# Molten Salt Reactor Chlorine Radioisotopes Separation by Electrophoresis

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# Overview

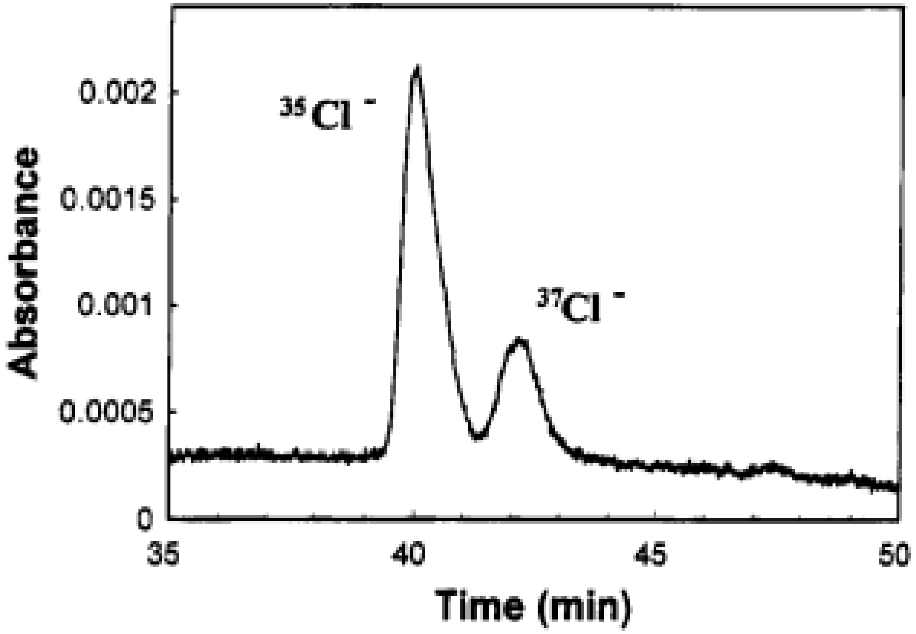
- **Introduction**
  - Electrophoresis fundamentals
- **Review of bench-scale electrophoretic equipment**
  - Cl isotopic analysis by QQQ-ICPMS
  - Comparison of experimental with simulation results
- **Experimental results**
- **Recycle continuous flow electrophoresis design**
- **Conclusions**

# Introduction

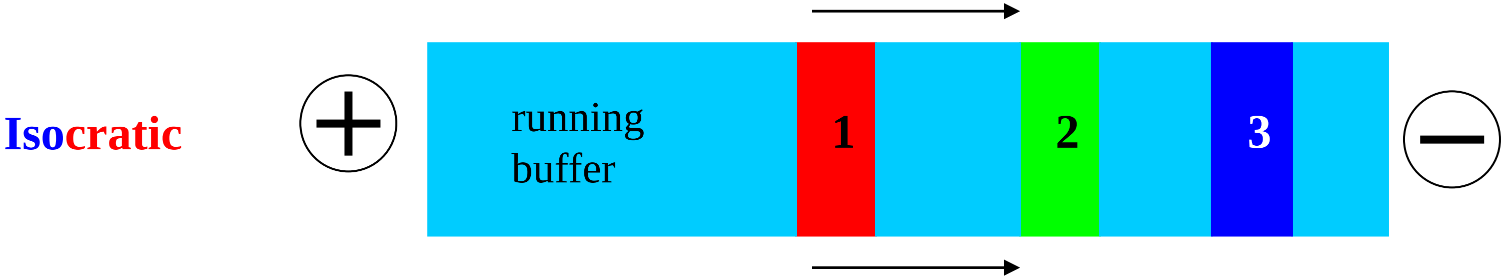
- **Design for molten salt reactors**
  - Rely on fluoride or chloride-based salts to act as coolants or fuel carriers
  - Chloride salts have attractive features
    - Actinide trichlorides forms lower melting point solutions and have higher solubility for actinides so they can contain significant amounts of transuranic elements
    - $^{35}$Cl has a strong (n, proton) threshold reaction that will poison the reactor and gives rise to $^{36}$Cl as an activation product, which is a long-lived, energetic beta source that complicates waste disposal
      - Cl isotope ratio = $^{35}$Cl (75.77%), $^{37}$Cl (24.23%)
  - Currently no domestic capability to enrich $^{37}$Cl from the more abundant $^{35}$Cl

# Electrophoresis

- Enrichment and separation of $^{37}$Cl from $^{35}$Cl at nanogram scales by capillary electrophoresis (CE) has been demonstrated in the technical literature
- Electrophoretic mobility difference is 0.29%
    - $^{35}$Cl mobility = $79.18 \cdot 10^{-9}$ m$^2$/(V·s)
    - $^{37}$Cl mobility = $78.95 \cdot 10^{-9}$ m$^2$/(V·s)
- Elemental chloride has been separated by isotachophoresis (ITP)
- Propose stationary ITP and Moving Bed Electrophoresis (MBE) for enrichment

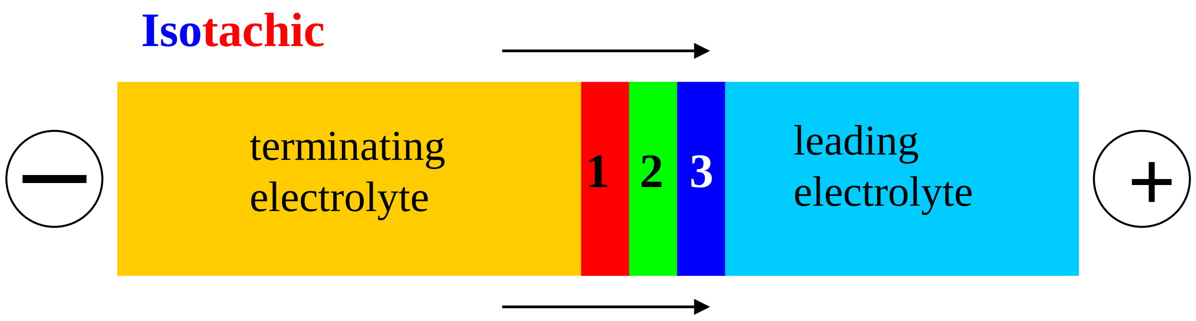


## Capillary Zone Electrophoresis (CZE)



Analytical Chemistry 2018, 90 (15) , 9410-9417.

