IMPROVED METHODOLGY FOR ION PROFILING IN AQUARIUM WATER

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1 Introduction

Aquariums are an important part of modern society, as they provide both a way to explore the wonders of the ocean and a source of entertainment. Assaying artificial seawater is essential for the proper maintenance of aquariums in order to ensure that its composition is similar to that of natural seawater, providing fish and other sea creatures with the healthy environment they need to thrive. Therefore, it is of critical importance to determine the profile of cations and anions present in the water from various dissolved salts. Established analytical methods typically employ ion chromatography, but these methods are lacking, requiring long run times or providing insufficient data. **The goal of this project is to improve, optimize, and validate an ion chromatographic method for the determination of ions in aquarium water.**

Table 1: Concentrations of the ions of interest in natural seawater.[1]

Ion Concentrations in Natural Seawater			
Cation		**Anion**	
Lithium	0.17 ppm	Fluoride	1.2 ppm
Sodium	10,500 ppm	Bromide	65 ppm
Potassium	380 ppm	Phosphate	0.07 ppm
Magnesium	1,350 ppm	Nitrate/Nitrite	15 ppm
Calcium	400 ppm	Chloride	19,000 ppm
Strontium	8 ppm	Sulfate	2,700 ppm

2 Ion Chromatography

Ion Chromatography works by separating various charged components in solution using an ion-exchange column followed by electrochemical detection.
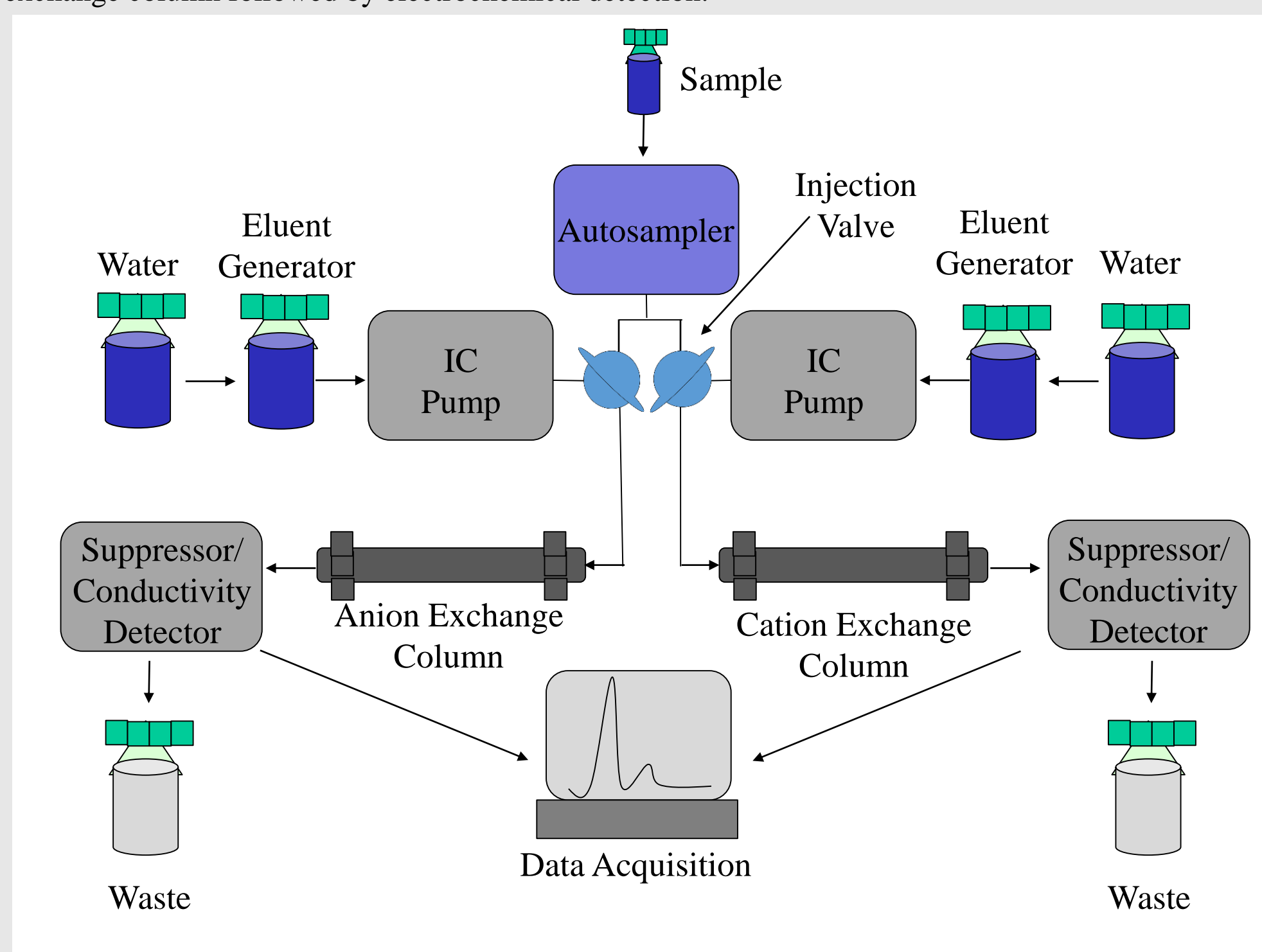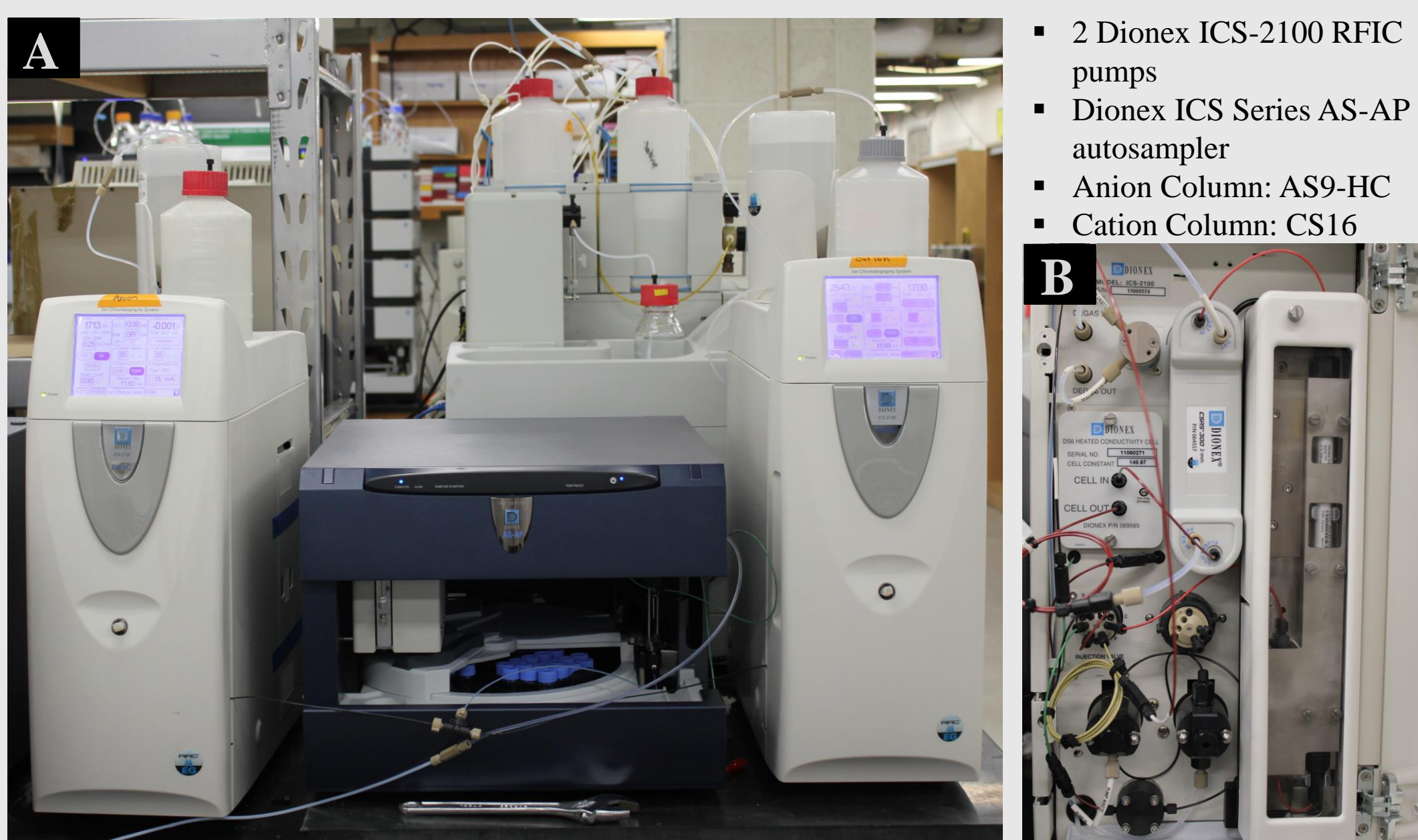

