Analysis of Total PFAS Concentration in Solution

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are chemicals we encounter daily in items like non-stick pans, carpet cleaner, and clothing due to their water and grease resistant properties. Deemed “forever chemicals”, PFAS persist in the environment without significant degradation. These compounds have been linked to health concerns such as an increased risk of some cancers, reproductive problems, and weakening of the immune system. PFAS remediation is costly, so analysis is necessary to ensure both safe concentrations in drinking water and better targeted cleanup efforts. Liquid Chromatography-Mass Spectrometry (LC-MS) is a highly sensitive but expensive method used for analysis of PFAS concentration down to parts-per-quadrillion. The existence of thousands of different PFAS makes target techniques like LC-MS underrepresent total PFAS contents, however. The aim of our project is to develop a sensor for measuring the total organofluorine content regardless of individual species. First, PFAS are introduced into a reactor wherein they are mineralized to produce fluoride which is then measured using a fluoride ion selective electrode (FISE) with a custom flow cell to produce a potentiometric response. We are currently optimizing the sensing conditions to work with this reactor, with the goal being to achieve sub part-per-billion level of analysis.

INTRODUCTION

- LC-MS can be cost prohibitive and can underrepresent total PFAS concentration
- Benefits of flow through analysis are that it is inexpensive comparatively, and it can be performed in quick succession
- Analyzing total PFAS is accomplished by breaking the carbon-fluorine bonds and measuring free Fluoride concentration
- Free Fluoride in solution is used as an indicator for the original PFAS concentration
- FISE sensor is used to measure potential of ions in solution
- Nernst equation can be used to represent the potentiometric response of an ion in solution
- After some rearrangement, the concentration of an ion in solution (C) can be calculated

Nernst Equation

$$E_{cell} = E°_{cell} - \left(\frac{0.0592\ V}{n}\right) logC$$

Rearranged to solve for Fluoride concentration

$$C = 10^{\left(\frac{(E° - E)}{(0.0592\ V/n)}\right)}$$

METHODS FOR ANALYSIS

The individual parts used for the sensor are listed below:

- Fluoride Ionplus Sure-Flow Solid State Combination Orion™ Fluoride Ion Selective Electrode (FISE)
- Manual 6 port valve
- 30SWG PTFE Teflon Tubing
- Custom 3D printed FISE flow cell
- Various PEEK fittings for the 6-port valve
- Peristaltic Pump (PP)

The steps taken to measure the potential of an individual sample are as follows:

1) The 6-port valve is manually set to the loading position (Position A) before starting the PP
2) The 100 μL injection loop is filled with a sample solution containing Fluoride using the PP. While in Position A, the carrier solution flows directly to the flow cell and no sample solution is detected at the FISE.
3) Once the injection loop is loaded, the valve is manually switched to Position B. This position allows the sample to be injected along with carrier solution through the flow cell, and the FISE can measure a potentiometric response.

The benefit of this 6-port valve setup is that data can be collected in succession, provided there is sufficient sample and carrier solution.