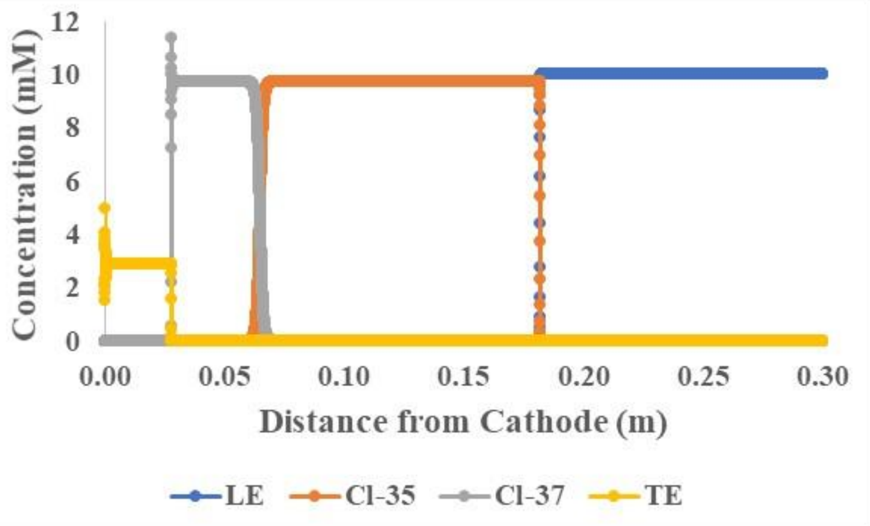
# Isotachophoresis

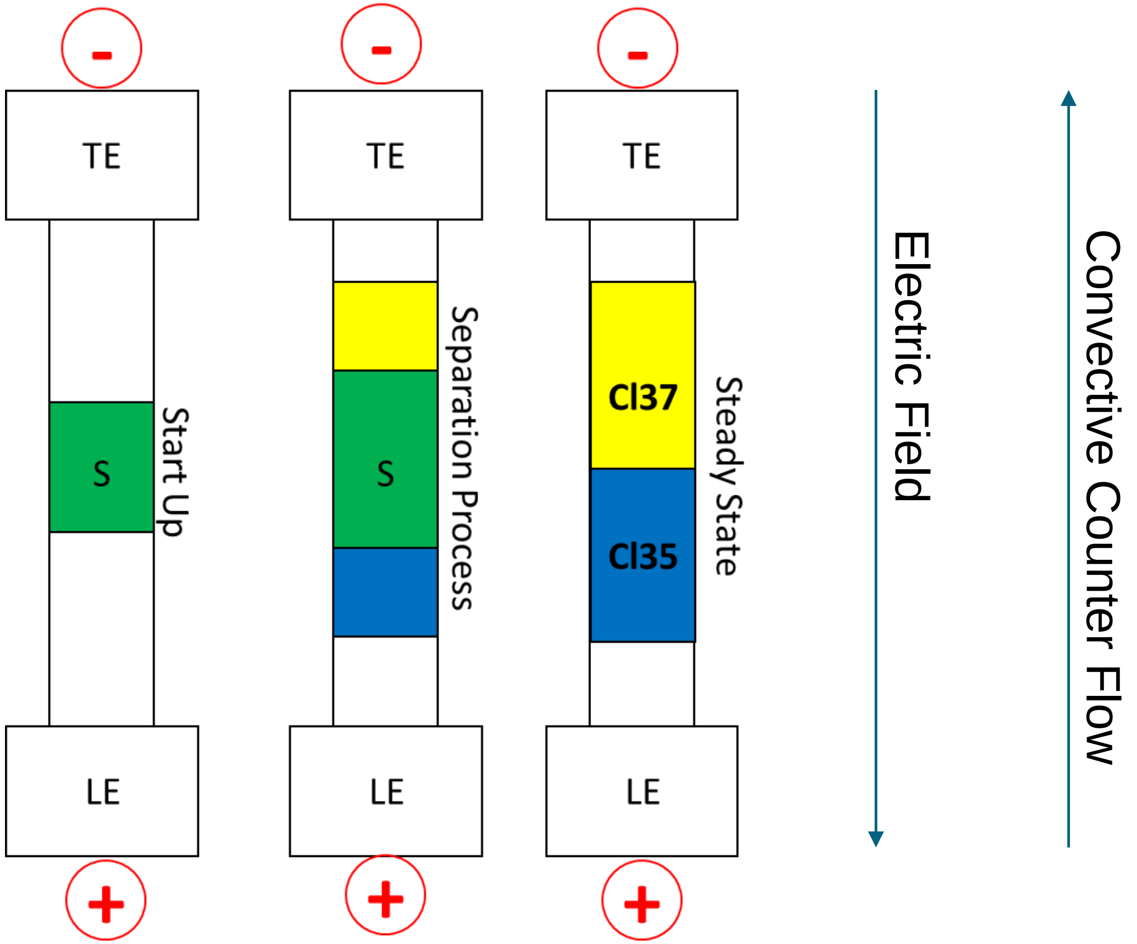


- **Separation and pre-concentration of charged analytes in an electric field**
- **Sample (S) is introduced between a fast-leading electrolyte (LE) and a slow terminating electrolyte (TE)**
- **Apply electric field and ions will migrate according to their $\mu_i$**
  - $\mu_{LE} > \mu_S > \mu_{TE}$
- **Advantages**
  - Concentration by several orders of magnitude
  - Simple, fast, and compatible with other analytical techniques
  - Simultaneous concentration/fractionation
  - Immune to racetrack dispersion
    - ITP self-sharpening effect
  - “Greener” technology
  - Chemical reagents needed are less hazardous than alternative approaches
  - Potential to out-perform liquid:liquid extraction approaches

# Stationary Isotachophoresis

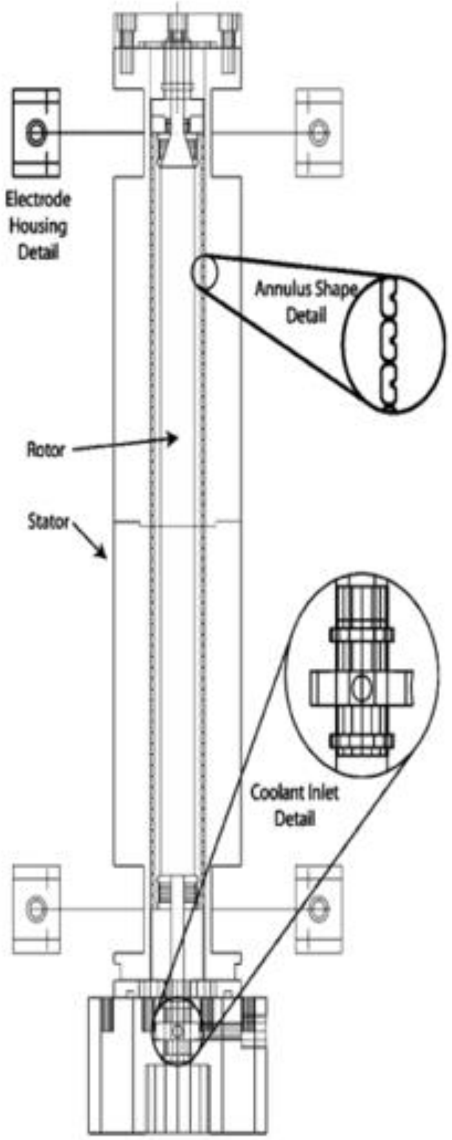
- Balance electric field with “upflow” counter flow
- Allows time for difficult separations
- May take up to days to get complete separation under ideal conditions
  - pH excursion issues, i.e. hydrogen build-up at cathode
- **New capability to PNNL**





# State of the Art Electrophoresis System

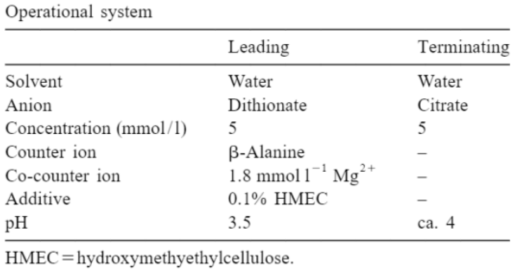
- Separation medium is in the annulus
- Complimentary tines and spinning rotor → No electroosmotic Flow
- Cooling oil is recirculated through the hollowed-out rotor that effectively remove Joule Heat
- Equipment can be modified to run in continuous operation
- Sample ports along the length of the chamber allow for easy sample collection
- Efficient removal of electrolysis products



Ivory, C. F. (2004). ELECTROPHORESIS 25(2): 360-374.

# Challenges

- Initial literature review found thiosulfate and dithionate as strong candidate for LE in ITP separations
- Neither ion was available and required a custom synthesis that made the cost and time to synthesis prohibitive
- Other options Br, I, and CN were safety concerns
- Resulted in a pivoting of strategy
  - Initial testing at PNNL utilized moving bed electrophoresis (MBE)
  - QQQ-ICPMS for analysis of separation efficiency

