

Introduction to Urban Watershed Geochemistry
Part 2: Analysis of Anions in Water Using an Ion Chromatograph
Lab Exercise #2

1 Introduction:

In this laboratory, you will use an ion chromatograph to analyze water samples from Filbin Creek. You will also learn principles of ion chromatography and create solutions to calibrate the ion chromatograph (IC). You will prepare calibration curves for Cl^- , F^- , Br^- , NO_3^- , PO_4^- , and SO_4^{2-} .

Chromatography is a technique for separating ionic, nonionic, or gas solutes from complex mixtures. A liquid or gas solvent (mobile phase) containing the solute mixture is passed through a column packed with an appropriate solid phase (stationary phase). Depending on the properties of the individual solutes, the solutes interact with the stationary phase at different strengths. Therefore, as the mobile phase (containing the solutes) flows through the column, some solutes move more slowly compared with others (Figure 1). The solutes are then detected at other end of the column

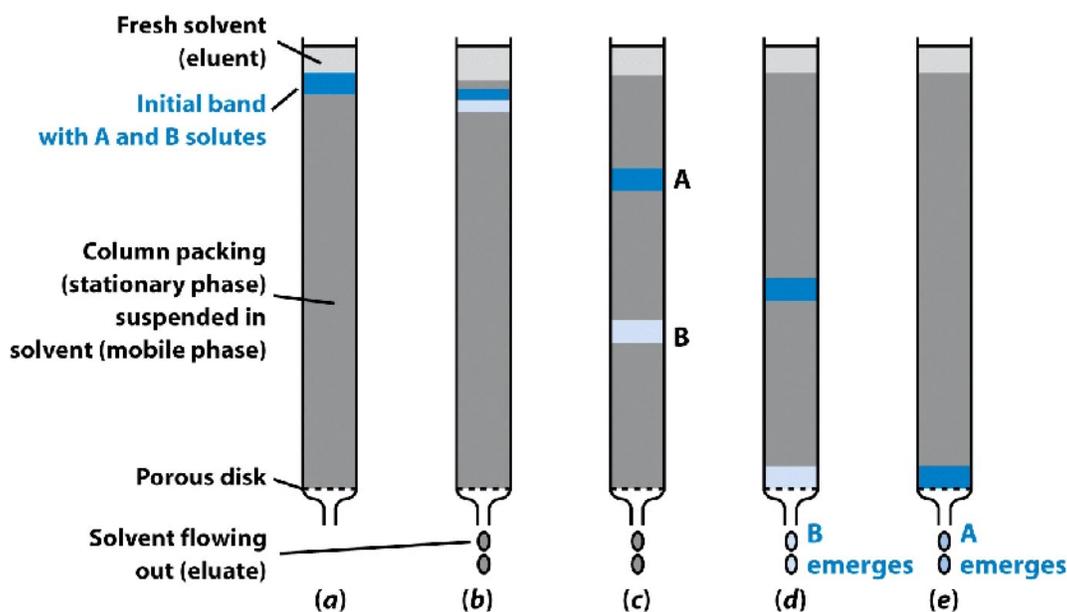


Figure 1: The basic principle of chromatographic separation of multiple solutes in a column packed with absorbent stationary phase. Image source: Harris, 2007, Quantitative chemical analysis, 7e, WH Freeman.

using a specific detector. A graph indicating the signal intensity versus time is plotted and this plot is called the chromatogram (Figure 2). The time at which each solute appears at the end of the column is called retention time (t) and shows very distinctly on the chromatogram. The area under each solute peak is directly proportional to the solute concentration. With this technique, we can not only separate mixtures, but can also quantify their concentrations.

2 Required Materials:

The following materials and equipment to required for today's lab exercise:

1. Wear appropriate attire (gloves, safety glasses, lab jacket, pants, close toed shoes, etc.)
2. Lab notebook to record data

