**Determination of the Equivalent Weight of an Inorganic Salt by Cation Exchange**

**Introduction:**

Many common chemical species such as the alkali metal cations and the halide anions are difficult to measure in macro amounts since they do not readily form insoluble compounds or colored complexes which would aid in their analysis. In addition, some metal ions may occur in solution as a stable complex species such as the case of Fe(CN)$_6^{3-}$, CoCl$_4^{2-}$ or in different oxidation states such as UO$_2^{2+}$ or U$^{4+}$. Common techniques for metal analysis such as atomic emission or atomic absorption spectroscopy analyze for the total metal present, but cannot distinguish between the complex species or various oxidation states. Ion exchange may be used to concentrate and separate solution species based on their charges or it may be used to quantitatively determine the concentration of a solution species based on the stoichiometry of a charged species displaced from the solid phase when the analyte binds to the ion exchanger.

An important method of analysis for alkali metal cations and for determining the distribution of complex species is a technique called ion-exchange chromatography. Ion-exchange involves the interaction of a solid, insoluble phase that contains positively or negatively charged sites with a mobile phase (eluent solution) that contains the counterion. The ion-exchange equilibrium can be written as

\[
\begin{align*}
B^+(aq) + A^+\text{(Res)} & \rightleftharpoons A^+(aq) + B^\text{Res}(s) & \text{Cation exchange} \\
X^-(aq) + \text{Res}^Y(s) & \rightleftharpoons Y^-(aq) + \text{Res}^X(s) & \text{Anion exchange}
\end{align*}
\]

where Res$^-$ and Res$^+$ represent a solid, porous, polymer phase with specific binding sites. These polymer phases may be inorganic such as zirconium phosphates or aluminosilicates (clays) or, more commonly, an organic polymer that has been cross-linked and reacted to form the active ion-exchange sites.

One of the more common ion-exchange resins is a copolymer of styrene and 4-12% divinylbenzene which has been sulfonated to produce a strong-acid cation exchanger or aminated to give a strong-base anion exchanger. The cation exchanger typically has 1.1 sulfonate groups per benzene ring while the anion exchanger has approximately 1 amine group for every two benzene rings. Typical structures are illustrated below.

- Cation exchange: $B^+(aq) + A^+\text{(Res)} \rightleftharpoons A^+(aq) + B^\text{Res}(s)$
- Anion exchange: $X^-(aq) + \text{Res}^Y(s) \rightleftharpoons Y^-(aq) + \text{Res}^X(s)$

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If a salt solution is passed through a cation exchange column which is in the hydrogen form, a quantitative reaction occurs:

\[ M^{n+} + nX^- + nH^+Res^- \rightleftharpoons M^{n+}(Res^-)_n + nH^+ + nX^- \]

The H\(^+\) liberated by the reaction can be titrated with a standard base to determine the amount of M\(^+\) in the sample taken for analysis. Note that a salt containing M\(^{+2}\) would give 2 H\(^+\) in the reaction. This procedure offers an excellent method for determining total cation charge in complex mixtures, preparing standard solutions of salts that cannot be prepared gravimetrically due to hygroscopic behavior (such as most nitrate salts), or allowing the quantitative analysis of a single cation in a relatively pure salt. It should also be noted that the technique will not give quantitative results if the charged species is involved in a significant acid-base equilibrium, K\(_a\) < 10\(^{-5}\), or is involved in a gaseous equilibrium such as CO\(_3^{2-}\), HCO\(_3^-\), HSO\(_3^-\), etc., or if the complex species is quite labile.

In this experiment, since the charge on the metal ion is unknown, the determination of the grams of unknown equivalent to one mole of H\(^+\) is called equivalent weight. For a +1 ion, the equivalent weight and the molar mass are identical. For a +2 or +3 ion, the equivalent weights are one half and one third of the molar masses, respectively.

**Before you come to class:**

- List all of the reagents (formulas and names) in your notebook. Also include the NFPA ratings for any compounds with a non-zero rating. Familiarity with the reagents will help you avoid costly mistakes during the experiment.

