Objectives:

1. To become familiar with applications, parameters, and instrumentation used in ion chromatography
2. To quantitatively determine the anions present in Boggs tap water

Text References


Other Resources

- [www.dionex.com](http://www.dionex.com)
- [http://www.anachem.umu.se/jumpstation.htm](http://www.anachem.umu.se/jumpstation.htm)
- [http://hazard.com/msds/](http://hazard.com/msds/)
- [www.epa.gov](http://www.epa.gov)

Introduction

Ion chromatography (IC) is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the particular resin. Its greatest utility is for analysis of anions. It is also used in the analysis of cations and biochemical species such as amino acids and proteins.

The column packings for ion chromatography consist of ion-exchange resins bonded to inert polymeric particles (typically 10 µm diameter). The DX-300 used in this experiment contains an anion exchange column, a ©Dionex ([www.dionex.com](http://www.dionex.com)) IonPac® AS9-HC (2-mm) Analytical Column. *Cation exchange is used to illustrate the general theory of IC in this introduction. It will be up to the student to formulate the general theory for anion exchange.*
Figure 1. Structure of an IonPac® AS9-HC packing particle.

For cation separation the cation-exchange resin is usually a sulfonic or carboxylic acid, and for anion separation the anion-exchange resin is usually a quaternary ammonium group. For cation-exchange with a sulfonic acid group the general reaction is:

\[ x\text{RSO}_3\text{H}^+ + M^{x+} \rightarrow (\text{RSO}_3)^mM^{x+} + x\text{H}^+ \]

The equilibrium constant for this reaction is:

\[ K_{\text{eq}} = \frac{[(\text{RSO}_3)^mM^{x+}]_s [\text{H}^+]_{\text{solution}}}{[\text{RSO}_3\text{H}^+]_s [M^{x+}]_{\text{solution}}} \]

Different cations have different values of \( K_{\text{eq}} \) and are therefore retained on the column for different lengths of time. The time at which a given cation elutes from the column can be controlled by adjusting the pH ([H\(^+\)]_{\text{solution}}).

Ions in solution can be detected by measuring the conductivity of the solution. However, in ion chromatography, the mobile phase contains ions that create a background conductivity, making it difficult to measure the conductivity due only to the analyte ions as they exit the column. This problem can be greatly reduced by selectively removing the mobile phase ions after the analytical column and before the detector. This is done by converting the mobile phase ions to a neutral form or removing them with an eluent suppressor, which consists of an ion-exchange column or membrane.
This experiment uses a Dionex ASRS-ULTRA (2-mm) Anion Self-Regenerating Suppressor. This suppressor includes two regenerant compartments and one eluent compartment separated by ion exchange membranes. As shown in Figure 2, eluent flow is in a direction that is countercurrent to the regenerant flow. Electrodes are placed along the length of the regenerant channels. When an electrical potential is applied across the electrodes, H₂O is electrolyzed, supplying regenerant H₃O⁺ for the neutralization reaction. The membrane allows these hydronium ions to pass into the eluent chamber resulting in the conversion of the electrolyte of the eluent to a weakly ionized form. Eluent cations are simultaneously passed into the regenerant chamber to maintain charge balance.

For cation analysis, the mobile phase is often HCl or HNO₃, which can be neutralized by an eluent suppressor that supplies OH⁻. The Cl⁻ or NO₃⁻ is either retained or removed by the suppressor column or membrane. The same principles hold for anion analysis.

Figure 2. Electrode, membrane and screen configuration in the Anion Self-Regenerating Suppressor.

Experimental:

*As a pre-lab exercise (5 points of your overall grade), devise a dilution scheme to obtain 1ppm, 0.5ppm, and 0.25ppm standard addition solutions in each NO₃, Br, PO₄, Cl, F, SO₄ considering the following: You will use 100mL volumetric flasks. The starting solution contains all six anions (NO₃, Br, PO₄, Cl, F, SO₄), each at equal concentrations of 100μg/mL.
Preparing the Instrumentation:

1. Turn on the main power (blue buttons) for both the Pump and Detector. Also, turn on the Multimeter. Make sure both the eluent and regenerant bottles contain sufficient levels of liquid (at least half full). Turn on the He gas *SLOWLY* and note that it reads a pressure between 80 – 100 psi into the instrument.

2. Turn the Eluent Degas Module ON. Turn the pressure valve clockwise to obtain a pressure between 5 and 10psi. Make sure the leftmost Mode is set to Sparge. Activate Reservoir 1 and sparge for 10 minutes.

3. Set the leftmost Mode to Pressurize for Reservoir 1. Again, make sure the pressure is 5 – 10psi. Now, start the Pump (STOP/START option to the right of the pump). Make sure the pump pressure is 1400 – 1700psi.