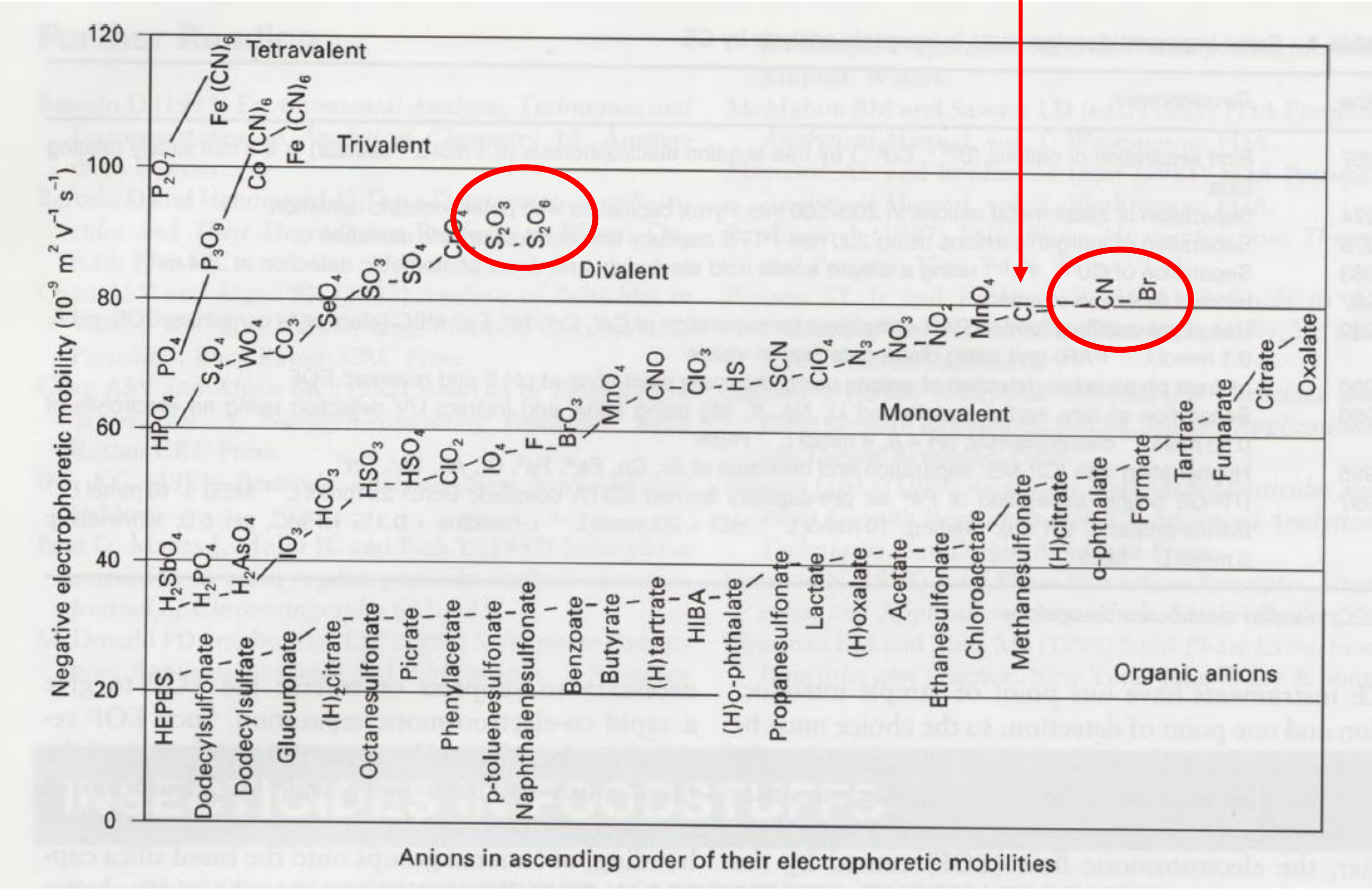


Operational system

| | Leading | Terminating |
|---|---|---|
| Solvent | Water | Water |
| Anion | Dithionate | Citrate |
| Concentration (mmol/l) | 5 | 5 |
| Counter ion | β-Alanine | – |
| Co-counter ion | 1.8 mmol $l^{-1}$ $Mg^{2+}$ | – |
| Additive | 0.1% HMEC | – |
| pH | 3.5 | ca. 4 |

HMEC = hydroxymethyethylcellulose.

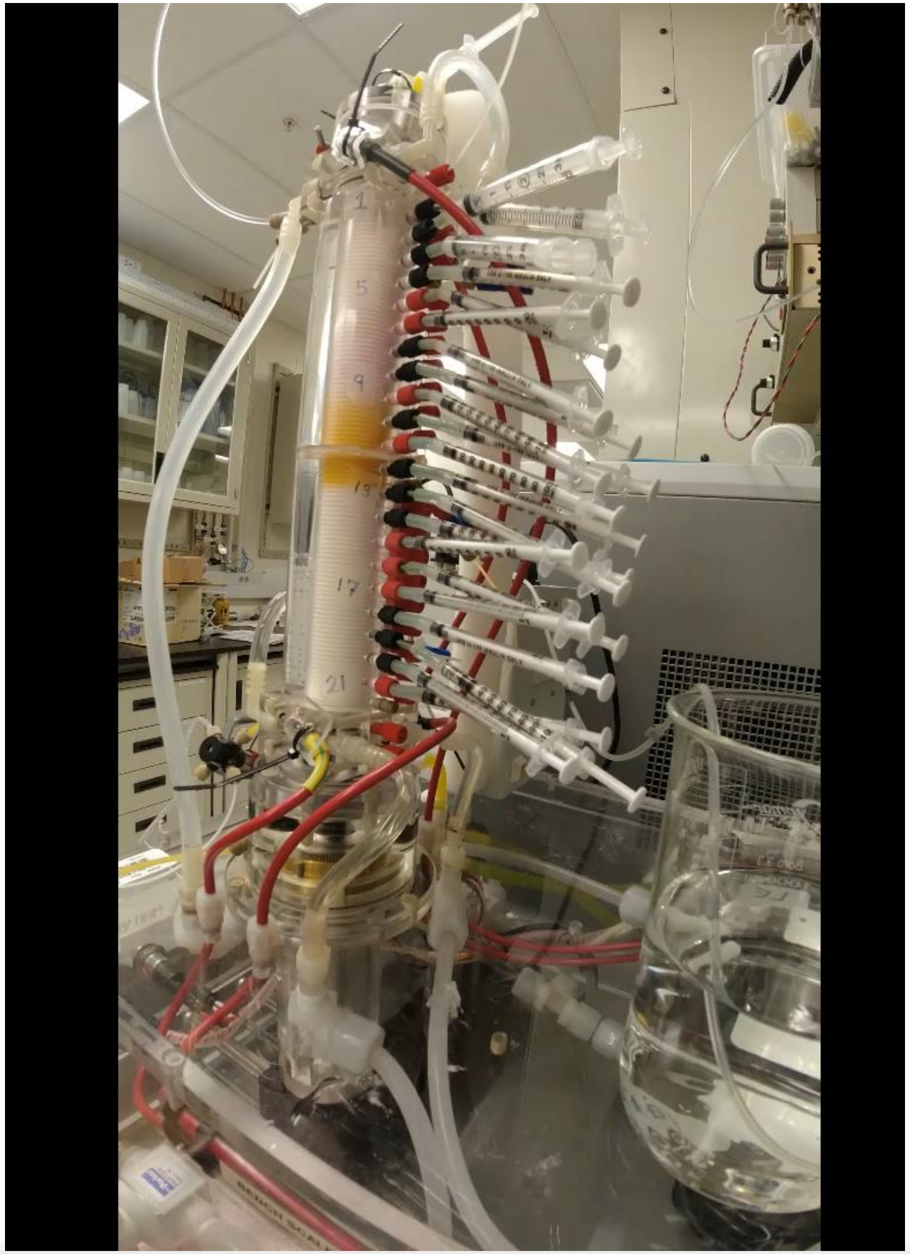
For ITP to work need a faster ion than Cl act as LE



J. Chromatog. A 838 (1999) 81-88.

# Initial testing – Moving Bed Electrophoresis

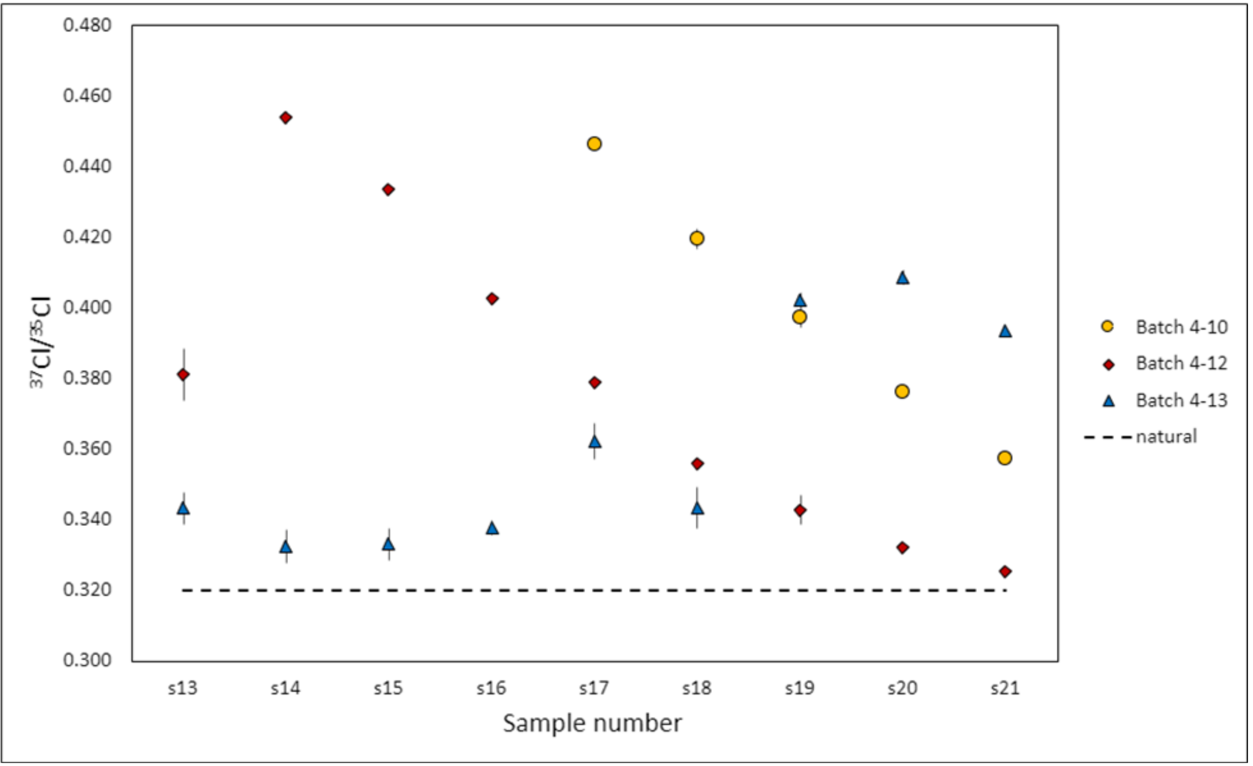
- Similar to ITP
    - Instead of LE you use sample as leading zone and slower ion, in this case, $^{37}$Cl will be enriched at TE interface
- ITP System
    - LE – 10mM HCl titrated to pH 8.8 with Tris
    - TE – 60 mM ε-Aminocaproic acid (EACA) titrated to pH 9.5 with EACA
    - Sample – 0.4 mM Orange G used as a visual indicator to balance "upflow" counter flow with electric field