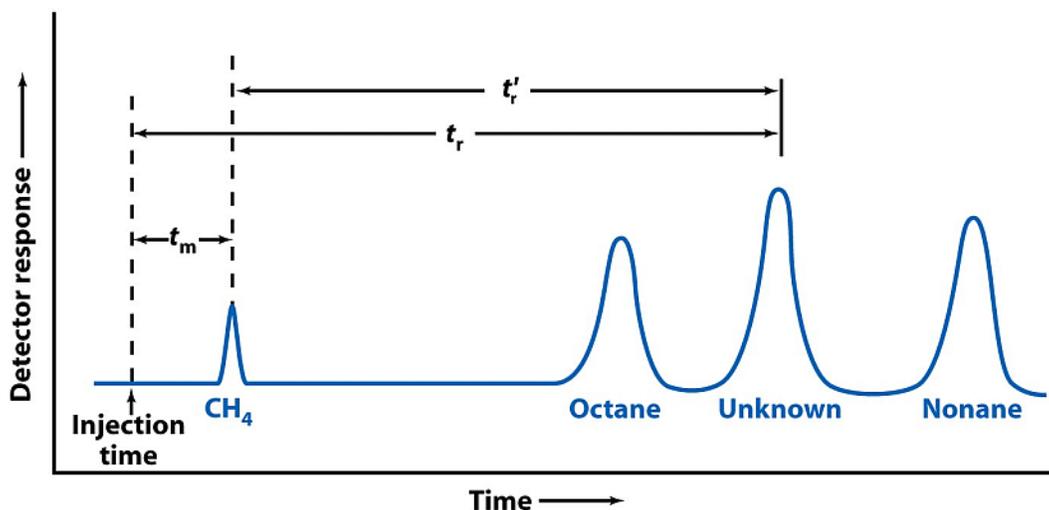


Figure 2: A schematic of a chromatogram that shows elution of different solutes at different retention times (t). Area under each solute peak is directly proportional to solute concentration in the sample injected. Image source: Harris, 2007, Quantitative chemical analysis, 7e, WH Freeman.

3. 6-7 50 mL plastic bottles with caps
4. 10-15 mL of 1000 mg/L multi-anion IC standard solution
5. Water samples from Filbin Creek
6. Deionized (DI) H₂O in squeeze bottle
7. Several IC tubes

3 Tasks to be Performed:

1. Preparation of Standard Solutions to Calibrate the IC

1. Calculate exact volumes of 1000 mg/L “stock” solution needed to prepare 50 or 100 mL of dilute multi-anion (stock standard contains Cl⁻, F⁻, Br⁻, NO₃⁻, PO₄⁻, and SO₄²⁻) solutions of 50, 20, 10, 5, 1, and 0.5 mg/L concentrations using standard and/or serial dilutions.
2. Prepare standards gravimetrically (by mass using the balance instead of volumetric flasks.) *Note: Prepare your standards directly in the clean plastic bottles that were provided. Do not need volumetric flasks.*
3. Transfer standard solutions to pre-labeled IC tubes. Also include a blank standard (deionized H₂O) in one IC tube.

2. Preparation of Unknown Water Samples

1. Dilute your unknown water samples serially, 10×, 100×, and 1000× directly into 15 mL IC tubes.
2. Label each sample container clearly with your group’s name.

3. IC Analyses

1. Load samples in IC queue from low to high concentrations and identify samples based on partner’s names and enter this information into the IC queue.
2. Run samples.
3. The raw data will be emailed to you before end of the week.

4 What to Include in your Lab Report:

Address the following issues and questions:

1. From the provided raw data, plot the chromatograms for all standards and samples on the same plot (Signal on y -axis and time on x -axis.)
2. From the provided raw data, calculate retention times (see Figure 2) for each ion and the areas under the peaks of these curves. You will use numerical integration (trapezoidal rule) to calculate area under the peak (see Figure 3).

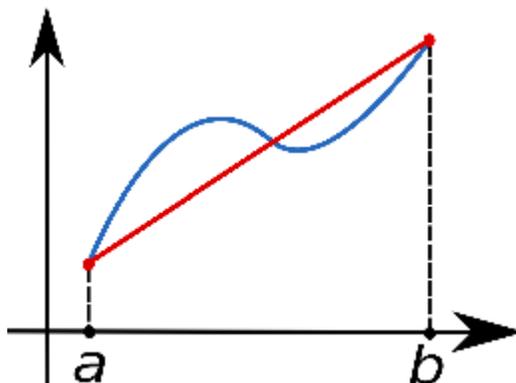


Figure 3: A schematic of a small section of the chromatogram that is approximated in the form of a trapezoid. The area of this trapezoid is calculated using standard geometry techniques.

- (a) Identify the beginning and end of each peak area
- (b) For each segment under the peak of ion, calculate the area of the trapezoid as shown in Figure 3 and the equation below.

$$\int_a^b f(x)dx \approx (b-a)\frac{f(a)+f(b)}{2} \quad (1)$$

Note that $y = f(x)$. Set this equation in a separate column next to the signal column.

- (c) Repeat this for all segments under the peak of each ion.
 - (d) Add all trapezoid areas under the peak of each ion to calculate total area under the peak.
3. Construct calibration curves for each ion (peak area (y -axis) versus concentration (x -axis)).
 4. Determine the limit of linear response (LOL) of the calibration curve for each anion.
 5. Determine the limit of quantification (LOQ) for each anion.
 6. Apply dilution factors to unknown samples and recalculate actual concentrations.
 7. Compare the anion data collected in the field using the Hach kits with those obtained using the IC. Explain why the data is different and which of these two data sets is likely to be correct.
 8. Compare the data with drinking water standards on EPA website (<http://water.epa.gov/drink/contaminants/index.cfm>).
 9. Based on your research of similar stream sites in urban areas (conduct literature review), are the anion concentrations within acceptable limits?
- ‘ The lab report format is identical to earlier lab reports and should include the following components:
1. Title of the exercise, your name, name of partner, and date of lab exercise.
 2. Abstract (≈ 150 words)
 3. Methods (≈ 300 words)
 4. Results (≈ 400 words)
 5. Discussion (≈ 400 words)
 6. Conclusions (≈ 100 words)
 7. References