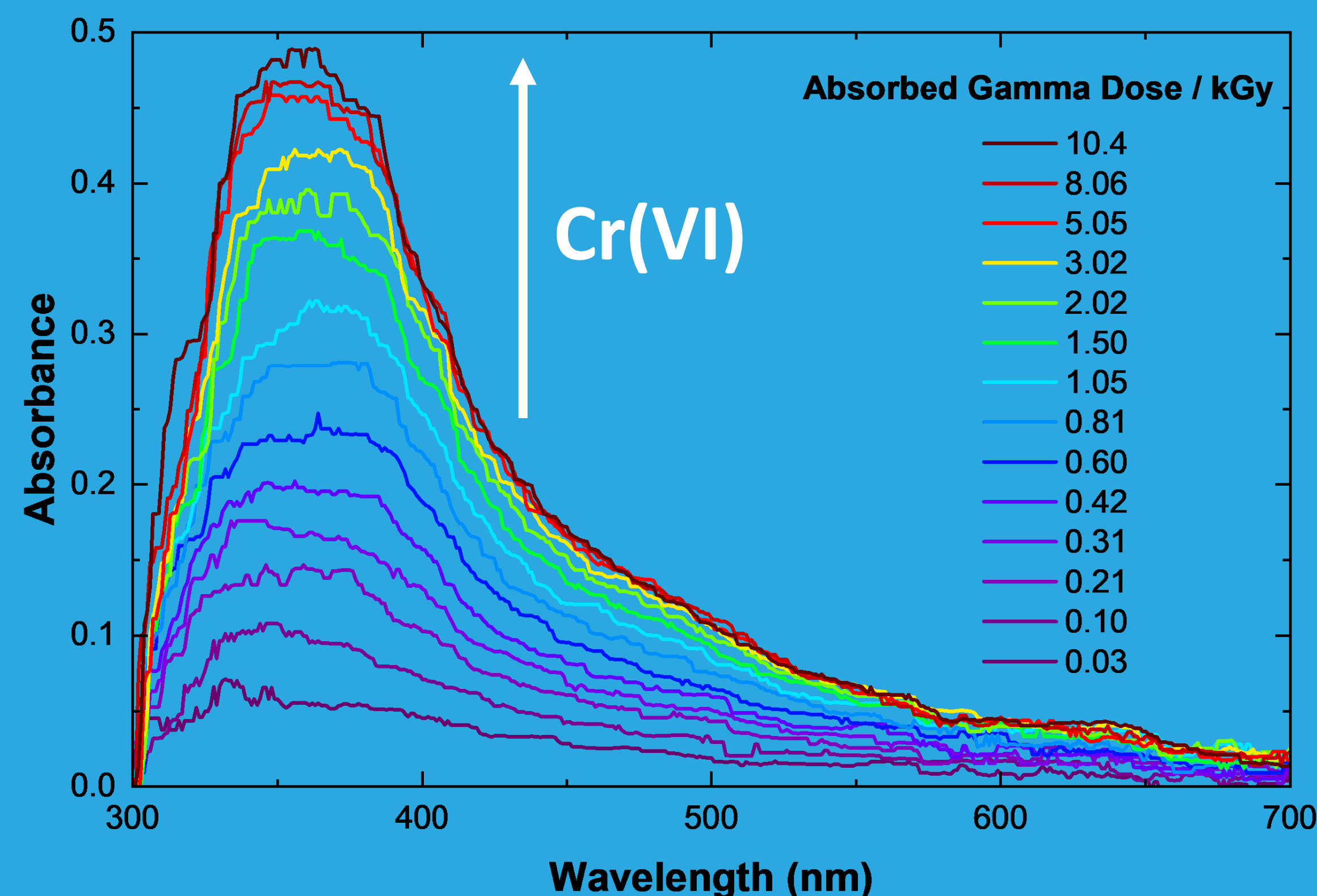
METHODS

1. Pulsed electron radiolysis to measure the rates of chemical reactions as a function of temperature.
2. Custom-built high temperature cell for steady-state cobalt-60 irradiations with *in-situ* UV-Visible spectroscopy.
3. Kinetic models of chemical reactions.

RESULTS



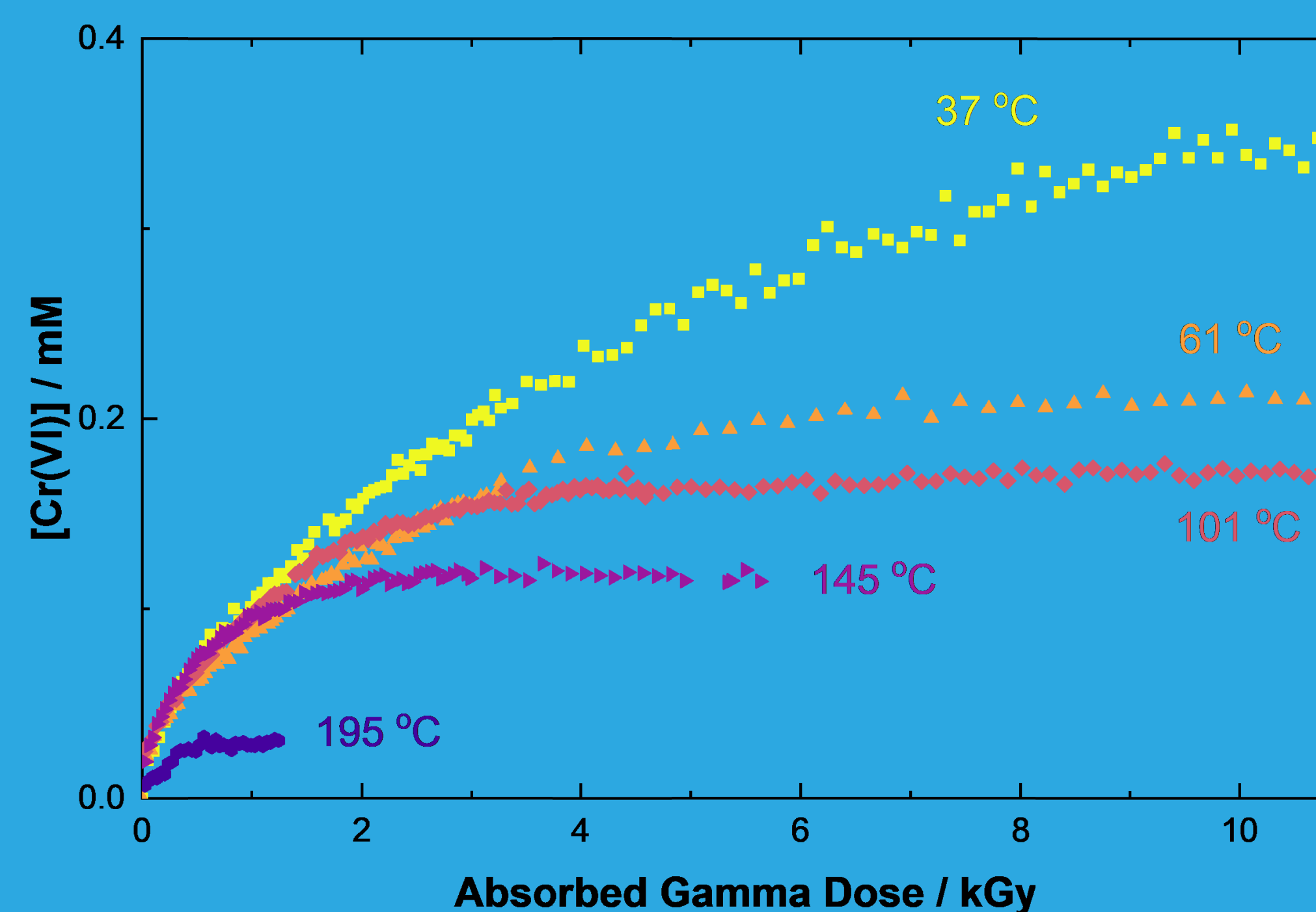
Absorption spectrum of the Cr(VI) from gamma irradiation