**Reagents:**

- 6 M HCl
- 0.1 M NaOH
- phenolphthalein
- blue litmus paper
- Dowex 50-X8, 20-50 mesh cation exchange resin

**Waste Disposal:** All solutions in today’s lab can be disposed of down the sink with running water.

**Experimental Procedure:**

Transfer your unknown to a weighing bottle.

Use the 0.1M NaOH solution that you standardized from the earlier weak acid titration lab. Otherwise, you will need to standardize a fresh solution of 0.1M NaOH against KHP.

**Column Preparation:**

The resin level should be above 7 in the column. If you need new resin, add some water to your column, shake, and pour the resin-slurry into a beaker. When your column is empty, clamp your ion-exchange columns to a column support and place waste beakers underneath the columns. Add some distilled water with the column cap on. Make a slurry of the new resin in distilled water and pour into the column until the resin settles into a layer that just reaches the neck bottom of the top reservoir. Make sure there are no air bubbles visible in the column. Take off the cap to help drain the column.

Clamp your ion-exchange columns to a buret support and place waste beakers underneath the columns. Try to keep solution over the resin at all times to prevent "channeling" in the column, a
process that creates paths for the solution to pass through the column without equilibrating with the resin phase.

**Preparation of the Unknown Salt Solution:**

You will be given an unknown salt solution and its approximate equivalent weight. Weigh out enough sample to be dissolved in a 100.0 mL volumetric flask so that a 10.00 mL aliquot (a 1/10 portion of the total sample) contains approximately 3.5 milliequivalents (meq) of salt so that approximately 35 mL of 0.1 M NaOH would be required for titration of each aliquot.

**The Ion Exchange Process:**

The cation exchange resin is converted to the $\text{H}^+\text{Res}^-$ form by washing with 3 M HCl. Prepare the 3 M HCl solution by adding 50 mL of concentrated 6 M HCl to 50 mL of distilled water in a beaker. For maximum efficiency, run several columns at once.

1. Fill the column with the 3 M HCl solution and allow the solution to drain until just before the resin bed is uncovered. Discard the 3 M HCl as soon as possible into the container in the hood. HCl fumes can interfere with the titration. You might also want to discard the first column rinse to minimize HCl fumes. Quickly fill the column with distilled water and allow this to drain. Try not to let the water level fall below the top of the resin bed once it has been converted to the $\text{H}^+\text{Res}^-$ form.
2. Add two more column volumes of distilled water before checking the eluent with litmus paper.
3. Continue washing the column with distilled water until the litmus shows no further positive test for $\text{H}^+$.
4. Make sure that the drip rate from the column is slow enough to ensure equilibration. A rapid drip rate will not allow quantitative displacement of $\text{H}^+$ by the $\text{M}^{n+}$ ion.
5. Place a 250 mL Erlenmeyer flask under the column and slowly pipet your 10 mL aliquot into the column.
6. Wash with approximately the same amount of distilled water it took to remove the excess $\text{H}^+$ originally.
7. Check for no further $\text{H}^+$ release with litmus paper.
8. After passing the sample through the column, add phenolphthalein to the eluent and titrate with the 0.1 M NaOH to the first appearance of pink. Use this data to determine the amount of HCl liberated in the ion-exchange process. Note that this will also be the moles of positive charge contained in 1/10 sample weight. From this data, calculate your equivalent weight.

If your equivalent weight is not within 10 g/mole of the value given to you by the instructor consider the following sources of error. Assuming that the correct size sample was weighed out and the 10 mL aliquot was applied to the column, if your equivalent weight is too large, then the volume of titrant used was too small. This can occur if the sample aliquot does not adequately equilibrate in the column. If your equivalent weight is too small, then too many mL of titrant were used. The most likely source of this error is contamination of the sample by HCl fumes or glassware that was in contact with the 3 M HCl. If either of these errors occur, run two more samples using precautions to prevent a repetition of the error.

Another problem encountered in quantitative ion-exchange is ensuring that your sample does not exceed the exchange capacity of your column. This can be quickly checked by pipetting a 5 mL aliquot sample on your column and following the procedure outlined above. This sample should require exactly one-half the mL of NaOH that the 10 mL samples take. If this is not observed, see the instructor.

- **Report the equivalent weight of your unknown.** The range on unknown values should be between ±10 gm/mole from the estimate given by the instructor.