4. Pressurize the regenerant bottle to 15 – 20 psi. Turn the CELL to the ON position. (This also activates the anion suppressor.) Make sure the MODE is set to Conductivity and monitor the TOTAL conductivity (under DISPLAY); make sure it stabilizes to a range of 25 – 30 μS. This could take up to 30 minutes.

5. Open the LabView Program (3211.vi) and set the # of points option to 1800. Designate your file name for the 1ppm High-Purity Solution A and press Enter. (Change file name for subsequent injections.)

Preparation of Standard Solutions

Prepare the following standard addition solutions from the pre-lab dilution scheme using the High-Purity Standard that contains 100ug/mL in each NO3, Br, PO4, Cl, F, SO4 anions:

1ppm, 0.5ppm, 0.25ppm (use tap water as the solvent for each)

The eluent is 9mM Na2CO3

Injecting the Solutions

Injections include (in this order): 1ppm High-Purity Solution A, tap water, 0.25ppm standard, 0.5ppm standard, 1ppm standard

1. Wash the syringe several times with the solution of interest. Obtain 0.5mL of sample in the syringe with no large air bubbles.

2. Reset the pump by pressing RST (make sure the time is set to 0.0). Now, activate AUTO OFFSET on the Electrochemical Detector panel.
3. *Read Step 3 in its entirety before proceeding.*
   Inject the 0.5mL sample and REMOVE the syringe from the injection port. Active RUN (the HOLD/RUN option near the pump). As soon as the automatic pressure controlled injection valve initiates, begin recording data. (This starts time zero at the automatic injection.) Note: each injection takes ~22 minutes to complete.

4. At the completion of the 22-minute timed run, stop collecting data in LabView. Activate HOLD then press RST. Repeat Steps 1 – 4 for subsequent injections.

5. Determine the elution times for each anion present in the High-Purity Solution A (a reference sheet is available in the lab). After injecting the tap water sample (in duplicate), it should be obvious what anions are present. Note these, and inject the standard addition solutions in duplicate. Prepare standard addition plots for each anion present.

**Cleanup:** *Failure to leave the workspace and equipment in proper order will result in a deduction of points during grading.*

1. Turn the cell to the OFF position. Depressurize the regenerant bottle. Turn the pump to STOP. Depressurize the eluent bottle. Turn the eluent SYSTEM OFF. Turn OFF the main power and Multimeter. TURN OFF the He gas!!

2. After disposing of your standard solution(s) (sink), fill each piece of glassware used with Nanopure water (this allows any ions present in the glass to be leached out until the next use).

**Lab Reports**

Create standard addition plots for each anion present in Boggs tap water by plotting signal (A.U.) versus concentration. Report the final amount of each anion in ppm. Compare these levels with the recommended safe levels as reported by the federal agencies (you must find this information). Label all figures and tables. Note your references.

**Questions:**

1. (2 points) The IonPac® AS9-HC column allows the determination of bromate as low as what value (g/L) in typical drinking water samples without sample pretreatment? (Hint: You will have to use your resources listed above.)

2. (3 points) Name three advantages of chemical suppression in ion chromatography.
3. (16 points total) (a) What is the purpose of the eluent suppressor in this experiment? (b) Write chemical equations for the interactions inside of the suppressor. (c) Why would a suppressor for cation chromatography contain an anion-exchange resin? (d) The exchange capacity of an ion-exchange resin can be defined as the number of moles of charged sites per gram of dry resin. Describe how you would measure the exchange capacity of an anion-exchange resin by using standard NaOH, standard HCl, or any other reagent you wish.

4. (7 points) Propose a scheme for separating trimethylamine, dimethylamine, methylamine, and ammonia from one another by ion chromatography.

5. (7 points) Knowing that the IonPac AS9-HC contains quaternary ammonium groups, formulate a chemical equilibrium reaction and show the equilibrium constant for the exchange inside the column between the mobile and stationary phases. What is the purpose of a guard column?

Bonus!: (5 points) State the effects of increasing cross-linking on an ion-exchange column.
Ion Chromatography – Grading Scheme

Clint Jones TA

CHEM 3211, Spring 2000

• Pre-lab dilution scheme 5 points

• Title Page
  Experiment title, name, partner’s name(s), class section,
  date performed, date submitted

• Introduction 20 points
  Must at least include: Purpose; Theory of: IC, Anion Suppressor,
  Conductivity Detector; Relevant chemical equations

• Procedure (only deviations from) 5 points

• Sample Calculations, Dilution Scheme, Tables, Charts 15 points

• Discussion 25 points
  Must at least include: precision, pertinent errors, the experimental
  results, why did the anions elute in that order?, sensitivity of the
  detector for the different anions, general theory as it pertains to
  this experiment and the results

• Questions 35 points

• References

100 Total