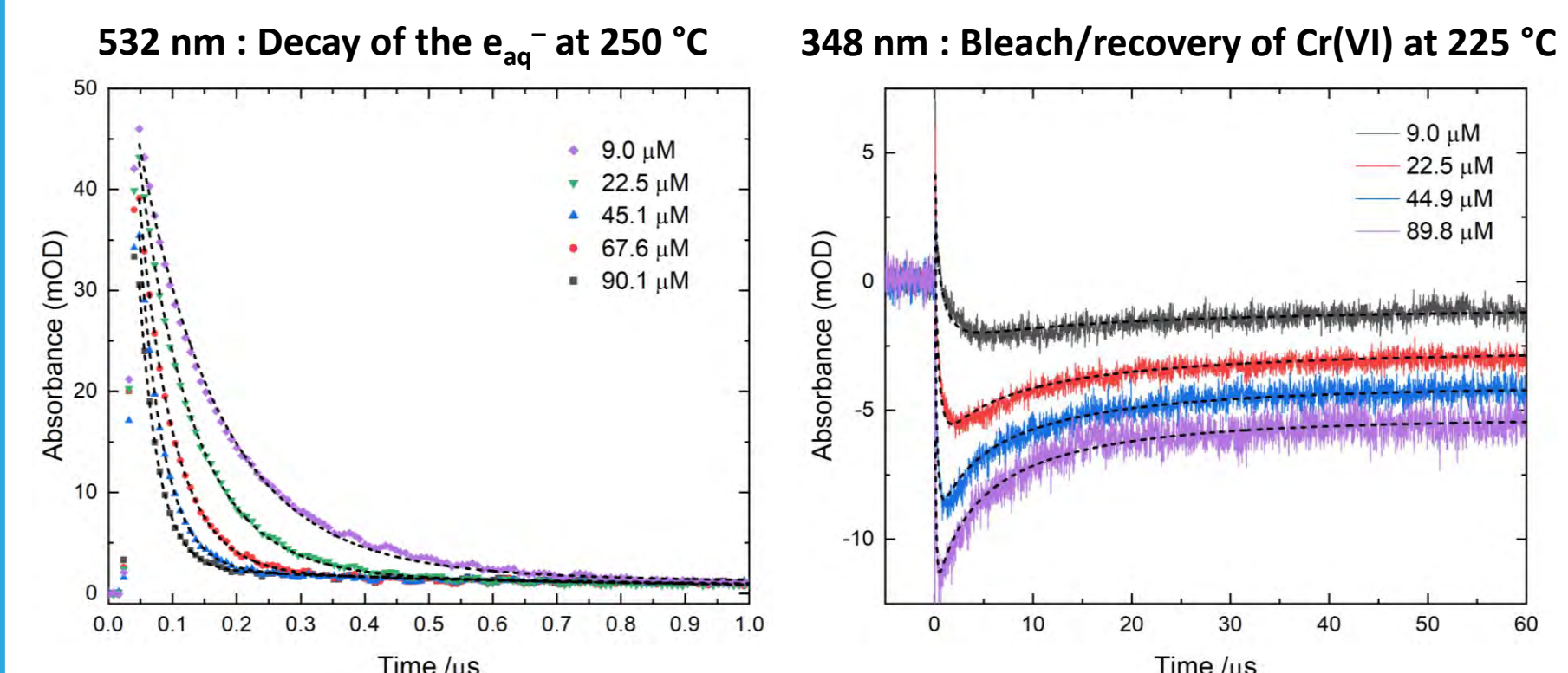
Foss Therapy Services Model 812 Cobalt-60 Gamma Irradiator

Radiation influences the redox chemistry of aqueous metal ions.

Radiation-induced Cr(VI) from a 0.5 mM Cr(III) solution



Custom-built high temperature cell



Rate coefficients (k) Arrhenius parameters determined for reactions between aqueous chromium ions and water radiolysis products

Reaction	k_0 (25 °C) ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$)	Activation Energy, E_a (kJ mol ⁻¹)	Preexponential Factor, A ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$)
$\text{HCrO}_4^- + e_{\text{aq}}^-$	3.28 ± 0.58	12.87 ± 0.56	5913 ± 104
$\text{CrO}_4^{2-} + e_{\text{aq}}^-$	1.47 ± 0.10	13.19 ± 0.12	300.1 ± 13.0
$\text{HCrO}_4^- + \text{H}^\cdot$	1.19 ± 0.17	12.98 ± 0.29	223.6 ± 17.3
$\text{Cr(V)} + \cdot\text{OH}$	0.48 ± 0.05	7.03 ± 0.22	8.17 ± 0.54
$\text{Cr(III)} + e_{\text{aq}}^-$	4.86 ± 0.05	$k = A e^{-\frac{E_a}{RT}}$	
$\text{Cr(OH)}^{2+} + \cdot\text{OH}$	0.072 ± 0.003		

PUBLICATIONS

1. Conrad, J.K., Lisouskaya, A., Mezyk, S.P., Bartels, D.M. (2023) Temperature Dependence of the Reaction Kinetics of the e_{aq}^- and $\cdot\text{OH}$ Radicals with Cr(III) Ions in Aqueous Solutions. *ChemPhysChem* (Under Review).
2. Barr, L., Conrad, J.K., McGregor, C., Yakabuskie, P.A., Stuart, C.R. (2023) Kinetics of the reaction of ferrous ions with hydroxyl radicals in the temperature range 25-300°C. *Physical Chemistry Chemical Physics*. (Under Review)
3. Conrad, J.K., Lisouskaya, A., Barr, L., Stuart, C.R., Bartels, D.M. (2023) High Temperature Reaction Kinetics of the e_{aq}^- and HO_2^\cdot Radicals with Aqueous Iron(II) Ions. *Journal of Physical Chemistry A*, 127(27), 5683–5688.
4. Conrad, J.K., Lisouskaya, A., Bartels, D.M. (2022) Pulse Radiolysis and Transient Absorption of Aqueous Cr(VI) Solutions up to 325 °C. *ACS Omega*, 7(43), 39071-39077.

