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Molten Salt Reactor PROGRAM

Molten Salt Reactor Radioisotopes Separation by ~~Isotachophoresis~~

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Overview

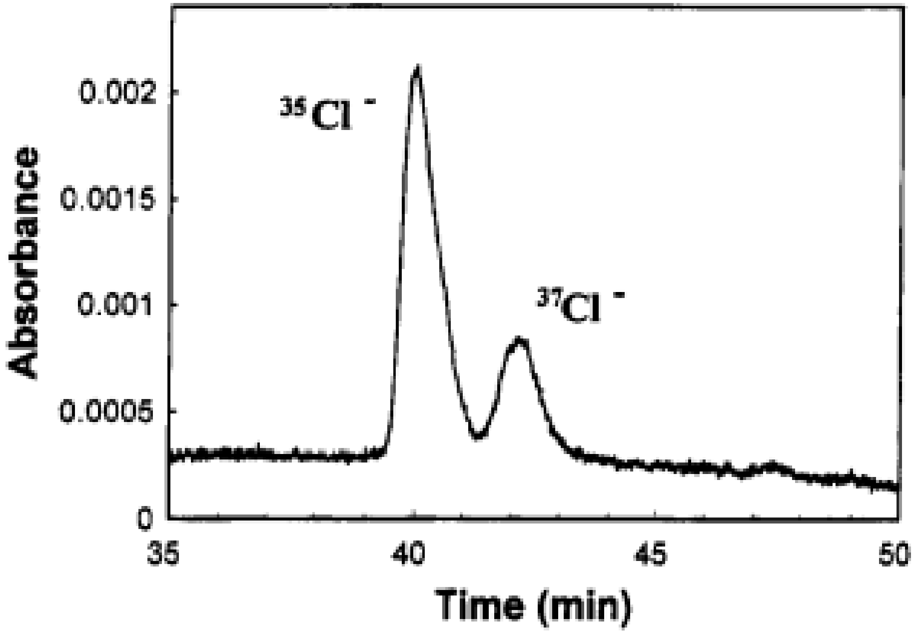
- **Introduction**
- **Experimental**
    - Cl isotopic analysis by QQQ-ICPMS
    - Electrophoresis experiment in bench-scale electrophoretic equipment
- **Numerical simulations using COMSOL Multiphysics**
- **Experimental results**
- **Recycle continuous flow electrophoresis design**
- **Conclusions**

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 also gives rise to ^{36}Cl as an activation product, which is a long-lived, energetic beta source that complicates waste disposal
  - Currently no domestic capability to enrich ^{37}Cl from the more abundant ^{35}Cl

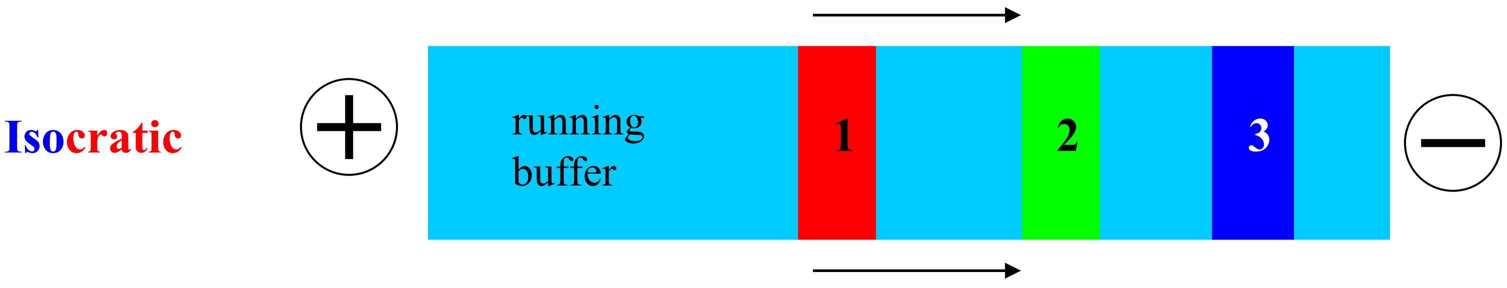
Electrophoresis

- 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 = $79.18 \cdot 10^{-9}$ $m^2/(V \cdot s)$
    - ^{37}Cl mobility = $78.95 \cdot 10^{-9}$ $m^2/(V \cdot s)$
- Elemental chloride has been separated by isotachophoresis (ITP)
- Propose stationary ITP and Moving Bed Electrophoresis (MBE) for enrichment

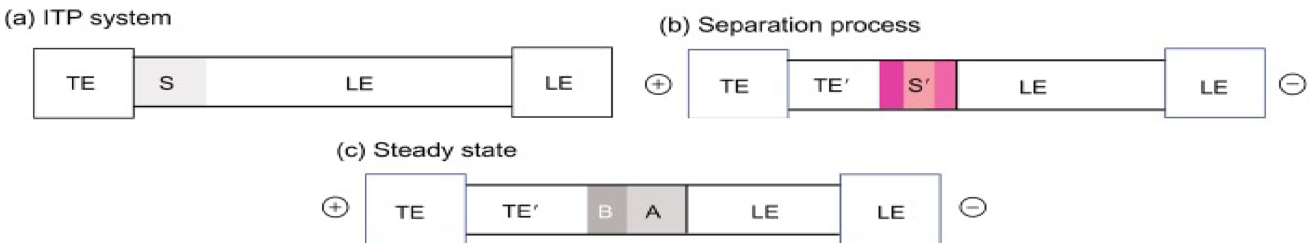


Lucy, C., McDonald, T. Anal. Chem. 1995, 67, 6, 1074–1078

Capillary Zone Electrophoresis (CZE)



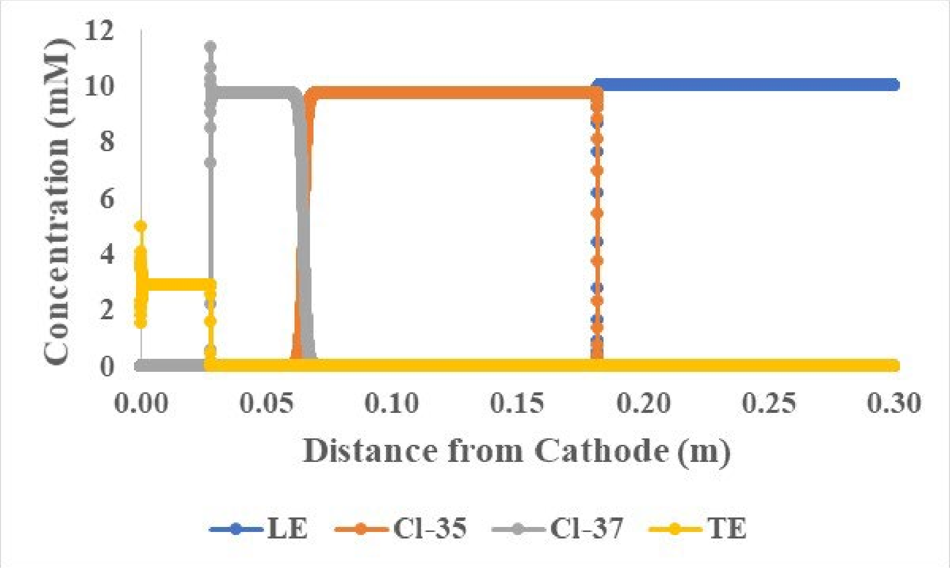
Isotachophoresis

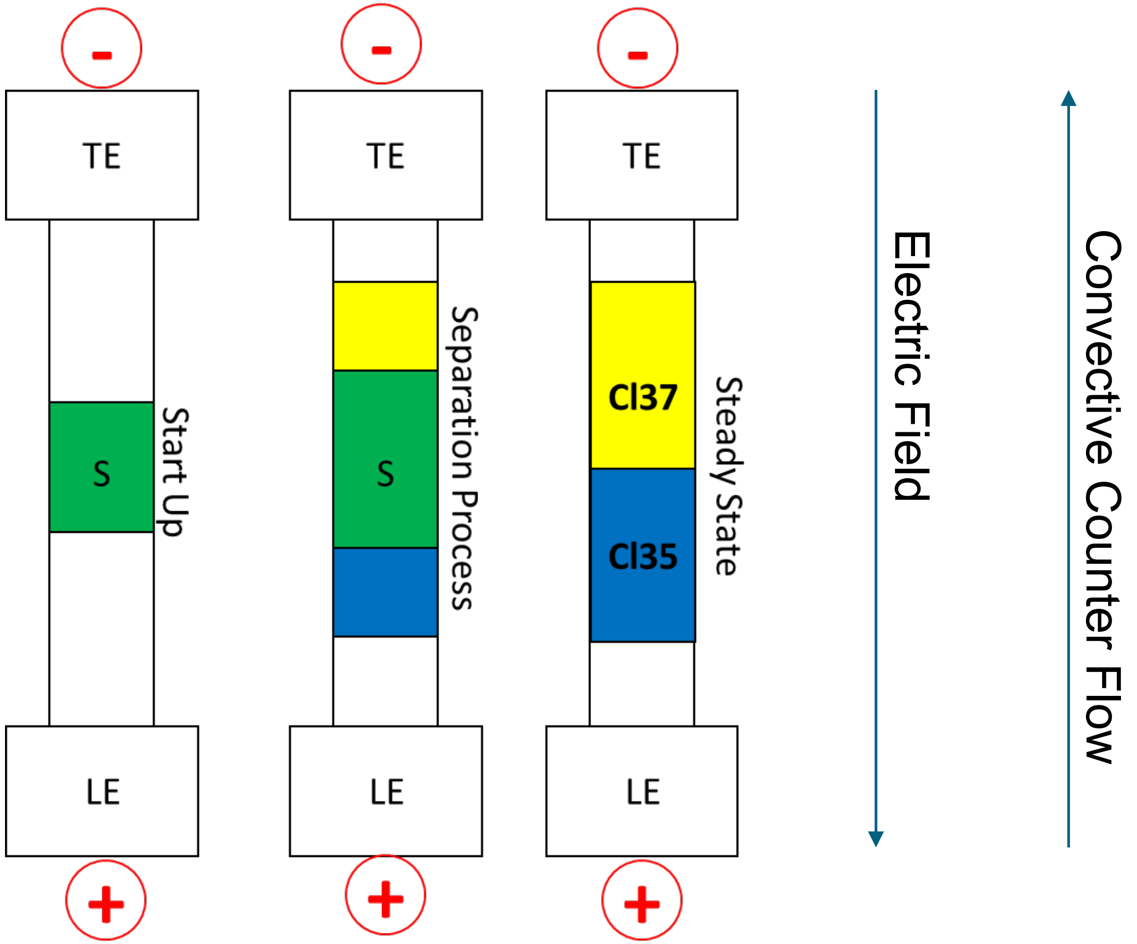


- **Separation and pre-concentration of charged analytes in an electric field**
- **Sample (S) is introduced between a fast leading electrolyte (LE) and a slow terminating electrolyte (TE)**
- **Apply electric field and ions will migrate according to their m_i**
  - $m_{LE} > m_S > m_{TE}$
- **Advantages**
  - 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