# Analytical Results from QQQ-ICPMS

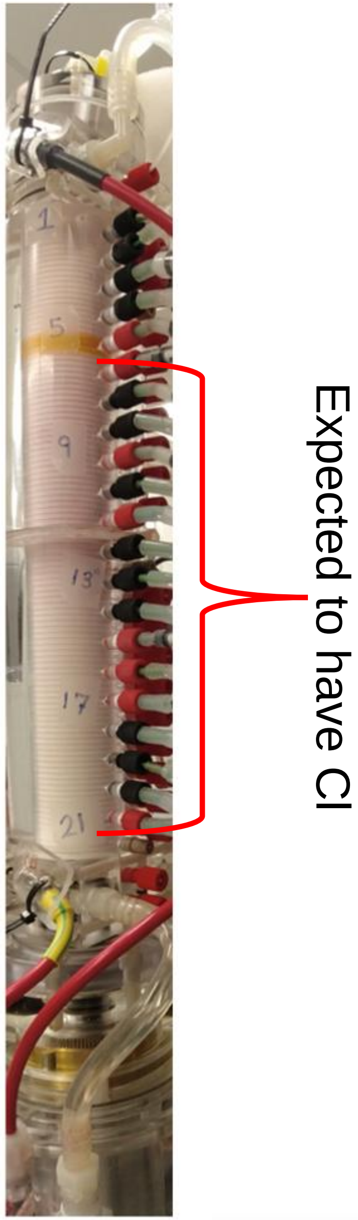
- This is about what we expected in terms of enrichment based on previous results
  - Dispersion is the primary source of low enrichment levels
- Unexpected – samples close to the visible dye did not contain sufficient amount of chlorine to get an accurate measurement
  - Unknown – best guess currently is another anion contamination forming a zone between Cl-37 and visible dye
- Single stage separation factor ($\alpha$):

$$\propto = \frac{Cl37_{product}\cdot\left(1-Cl37_{tails}\right)}{Cl37_{tails}\cdot\left(1-Cl37_{product}\right)} = 1.81$$



| Experiment | *Experimental System* | *Voltage (kV)* | *Time (hr)* | *Meaningful Sample Numbers†* |
|---|---|---|---|---|
| Batch 4-10 | 10mM HCl pH 8.8 w/ Tris | 4.0 | 16 | S17-S21 |
| Batch 4-12 | 10mM HCl pH 8.64 w/ Tris | 4.0 | 22 | S14-S21 |
| Batch 4-13 | 10mM HCl pH 8.8 w/ Tris | 3.5 | 24 | S19-S21 |
| Batch 4-19* | 10mM HCl pH 9.4 w/ Tris | 3.5 | 24 | * |

*Awaiting Results; †Samples that had sufficient counts to be reliable in their measurement.

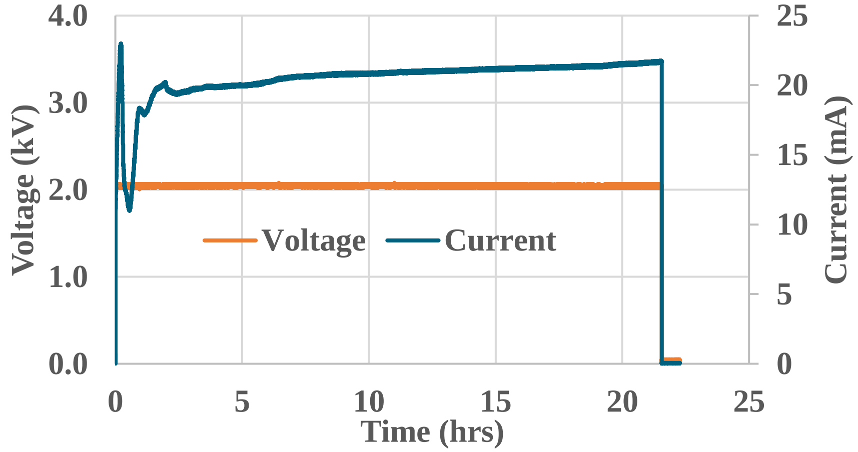


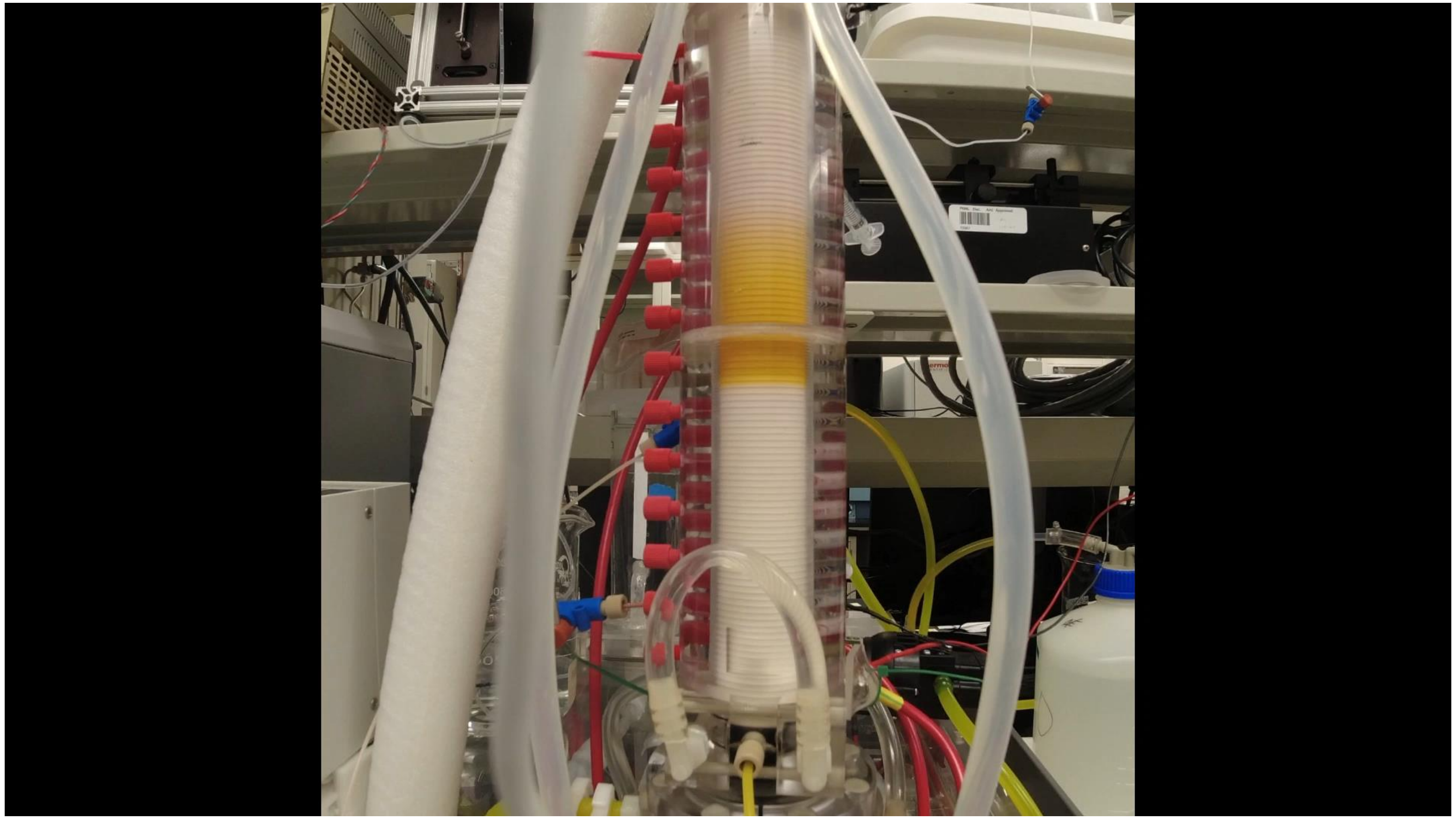
24 hr

QQQ-ICPMS analysis by Nicole Rocco and Tyler Schlieder (PNNL)