Figure 1. Block diagram of the current anion-cation ion chromatography instrumentation.

3 Instrumentation Setup

- 2 Dionex ICS-2100 RFIC pumps
- Dionex ICS Series AS-AP autosampler
- Anion Column: AS9-HC
- Cation Column: CS16

Figure 2. A) Overall view of the anion-cation instrumentation setup. B) View of the inside of the cation module.

4 Conditions

Each sample is prepared by a 1:5 dilution in ACS grade water. The eluent for the cation pump is methanesulfonic acid (MSA) and the eluent for the anion pump is potassium carbonate (K_2CO_3).

Table 2: Conditions for the original and current anion-cation method.

Condition	**Cation**		**Anion**	
	Original Value	Improved Value	Original Value	Improved Value
Eluent Molarity (mM) (Isocratic)	32	46	12	12
Flow Rate (ml/min)	0.40	0.40	0.25	0.25
Injection Volume (μL)	10	10	10	10
Column Size (mm)	3 x 250	3 x 250	2 x 250	2 x 250
Column Temperature (ᵒC)	60	35	30	35
Suppressor Current (mA)	38	38	15	15
Cell Temperature (ᵒC)	55	35	35	35

5 Anion Analysis

Each peak must be correctly identified in a chromatogram by spiking experiments. When run individually, ions elute at specific times; however, in a mixture, retention times can change. Elution order is important in identifying the correct concentrations of each ion in seawater.
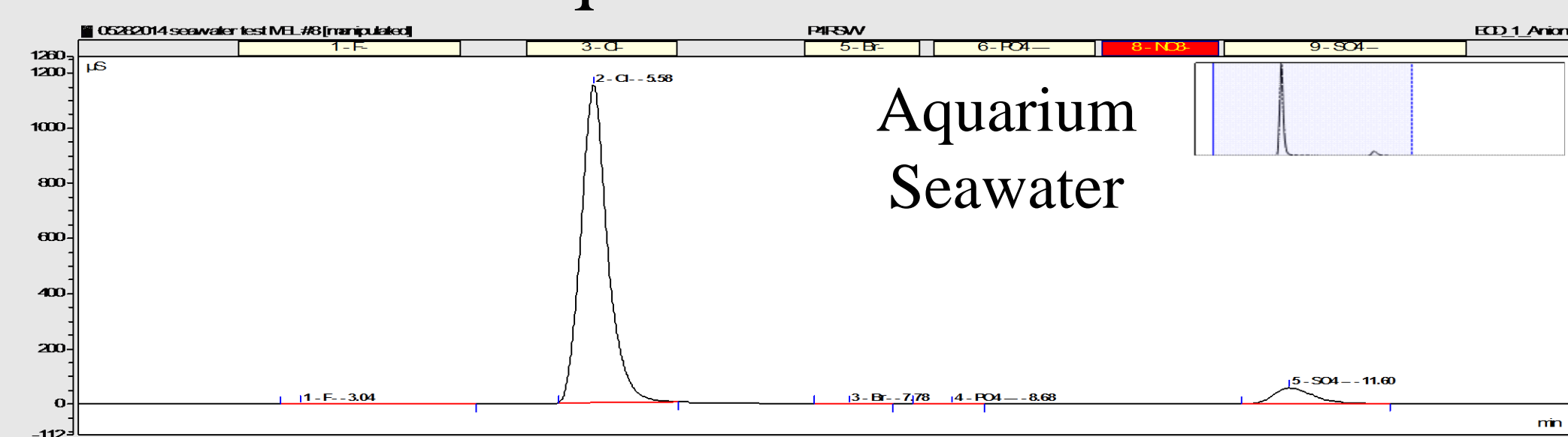
Aquarium Seawater