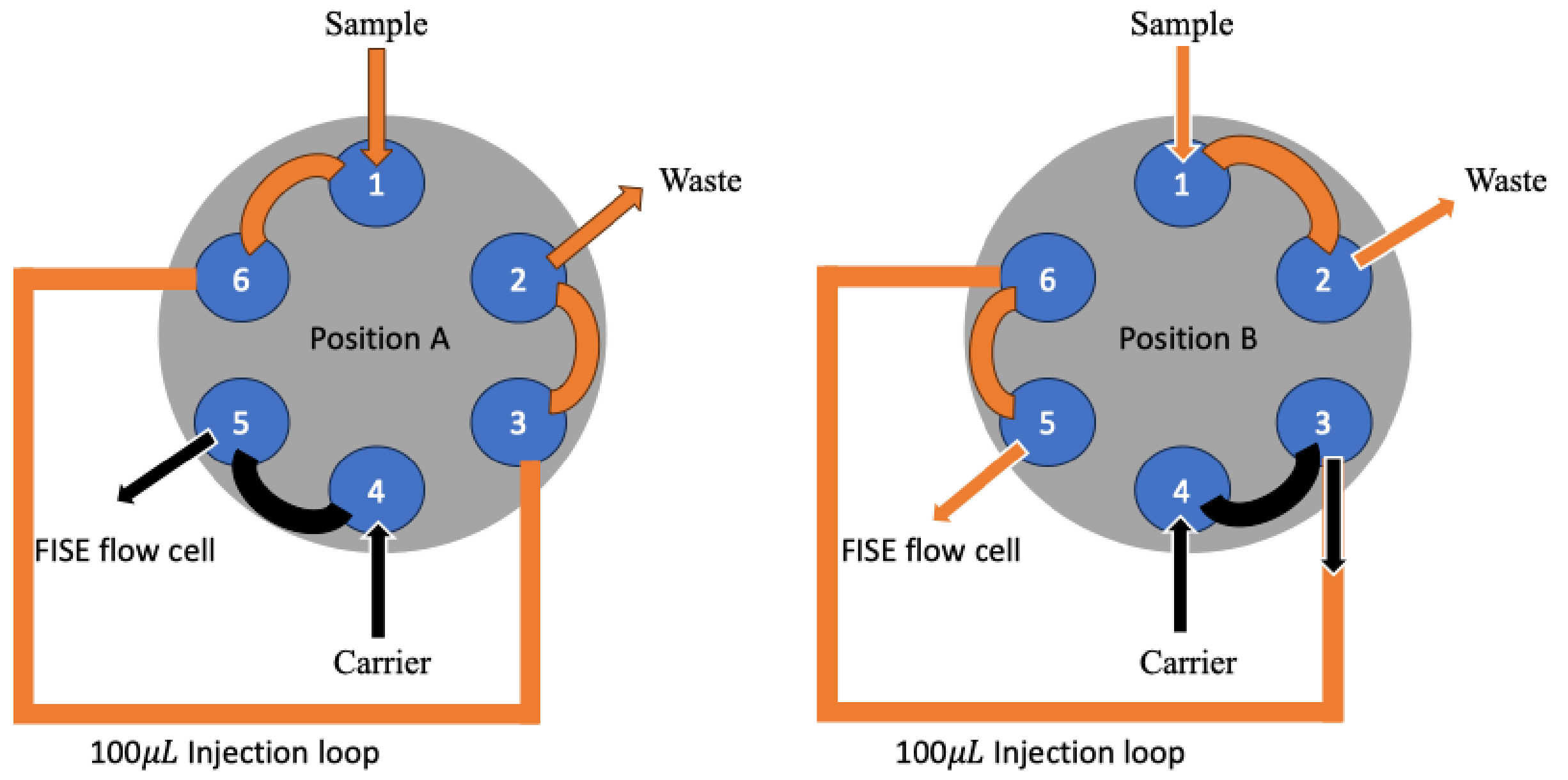

Figure 1: Positions A and B for the 6-port valve

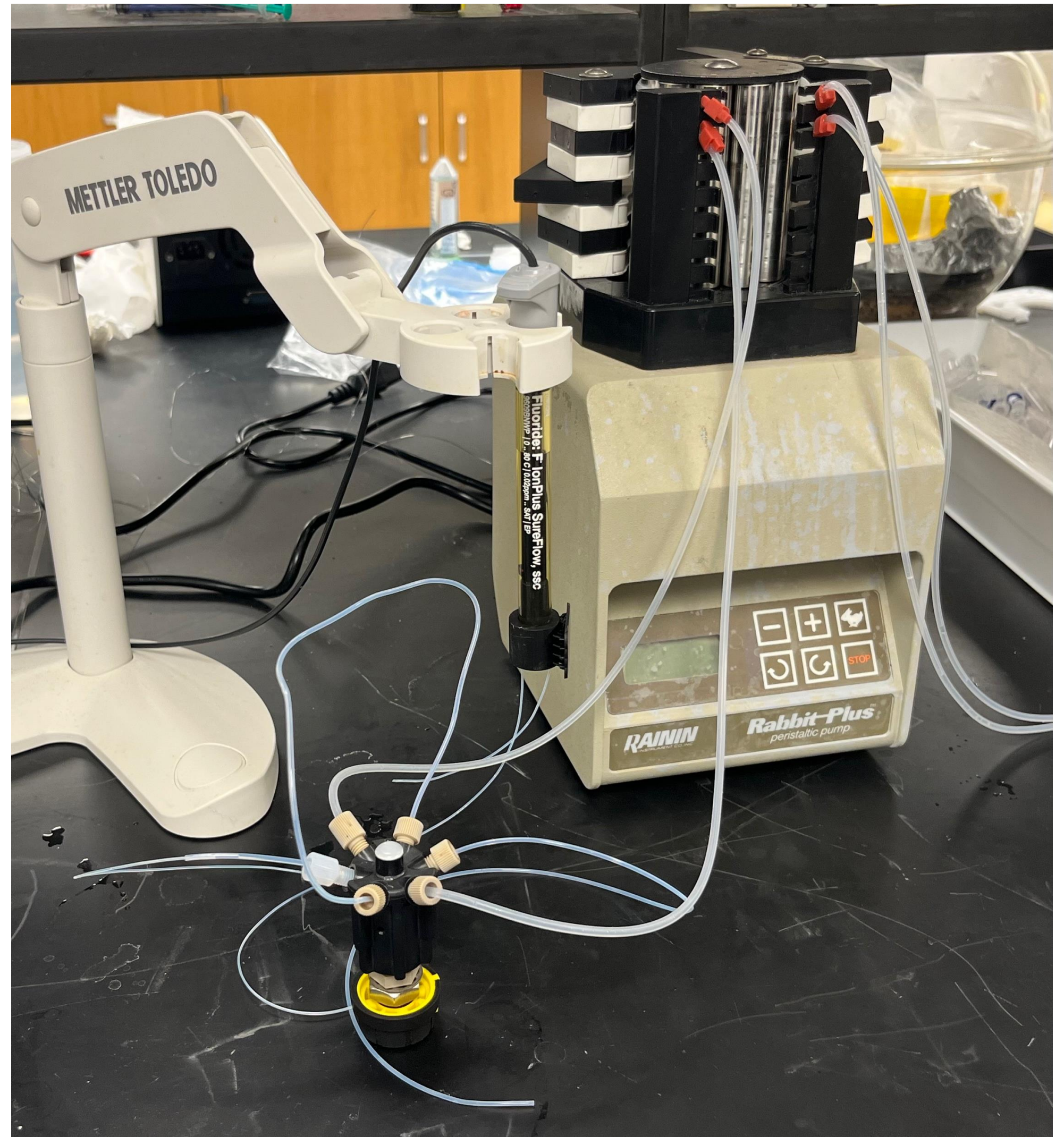

Figure 2: 6-port valve, FISE, custom flow cell, and PP