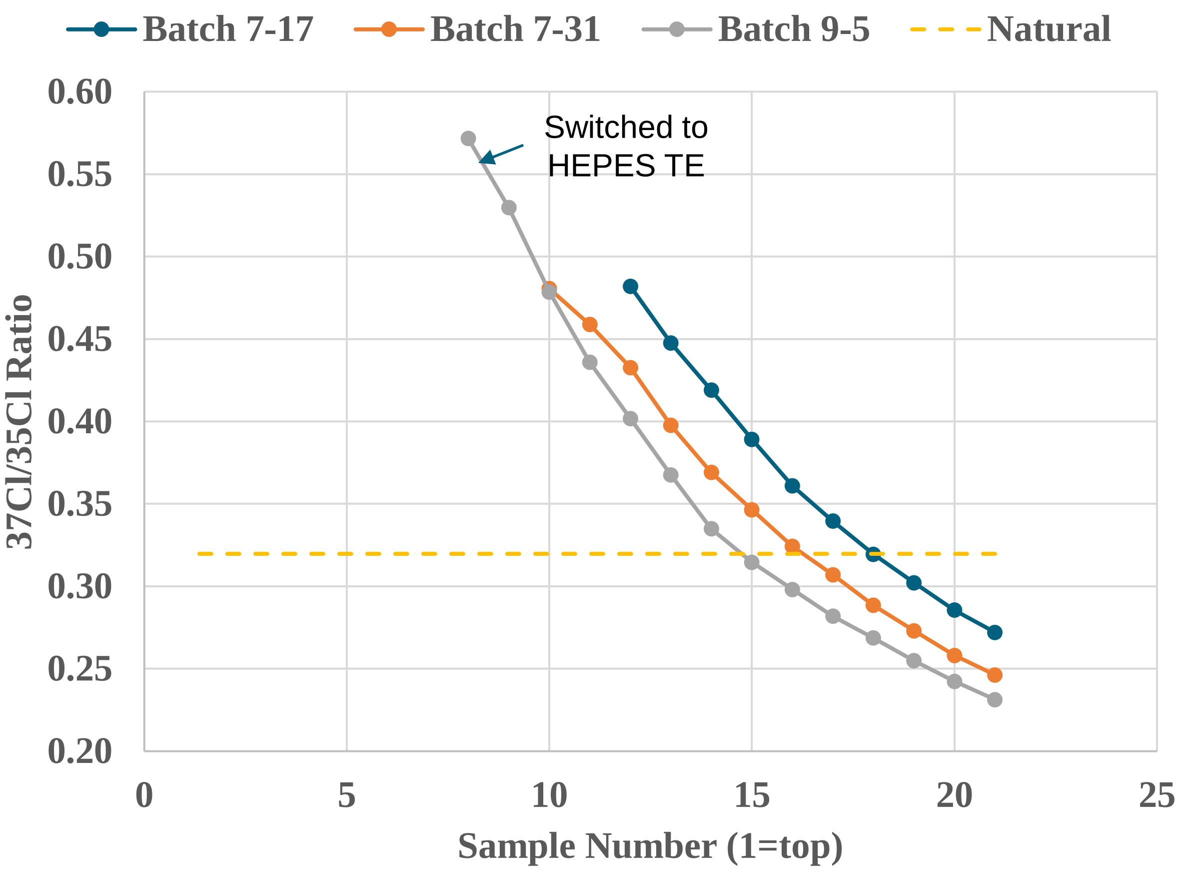
# Isotachophoresis Demonstration

- LE: 10mM Ammonium Thiosulfate pH 9.3 with Ammonium Hydroxide
- TE: 10mM ε-Aminocaproic Acid, 5mM barium hydroxide, pH 11.2
- Sample: 0.4mM Orange G Dye + 60mM Potassium Chloride in 3mL of TE

