**Ion Exchange Determination of Na+ by Displacement and Zn^{2+} Using Preconcentration**

**Reading:** Harris pp. 641-647, 699

**Prelab Assignment:**

1. The pH of a solution is 4.56. Determine the H^{+} concentration and use significant figure rules to calculate the number of significant figures in the final result.

2. Using the procedure in Part 2, the colorimetric procedure determined the Zn^{2+} concentration in the 25 mL sample of eluant as 1.89x10^{-5} M. The original stock solution before preconcentration was 5.00x10^{-6} M Zn^{2+}. Calculate the percent recovery.

3. Bring the instrument instructions for the Hewlet Packard 8452A Diode Array UV/Visible Spectrophotometer to lab.

**Theory**

**Ion Exchange:** Ion exchange resins consist of charged functional groups attached to a polymeric backbone. For cation exchange resins the charged group is most often the sulfonate group, -SO_{3}^{-}. For anion exchange resins the charged group is most often a quaternary ammonium ion, -N(CH_{3})_{3}^{+}. The mechanism of ion exchange can be pictured with the aid of Figure 1. In acidic solution the charged groups in a cation exchange resin will be associated with H^{+}. If a sample containing Na^{+} is added to the solution, some of the H^{+} ions will exchange with Na^{+} ions. The following exchange reaction takes place:

\[
[\text{Resin}]^{-} \cdot H^{+} + Na^{+} \rightleftharpoons [\text{Resin}]^{-} \cdot Na^{+} + H^{+} \quad (1)
\]

The resulting H^{+} can be determined by titration and used to calculate the original concentration of the exchanged ion in solution. The exchange in Eq. 1 can be described by an equilibrium expression:

\[
K = \frac{[\text{Resin}^{-} \cdot Na^{+}][H^{+}]}{[\text{Resin}^{-} \cdot H^{+}][Na^{+}]} \quad (2)
\]

![Figure 1. Cation exchange](image)

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**Figure 1. Cation exchange**
Different ions have different equilibrium constants. The greater the affinity of an ion for the ion exchange resin the further the position of equilibrium will lie to the right and the greater the equilibrium constant will be. In many uses, a mixture of ions is exchanged onto the column. The exchanged ions can later be removed (eluted) from the resin using acid solutions of increasing strengths. The order of elution of ions can be predicted by knowing the equilibrium constants for each of the ions in the sample. Ions with small K's will have smaller affinity for the resin and will elute at lower acid concentration. For elution, any ion will do, as long as the ion is not one that is being determined. Common elution solutions include HCl, NaCl, sodium acetate, and ammonium acetate.

Ion exchange resins are used in many different formats. Ion exchange resins are often used in low pressure chromatography columns with gravity elution or low pressure pumps. Small particle ion exchange resins are used in high performance liquid chromatography, HPLC, columns for very high-resolution separations. For sample preparation, ion exchange resins can be packed as beads into syringe cartridges or used to form filtration membranes. For small volume samples, milligram quantities can be packed into auto-pipettor plastic tips (Zip-tips). For this experiment we will use a larger volume cartridge format, called a solid-phase extraction cartridge.

**Solid Phase Extraction, SPE**

Solid phase extraction, SPE, cartridges are a commonly used tool for sample preparation. The cartridge can be packed as an open tube or as a syringe–type filter. SPE cartridges are available in a variety of chemistries. Silica particles that have C\textsubscript{18} chains attached are the most common SPE packing. For C\textsubscript{18}-SPE cartridges, non-polar compounds are retained in the cartridge while polar compounds and salts can be washed through. In our experiment, ion exchange SPE cartridges will be used to introduce you to these powerful tools. C\textsubscript{18} and ion exchange SPE are very commonly used in analytical and biochemical sample preparation. DNA and polar proteins are polyelectrolytes that can interact with an ion exchange resin in the same fashion as the simple ions in this experiment.

**Part 1. Ion Exchange Determination of Na\textsuperscript{+} by Displacement**

We will use commercial solid phase extraction cartridges to determine the total cation concentration in a sample. The cations will displace H\textsuperscript{+} ions from the hydrogen ion form of the resin, and the hydrogen ion concentration resulting will be determined using a pH meter.

\[
\text{H}^+\text{SO}_3^-\text{–R} + \text{Na}^+ \rightarrow \text{Na}^+\text{SO}_3^-\text{–R} + \text{H}^+
\]

The plastic cartridges hold 300mg of the ion exchange resin. The ion exchange capacity is about 0.45 meq. Here meq means milliequivalents. For unipositive ions like Na\textsuperscript{+}, milliequivalents is the same as millimoles.