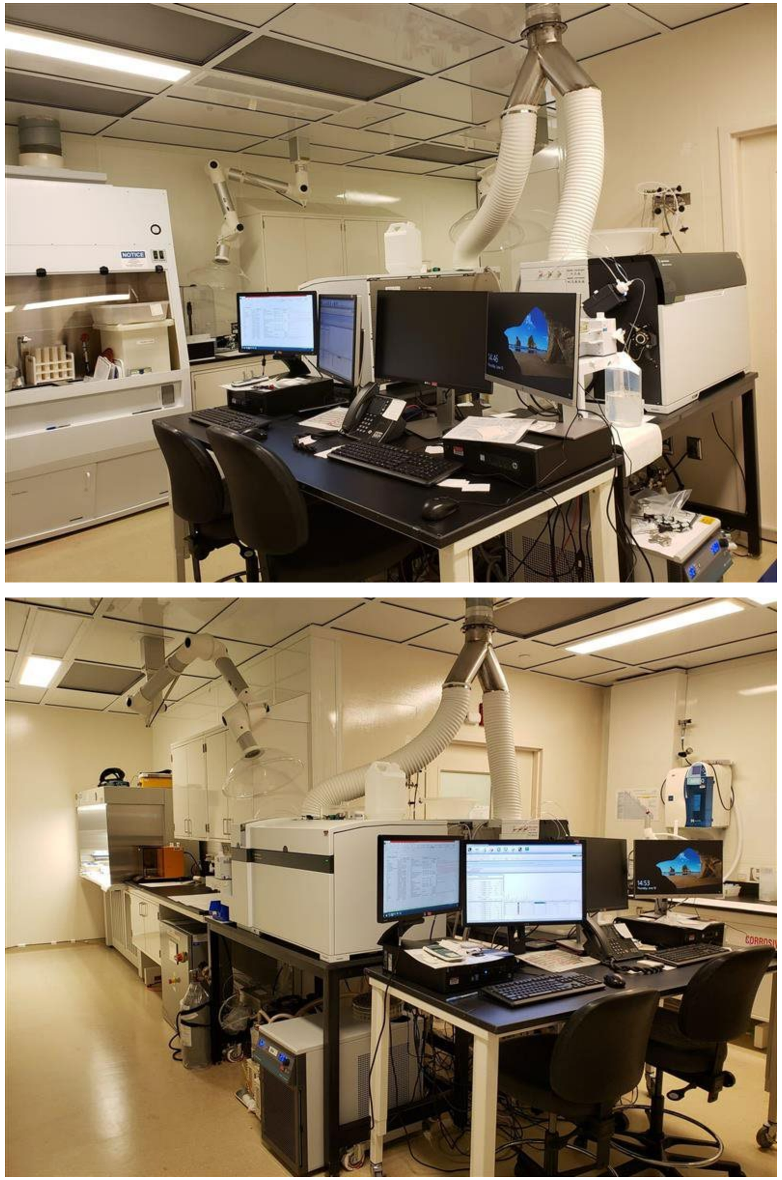
- Balance electric field with “upflow” counter flow
- Allows time for difficult separations
- May take up to days to get complete separation under ideal conditions
  - pH excursion issues, i.e. hydrogen build-up at cathode
- **New capability to PNNL**





Experimental

- **Validate ^{37}Cl enrichment by isotachophoresis by QQQ-ICPMS**
- **Typically measured by TIMS, IRMS, or AMS**
  - Extensive sample preparation and analytical time
- **ICPMS – fast, accurate, and requires minimal sample processing**



ICP-MS lab, Physical Sciences Facility, PNNL

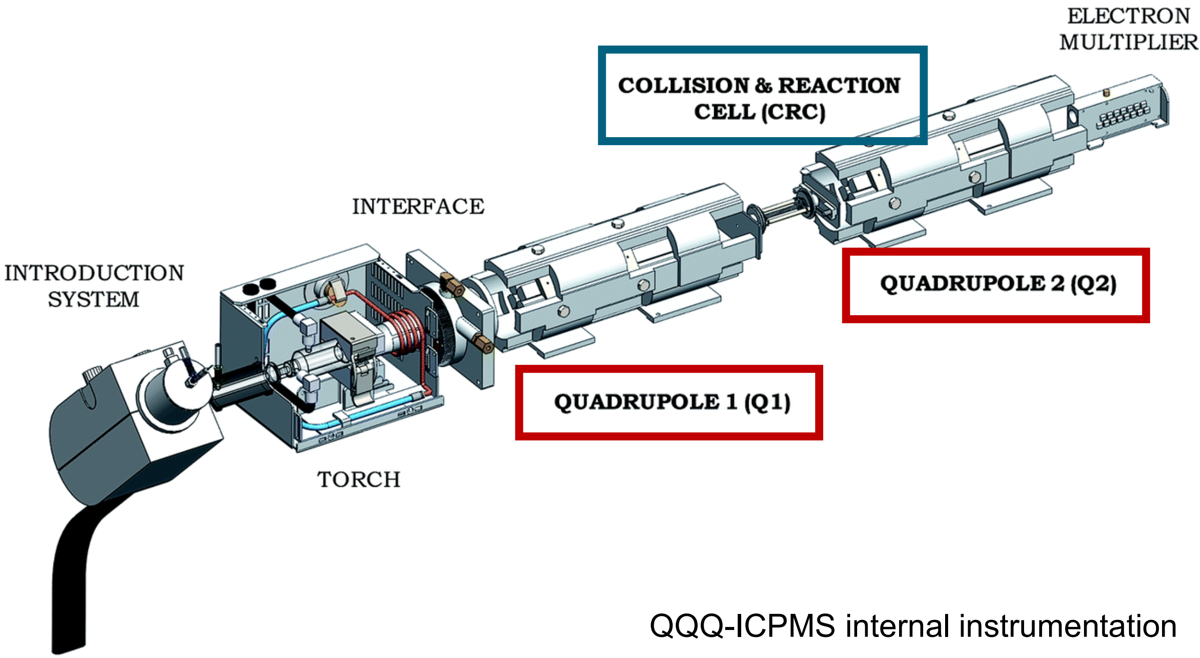
Challenges/approach

- **Challenge: polyatomic interferences**
  - Interference on $^{35}Cl = {}^{1}H^{16}O^{18}O$
  - Interference on $^{37}Cl = {}^{36}Ar^{1}H$ and $^{18}O^{18}O^{1}H$
- **Solution: reaction gas in collision-reaction cell (CRC)**
  - Shifts target analyte (Cl) to higher mass to avoid poly atomic interferences
- **Instrumentation**
  - QQQ-ICPMS
  - Agilent 8900 (pictured right)

Agilent 8900 QQQ-ICPMS

Methodology

- **Tandem MS/MS**
  - Two quad mass specs
  - Collision reaction cell (CRC) between
  - Cl analysis using O_2
- **Measure shifted product ions at m/z = 51 and 53 amu**
  - $^{35}Cl \rightarrow {}^{35}Cl^{16}O$; $m/z = 51$
  - $^{37}Cl \rightarrow {}^{37}Cl^{16}O$; $m/z = 53$
- **Measure 53/51 ratio is equivalent to $^{37}Cl/^{35}Cl$**

