An Electrochemical Trigger for Drop-on-Tape Sample Delivery System *with In-Line UV-Vis Validation*

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Introduction

Linac Coherent Light Source is a means to study metalloenzyme structures.

- **Drop-on-Tape System:** a conveyer belt like setup where liquid samples are dropped as droplets on tape and observed with LCLS's Xray free-electron laser through the "diffraction before destruction" process.
- Can learn about the structure of enzyme through process

ELECTROCHEMICAL PROCESS STUDIED: Reduction-Oxidation (Redox) of Fe(III)/Fe(II)

- Study reaction in real-time conditions
- Capture fast dynamics
- Reveal how changing reaction conditions influence structure and behavior of enzymes

Why use Fe(III)/Fe(II)? Well-established literature values are used to validate the Drop-on-Tape setup before applying it to unknown redox reactions

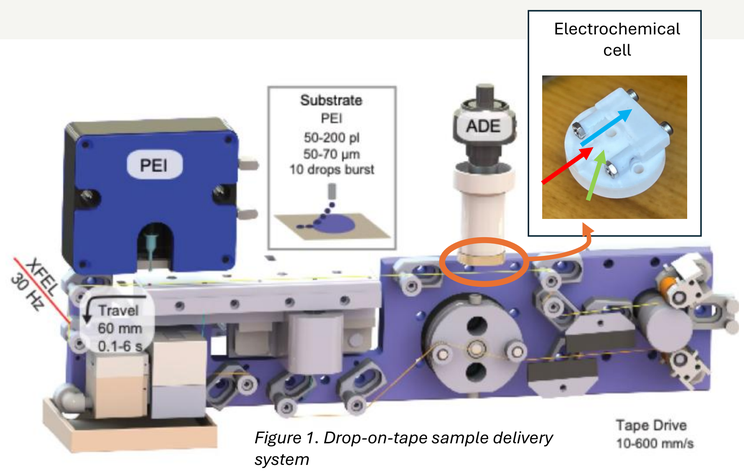
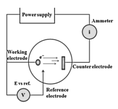


Figure 1. Drop-on-tape sample delivery system

Methodology

Prepare baseline solutions of different ratios of Fe(III) and Fe(II) in 0.8M NaCl



Assemble a three electrode electrochemical cell (working, reference, and counter) and connect capillary working electrode to a syringe pump to control the flow of the sample. (See Fig. 1 image for matching colored arrows)

Measure the open-circuit voltage (OCV) to have initial diagnostic measurements to determine the equilibrium potential of the system

Perform the electrochemical processes to drive the Fe^{3+} → Fe^{2+} reduction-oxidation (redox) reaction

Monitor the Chronoamperometry process using Open-Circuit-Voltage at intervals

Compare final UV-Vis spectrum and OCV to the diagnostics taken and determine the extent of Fe^{3+}/Fe^{2+} conversion

Open Circuit Voltage (OCV): the voltage of the sample when no current is flowing through it

Chronoamperometry (CA): Use electricity to drive the reaction from Fe(III) to Fe(II)

Reduction Reaction: $Fe^{3+} + 1e^- \rightarrow Fe^{2+}$

Oxidation Reaction: $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$

Results

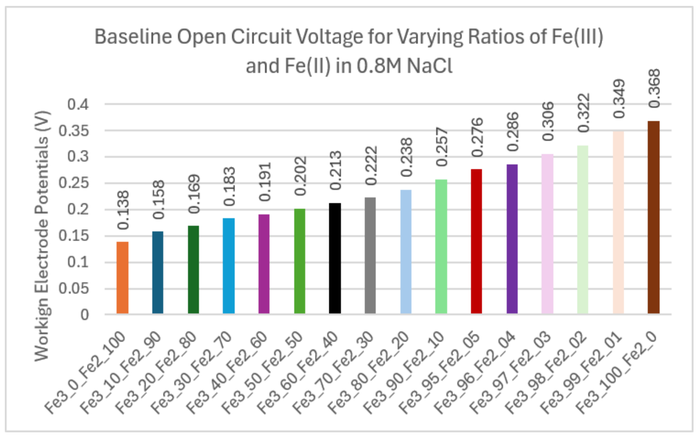


Figure 2. OCV of 16 samples of varying ratios of Fe(III) and Fe(II)