Ion exchange columns may be regenerated and reused. To regenerate a column, 0.1 M HCl is passed through the column in excess. Then the column is washed at least three times with reagent grade water. To determine if the excess acid has been washed from the column, you can test the wash water with a pH electrode, or even better, you can use AgNO\textsubscript{3} solution to check for the presence of Cl\textsuperscript{–}. 
The sample in this exercise contains only NaCl. However, environmental samples are often complex mixtures. This determination will not discriminate among any particular cation. All cationic species will in general be determined. For example, in a mixture of NaCl, KCl, and CuCl₂, the H⁺ generated will be equal to the total number of moles of positive charge (equivalents) of all ions.

**Procedure:**

**Equipment Required:**
- Fisher P457 PrepSep-SCX Solid Phase Extraction Cartridge
- 2x 25-mL volumetric flasks
- 10-mL volumetric pipet
- 3x 30-mL beakers
- 2x 50-mL beakers
- 10-mL graduated cylinder
- pH meter and pH electrode
- Blue litmus paper

**Solutions:**
- Unknown (about 25 mL of 2.50x10⁻³ M NaCl as supplied by instructor)
- 10 mL of 0.1 M HCl
- 10 mL of 0.3 M NaCl
- pH 7 and pH 4 phosphate buffers

**pH Meter Calibration:**
Use standard pH 7 and pH 4 phosphate buffers to calibrate the pH meter. To help insure accurate readings, keep two beakers of reagent grade rinse water so that you can rinse the electrode twice between each change of sample. Always rinse in the same order so that the second rinse stays cleaner.

**Sample Preparation:**
Place a plastic bottle in the white plastic filtration apparatus to collect the filtrate. Assemble the filtration apparatus. If the blue valve handle is vertical, the valve is closed. If the blue valve handle is horizontal the valve is open and vacuum will be applied to the SPE cartridge. To regenerate the ion exchange resin, rinse the SPE cartridge with 10 mL of 0.1 M HCl, and then three washes of 10 mL of water. A graduated cylinder can be used for the acid and a wash bottle for the rinses. Remove the top of the filtration apparatus and touch the stainless steel tip to a piece of litmus paper to check for sufficient rinsing. If the litmus paper turns red, wash with several more 10 mL portions of water. Rinse the plastic bottle several times with reagent grade water and put it back in to the filtration apparatus. Collect two more 10 mL rinses. Determine the pH of this solution. Continue rinsing until the pH is greater than 5.8.

Place a 25-mL volumetric flask inside the plastic filtration apparatus to collect the filtrate and reassemble the filtration apparatus. Transfer your unknown quantitatively into a 25 mL volumetric flask. Dilute to the mark with reagent grade water and mix well. Transfer 10 mL of this solution into your SPE cartridge using a volumetric pipet. After pulling this solution through the SPE cartridge, follow the sample solution with two small portions of water (2-3 mL) from your wash bottle to ensure quantitative transfer. Remember that the volumetric flask holds only
25 mL, so don’t add too much wash water. Remove the 25-mL flask and dilute to the mark with reagent grade water.

**pH Determination:**

Rinse the pH electrode twice with reagent grade water. Carefully and gently dry the pH electrode with a ChemWipe to avoid dilution of your filtrate solution. Pour half of your sample into a clean, dry 30-mL beaker and determine the pH. Empty the beaker and refill with the other half of your filtrate solution and repeat the pH determination. Report the average of the two results. Use the difference in the two readings to estimate the uncertainty of your results. Rinse the pH electrode twice and determine the pH of the pH 4 buffer solution to check for drift in the meter calibration. If the meter calibration has changed, use the difference to help estimate the uncertainty in your results.

**Calculations and Report:**

Report the average pH and your estimated uncertainty. Calculate the Na⁺ concentration and uncertainty in your original sample (in the 25-mL volumetric flask diluted to the mark). Do the error analysis two different ways and compare the estimated uncertainties: first using significant figure rules and second using propagation of errors rules. Compare your uncertainty to the expected uncertainty that would be expected if you had used a titration to determine the H⁺ ion concentration.

**Part 2. Ion Exchange Preconcentration and Colorimetric Determination of Zn²⁺**

Many techniques lack the necessary detection limits to work well for environmental samples. One commonly used method to overcome these limitations is preconcentration. Sample evaporation is an obvious and commonly used technique, but evaporation is a slow process. Ion exchange is often used to preconcentrate ionic analytes. In this experiment we will use the colorimetric reagent Zincon to determine the Zn²⁺ concentration in a dilute unknown, Figure 1. Zincon in pH 9.2 sodium borate buffer can be used to determine Zn²⁺ from 0.01-3.0 mg/L, that is 0.01-3.0 ppm. However, this range is not sensitive enough for most natural surface water samples. In this exercise we will preconcentrate only by a factor of eight, to save time. However, greater concentration factors can easily be achieved. The Zn²⁺ ions will be eluted from the SPE cartridge using NaCl solutions of different concentrations.