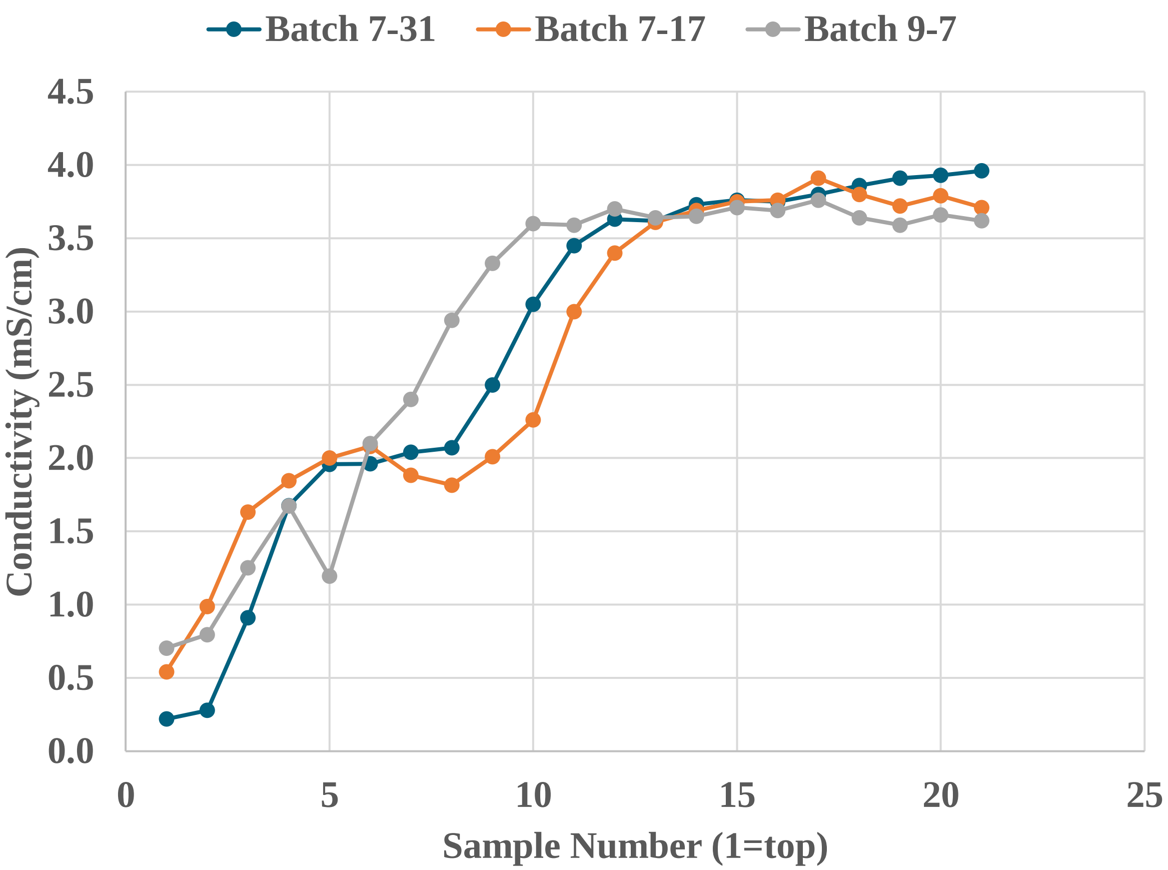




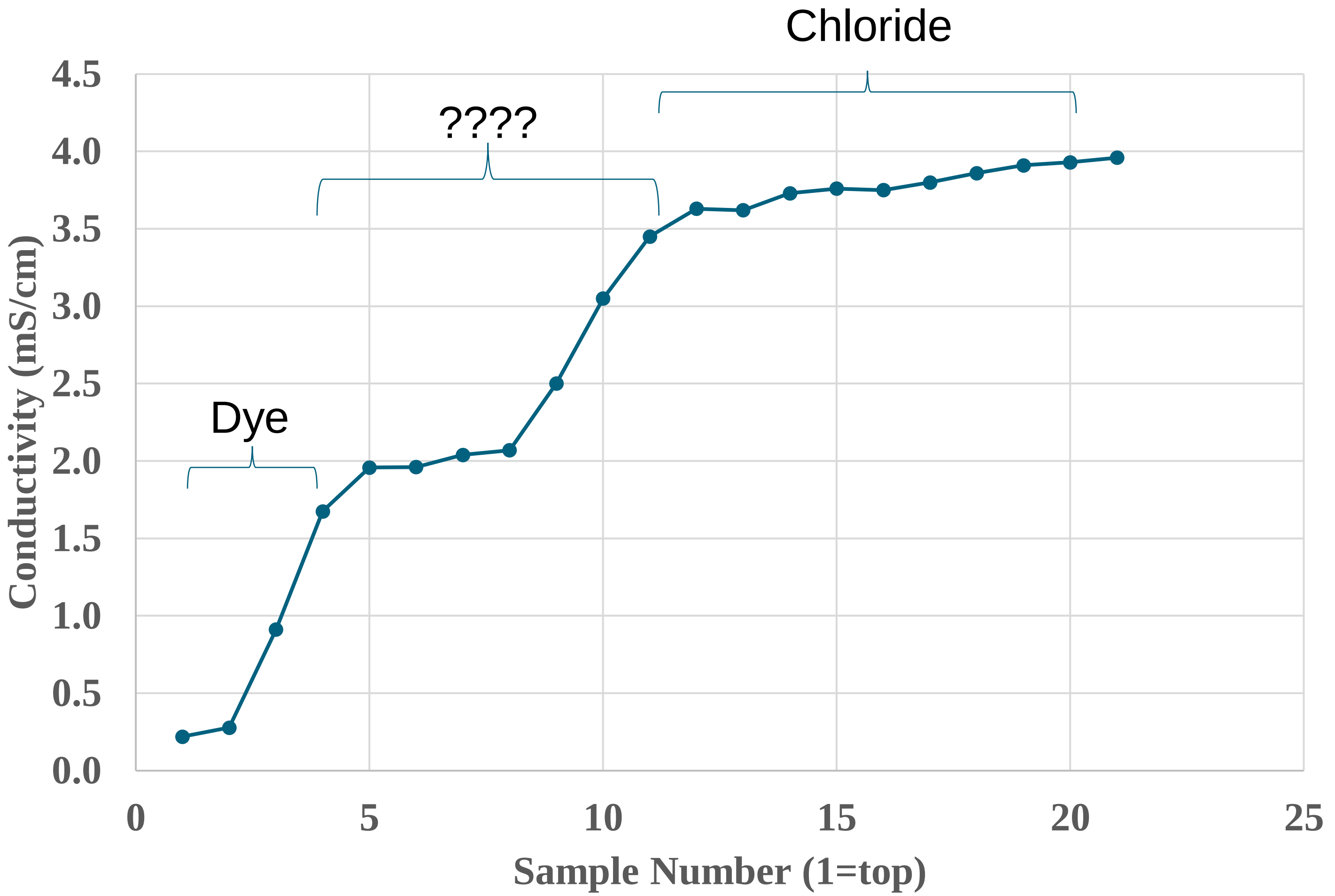
# Experimental Results



Switched to HEPES TE

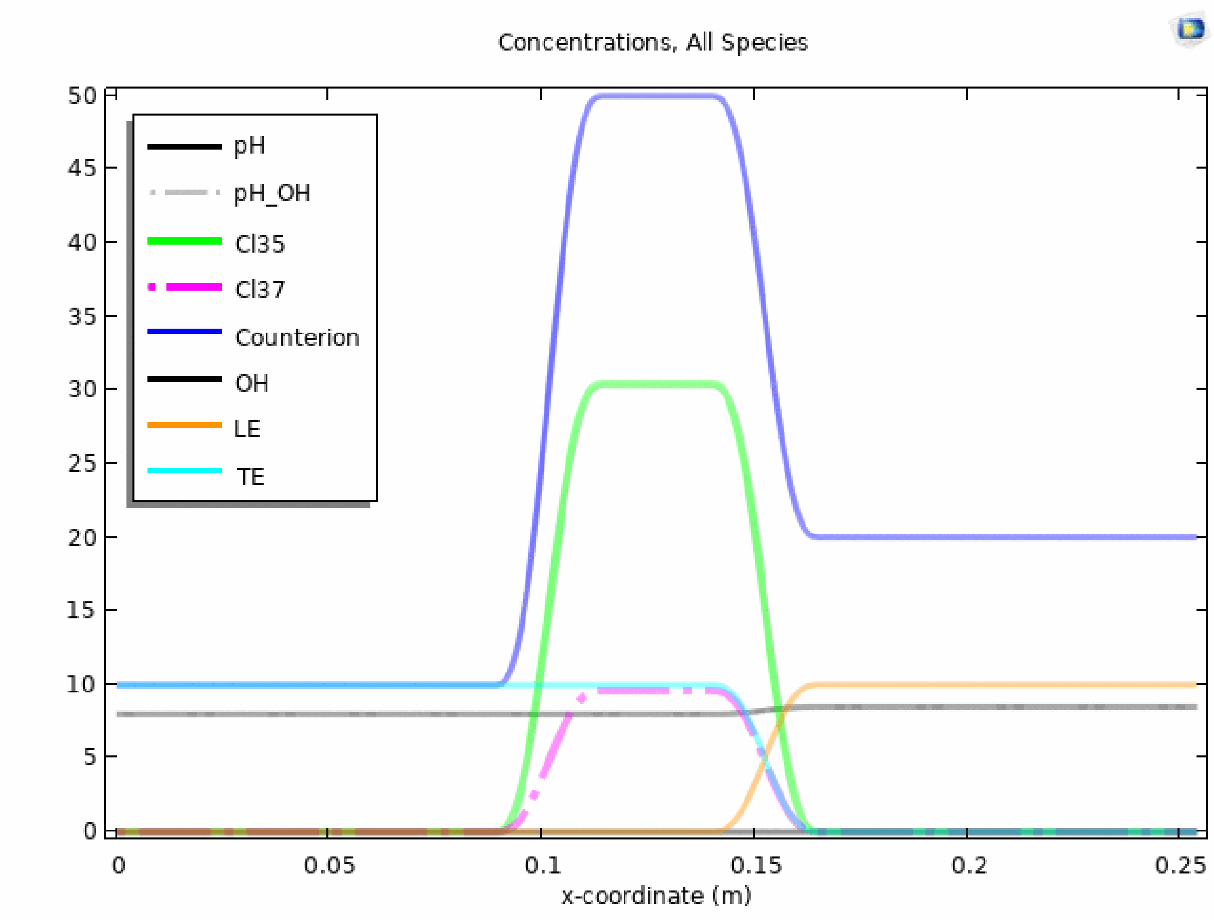


# Conductivity of Samples



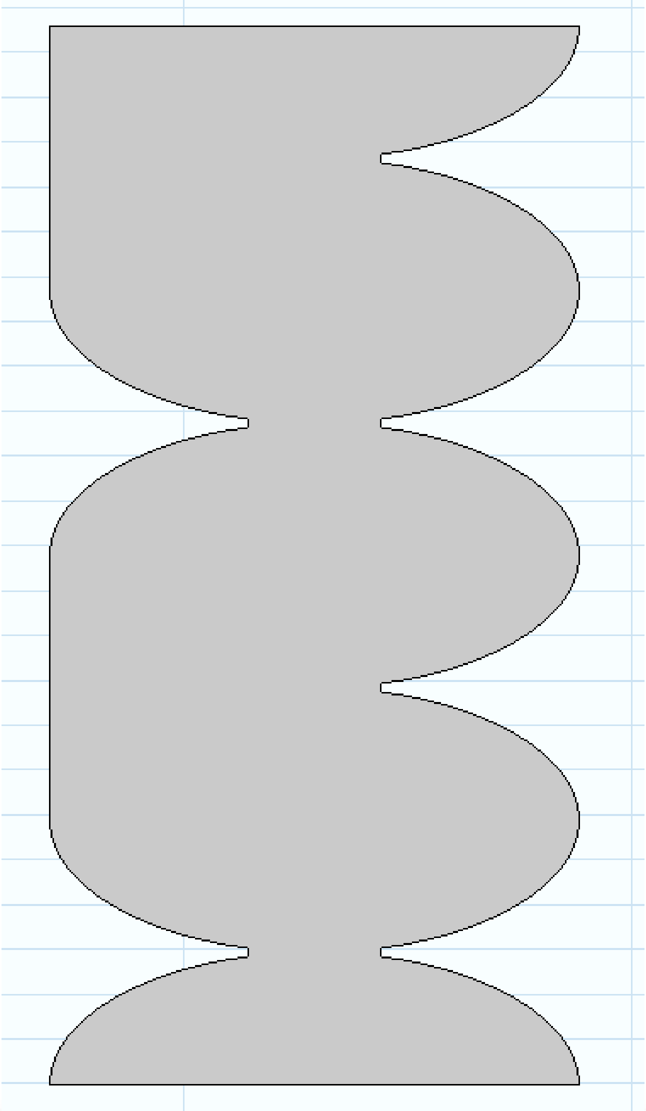
- Possibilities:
  - $CO_2$ dissolved in water→carbonate or carbamate zones →$Ba(OH)_2$
  - Nonvisible form of dye
  - Thiosulfate + Cl → Bisulfate
  - TE has multiple forms → Run with different TE
  - Some other contaminant???