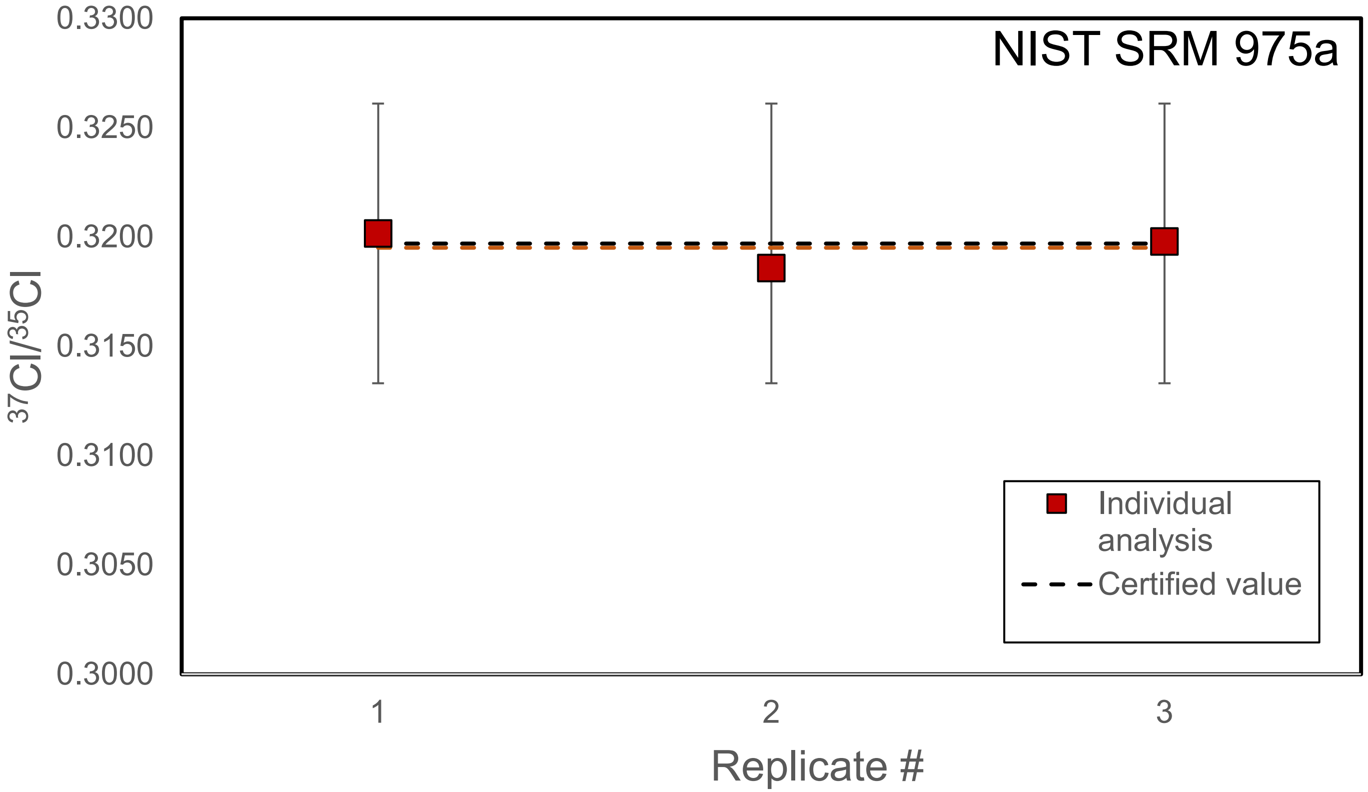


QQQ-ICPMS internal instrumentation

Results – natural $^{37}Cl/^{35}Cl$

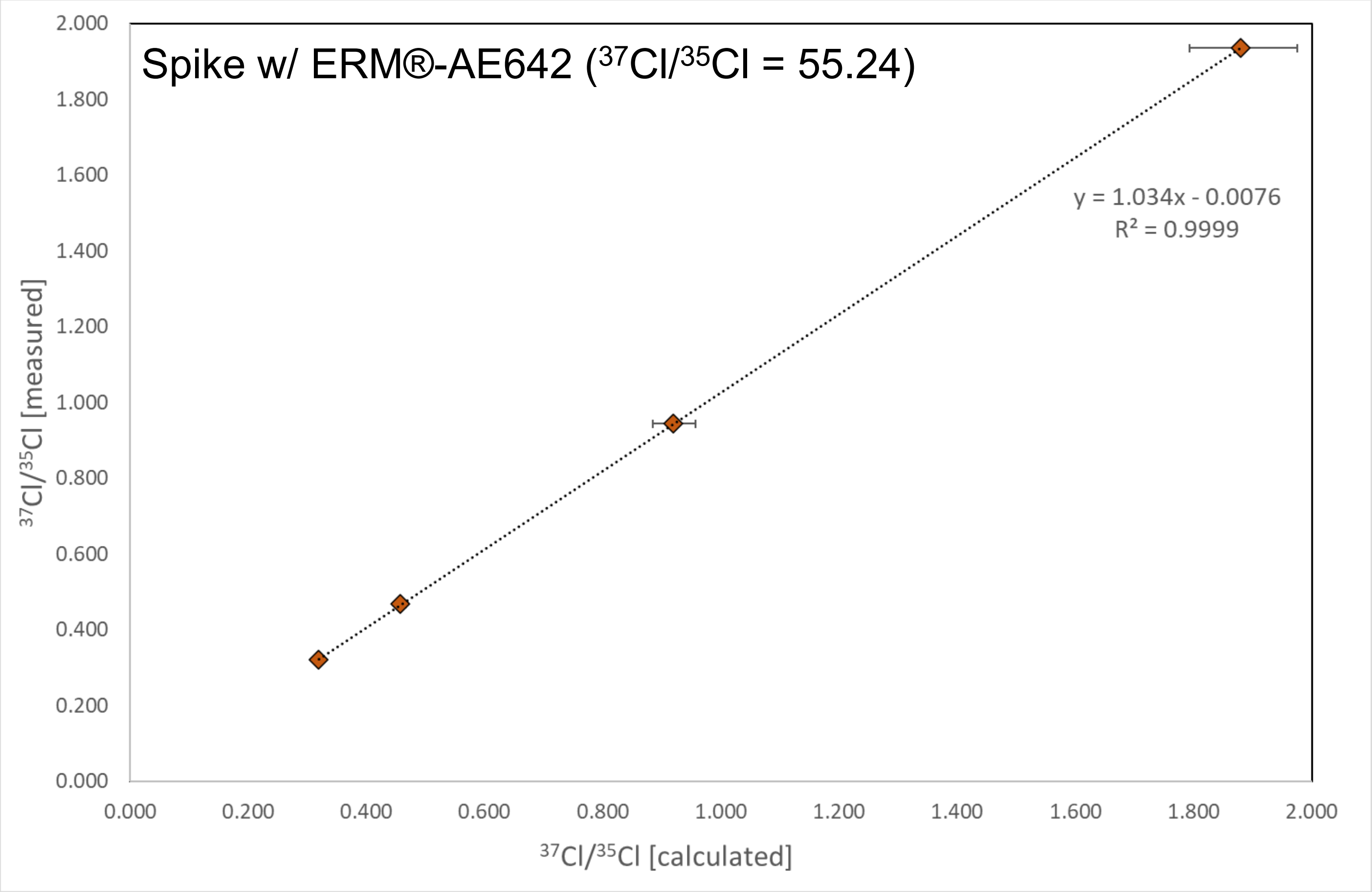
NIST SRM 975a

- **Certified value**
  - $^{37}Cl/^{35}Cl = 0.31970 \pm 0.00006$
- **Measured value**
  - $^{37}Cl/^{35}Cl = 0.31951 \pm 0.0008$
  - Within <0.1% of certified



Results – enriched $^{37}Cl/^{35}Cl$ in HCl

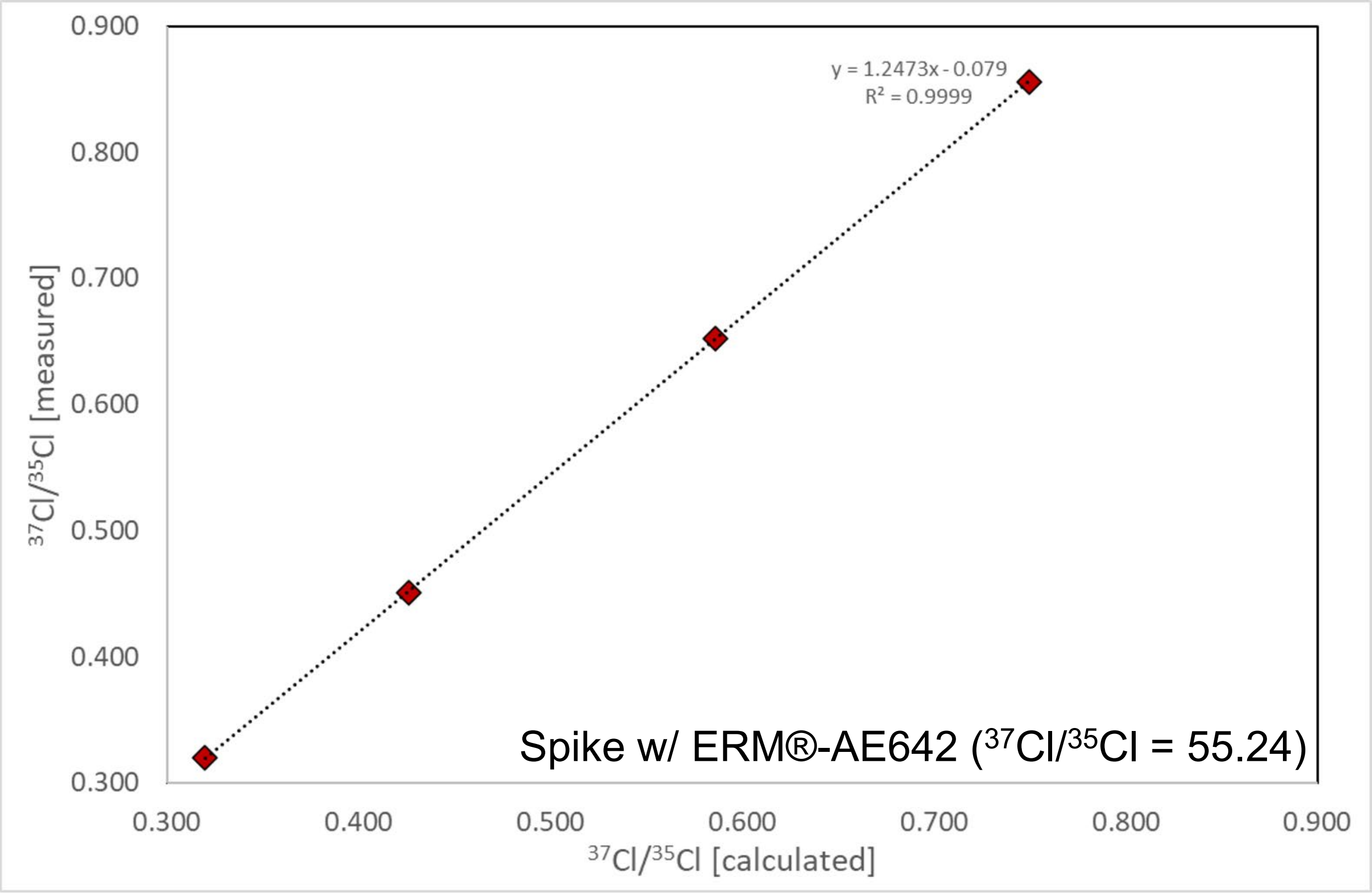
- **Enriched $^{37}Cl/^{35}Cl$ cal curve**
  - Use enriched ^{37}Cl spike
  - $^{37}Cl/^{35}Cl = 0.3197$ (natural) - 1.8791



Results – enriched $^{37}Cl/^{35}Cl$ in buffer

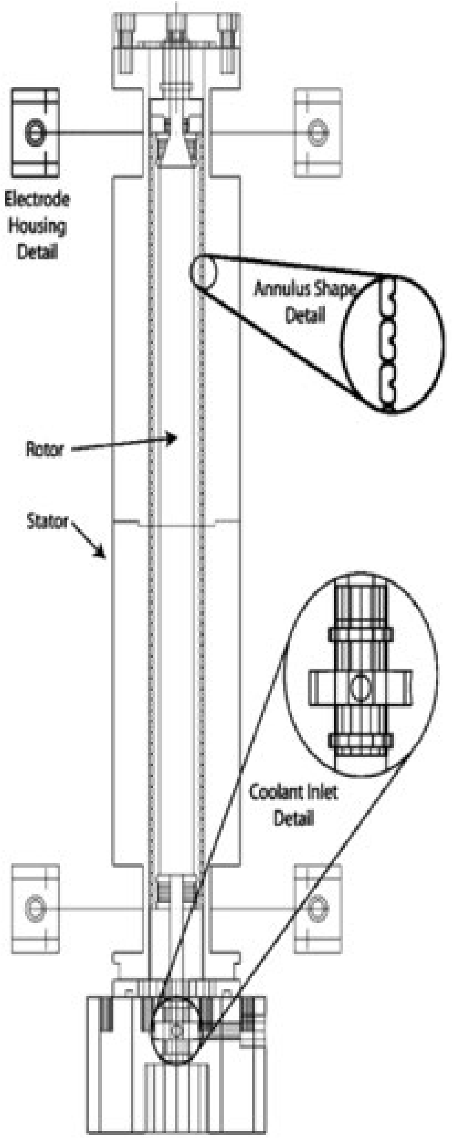
- **$^{37}Cl/^{35}Cl$ cal curve in buffer**
  - $^{37}Cl/^{35}Cl = 0.3197\text{-}0.7496$

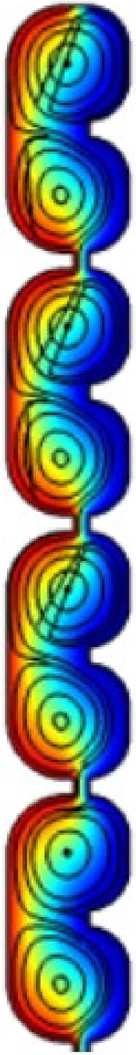
- **Compare unknowns to calibration curve to determine $^{37}Cl/^{35}Cl$ ratio**