![Zn²⁺-Zincon complex](image)

Figure 2: Zn²⁺-Zincon complex.
Other than improved detection limits, ion exchange preconcentration is also useful for separating the desired analyte from interfering species. For example, colored substances in lakes and streams can interfere with colorimetric tests. In this exercise, we will first elute the column with 0.01 M NaCl to wash off any interfering substance that is less weakly bound than Zn$^{2+}$. This dilute NaCl elution will help to wash off colored species (which are typically anionic tannins). Typical colorimetric reagents, including Zincon, are not completely specific for only one metal. Iron(III) also forms colored complexes with Zincon. By carefully choosing the NaCl concentration of the elution, ions that are more strongly held to the resin than Zn$^{2+}$ can be left on the column. Typically, ions with higher charge have a larger equilibrium constant for binding on the resin. In this experiment, we elute Zn$^{2+}$ from the column using 0.3 M NaCl to avoid washing off Fe$^{3+}$.

Rather than doing this experiment with an unknown, we will run this experiment as a method development lab. In this development effort you will determine the effect of the concentration of the NaCl elution solution and also determine how efficiently the total amount of Zn$^{2+}$ in the starting solution can be preconcentrated and determined. The efficiency of the overall process is often quoted as the percent recovery. That is, the percent recovery is the total number of moles of sample recovered after preconcentration divided by the initial sample moles multiplied by 100 to get a percentage.

**Procedure:**

**Equipment Required:**
- Fisher P457 PrepSep-SCX Solid Phase Extraction Cartridge
- 200-mL volumetric flask
- 2x 25-mL volumetric flasks
- 10-mL graduated cylinder
- 7x 10-mL volumetric flasks
- 7x plastic visible cuvettes
- blue litmus paper
- 1-mL auto-pipettor

**Solutions:**
- 200mL of 5.00x10^{-6} M ZnCl$_2$
- 10 mL of 0.01 M NaCl
- 10 mL of 0.3 M NaCl
- 35 mL of 1x10^{-4} M Zincon in 20 mM NaB$_4$O$_7$ pH 9.2 buffer
- 6 mL of 1.00x10^{-4} M ZnCl$_2$
- 10 mL of 20 mM NaB$_4$O$_7$ pH 9.2 buffer

**Sample Preconcentration:**
Place a plastic bottle in the white plastic filtration apparatus to collect the filtrate and assemble the filtration apparatus. If the blue valve handle is vertical, the valve is closed. If the blue valve handle is horizontal the valve is open and vacuum will be applied to the SPE cartridge. Rinse the SPE cartridge with 10 mL of 0.1 M HCl, and then three washes of 10 mL of water. Remove the top of the filtration apparatus and touch the stainless steel tip to a piece of litmus paper to check for sufficient rinsing. If the litmus paper turns red, wash with several more 10 mL portions of water.
Fill a 200-mL volumetric flask with 5.00x10^{-6} M ZnCl\textsubscript{2} solution to be used as your sample. Place your SPE cartridge into the rubber stopper on top of a glass side-arm filtration flask. Attach the flask to an aspirator and carefully allow all 200 mL of your sample to pass through your SPE cartridge. Rinse your 200-mL volumetric flask with a small (2-3 mL) portion of water from a wash bottle and pour this wash through the SPE cartridge. Repeat this rinsing step twice more. Rinse the inside of the SPE cartridge with a small additional rinse to ensure quantitative transfer. Move your SPE cartridge back onto the white plastic filtration apparatus.

Place a 25-mL volumetric flask inside the plastic filtration apparatus to collect the filtrate. Use 10 mL of 0.01 M NaCl to elute the SPE cartridge. A graduated cylinder is fine for the NaCl solution. Follow the NaCl solution with two small portions of water (2-3 mL) from your wash bottle to ensure quantitative transfer. Remember that the volumetric flask holds only 25 mL, so don't add too much wash water. Remove the 25-mL flask and dilute to the mark with 20 mM Na\textsubscript{4}B\textsubscript{4}O\textsubscript{7} pH 9.2 buffer.