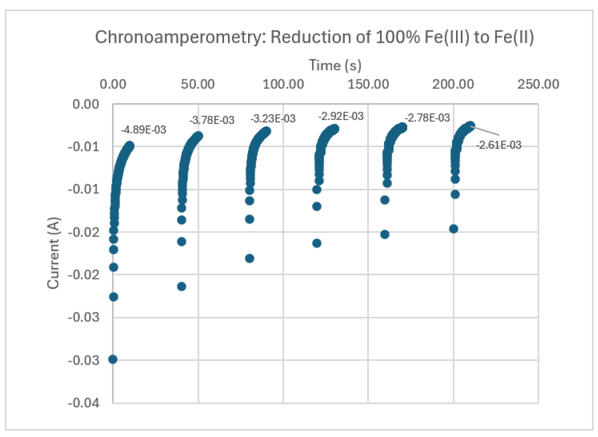


Figure 4. CA of Fe(III) to drive (reduction) reaction to Fe(II)

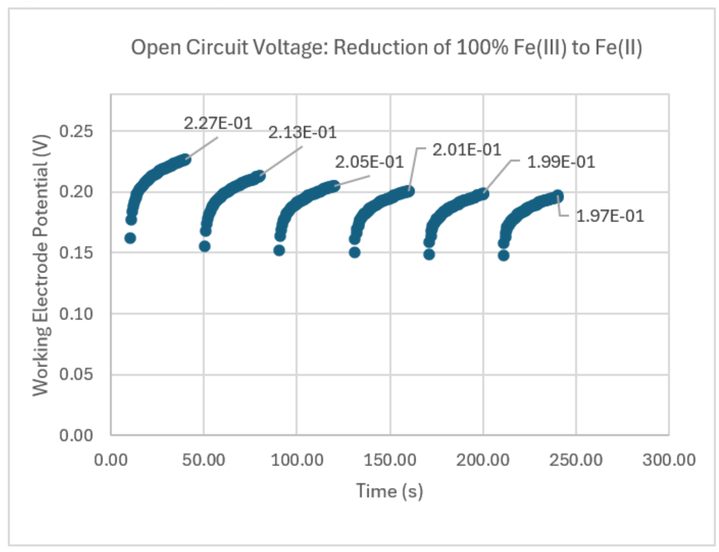


*Figure 5. OCV taken after 10 seconds of current applied during the CA. There is a visible reduction as can be shown by the highlighted values (compared to Figure 2 values). Example: **At 75s, about 55% of Fe(III) has reduce to Fe(II).***

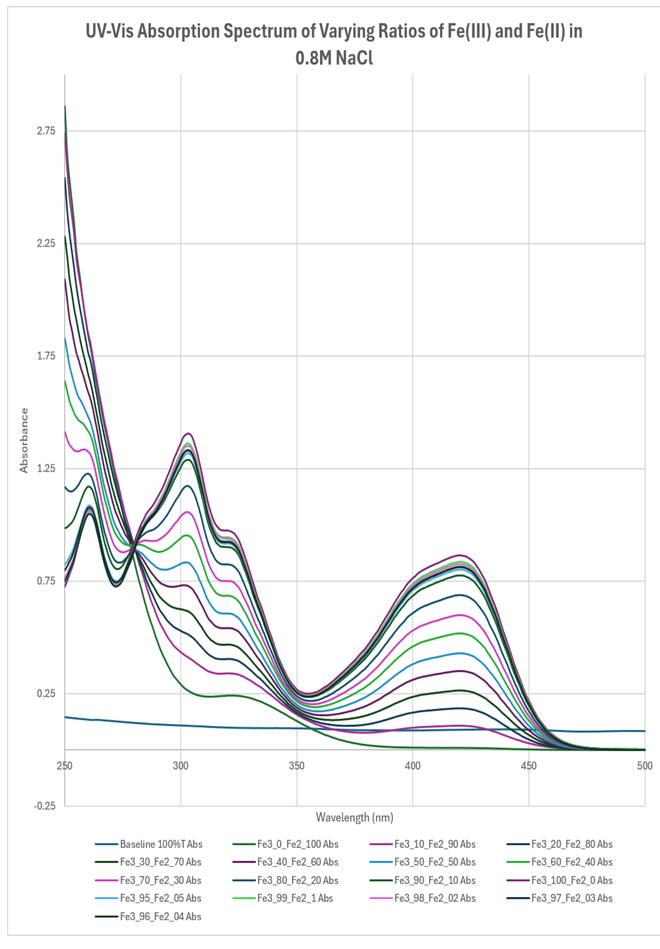


Figure 3. Baseline UV-vis spectrum of all 16 ratios of Fe(III) and Fe(II).