Figure 3. Typical separation of anions in aquarium seawater.
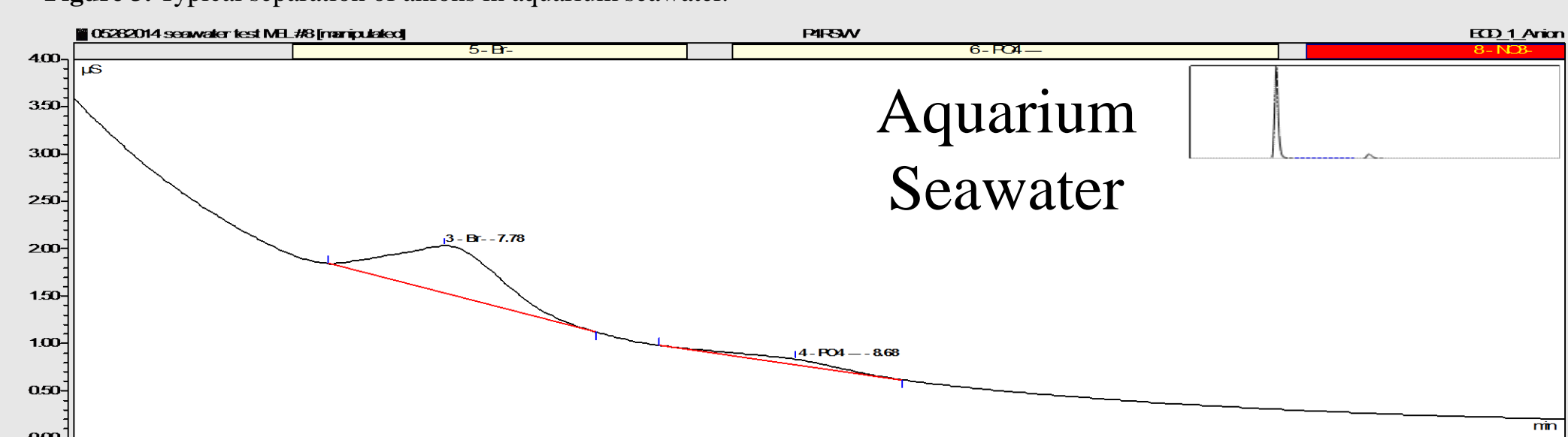

Figure 4. Typical separation of anions in aquarium seawater with a focus on bromide, phosphate, and nitrate elution times.
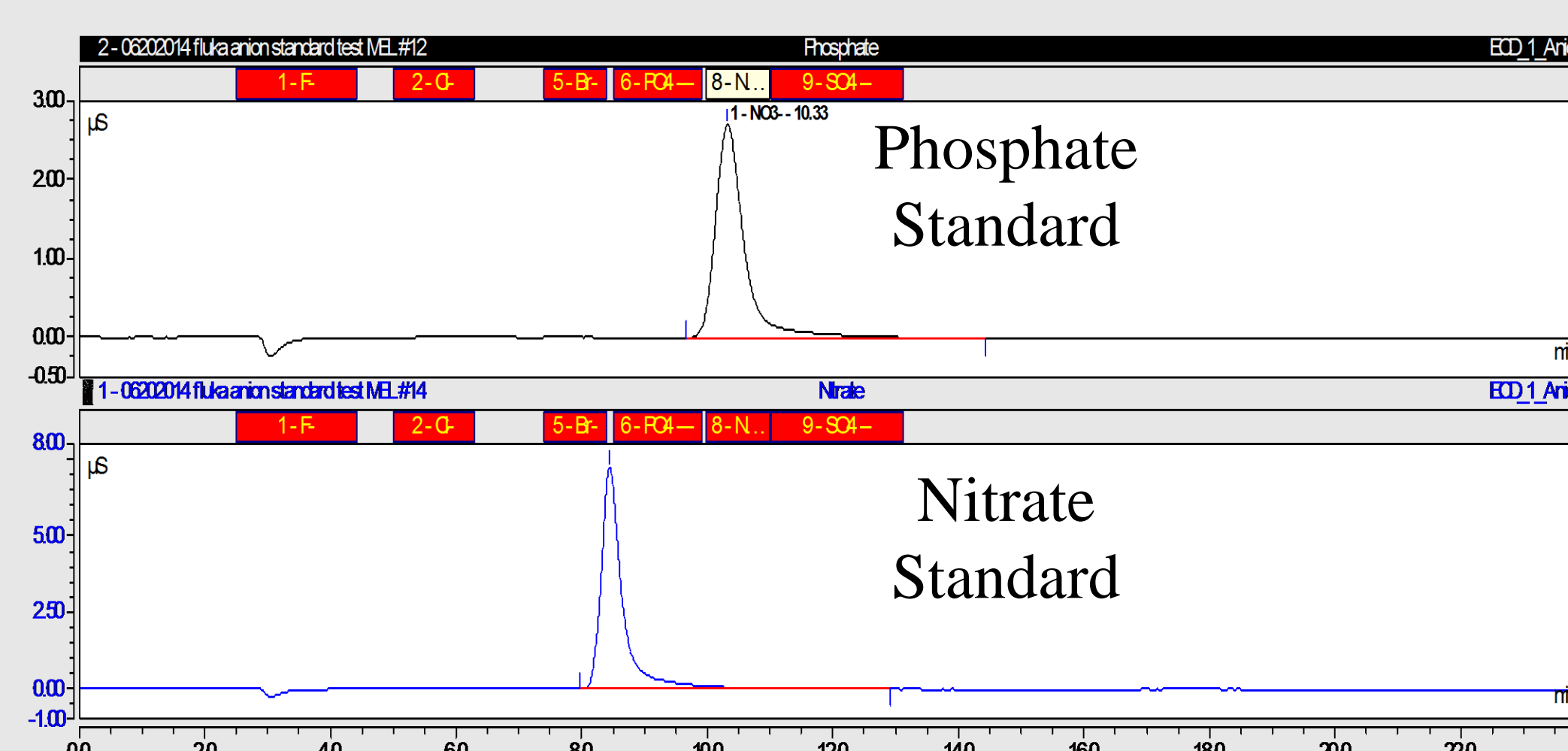
Standards