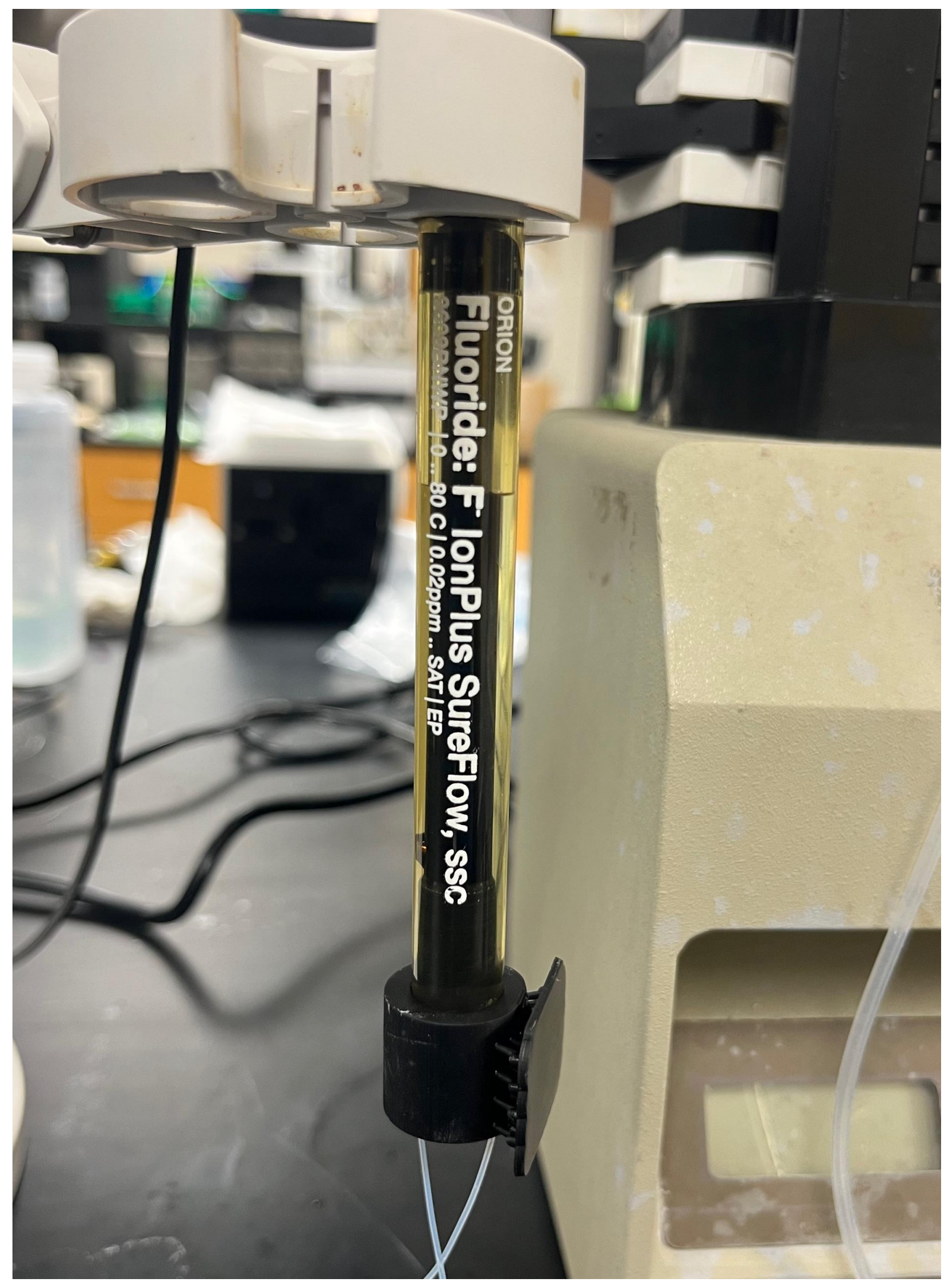

Figure 3: FISE and flow cell

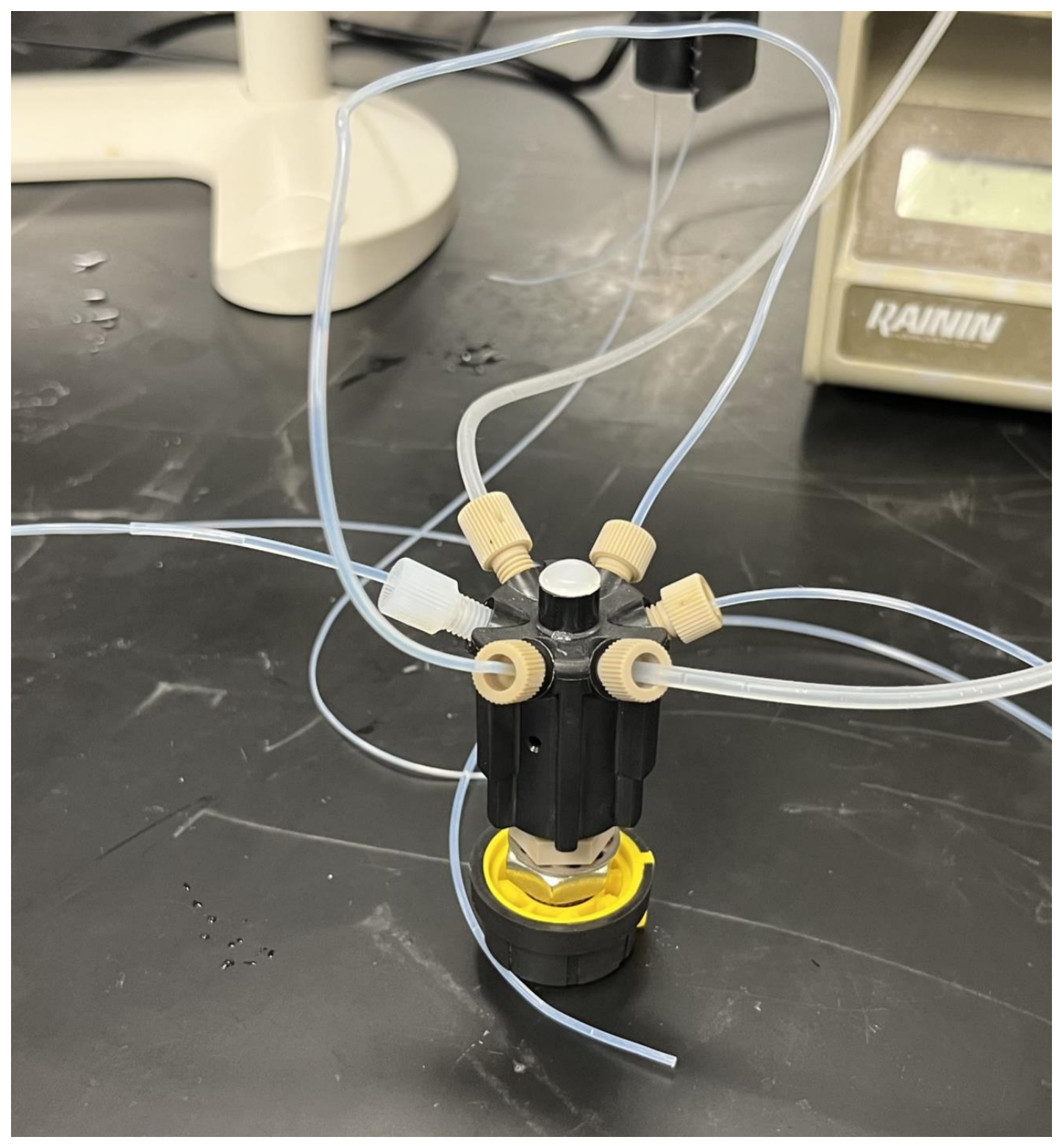

Figure 4: Manual 6-port valve