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

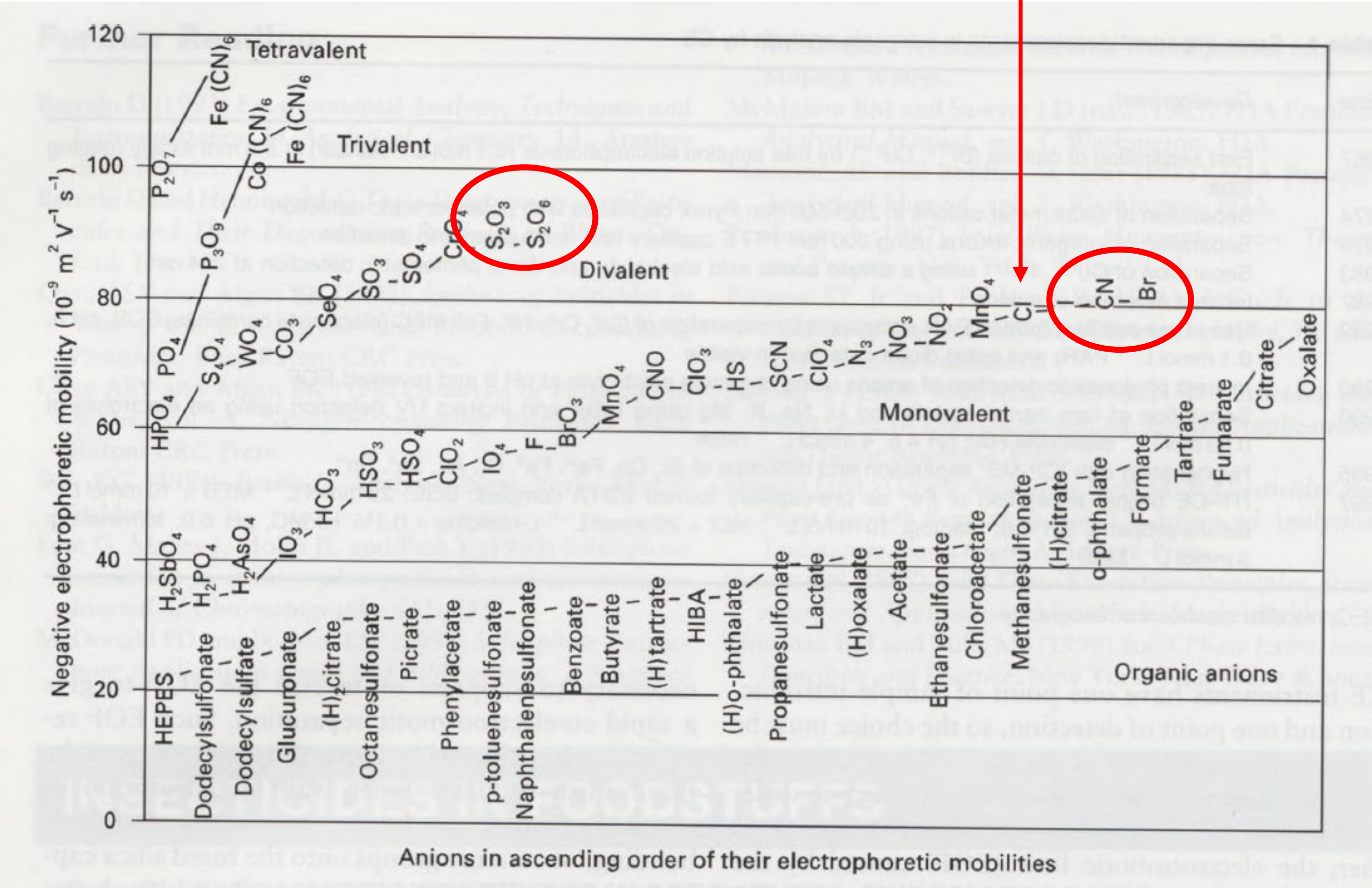




Challenges

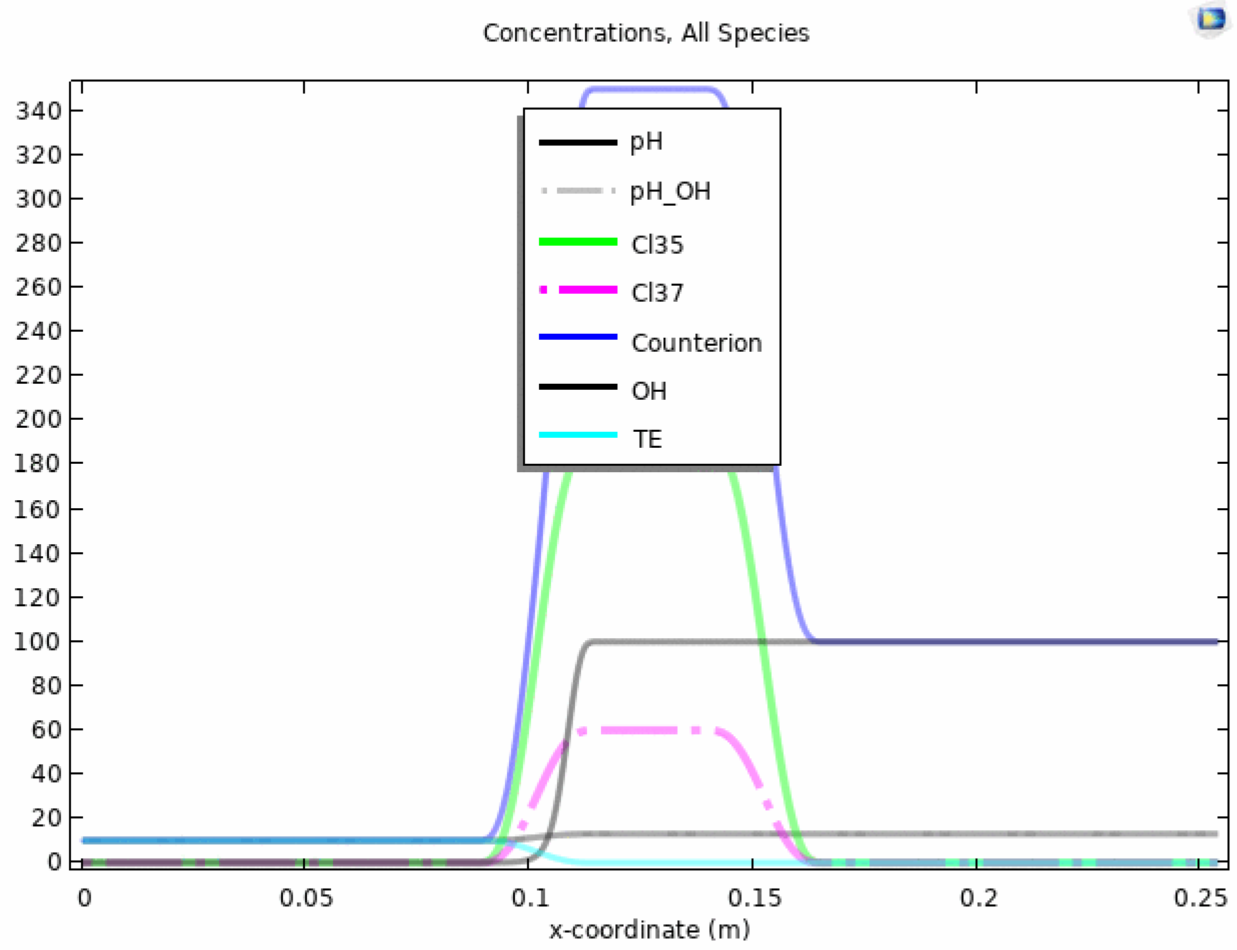
- Initial literature review found thiosulfate and dithionate as strong candidate for LE in ITP separations
- Neither ion was available and required a custom synthesis that made the cost and time to synthesis prohibitive
- Other options Br, I, and CN were safety concerns
- Resulted in a pivoting of strategy
  - WSU is currently attempting ITP at high pH using hydroxide as the LE
  - PNNL has transitioned to moving bed electrophoresis (MBE)

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



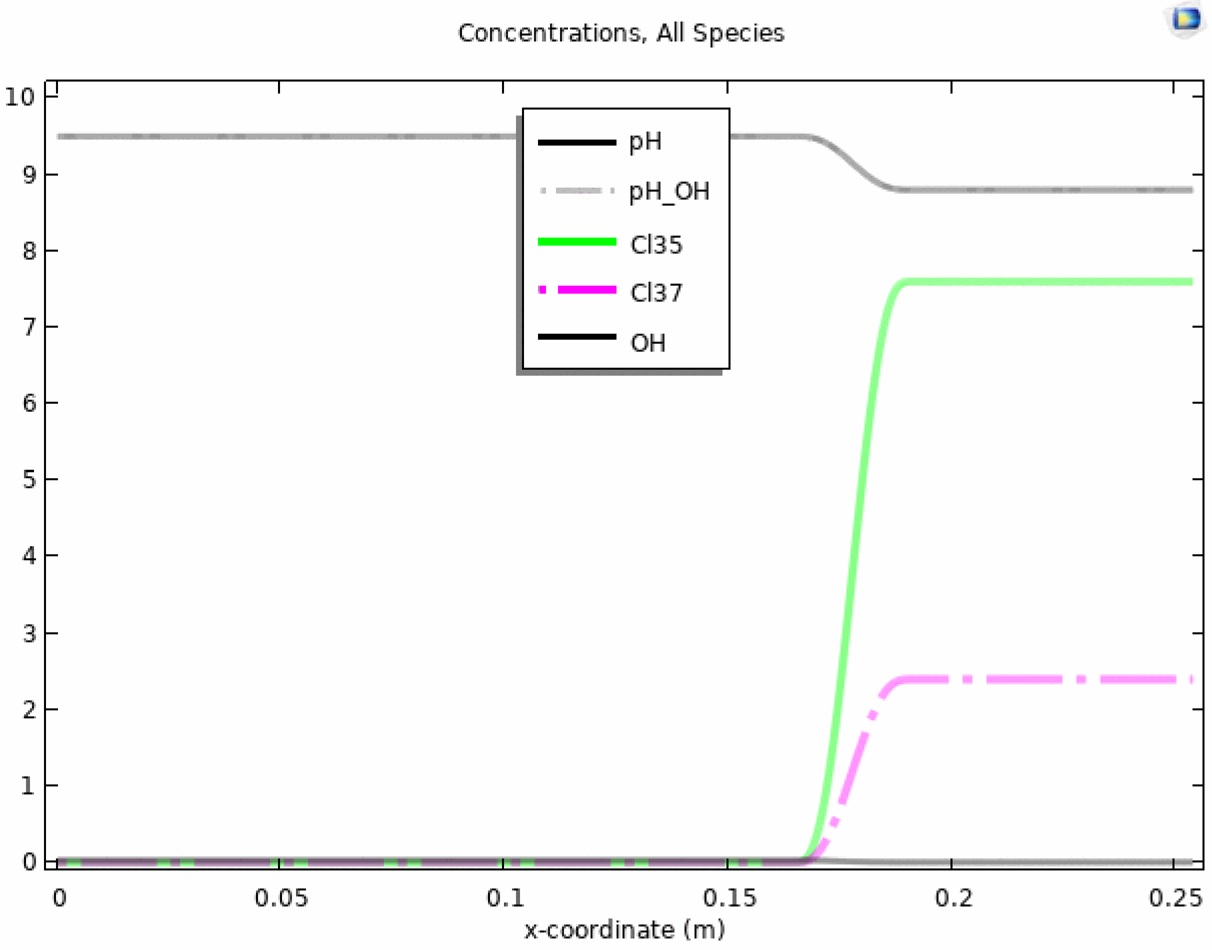
Will it Work – COMSOL Multiphysics Simulations