Once again, place a 25-mL volumetric flask inside the plastic filtration apparatus. Use 10 mL of 0.3 M NaCl to elute the SPE cartridge. Follow the NaCl solution with two small portions of water (2-3 mL) from your wash bottle to ensure quantitative transfer. Remove the 25-mL flask and dilute to the mark with 20 mM Na\textsubscript{4}B\textsubscript{4}O\textsubscript{7} pH 9.2 buffer.

Colorimetric Analysis:
You will prepare 2.50x10^{-6}, 1.00x10^{-5}, 2.00x10^{-5}, and 3.00x10^{-5} M standard solutions of Zn\textsuperscript{2+} in 5x10^{-5} M Zincon in 20 mM Na\textsubscript{4}B\textsubscript{4}O\textsubscript{7} pH 9.2 buffer. You will then prepare your two filtrate fractions in a similar fashion for analysis at 626 nm. The analytical wavelength at 626 nm is chosen slightly higher in wavelength than the absorbance maximum to provide a larger difference with the spectrum of uncomplexed Zincon.

Standards: This procedure is designed for speed and makes some compromises that will decrease the precision of the analysis. For example, multiple cuvettes will be used instead of using the same cuvette for each measurement. However, the results should still meet the normally expected accuracy and precision of general spectrophotometric determinations of about 1-2%. For best accuracy, the absorbance in a colorimetric determination should be in the range of 0.2 to 0.8 (better monochromators extend this range to higher absorbances). Preconcentration is necessary in this experiment to bring the analyte signal into this range.

Use a large volume auto-pipettor or bottle-top pipettor to place 5.00 mL of 1x10^{-4} M Zincon in 20 mM Na\textsubscript{4}B\textsubscript{4}O\textsubscript{7} pH 9.2 buffer into each of seven 10-mL volumetric flasks. Dilute one to the mark with 20 mM pH 9.2 buffer to act as a blank (i.e. zero concentration sample). In the second, dilute to the mark with 5.00x10^{-6} M ZnCl\textsubscript{2} solution. For the next three, place 1.00, 2.00, and 3.00 mL of 1.00x10^{-4} M ZnCl\textsubscript{2} solution, respectively, using an auto-pipettor. Dilute to the mark with pH 9.2 buffer. For your samples, simply dilute to the mark in the two remaining volumetric flasks. Fill seven plastic cuvettes with your samples. Using the HP Diode array spectrophotometer scan the background with a cuvette filled with water and then determine the absorbances at 626 nm and 650 nm (as the background). Subtract the background absorbance at 650 nm from the absorbance at 626 nm to help correct for differences in cuvettes. Plot out the spectrum of the blank and the highest concentration standard.

Calculations and Report:
Plot the calibration curve and determine the slope and intercept using the "linest" Excel spreadsheet function. In addition, using "linest" you will be able to determine the uncertainty of
the slope and the intercept. From the slope and intercept calculate the concentration of Zn$^{2+}$ in your samples. Use the uncertainty in the slope and intercept to calculate the uncertainty in your results. In experiments of this type, the final results are often reported as percent recovery. Report the percent recovery. In your report, use your printed spectra to discuss why 626 nm was chosen for the analytical wavelength.

**Follow-up: Applications of Ion Exchange Resins**

Ion exchange resins are generally useful tools in analysis and synthesis laboratories. Ion chromatography allows the separation and determination of cations and anions with great efficiency and sensitivity. For example, rain, snow or tap water can easily be analyzed for parts-per-million (ppm) levels of nitrate and sulfate. Ion exchange chromatography is also widely used for protein and oligonucleotide separations.

SPE sample preparation is also common in biochemistry. One example is for cation replacement for sample preparation for mass spectrometry. In this use, Na$^+$ and K$^+$ ions are replaced by NH$_4^+$ using an SPE cartridge or Zip tip. Replacing the Na$^+$ and K$^+$ ions simplifies the mass spectra and increases the sensitivity.

Ion exchange resins are also used in synthesis. For example, a synthetic procedure may yield an ionic product with a Cl$^-$ counter ion. Bulkier counter ions are often desired for the formation of crystals for X-ray diffraction. Ion replacement by BF$_4^-$ or other bulky anions can sometimes make crystals easier to form.

Substances other than the synthetic polymers used in this lab have ion exchange properties. Many clays have large ion exchange capacities. Clays are an important component of soils, which gives the typical soil an ion exchange capacity. The characterization of soils is an important branch of agricultural and environmental chemistry. Zeolites, both natural and synthetic, can also act like ion exchange resins. Synthetic zeolites are often added to laundry detergents to help avoid scum formation in hard water. These zeolites exchange Na$^+$ for the Ca$^{2+}$ and Mg$^{2+}$ ions that are responsible for water hardness.

**Literature Cited.**