# Numerical Simulation



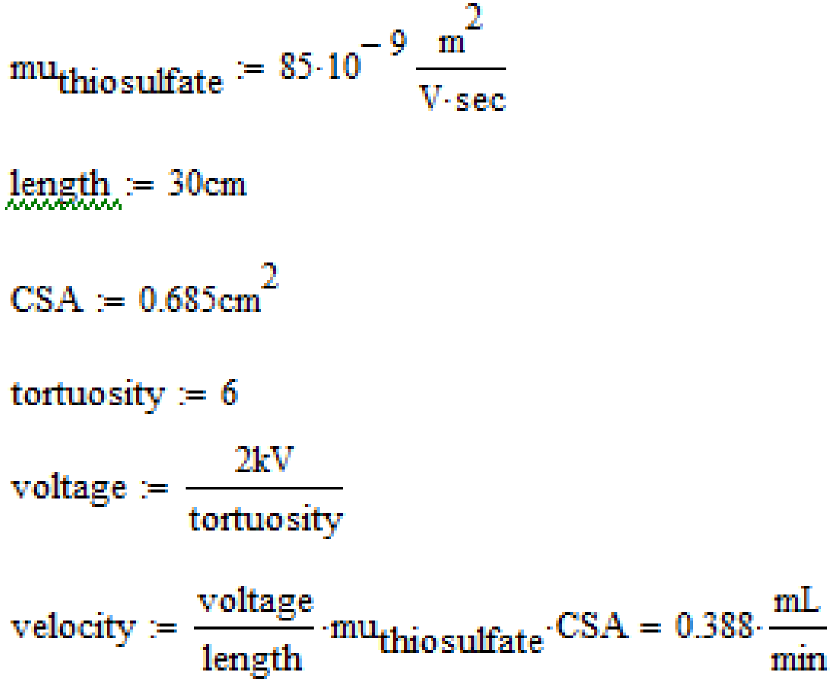
- Indicates a ratio close to 1 after 24 hours
- Deep dive into experimental system and simulation results
- Current in simulation appears to be a factor of 6 higher than what is measured experimentally for this electrolyte system

# Geometric Tortuosity



- Shaping of VpHor rotor and stator has an impact on effective electric field.
- Experiments using 10 mM NaCl in 18 MΩ water yielded a tortuosity of about 2 in order to match the current between simulation and experiment.
- However, in ITP experiments a tortuosity of 6 was needed to get good agreement with the current between experiment and simulation.
- Depending on the electrolyte system we get a different number for the tortuosity indicating that its not a mechanical or geometric issue.

# Further Evidence



$$\mathrm{mu}_{\mathrm{thiosulfate}} := 85 \cdot 10^{-9} \frac{\mathrm{m}^2}{\mathrm{V \cdot sec}}$$

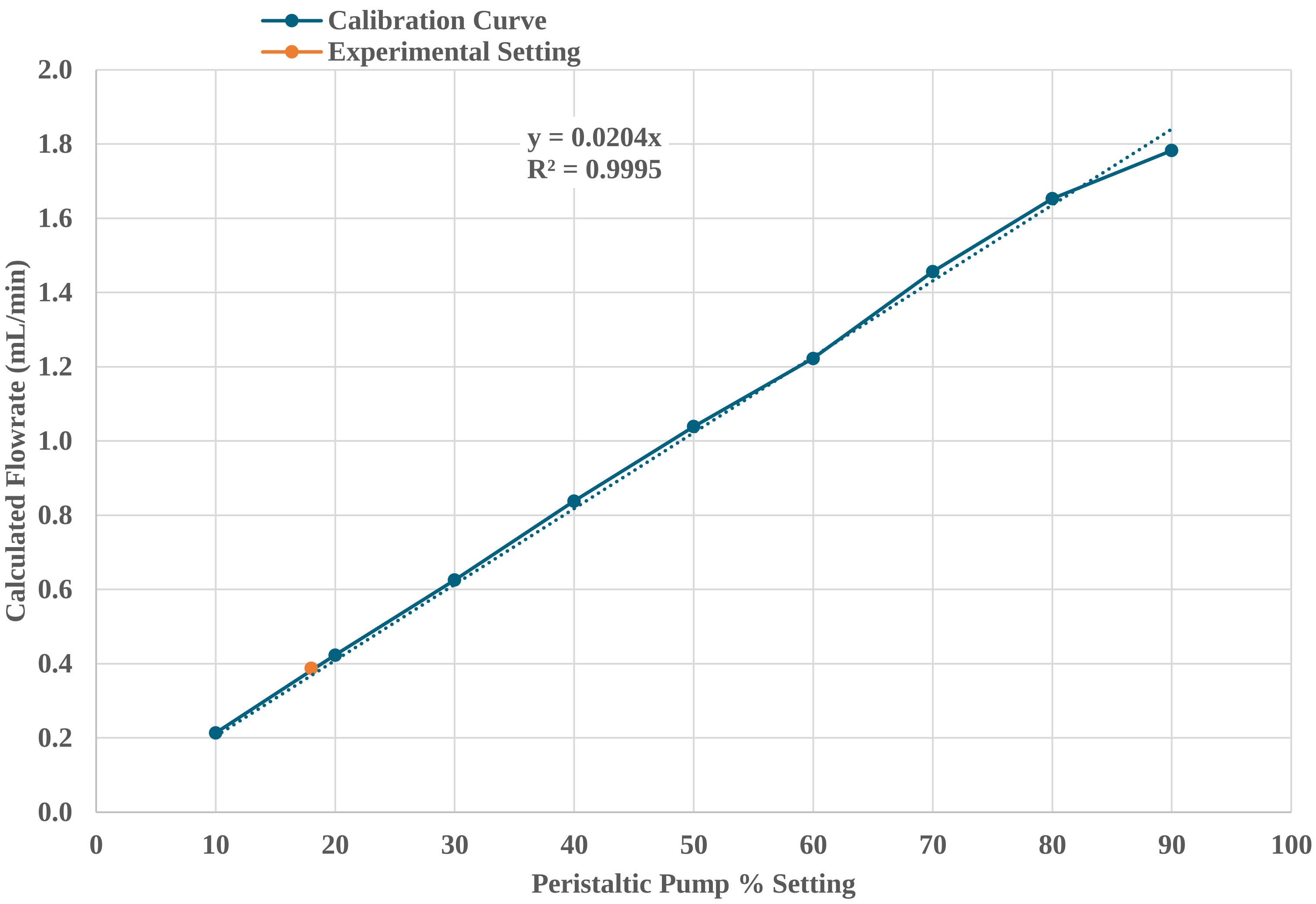
$$\mathrm{length} := 30\mathrm{cm}$$

$$\mathrm{CSA} := 0.685\mathrm{cm}^2$$

$$\mathrm{tortuosity} := 6$$

$$\mathrm{voltage} := \frac{2\mathrm{kV}}{\mathrm{tortuosity}}$$

$$\mathrm{velocity} := \frac{\mathrm{voltage}}{\mathrm{length}} \cdot \mathrm{mu}_{\mathrm{thiosulfate}} \cdot \mathrm{CSA} = 0.388 \cdot \frac{\mathrm{mL}}{\mathrm{min}}$$