COLLABORATORS

Robert V. Fox, Gregory P. Holmbeck, Harry Rollins, Dean R. Peterman, Aliaksandra Lisouskaya, David M. Bartels, Logan Barr, Craig R. Stuart, and Stephen P. Mezyk.



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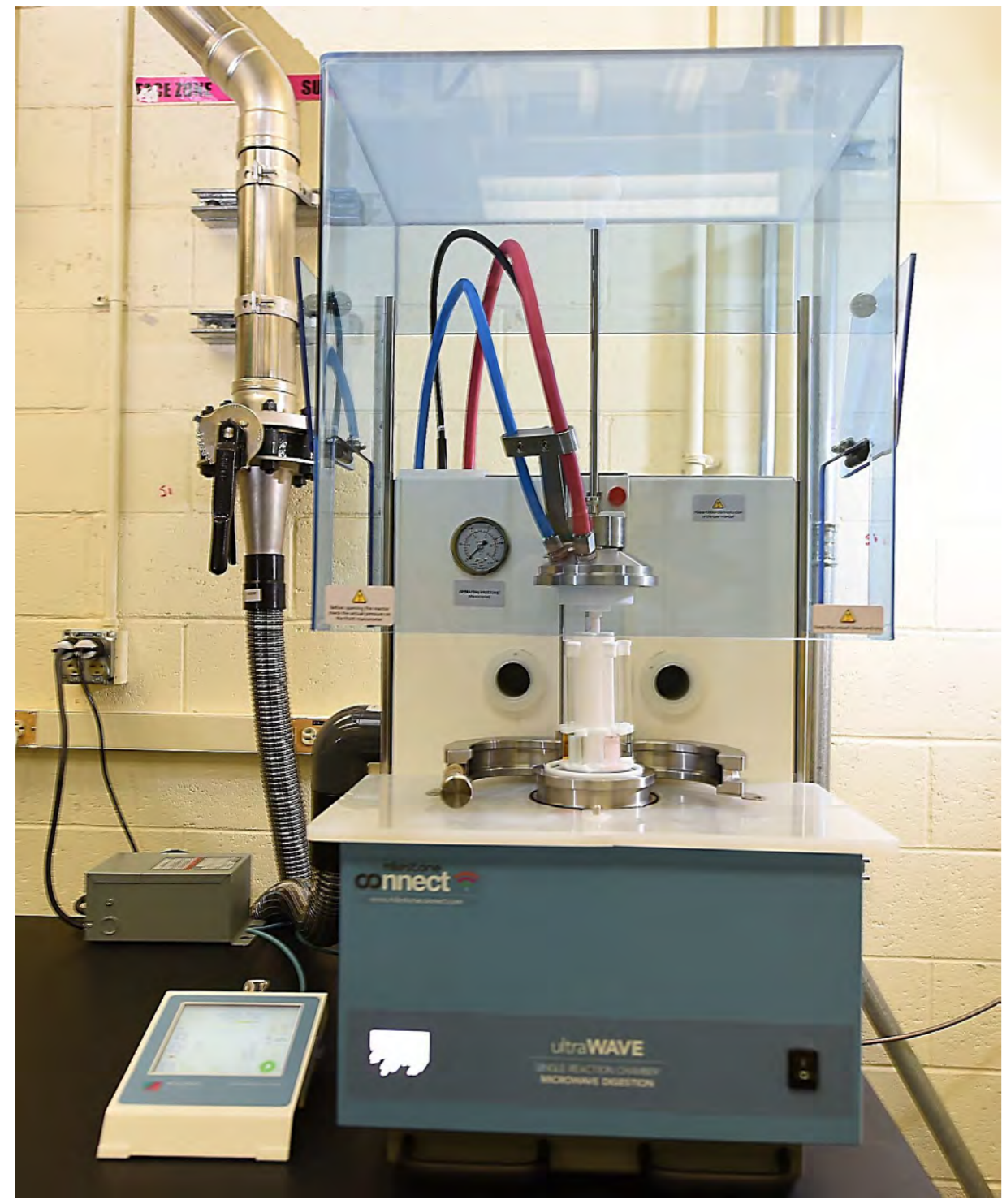
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Microwave-Assisted Digestion of Nuclear Materials

Luiza G. R. Albuquerque, Vivian M. de O. Carioni, Beau D. Ballard

Analytical Research Laboratory – Materials and Fuels Complex, Idaho National Laboratory – P.O. Box 1625, Idaho Falls – ID 83415



UltraWave (Milestone) installed in the ARL

Goal: develop microwave-assisted digestion methods for nuclear materials and correlated samples



Traditional hot plate dissolution in the ARL

Traditional Hot Plate Dissolution (HP)