Figure 5. Stacked view of 100 ppm phosphate and nitrate standards with a focus on order of elution.
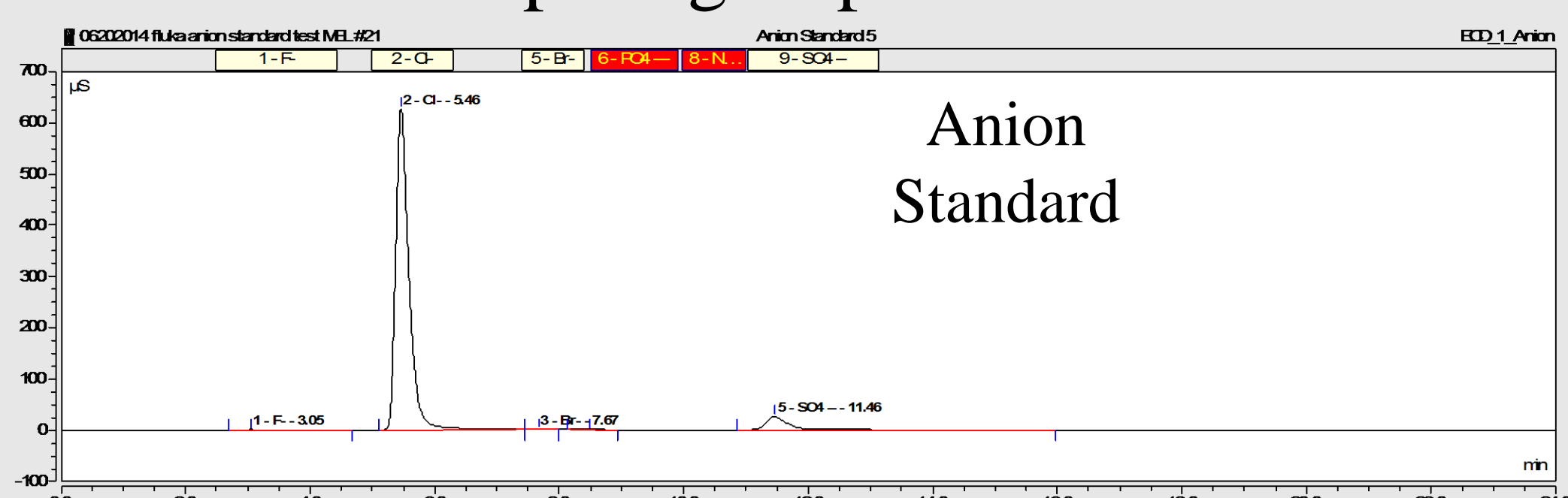
Spiking Experiments

Figure 6. Typical separation of a standard with anions in the ratio of natural seawater.
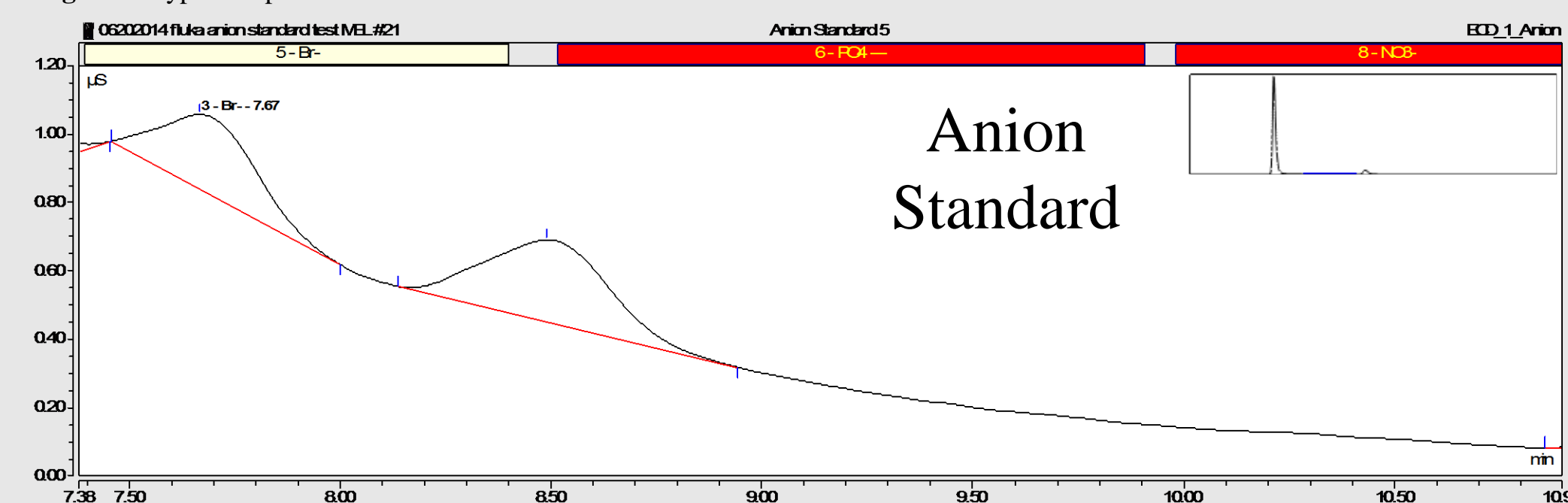