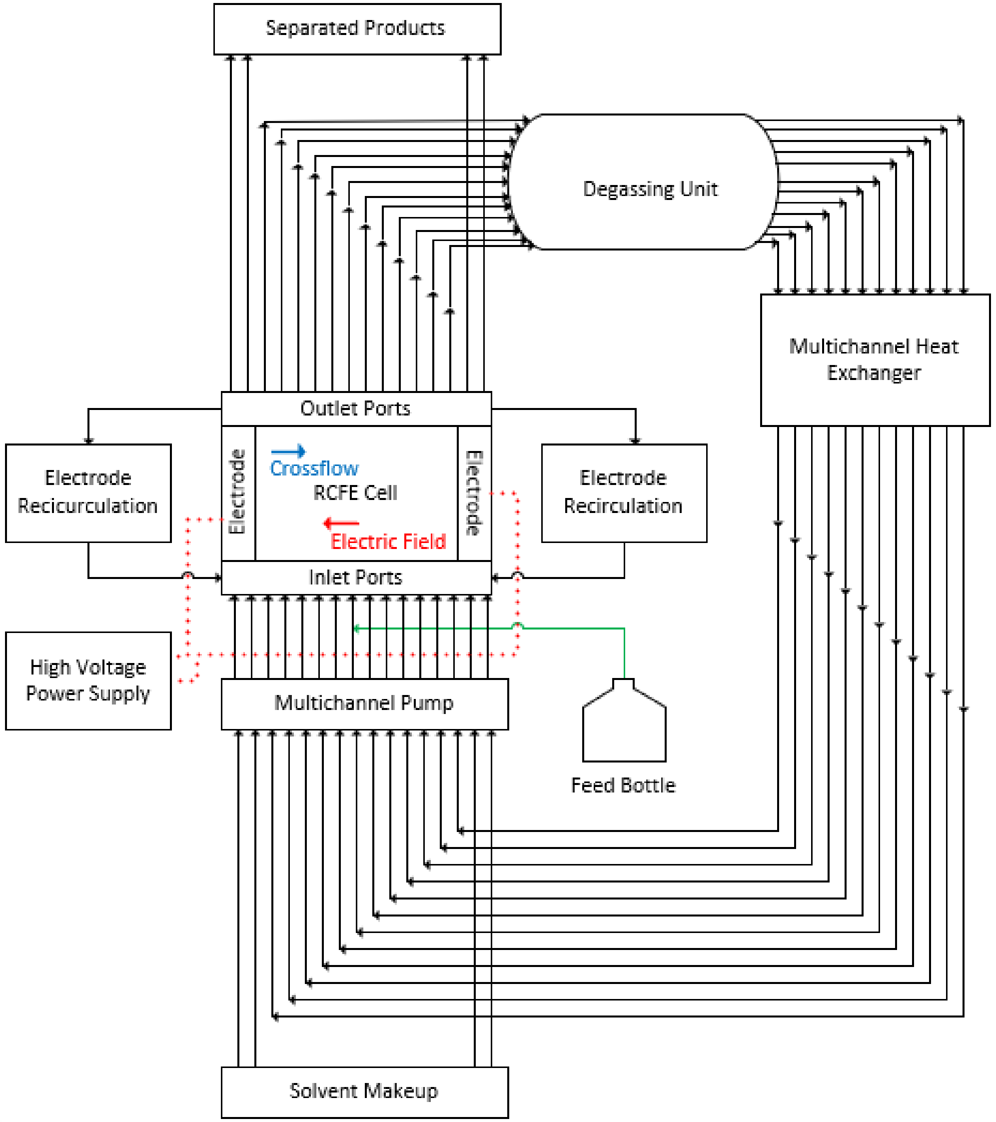


# Things to Keep in Mind

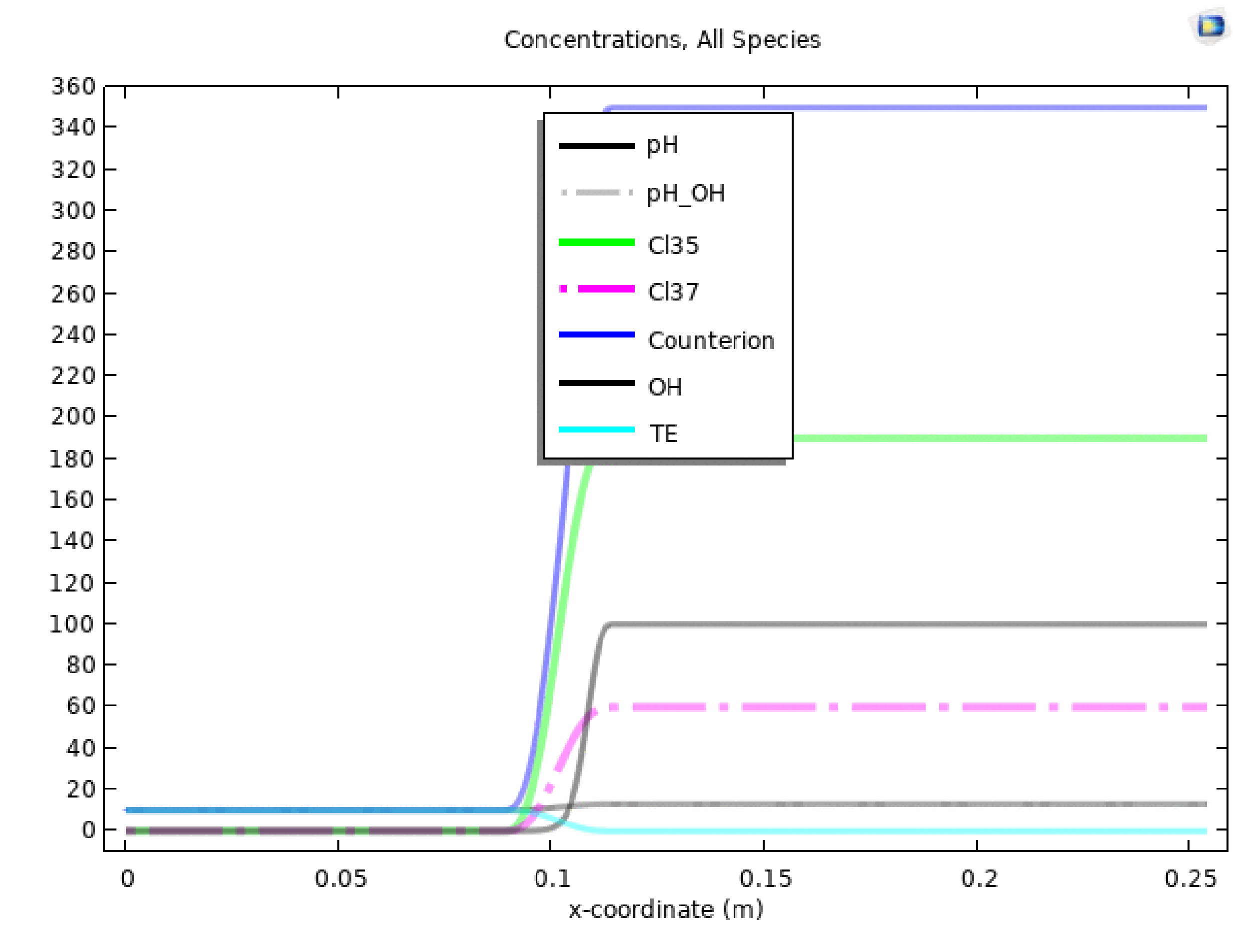
- Each decade increase in pH increases throughput by 10x
- ITP/MBE are expected to fail at pH>13
- Operation at higher pH will require better cooling due to the generation of Joule heat
- **Reduction of machine dispersion by 4x will dramatically increase enrichment as illustrated by the recycling continuous flow electrophoresis (RCFE) system**
- **It would be difficult to reduce dispersion in the existing electrophoresis unit but relatively easy to do this in the Flat-Bed RCFE by using surface coatings and adjusting the counterflow**

# Scale-Up and Design of New Electrophoresis System

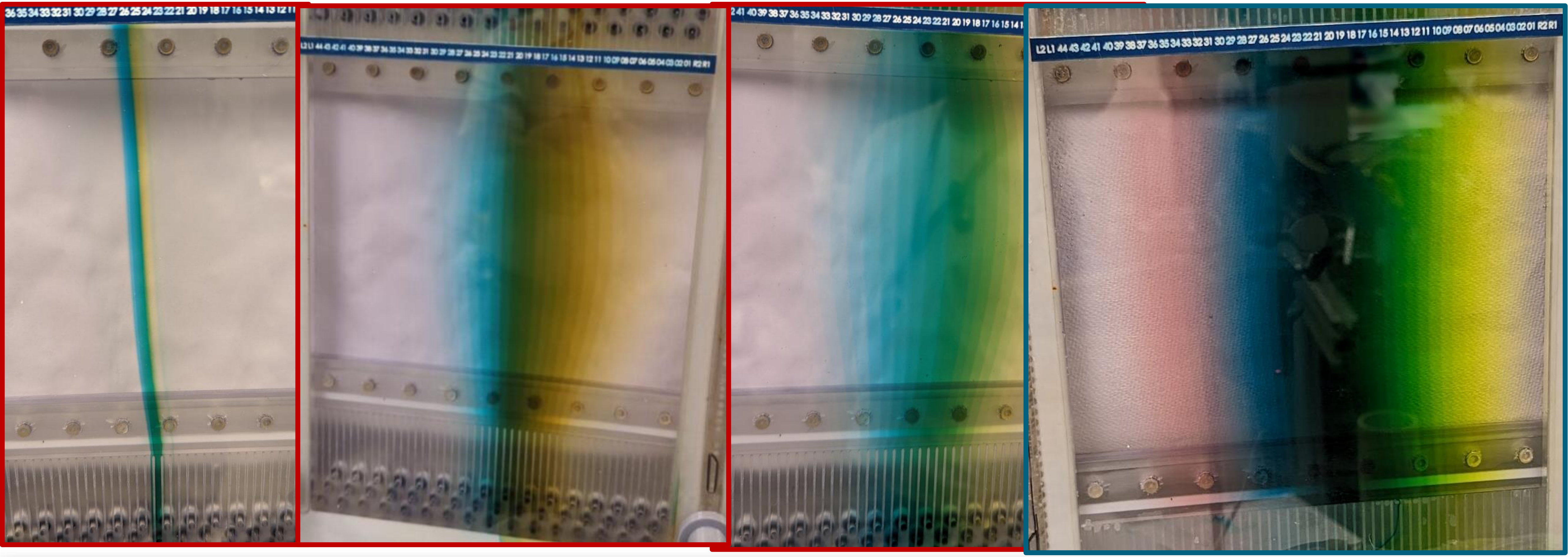
- Flat-Bed Recycling Continuous Flow Electrophoresis Device
- Two 24 Channel Peristaltic Pumps that Recycle Flow through the Device
- Degassing Unit to Remove Bubbles from System
- Heat Exchanger to Cool Fluid
- Electric Field from Right to Left
- Cross Flow from Left to Right
- Channel is 1 mm gap between Front Plate and Back Plate



# Constructed Test Stand



# Shakedown Experiments with Food Coloring



# Conclusions

- **Developed a capability for PNNL to quantify isotopic ratio of chlorine**
- **Demonstrated enrichment in state-of-the-art bench scale electrophoresis equipment despite higher than desirable dispersion**
  - Investigation into high dispersion presents need for Recycling Continuous Flow Electrophoresis Device
- **Developed new electrophoresis equipment design, i.e. RCFE**
  - Proof-of-concept shakedown with dye testing

# Thank you

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