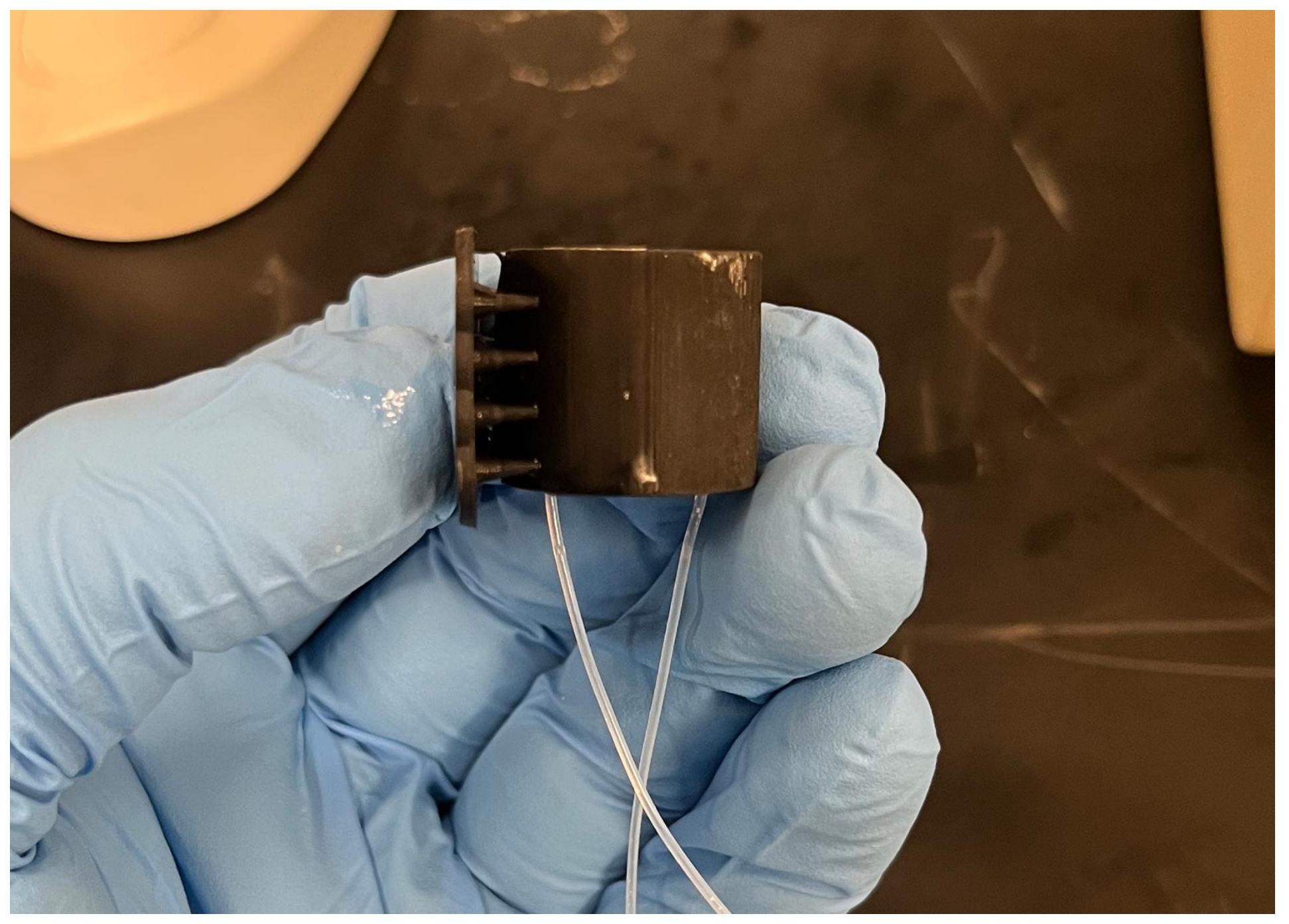

Figure 5: Custom flow cell

DATA

- Graph plots potential in millivolts (mV) vs. the sample number
- Multiple 100 μL samples with different concentrations injected in succession and measured
- Higher concentration of Fluoride correlates to a lower measured potential, as seen with the 0.1 M solution creating the lowest potentiometric response in mV.

Sample Number	Fluoride Concentration (M)	Measured potential (mV)
1	0.1	-114.5
2	0.01	-59.1
3	0.001	-1.7
4	0.0001	57.1
5	0.00001	116.1
6	0.000001	126.1