Figure 7. Typical separation of a standard with anions in the ratio of natural seawater with focus on bromide, phosphate, and nitrate elution times.
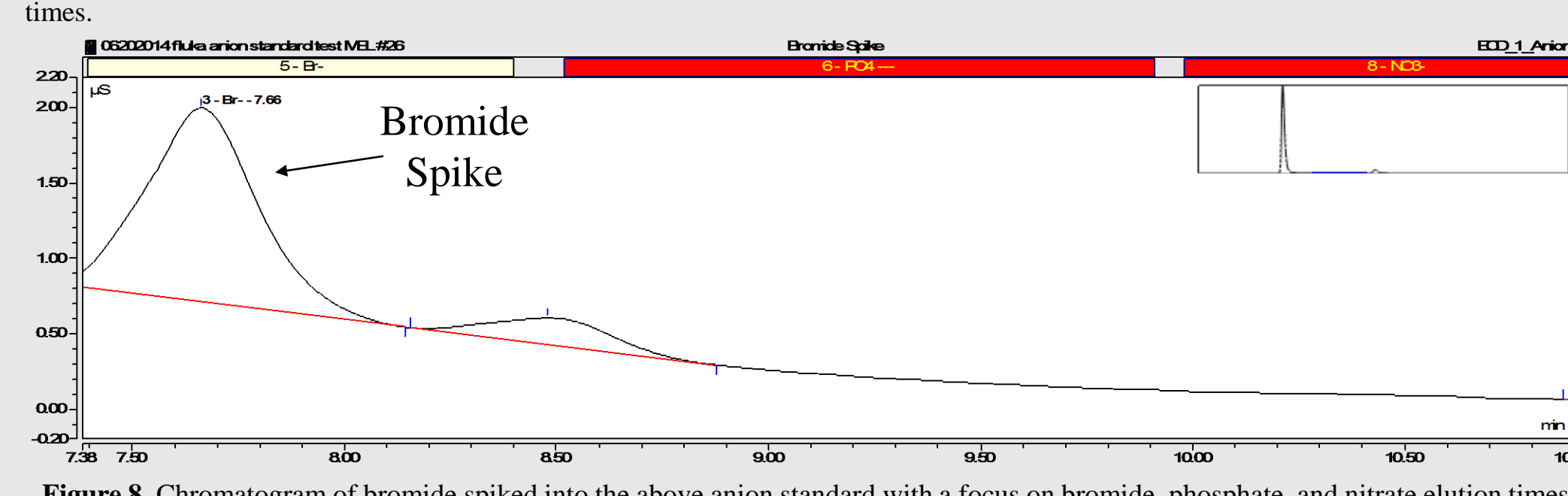

Figure 8. Chromatogram of bromide spiked into the above anion standard with a focus on bromide, phosphate, and nitrate elution times.
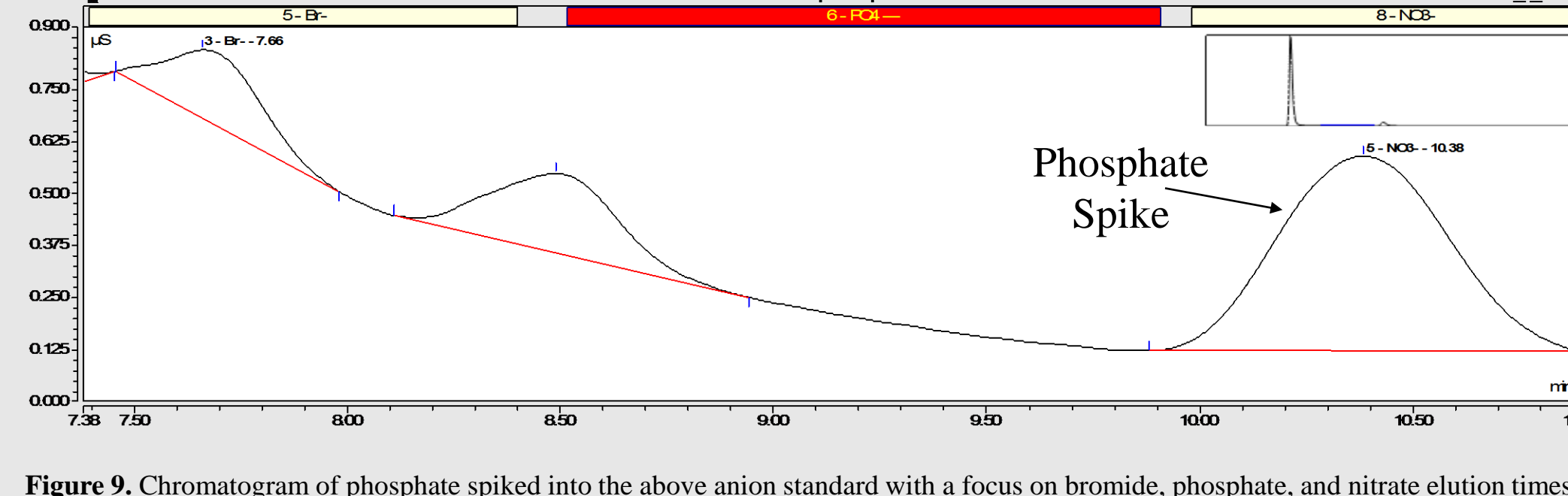

