

Day and Underwood Handout

Ion-Exchange Separation and Spectrophotometric Determination of Nickel and Cobalt

The ion-exchange method of separation is discussed in sections 23-2 and 26-1 of Quantitative Chemical Analysis 10th ed. D.C. Harris and there is a short discussion below. The present experiment illustrates this method by the separation of nickel and cobalt with a strong-base anion exchanger. In solutions containing a large concentration of hydrochloric acid, many metals are converted into complex anions (chlorides) and are adsorbed by an anion resin. Other metals that are not readily converted into complex anions are not adsorbed by such a resin. Cobalt forms the deep blue complex, CoCl_4^{2-} , and this is strongly adsorbed by 9 M hydrochloric acid. Nickel is not adsorbed from such a solution, and a separation of nickel from cobalt is easily effected. The cobalt is readily removed by washing the resin with hydrochloric acid less concentrated than about 4 M.

The two metals can be determined by standard spectrophotometric procedures. Nickel is oxidized with bromine in ammoniacal solution and then treated with dimethylglyoxime. A wine-red or brown complex is formed, the identity of which has not been established. Cobalt is determined by conversion of the metal to the blue complex cobalt thiocyanate, $\text{Co}(\text{CNS})_4^{2-}$. An acetone (or ethanol) solution is used because the complex is somewhat dissociated in water unless a large excess of thiocyanate is added. Both procedures are based on those given by Sandell in *Colorimetric Determination of Traces of Metals* (Interscience Publishers, Inc., 1959).

Procedure

A. Prepare Solutions: (will be prepared and available for use on the day of the lab.)

Standard nickel solution. Prepared by dissolving 0.405 g of uneffloresced crystals of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of 0.1 M hydrochloric acid. Then 10-mL of this solution is diluted in another 100-mL volumetric with 0.1 M hydrochloric acid. The standard solution contains 0.100 mg/mL of nickel.

Standard cobalt solution. Prepared by dissolving 0.404 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of 0.1 M hydrochloric acid in a volumetric flask. This solution contains 1.00 mg/mL of cobalt. *Ammonium thiocyanate.* Prepared by dissolving 50 g of the salt in 100 mL of aqueous solution.

Dimethylglyoxime. Prepared by dissolving 2 g of the solid in 200 mL of ethyl alcohol.

B. Acquire a chromatography column from the stockroom. Rinse the column with deionized water and drain. Place about 1 g of a strong-base anion in a 50 mL beaker and add about 10 mL of deionized water. Stir the resin to form a slurry and then add the slurry to the column. Allow the resin to settle and the water to flow through the column and then add more slurry until the entire 1 g is added to the column. Be sure that there are no air pockets in the column*. Now add the small portions of 9 M hydrochloric acid to the resin and allow this to flow over the resin until 4 to 5 mL of the acid has been used. The resin will shrink somewhat and darken slightly on treatment with the concentrated acid. Make two small marks, 1 cm apart, on the side of the column using a marker above the resin and adjust the screw clamp until the time required for the solution to flow this distance is 1 to 2 min.

*Be sure that you DO NOT allow your column to ever go dry. Make sure there is a small amount of liquid above the top of the slurry at all times.

C. Secure from the stockroom an unknown sample of a solution containing nickel and cobalt in 9 M hydrochloric acid. The instructor will have available 250 microliter pipettors for you to use to dispense 0.20 mL of the solution to the resin column. Place the tip into the column as close to the resin bed as possible and add the solution as slowly as possible to the column. Place a clean 250 mL volumetric flask below the column to receive the solution. Allow the solution to seep into the resin and note the blue band (cobalt) at the top of the column. Then add slowly, about 1 mL at a time, 4 mL of 9 M hydrochloric acid, allowing each portion to settle into the resin before addition of the next portion. Note that the cobalt band spreads somewhat during the washing, but does not come off the column. Near the end of the last wash, catch a drop of the solution on a spot plate (or in a small beaker), add a drop of concentrated ammonia, and then add a drop of dimethylglyoxime. No red color should be formed, showing that the nickel has been completely removed.