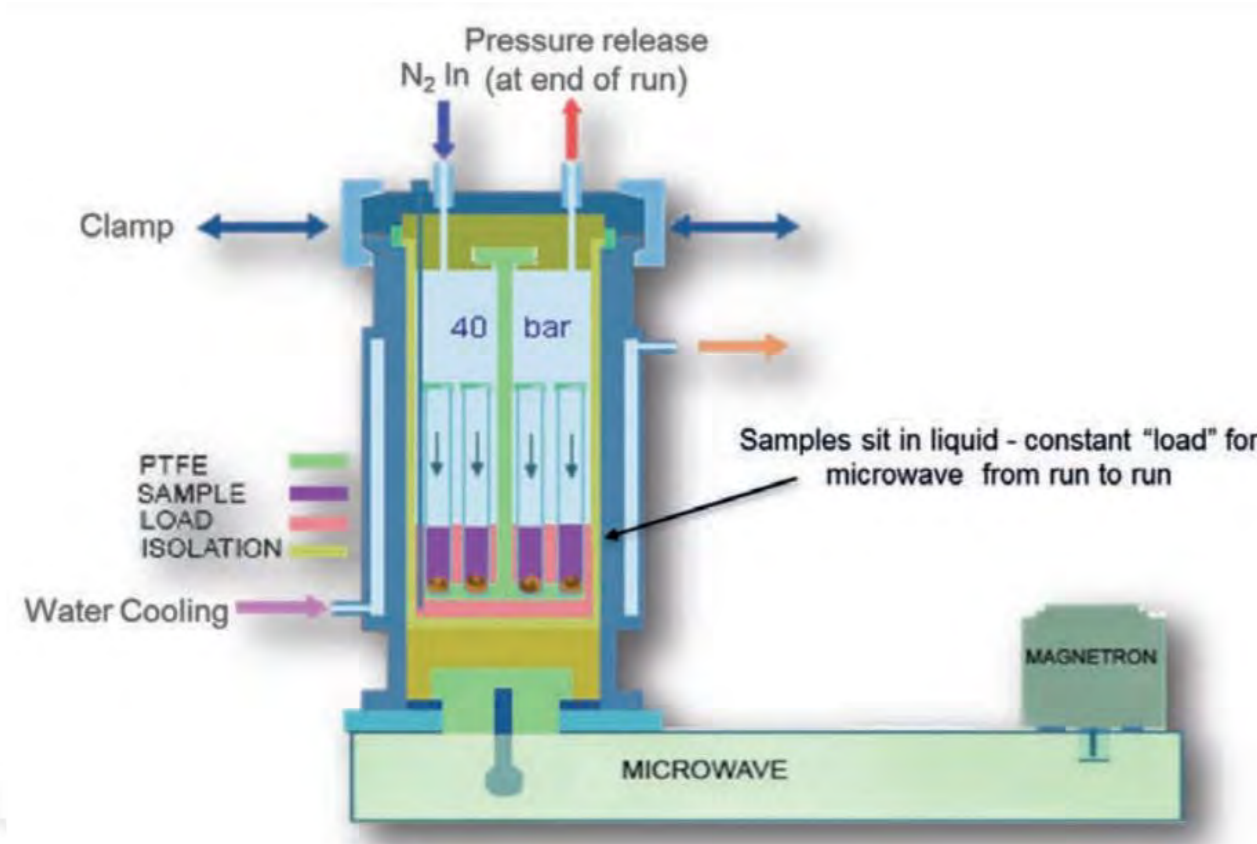
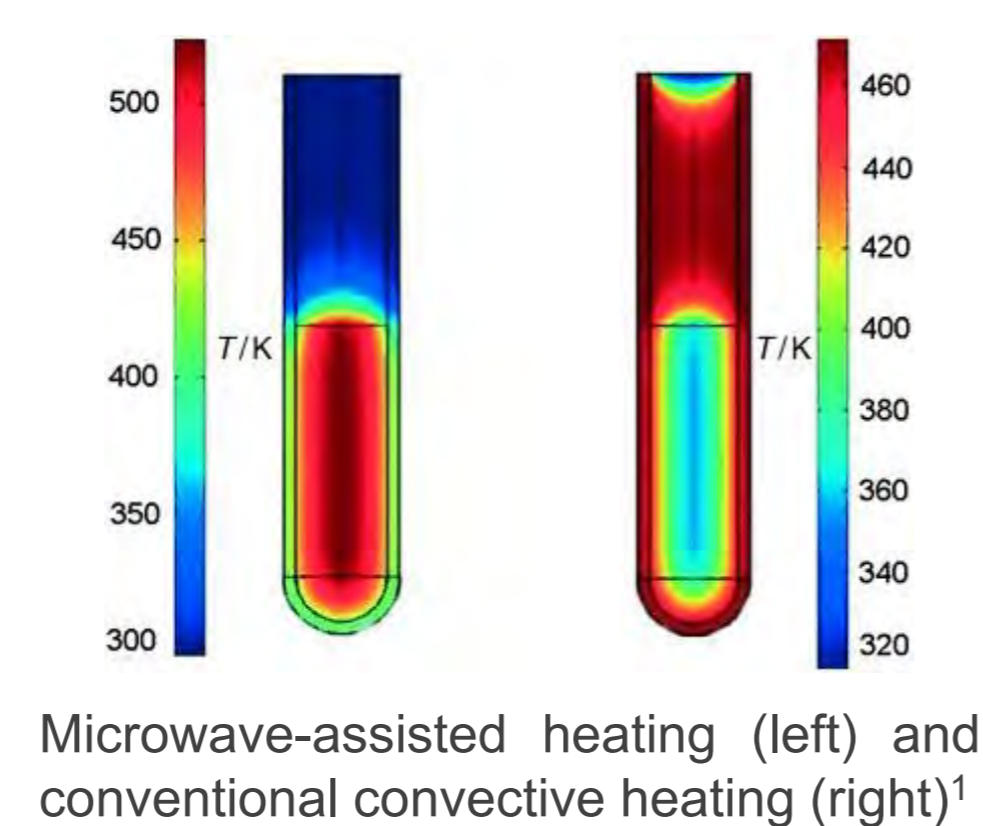
- Long history of sample processing.
- Multistep processes may be required.
- Prone to environmental contamination and loss of volatile species.
- Reproducibility is dependent on analyst skill and environmental variables.
- Sample dissolution time may vary from hours to days.

Microwave-Assisted Digestion (MW)

- High temperature (up to 300 °C) and high pressure (up to 199 bar) promotes digestion efficiency.
- Sealed vessel prevents evaporation of volatile species and reduces environmental contamination.
- Smaller acid volumes required, reducing waste.
- More reproducible and predictable.
- Lower digestion times → Increased sample throughput.
- Publication impact - literature on the use of microwave dissolution methods for nuclear materials is scarce.

Instrumentation

- Microwave heating affects only the solution (vessels are made of microwave-transparent material). Heat transfer to the core of the solution is more effective than conventional heating.
- Vessel walls remain at much lower temperature, creating a reflux condition and increasing effectiveness due to acid regeneration.



- Closed vessels are under pressure, reducing loss of volatile analytes and increasing the boiling temperature of acid mixture, improving its oxidizing power. A smaller acid volume can be used.
- Sensors are used to control the MW power being applied. The same temperature program can be followed each time guaranteeing reproducibility.

¹Kappe, C. O. (2004). Controlled microwave heating in modern organic synthesis. *Angewandte Chemie International Edition*, 43(46), 6250-6284.
²Revolutionizing Sample Preparation with Single- Reaction Chamber Microwave Digestion, 2018; Available from: <https://milestonesci.com/wp-content/uploads/2019/01/SRC-Technology-EBook-Spectroscopy-Milestone-August-2018-b.pdf>

Samples dissolution

- The following samples were kindly shared by other INL researchers:

Material identification	Description
316 Stainless steel	Cr-Mo-Ni stainless steel
800H Incoloy	Ni-Fe-Cr alloy
Zr-4 Zircaloy	Zr-Sn-Fe-Cr alloy
ID 1574	U ₃ Si ₂ sintered pellets
ID 1770	UO ₂ Sintered Pellet chunks
ID 1957	UN sintered
ID 1947	UC Sintered pellets

- Dissolution of these materials, along with C123 is complete and digested material is currently undergoing Q-ICP-MS and ICP OES analysis.

Conclusions

- Microwave-assisted digestion is producing good analytical results while increasing the sample throughput. The developed methods are already being implemented for routine analysis in the ARL, allowing for a higher sample throughput, benefiting a great number of programs.
- The high temperature and pressure environment in the MW instrument opens the potential for analysis of refractory materials, such as ceramics, glasses and carbides.
- A closed system for sample digestion decreases the contamination of the analytical blank, leading to lower limits of quantification. This allows the measurement of elements in concentrations lower than what is typically obtained when using open-system digestion.

Acknowledgements

- Cortney Pincock, Lindsey Lecrivain, Michael Rodriguez and Maria Lora-Lora for performing Q-ICP-MS analysis.
- Nick Erfurth, Paige Abel and Kelsi McDermott for performing ICP OES analysis.
- Lydia Meyer and Adrian Wager for samples.