Figure 9. Chromatogram of phosphate spiked into the above anion standard with a focus on bromide, phosphate, and nitrate elution times.
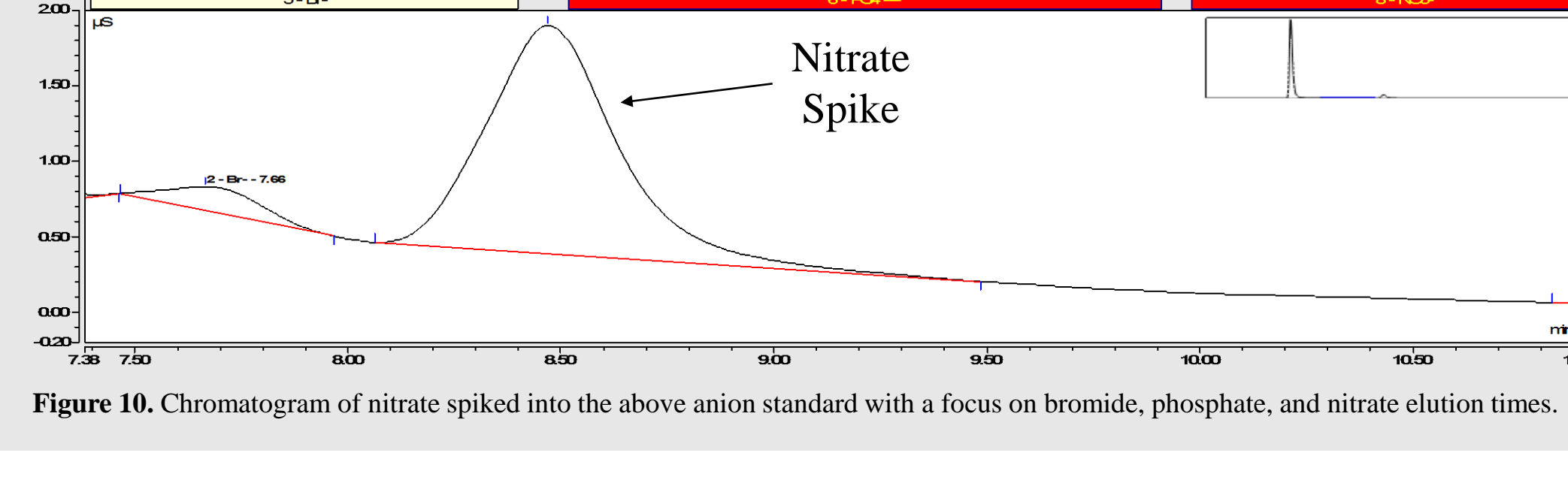

Figure 10. Chromatogram of nitrate spiked into the above anion standard with a focus on bromide, phosphate, and nitrate elution times.

6 Cation Analysis

The cation method needed improvement to shorten the run time and decrease the column temperature in order to lengthen the life of the column.
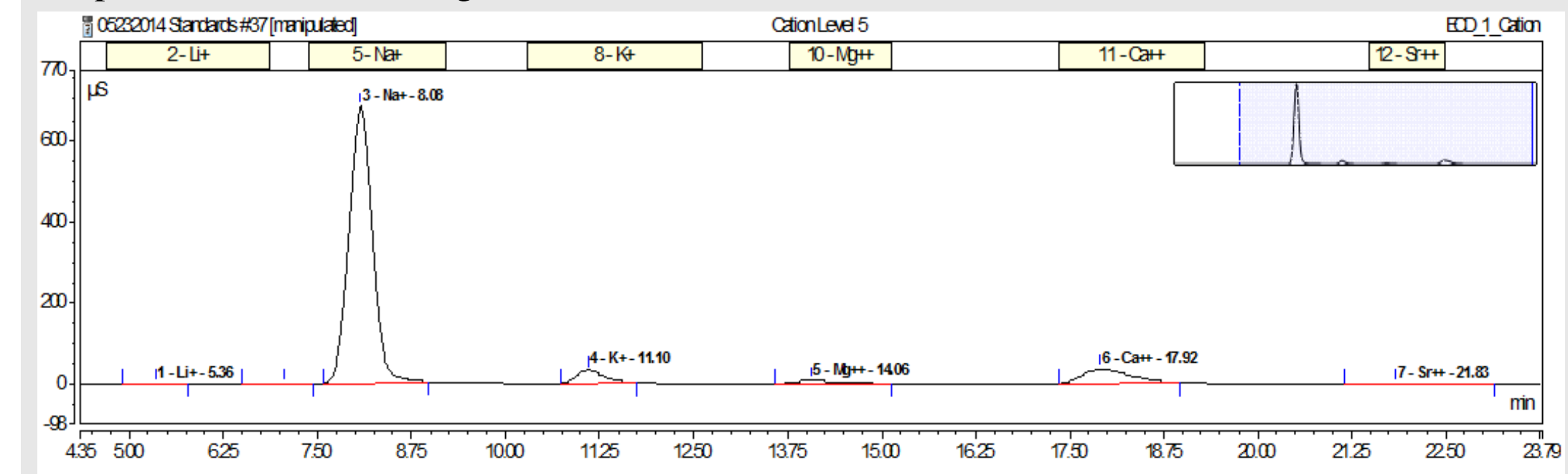

Figure 11. Typical separation of standard with cations in the ratio of natural seawater using the original method.