Set aside the flask containing the nickel and replace it with a 50 mL volumetric flask to receive the cobalt. Add to the column about 4 to 5 mL of 1 M hydrochloric acid in successive 1 mL portions. Note that the cobalt band quickly begins to move down the column and observe the color of the drops as the cobalt is removed. (Why is the color first blue, then pink?)

D. Into five 50 mL volumetric flasks pipet 0.5, 1.0, 1.5, 2.0 and 2.5 mL portions of the standard nickel solution. Use a sixth flask for the blank. Add to each flask 17.5 mL of 95% ethanol, and 10 mL of the dimethylglyoxime solution. In the hood, add 0.5 mL of saturated bromine water and 2 mL of concentrated ammonia to each flask. Dilute to the 50 mL mark with water and measure the absorbance of each solution, using the blank as a reference. (Do not wait longer than ½ hour before making the measurements.) A wavelength of 450 nm is employed with a spectrophotometer. To the volumetric flask containing the nickel unknown add 2.5 mL of bromine water, 14 mL of concentrated ammonia, 88 mL of 95% ethanol and 50 mL of dimethylglyoxime solution. Dilute to the mark with water and measure the absorbance.

E. Into five 50 mL volumetric flasks pipet 0.5, 1.0, 1.5, 2.0 and 2.5 mL portion of the standard cobalt solution. Use a sixth flask for the blank. Add to each flask 5 mL of ammonium thiocyanate solution and 25 mL of 95% ethanol. Dilute each solution to the 50 mL mark and measure the absorbance at 625 nm with a spectrophotometer. To the volumetric flask containing the cobalt unknown, add concentrated stock aqueous ammonia until the solution is only slightly acidic by pH paper** and then add 5 mL of ammonium thiocyanate and 25 mL of 95% ethanol. Dilute the solution to the mark with water and measure the absorbance.

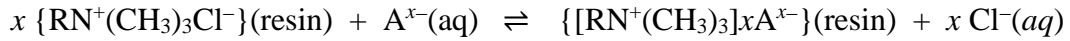
F. Plot absorbance vs. concentration for both the nickel and cobalt standard solutions. From the absorbances of each unknown solution calculate the concentrations in mg/mL of each metal.

** DO NOT dip the pH paper into the solution in the volumetric flask to test its acidity. Use a glass stirring rod to place a drop of the solution to be tested onto the pH paper.

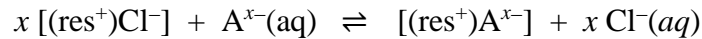
If the experiment is to be done in two lab periods the first day should include all steps through part D. On the second lab period one will then start with part E.

Ion Exchange Equilibria

Ion exchange equilibria can be treated by the law of mass action. In general for a basic ion exchange resin in equilibrium with an aqueous ion, A^{x-} , we can write: (see Fig. 26-1 and Table 26-1 for properties of typical ion-exchange resins)



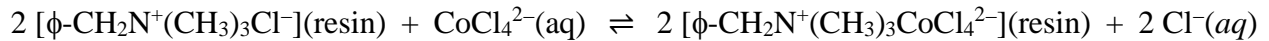
or in a more compact notation:



for which

$$K = \frac{[(res^+)^x A^{x-}][Cl^-(aq)]^x}{[(res^+)Cl^-]^x [A^{x-}(aq)]}$$

For example, when a dilute solution of $CoCl_4^{2-}$ ions is brought into contact with a strongly basic ion exchange resin (Dowex 1) $[\phi-CH_2N^+(CH_3)_3Cl^-]$, the following equilibrium develops:



The equilibrium constant (K) for this reaction is a very large number at low pH and $CoCl_4^{2-}$ is retained on the resin.

If a positive ion (such as Ni^{2+}) does not form a complex ion with chloride (to a great extent), then K (above) for the positive ion will be very small.

If a mixture of nickel and cobalt ions is treated with concentrated HCl, the cobalt complex ions will be retained on the ion exchange resin, while the nickel ions will not be retained on the ion exchange resin.