- Simulations performed by WSU
- System 1:
  - ITP at pH 13 using a OH as LE and TAPS as TE
  - Sodium at counterion
  - Sample is NaCl
- Over the course of 24 hours you do see some enrichment
- This simulation does include dispersion that is inherent to current electrophoresis system



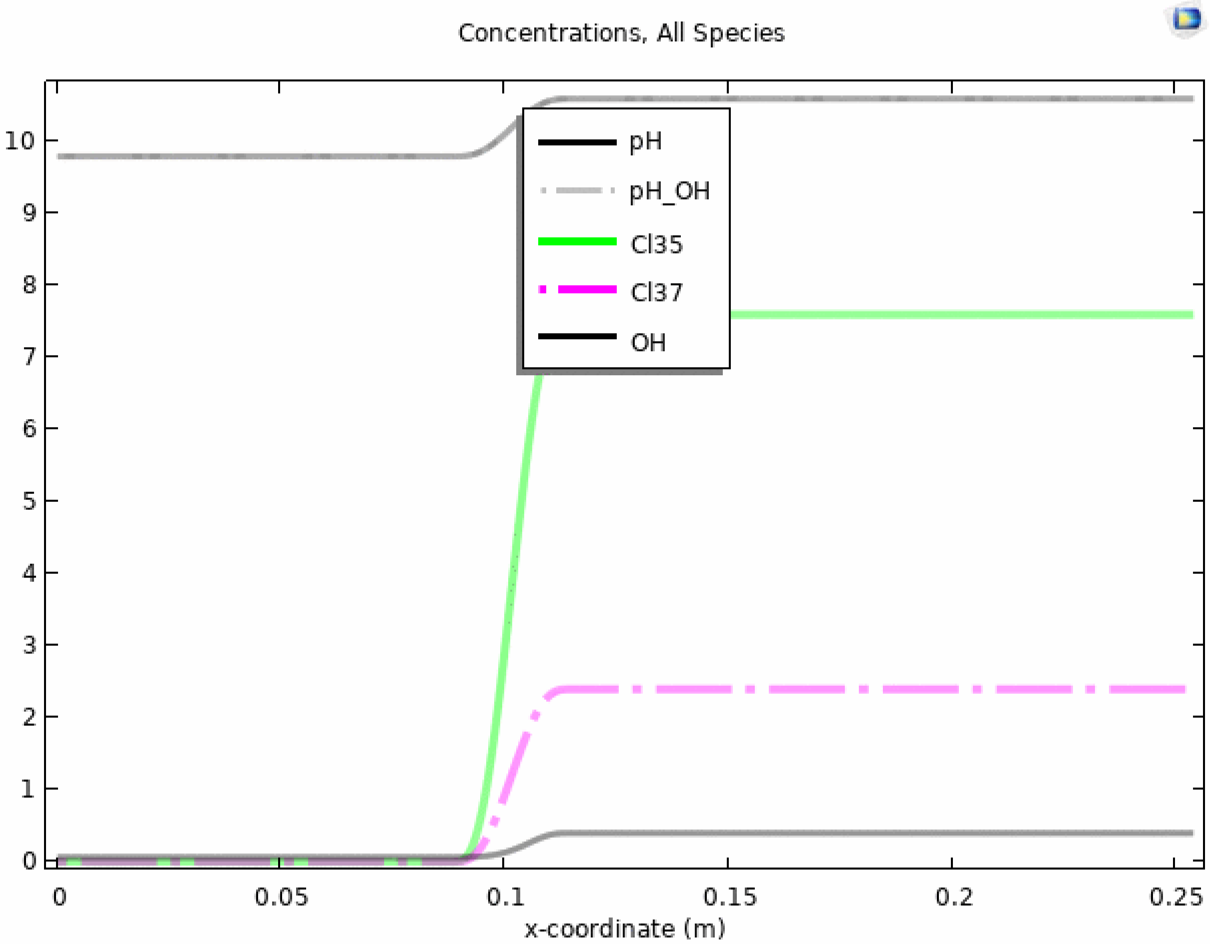
Moving Bed Electrophoresis

- 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
- System 2:
    - LE – 10mM HCl titrated to pH 8.8 with Tris
    - TE – 60 mM EACA titrated to pH 9.5 with EACA
- Over the course of 24 hours you do see some enrichment
- This simulation does include dispersion that is inherent to current electrophoresis system



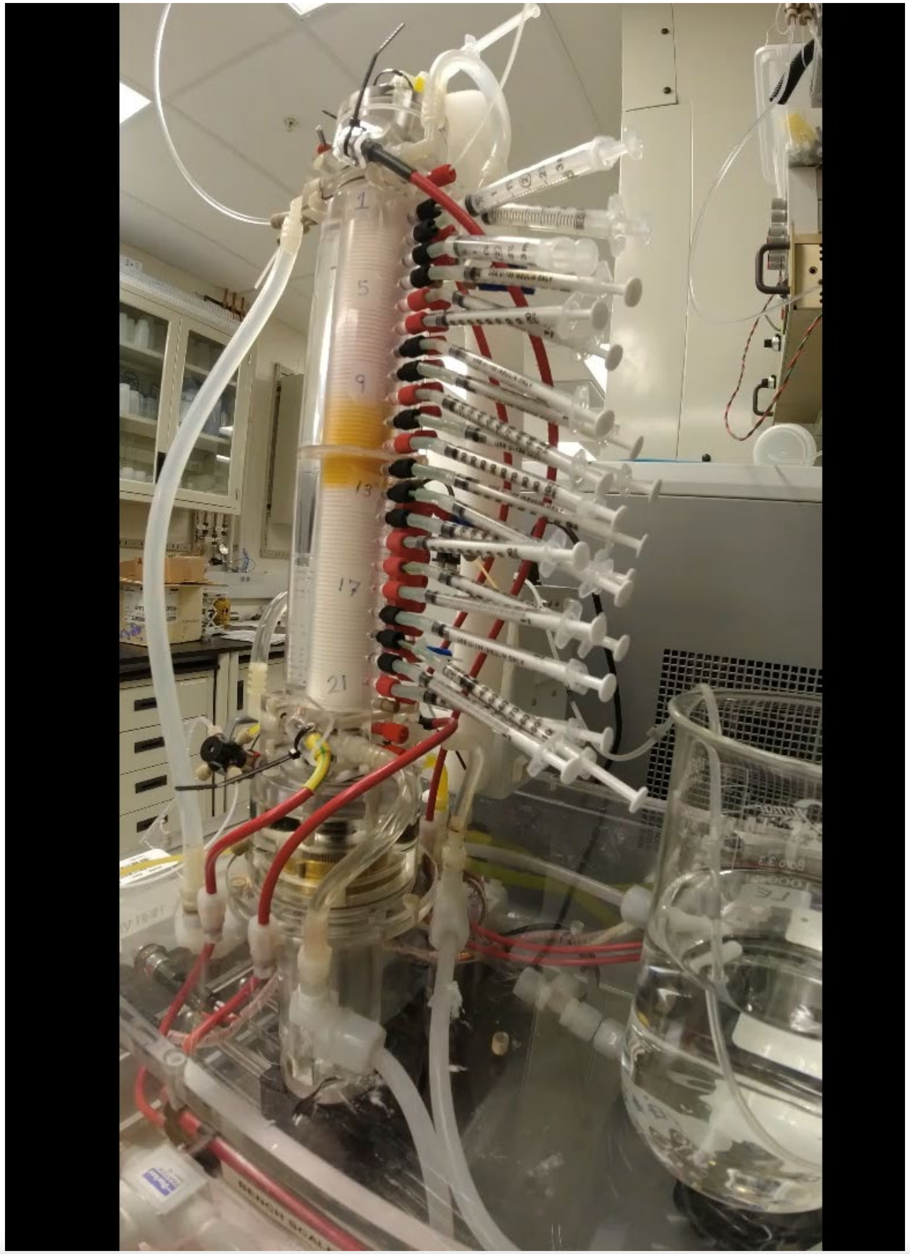
Moving Bed Electrophoresis

- System 3:
  - LE – 10mM HCl titrated to pH 10.5 with Tris
  - TE – 10mM EACA titrated to pH 11 with Tris
- Over the course of 24 hours simulations show good enrichment
- This simulation does include dispersion that is inherent to current electrophoresis system