Eluent Generator Molarity

- Changing the eluent generator molarity changes the retention time of each ion
- Changes in molarity affect the retention times of the divalent cations much more than the retention times of the monovalent cations
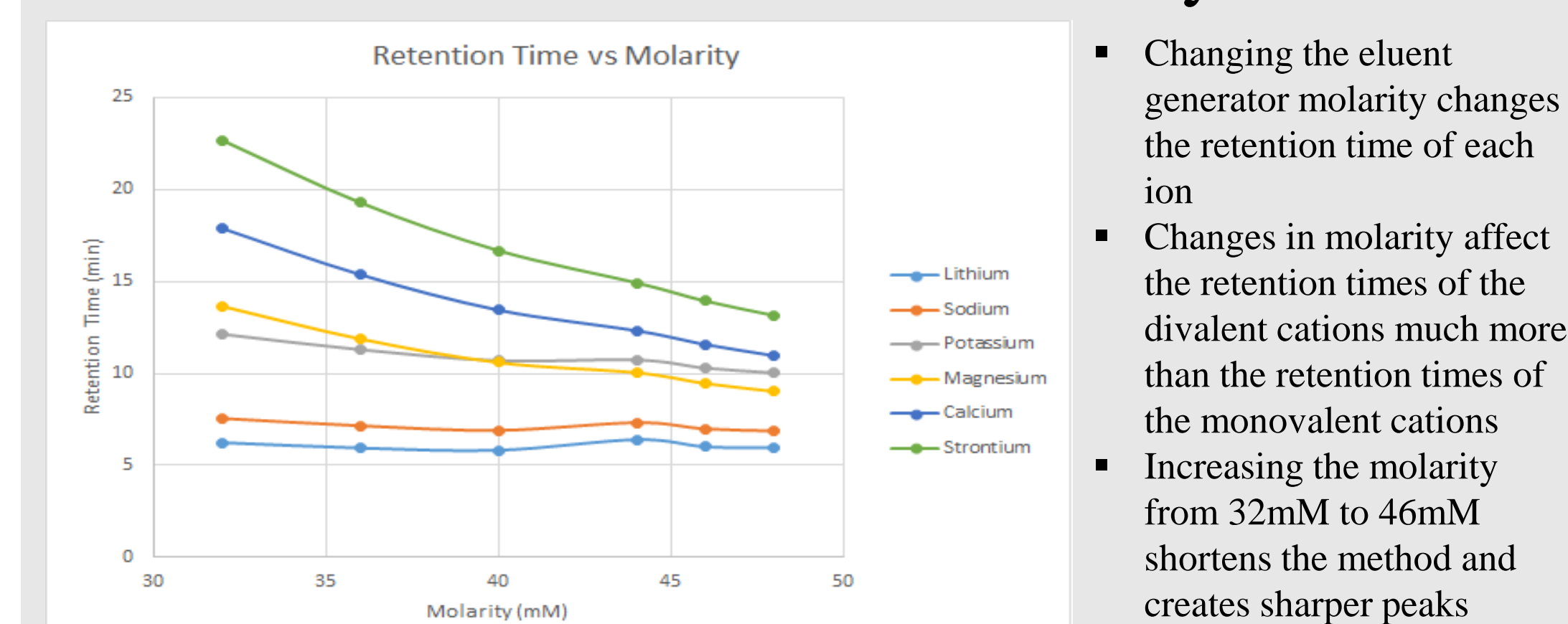- Increasing the molarity from 32mM to 46mM shortens the method and creates sharper peaks

Figure 12. Graph representing the change in retention time of each ion in minutes as correlated to the molarity of the eluent (mM).

Column and Cell Temperature

- Changing the temperature of the column and the cell changes the retention time of each ion
- Decreasing the cell temperature from 55ᵒC and the column temperature from 60ᵒC down to 35ᵒC creates a better separation and lengthens the life of the column
- The CS16 column was not designed to be run above 35ᵒC and doing so drastically shortens column life
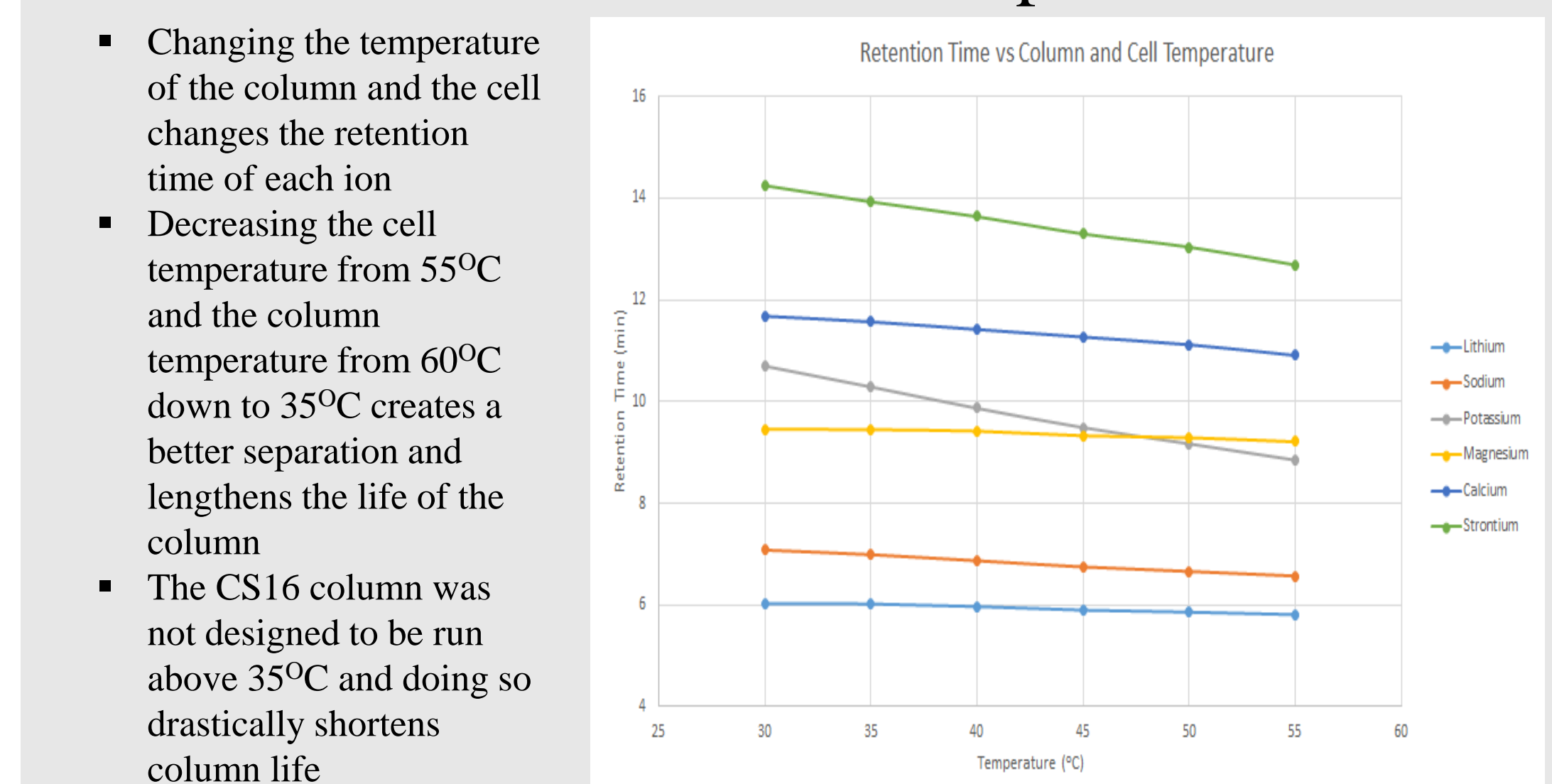

Figure 13. Graph representing the change in retention time of each ion in minutes as correlated to the temperature of the cell and column.