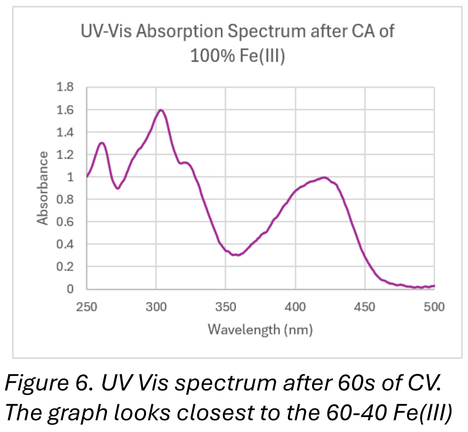


Figure 6. UV Vis spectrum after 60s of CV. The graph looks closest to the 60-40 Fe(III) to Fe(() ratio UV-vis curve.

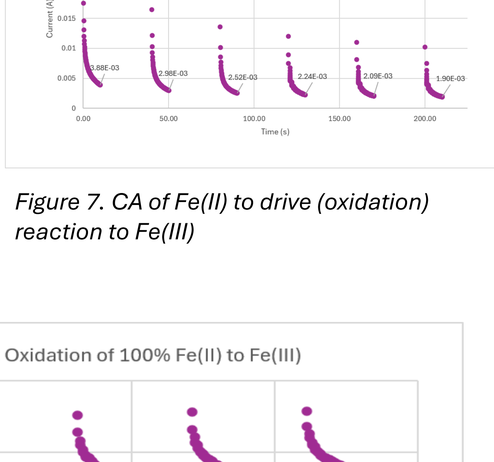


Figure 7. CA of Fe(II) to drive (oxidation) reaction to Fe(III)

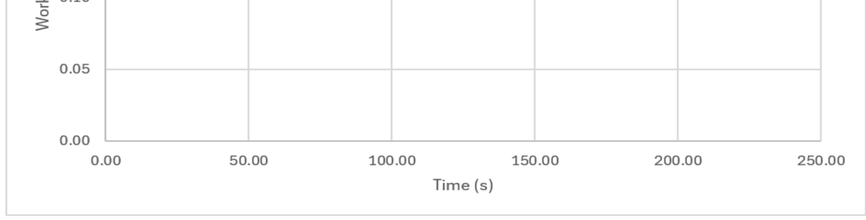


Figure 8. OCV taken after 10 seconds of current applied during the CA. There is a visible reduction as can be shown by the highlighted values (compared to Figure 2 values).

Conclusion

During beamtime, the conversion from Fe(III) to Fe(II) was around 48%.

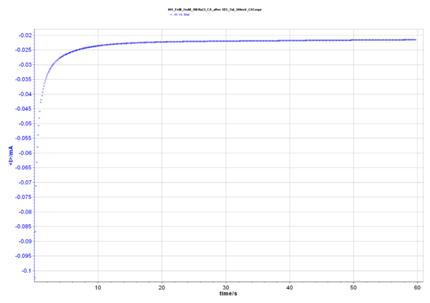


Figure 9. CA of Fe(III) during beamtime in July 2026.

Similar rates recreated in lab shows that set up is a working one.

Future work includes:

- Increasing surface area between liquid and working electrode
- More diagnostics to confirm validity of sample

Current and Future Work

In-Line UV-Vis Setup:

Only diagnostic for clarifying accuracy of sample is through off-line testing UV-vis

BUT

What if we could do it in-line (as droplets pass through)?

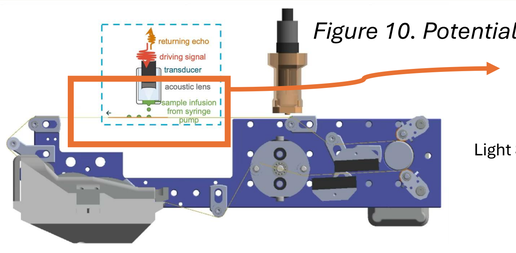
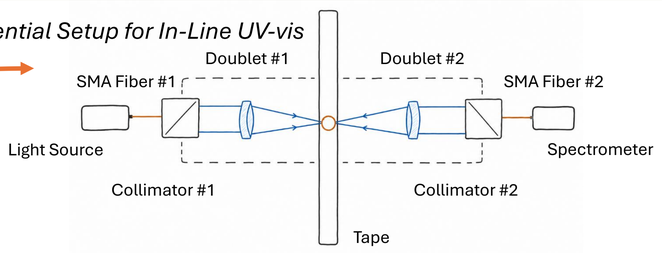


Figure 10. Potential Setup for In-Line UV-vis



Acknowledgements

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References

Chakrabarti, Barun & Roberts, Edward. (2008). Analysis of Mixtures of Ferrocyanide and Ferricyanide using UV-Visible Spectroscopy for Characterisation of a Novel Redox Flow Battery. Journal of the Chemical Society of Pakistan. 30. 817-823.
Tiwari, Vandana. Multimodal applications of Drop-On-Tape (DOT) sample delivery set-up for XFEL. Berkeley, CA.