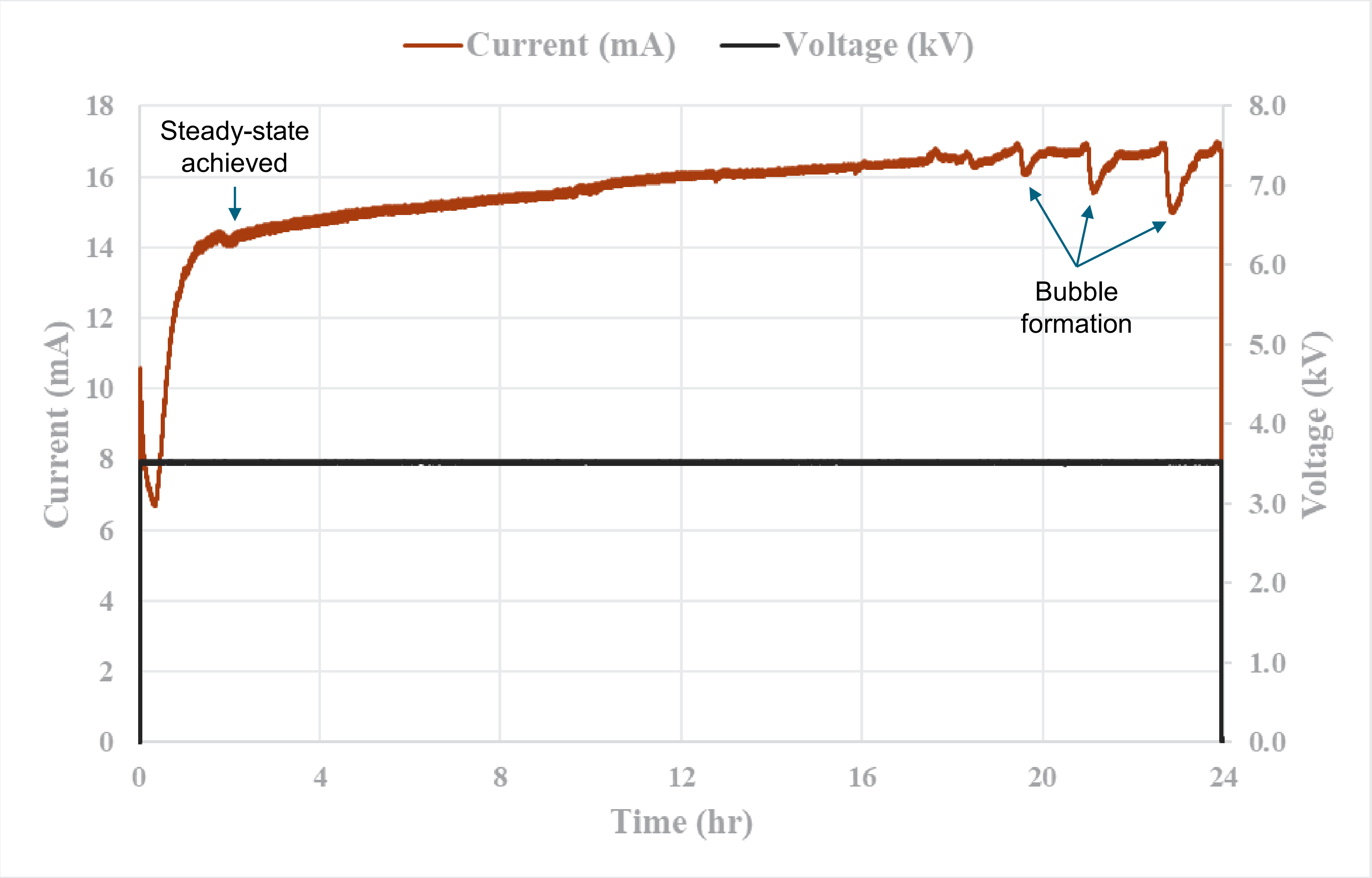
Experimental Results

- MBE – System 2:
  - LE – 10mM HCl titrated to pH 8.8 with Tris
  - TE – 60 mM 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
- 5-hr video compressed into ~ 1 min



Current/Voltage Profile

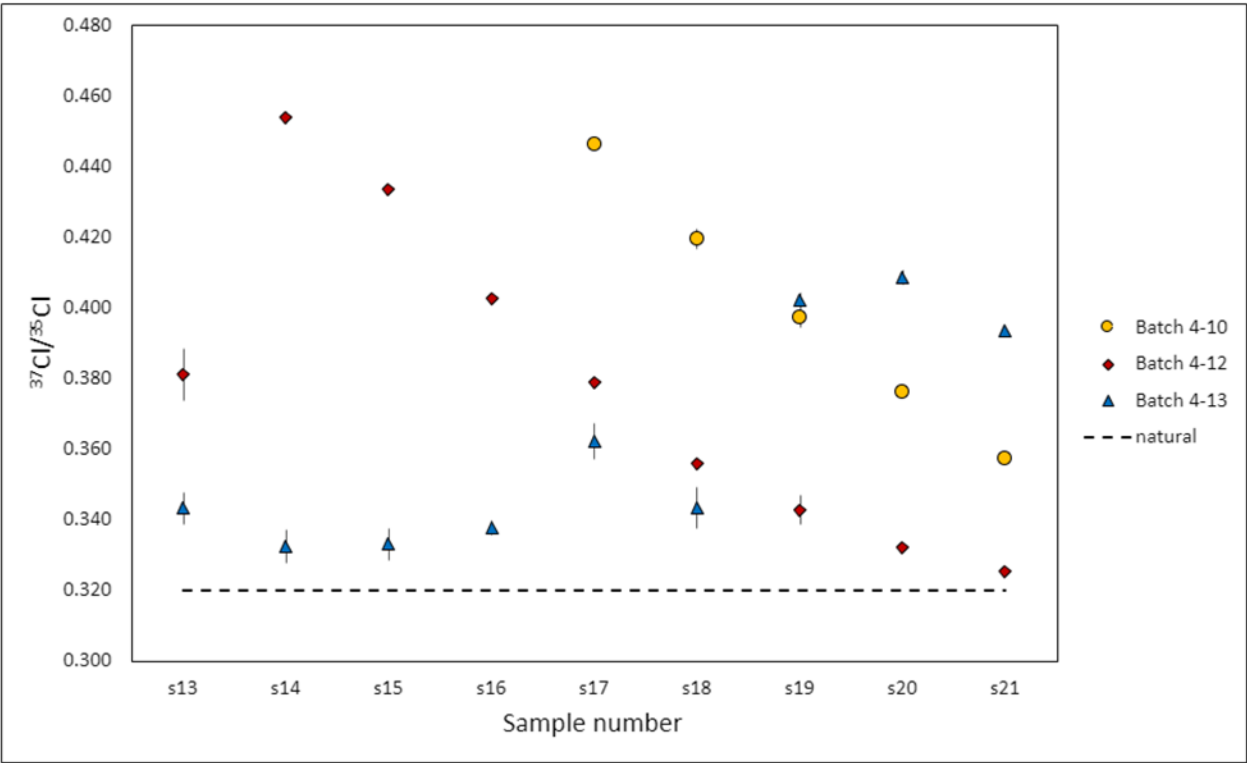
- Voltage applied = 3.5 kV
- Bubble formation could cause dispersion of analytes, inhibiting separation
  - Changing current due to buffer resistance changing over time
- Samples collected after 24 hours for quantitative determination of Cl$^-$ ratio



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 (α):

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



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.