MW digestion method development

Certified reference materials (CRMs) are certified for major constituents and trace impurities and were selected to act as surrogates for cladding, materials used in fuel casting and nuclear fuel. The following microwave heating program was applied for all samples:

- 1) 20 minutes ramp up to 240°C
- 2) 15 minutes hold at 240°C

Material identification	Description
CRM 123-1	Uranium oxide (U ₃ O ₈)
SRM 133b	Chromium-Molybdenum steel
SRM 360b	Zirconium (tin-iron-chromium) alloy
SRM 689	Ferrochromium silicon (39.5% Si)
SRM 867	Nickel-iron-chromium alloy

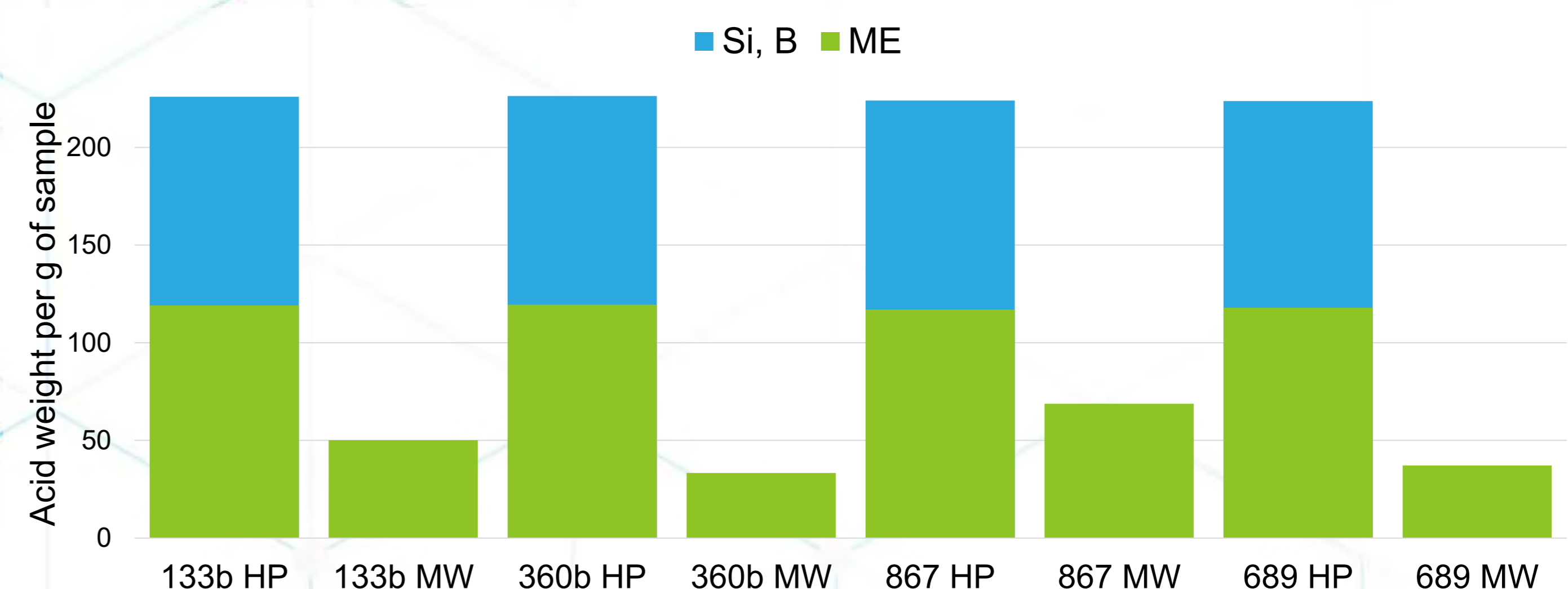
CRMs were dissolved using mixtures of reverse aqua regia (3:1 nitric acid/hydrochloric acid), hydrofluoric acid and water. Below are listed the mixtures with the optimal results:

CRM	Acid mixture
133b	4.5 mL reverse aqua regia + 0.5 mL HF
360b	4 mL reverse aqua regia + 1 mL HF
867	4.5 mL reverse aqua regia + 0.5 mL HF
689	2 mL H ₂ O + 1 mL reverse aqua regia + 2 mL HF

- Samples were analyzed by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP OES).
- Good recoveries for both methods (80-120%), with a few exceptions.
- Most noticeable difference for CRM 689 – high Si concentration.

$$\text{Recovery (\%)} = \frac{\text{Concentration}_{\text{Measured}}}{\text{Concentration}_{\text{Expected}}} \times 100\%$$

	HP recoveries				MW recoveries			
	133b	360b	867	689	133b	360b	867	689
Al	ND	105%	85%	56%	ND	ND	ND	ND
Cr	102%	118%	99%	61%	103%	125%	101%	100%
Cu	96%	5%	93%	63%	96%	ND	98%	ND
Fe	100%	91%	100%	64%	99%	130%	100%	105%
Mn	101%	82%	98%	61%	109%	ND	109%	107%
Mo	94%	ND	92%	ND	ND	ND	99%	ND
Ni	98%	344%	102%	71%	104%	ND	101%	79%
Si	96%	31%	92%	48%	ND	ND	ND	ND
Zr	ND	98%	ND	ND	ND	103%	ND	ND