Improved Method Results

- The original cation method was improved to become more efficient and effective and the column temperature was lowered to improve column lifetime
- Retention time decreases with increased mobile phase molarity, but the rate of change varies based on specific ions
- By controlling the variables of column and cell temperature and the molarity of the eluent, a shorter separation with better peak shapes is attained
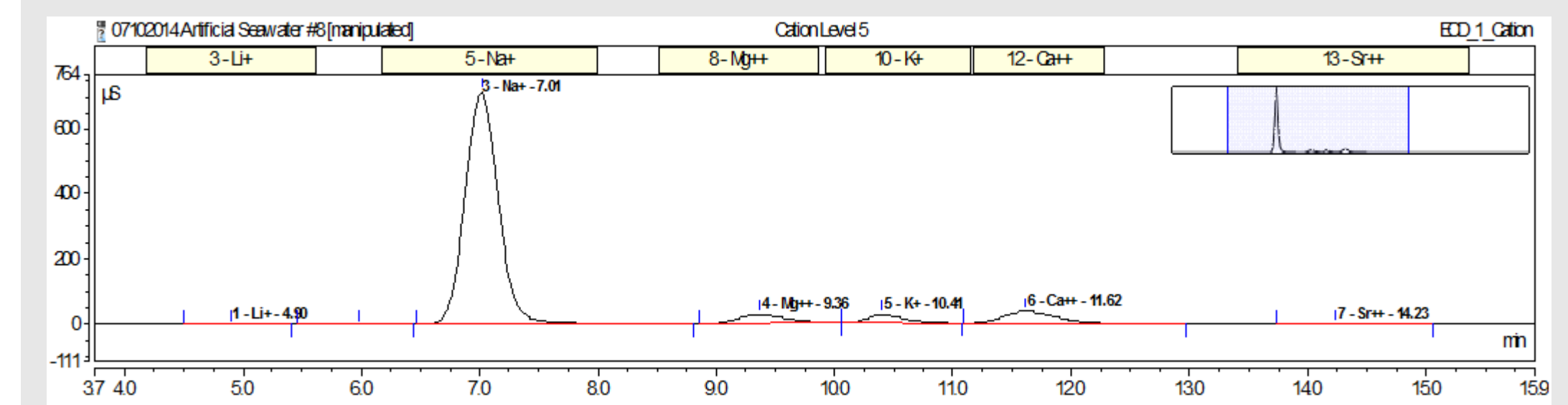

Figure 14. Typical separation of standard with cations in the ratio of natural seawater using the improved method.
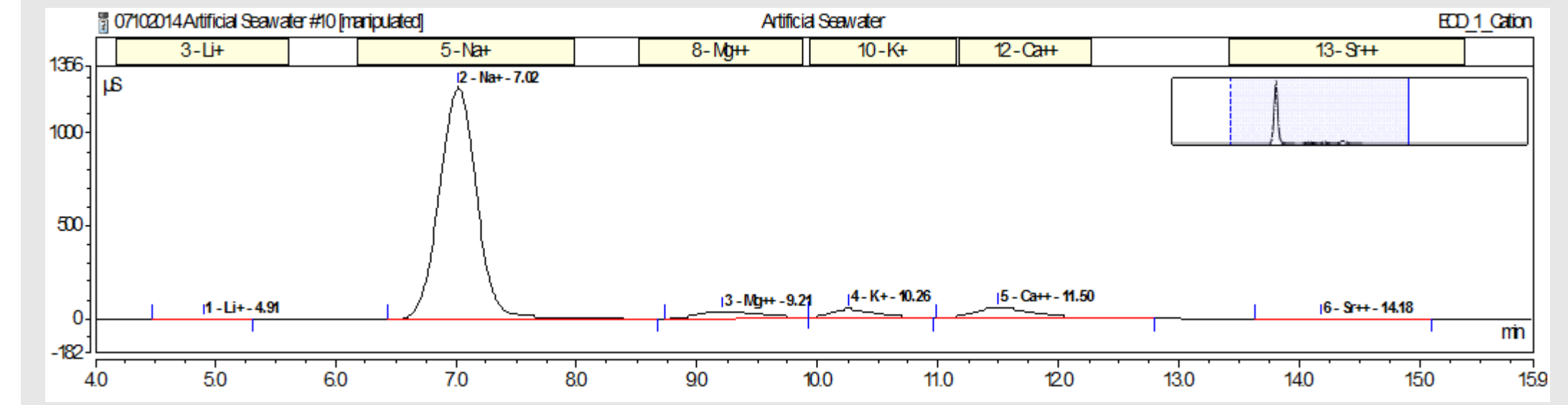

Figure 15. Typical separation of artificial seawater from the aquarium using the improved method.

7 Conclusion

The previous anion-cation separation method required improvement because the run time was lengthy, the high temperature shortened the life of the column, and the peaks were mislabeled in the method. Experimentation showed that retention time decreases with increased mobile phase molarity, and the rate of change varies based on specific ions. Additionally, retention time decreases with increased cell and column temperature, and the rate of change varies based on specific ions. The separation of ions in seawater can be optimized through control of these variables. Spiking experiments indicate that the nitrate and phosphate peaks were mislabeled in the method and allowed for the correct identification of each peak. Future experiments include further improving the anion method by optimizing variables such as cell and column temperature and eluent molarity. Additional steps also include validating the improved anion-cation method with spiking experiments and standards. Overall, the initial anion-cation method for the determination of ions in aquarium water was improved and optimized.

Reference: [1]All values in the table provided by the National Aquarium in Baltimore.