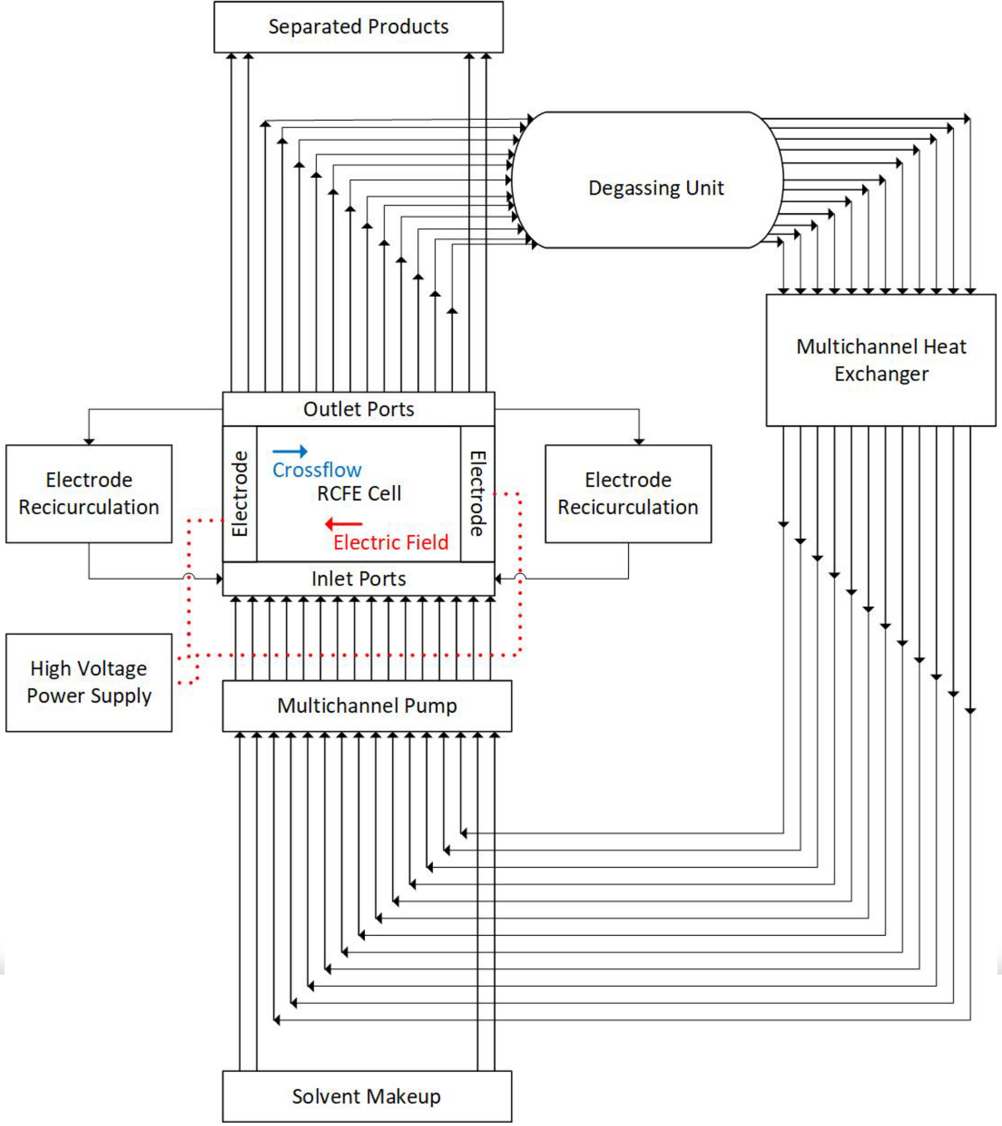
Expected to have Cl

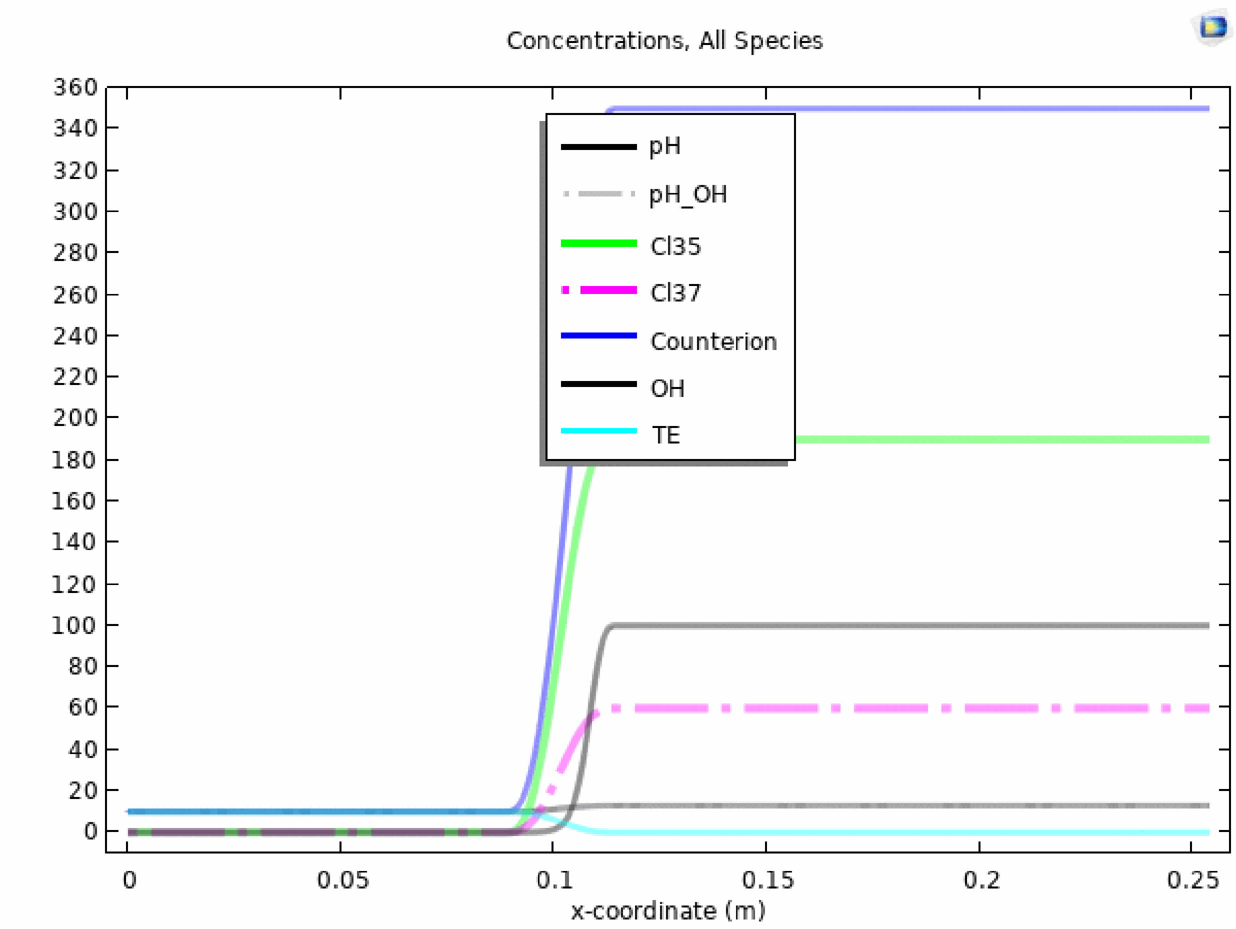
24 hr

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

RCFE Design and Simulation w/ Reduced Dispersion





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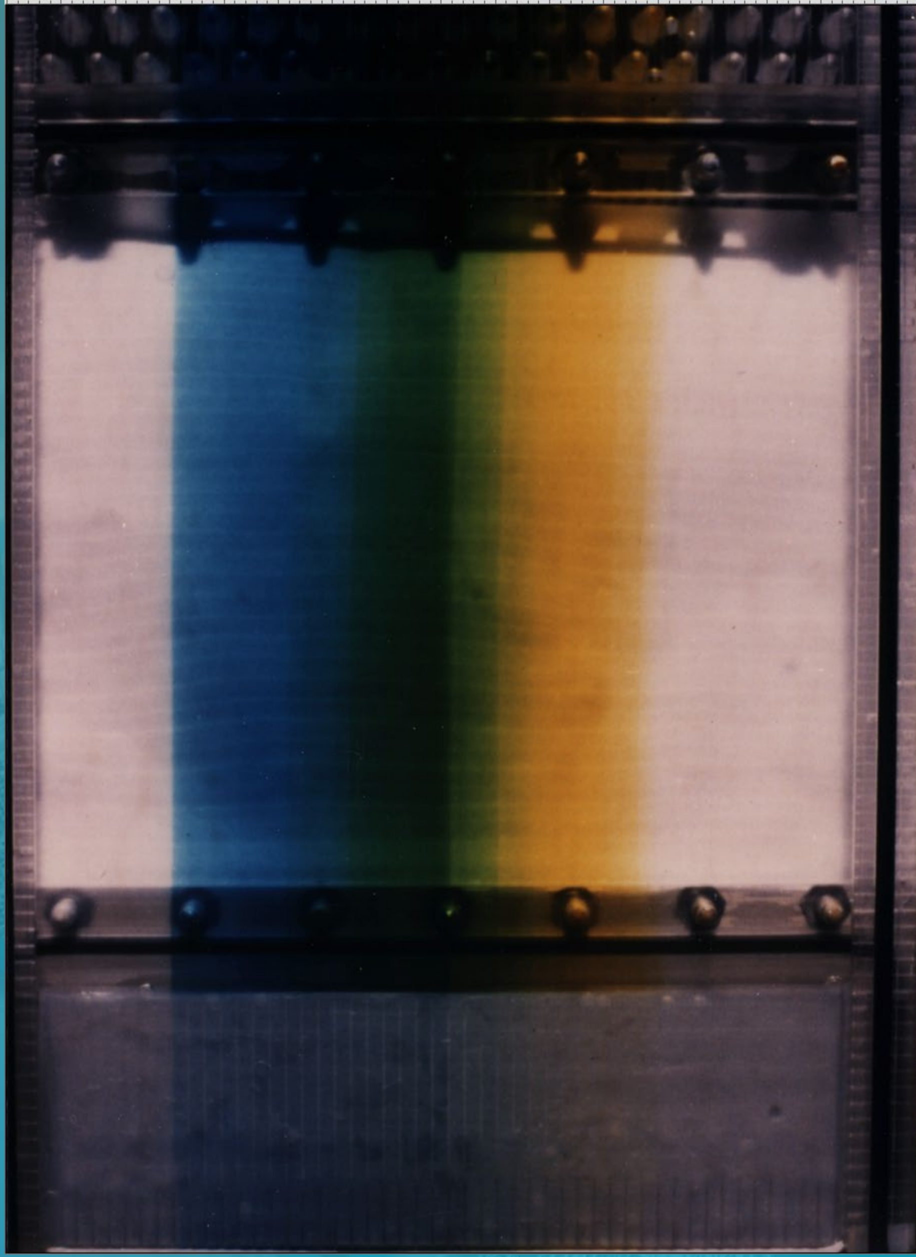
Conclusions

- **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**
  - Single stage separation factors of 1.8 achieved
- **Multitude of “working” COMSOL simulations to aid in development of new electrophoresis equipment design, i.e. RCFE**

Thank you



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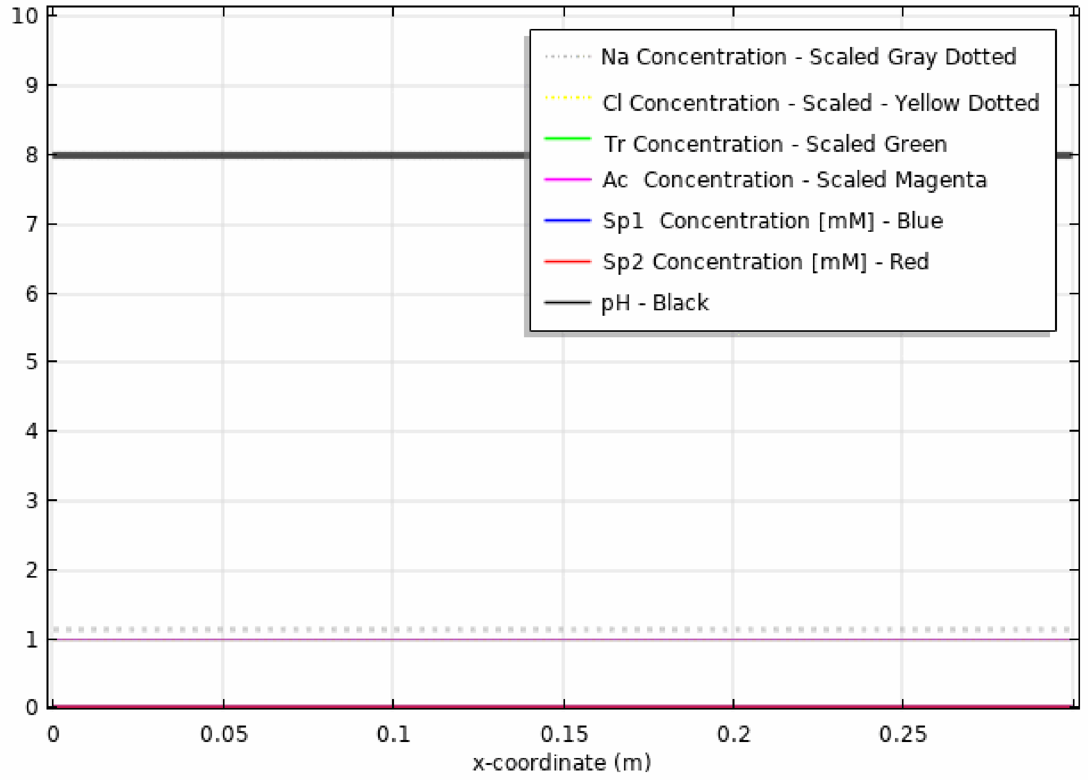
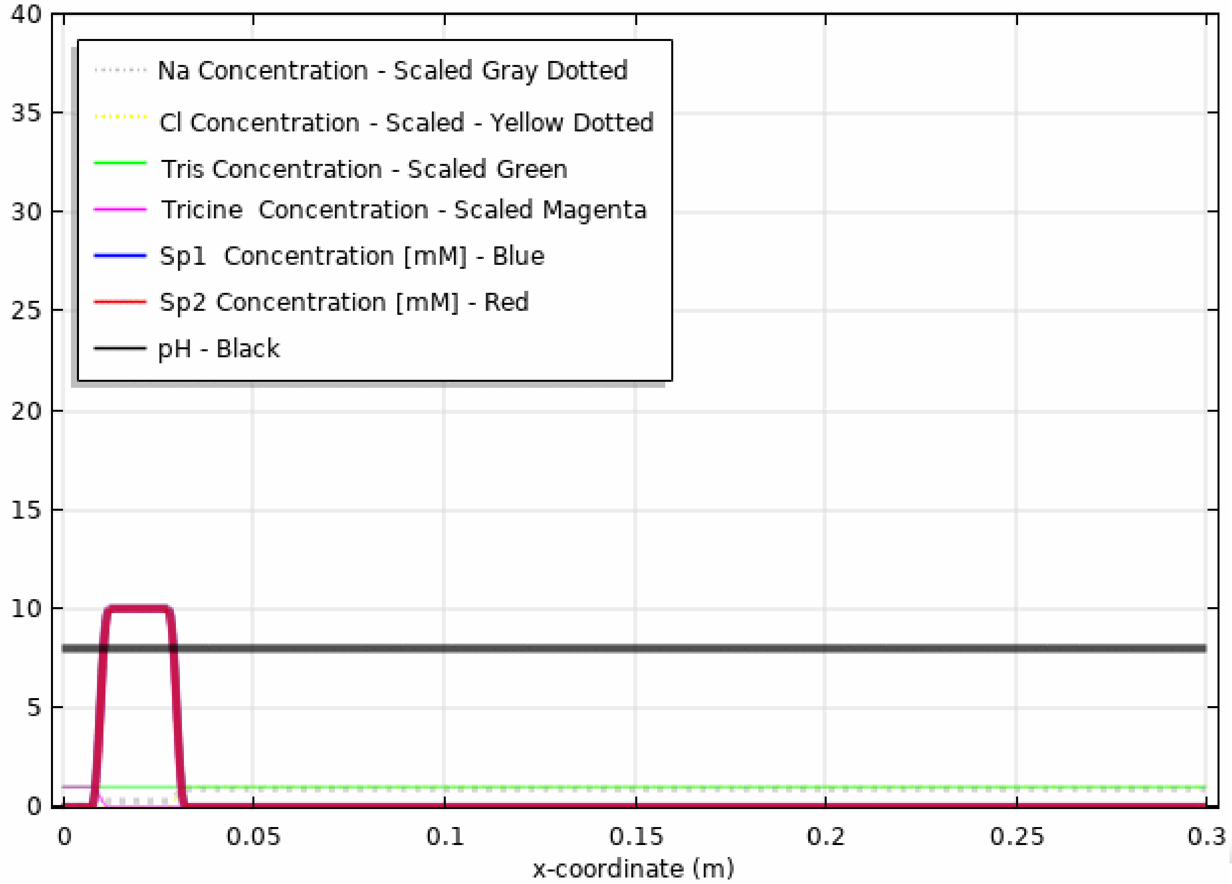
Electrophoresis