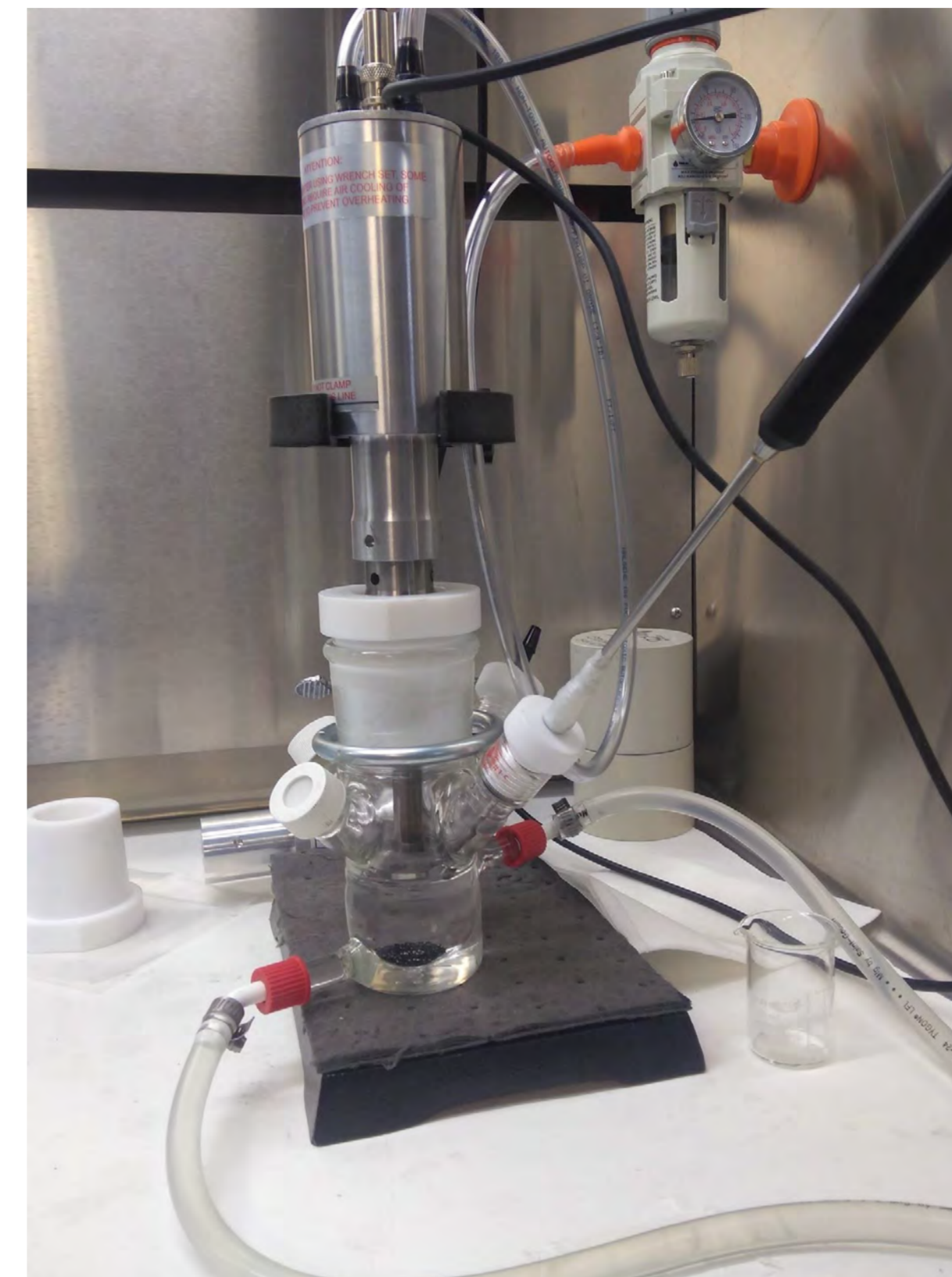


- Acid weight required per gram of sample was reduced down to 83%.
- Sample digestion time decreased from 2 working weeks (two steps were required for complete dissolution) to 2 hours.

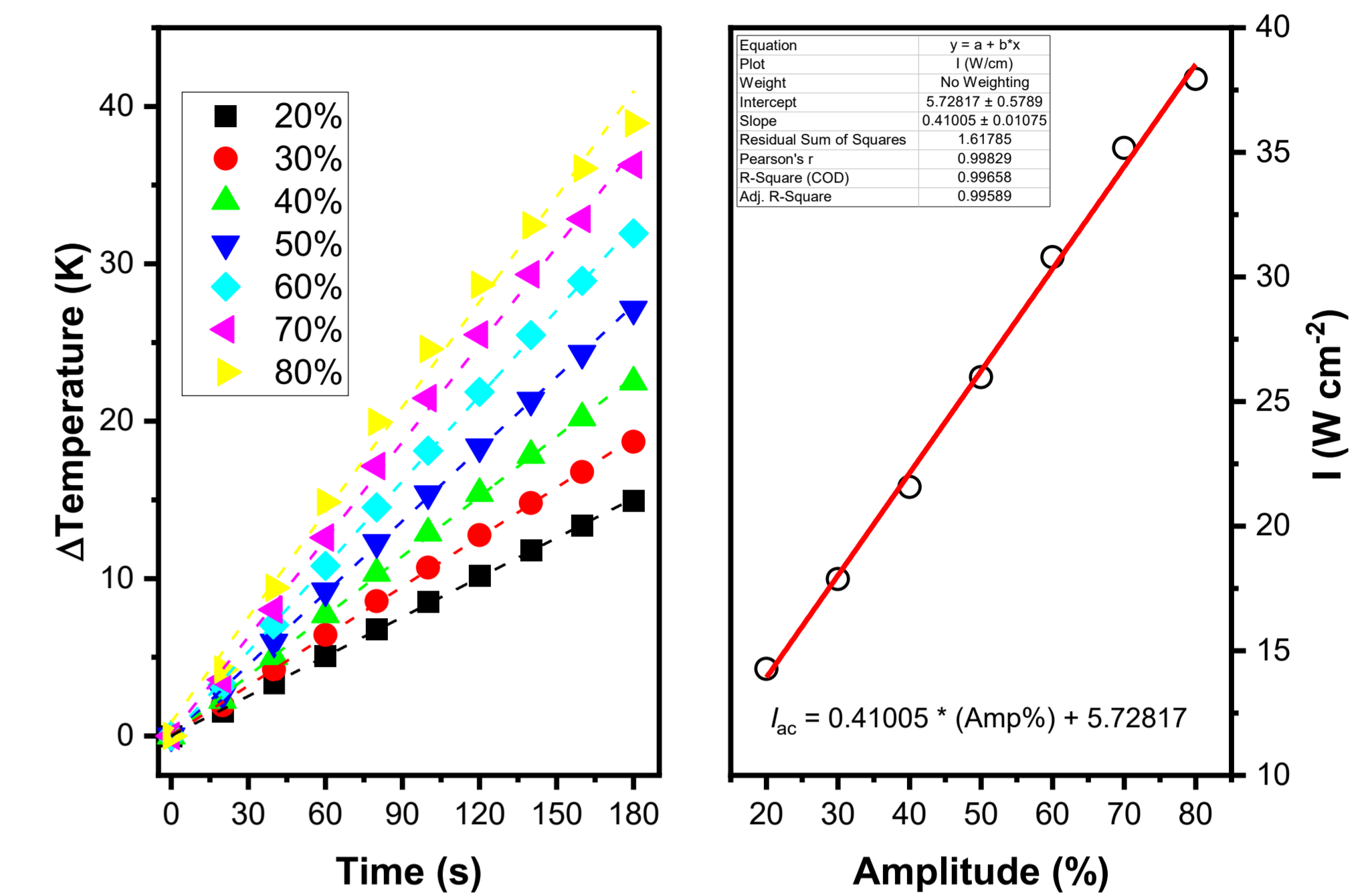
High-Power Acoustic Sound Waves Can Penetrate TRISO Fuel Particles!