Figure 6: Data table corresponding to Figure 7 graph

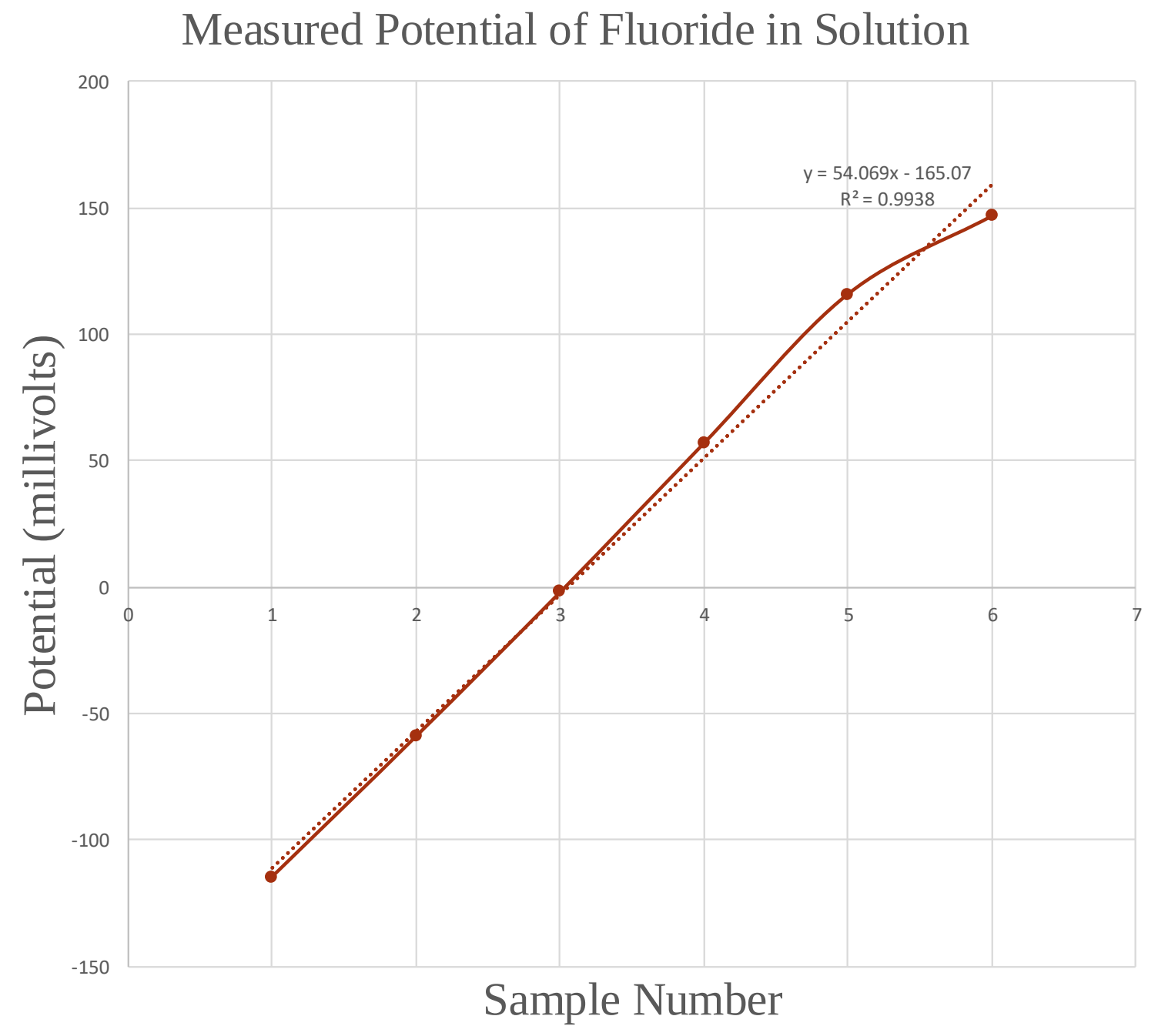

Figure 7: Graph plotting measured potentiometric response for each sample

CONCLUSIONS

- Compared to batchwise analysis, flow through analysis using the FISE sensor allows for small changes in concentration to be measured in real time
- FISE sensor provides an efficient means for total PFAS concentration in solution post degradation
- The goal is to obtain part-per-billion or trillion level sensitivity when measuring Fluoride concentration in solution
- Measuring low concentrations of Fluoride would provide an inexpensive means for PFAS concentration determination
- While focus remains on PFAS analysis, sensor can be used to analyze various ions in solution

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