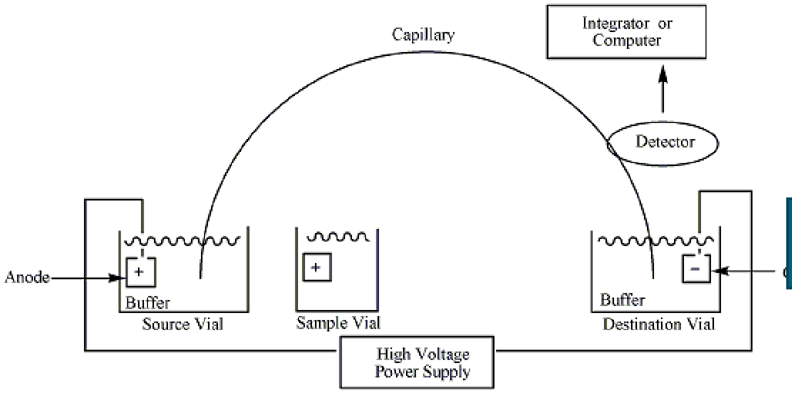
Zone Electrophoresis

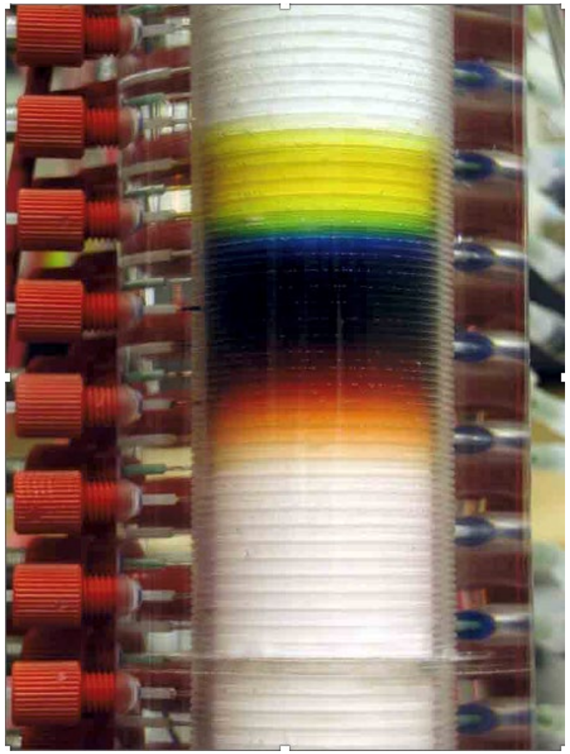


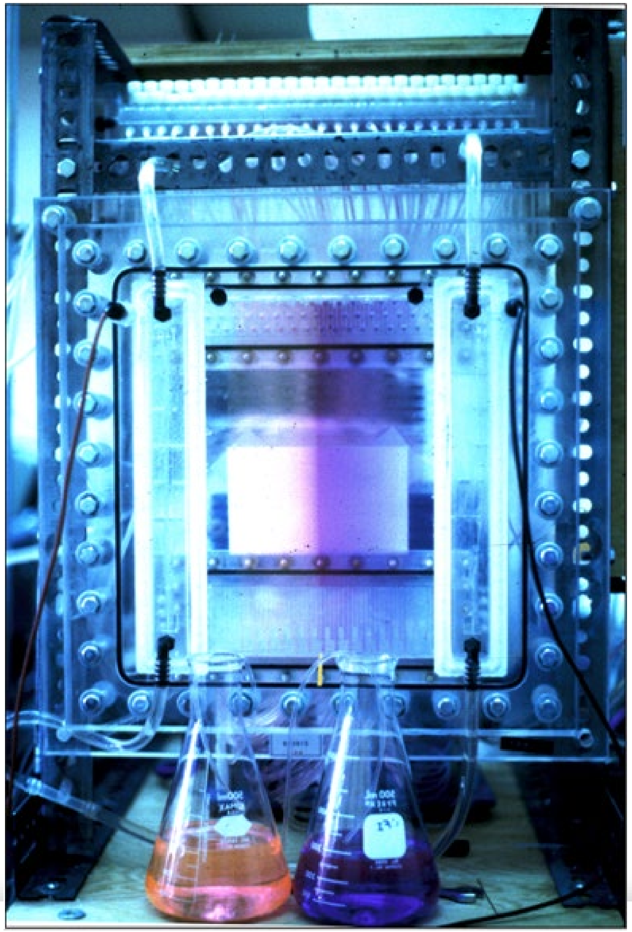
Isotachophoresis



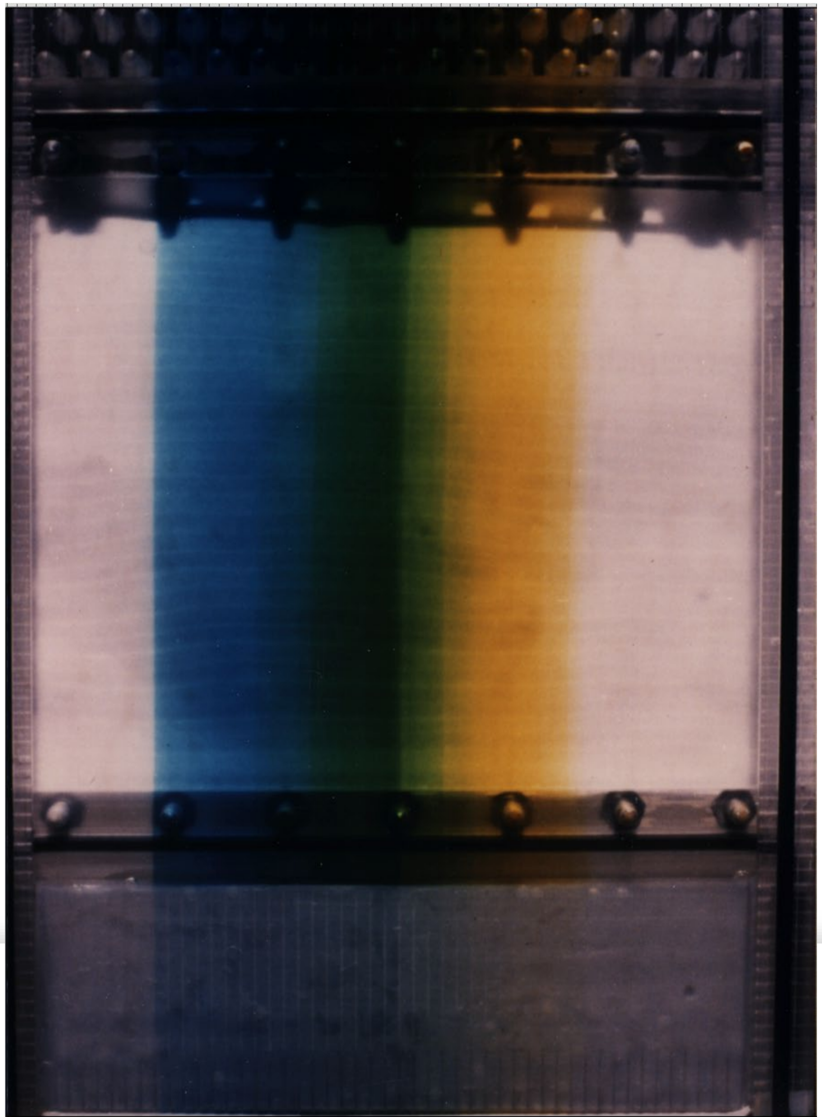
Strategy

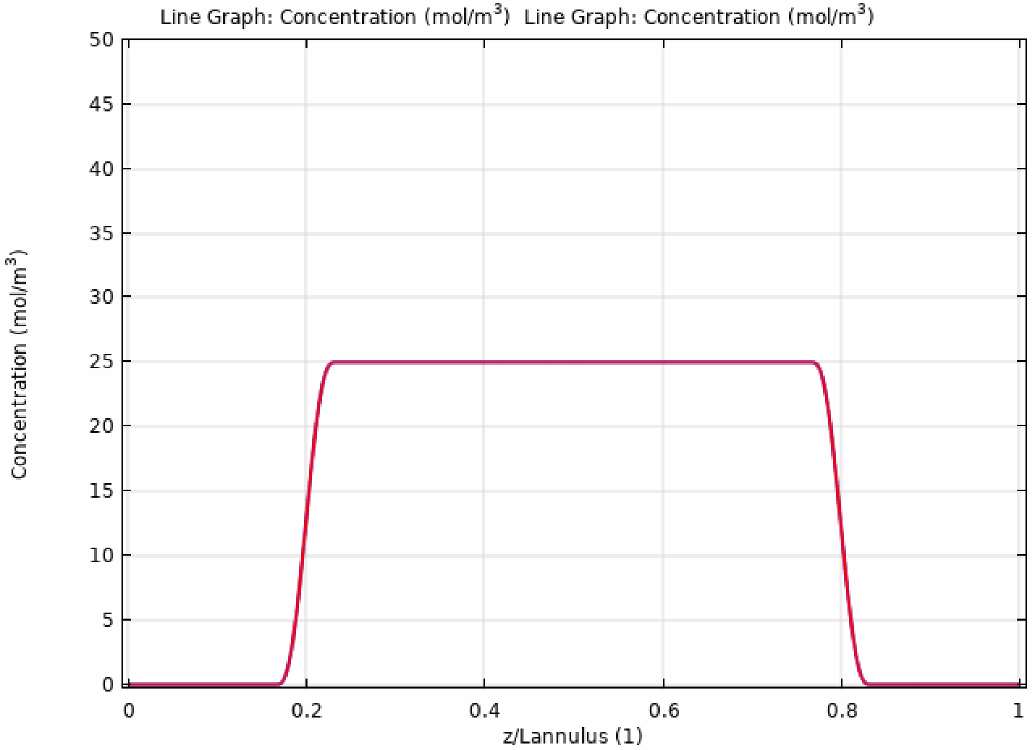

Integrator or Computer
Capillary
Detector
Anode
Buffer
Source Vial
Sample Vial
Buffer
Destination Vial
High Voltage Power Supply





RCFE





COMSOL Multiphysics® simulation of the evolution of a separation of two species with 0.25% difference in their electrophoretic mobilities in a 12-inch wide recycle CFE. Feed is continuously injected into the bottom center port and products are taken out of the chamber at the left and right offtake ports. Recycling allows the hold-up time to be increased until the two species are separated.