PIs: Travis S. Grimes, Peter R. Zalupski

Sonication Apparatus



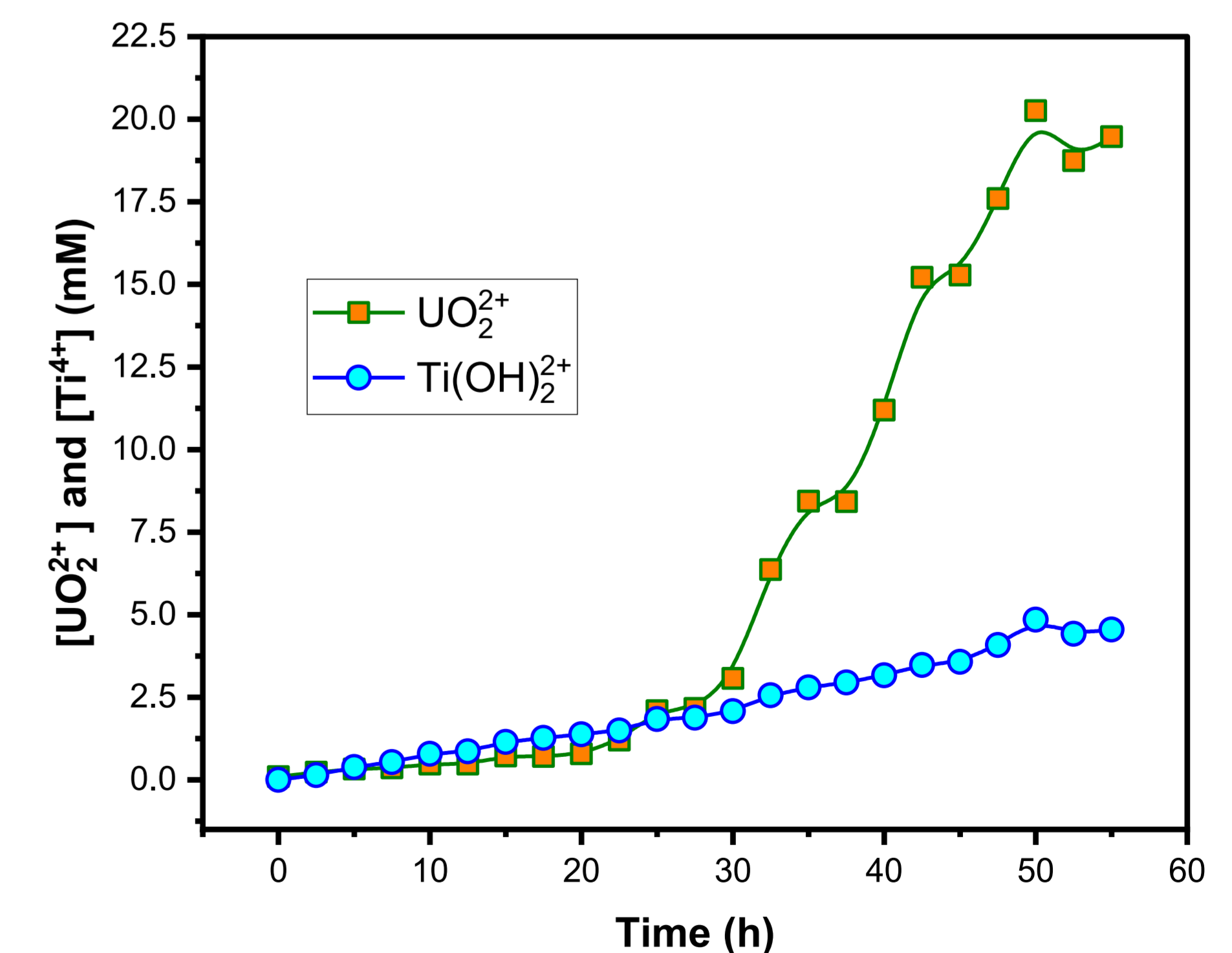
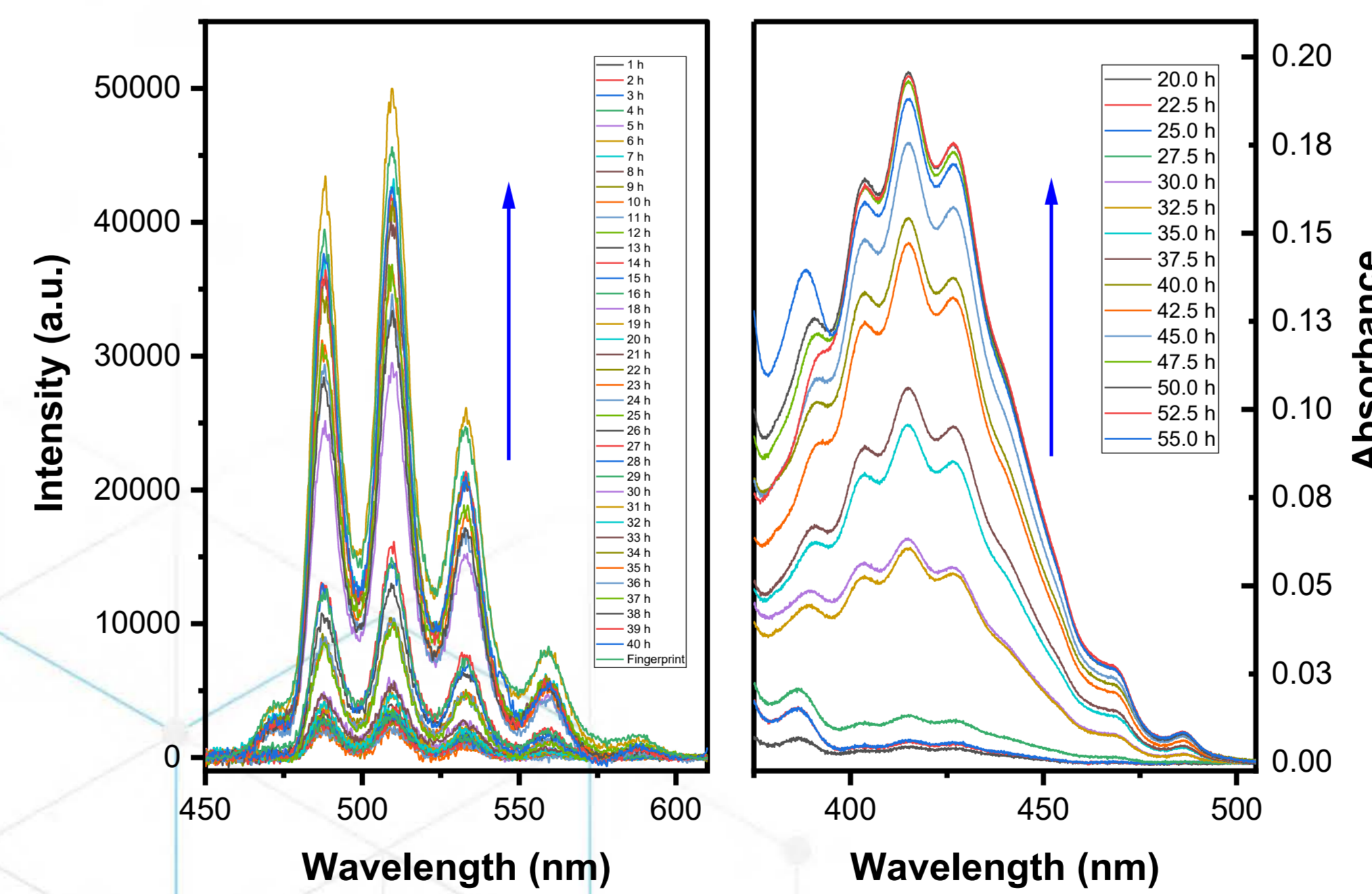
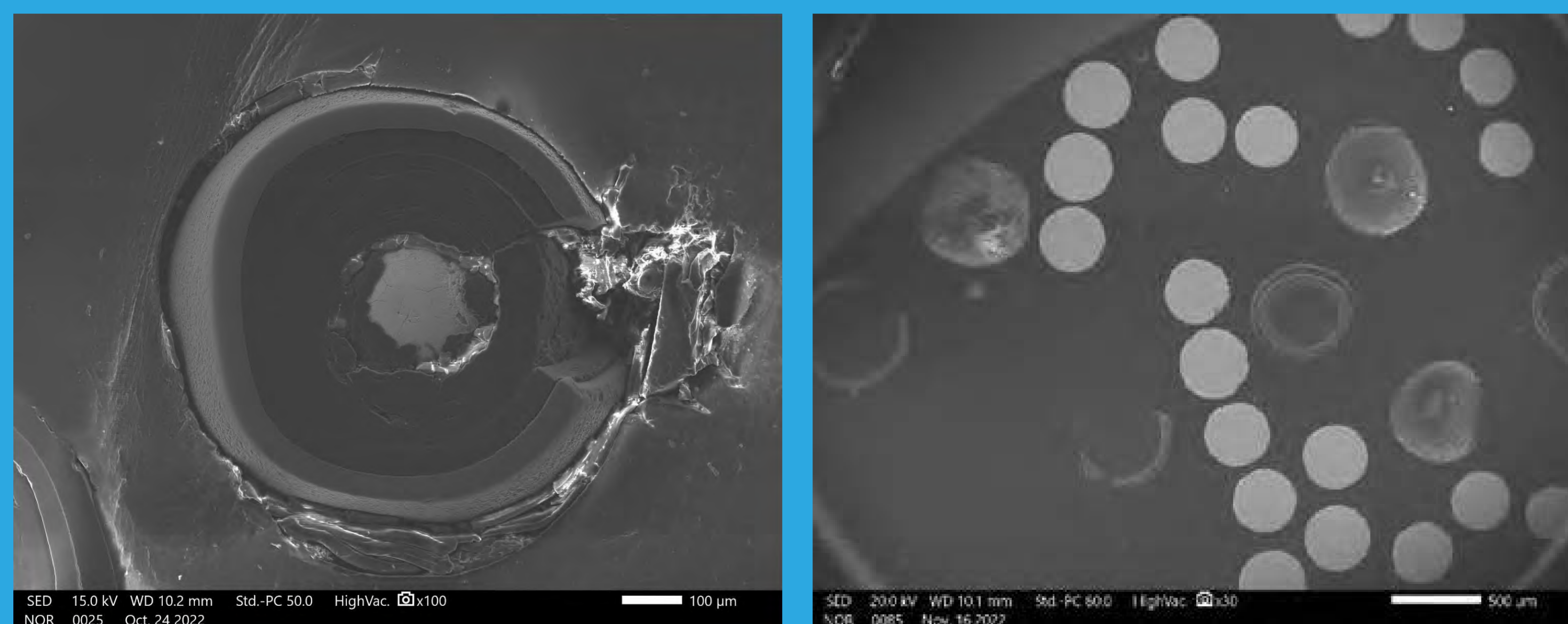
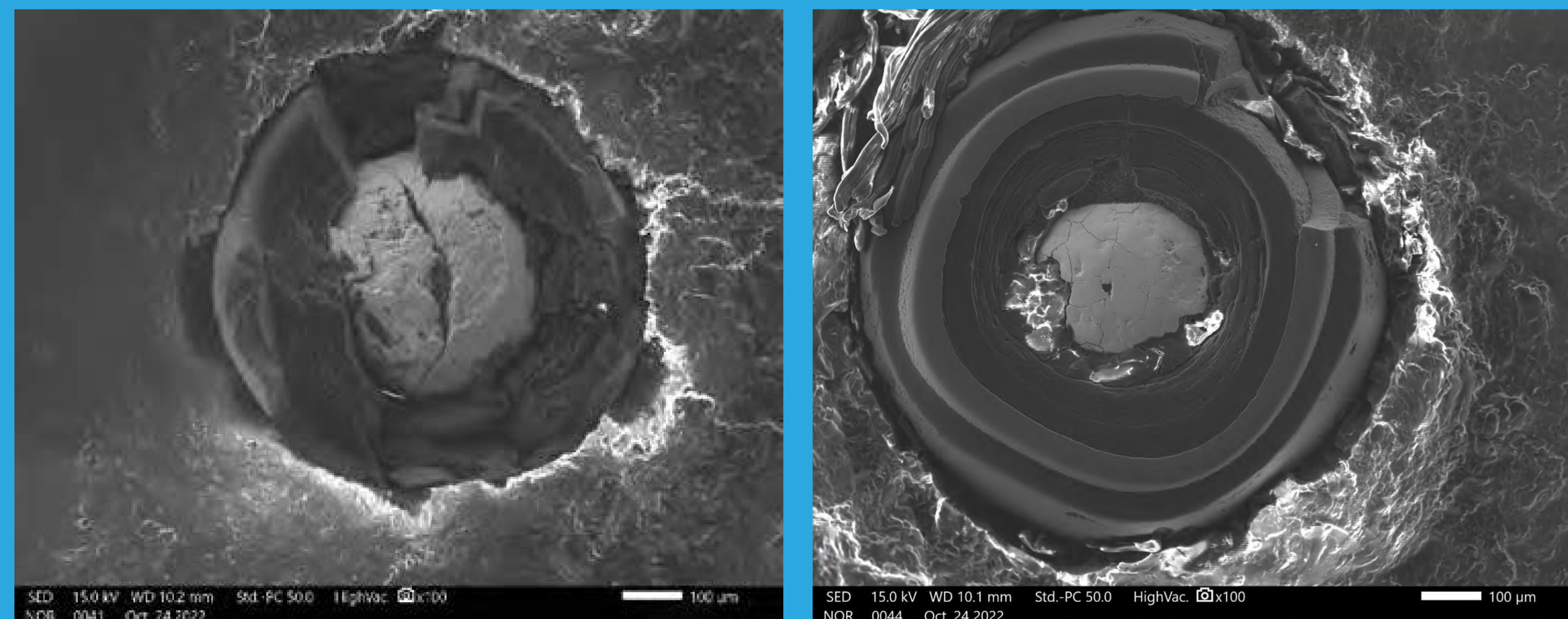
Thermal calibration to quantify power and acoustic intensity



$$P = \frac{dT}{dt} C_p m \quad I_{ac} = \frac{P}{A_{probe}}$$

Increases in fluorescence and absorbance signals indicate increasing uranium concentration in solution

Uranium concentration reached 20.3 mM corresponding to a 67% recovery from 1.0 g TRISO fuel particles



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