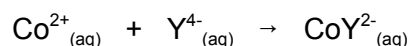


# Determination of Cobalt by Titration with EDTA

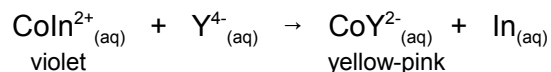
## I. Introduction

The quantitative determination of many metal ions in solution can be achieved by titrating with a standard solution of a Lewis base (ligand). A necessary requirement is that the ligand combines (complexes) quantitatively with a particular metal ion under the solution conditions. The most common ligand is the anion of ethylenediaminetetraacetic acid (EDTA,  $H_4Y$ ). The titrant is usually prepared by dissolving the disodium salt of this acid,  $Na_2H_2Y$ , since the acid is only slightly soluble in water.

The reaction of cobalt ion with fully ionized EDTA ( $Y^{4-}$ ) can be represented by the equation:



The end point of the titration can be obtained by observing the color change of a suitable indicator. In complexometric titrations, the indicator (In) must also act as a ligand toward the metal ion to be determined. The end point occurs as the color of the indicator changes from its complexed form ( $CoIn^{2+}$ ) to its uncomplexed form (In) when the EDTA titrant combines with the last bit of metal ion in solution. In this experiment, this can be represented by the equation:



Of course, for the above to work, EDTA must complex with the metal somewhat more strongly than the indicator ligand.

## II. Procedure

### A. Titrant Preparation

A solution of approximately 0.01M EDTA is prepared by dissolving 1.9 g of reagent grade ethylenediaminetetraacetic acid, disodium salt in 500 mL deionized water. (The disodium salt dissolves in water, but not easily, so add 250 mL of water to the salt and stir using a magnetic stirrer, then dilute to 500 mL and mix thoroughly.)

Store the solution in a plastic bottle (NOT GLASS). This solution will be standardized by titration against a standard cobalt solution (see below).

## B. Column Preparation

Each ion exchange column is constructed from a glass tube (about 1.5 cm x 15 cm) fitted with a stopcock at the bottom. Half-fill each column with deionized water and place a small amount of glass wool (about the size of a large pea) at the bottom of each column. (Do not force the glass wool into the narrow region just above the stopcock.) Remove any trapped air in the glass wool by using a glass stirring rod. Make a deionized water slurry of a few grams of DOWEX 1-X8, 200 mesh anion exchange resin and pour the slurry down a stirring rod into each column, with the stopcock partially open, until the resin height is about 8-9 cm. Make sure that the resin is not leaking through the glass wool. Drain the water level to the top of the resin beads, but do not allow the liquid level to drop below the top of the resin because air pockets will form in the column. Elute the resin with 40 mL of 4 M HCl. Make sure the tip of the column rests against the inner wall of the collection container. This minimizes HCl aerosol formation and splattering. Discard the eluate. For storage between lab periods, the tops of these columns should be stoppered and sealed with plastic wrap and the stopcocks turned off firmly.

## C. Metal Ion Separation by Ion-Exchange Chromatography

1. The unknown solution contains  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  ion salts in HCl. Add one or two mL of 4 M HCl to each column. Drain the 4 M HCl to the resin level until the meniscus just disappears completely into the resin. Stop the flow.
2. Carefully pipet 2.00 mL of unknown solution onto the resin. Place a beaker under the column with THE COLUMN TIP TOUCHING THE SIDE OF THE BEAKER and fix the unknown sample onto the column by allowing the solution in the column to drain until the meniscus disappears into the top of the resin. Add two, 2-mL aliquots of 4 M HCl to the column, allowing each to drain into the resin phase. After the sample has thus been washed into the resin phase, elute the  $\text{Co}^{2+}$  from the column into a 250-mL beaker using 30 mL of 4 M HCl. When complete, stop the flow and **save this solution** for analysis (see below).
3. Elute the  $\text{Fe}^{3+}$  from the column using about 45 mL of 0.5 M HCl into a clean 100-mL volumetric flask. When complete, stop the flow and **save this solution** for analysis (see Section F below).
4. Re-establish each column by eluting with 40 mL of 4 M HCl. The columns are now ready for another sample separation (II.C.2.). **Four cobalt unknown samples** should be separated for analysis as described below.
5. After you have obtained four (4) cobalt and four (4) iron samples, elute your columns with 50 mL of deionized water. Transfer the resin to a 250-mL beaker, **remove the glass wool** and rinse the resin into the large collection jar provided.
6. Evaporate each of the eluted  $\text{Co}^{2+}$  solutions on the hot plates in the hoods to about 2 mL. Avoid heating to dryness.

7. Add 60 mL of deionized water to each of the evaporated  $\text{Co}^{2+}$  samples **before removal from the hood**.

#### D. EDTA Standardization

1. Pipet a 10.00-mL aliquot of the standard  $\text{Co}^{2+}$  into four labeled 250-mL beakers, add 50 mL of deionized water to each of the standard  $\text{Co}^{2+}$  samples and process one sample at a time as described below.
2. Add 10 mL of 4 M sodium acetate and, using a pH meter, adjust the pH to 5.8 with 3M sodium hydroxide. Make sure that the pH meter is calibrated by checking it with pH 7.00 and 4.00 buffer solutions. **Be sure to rinse off the electrode with deionized water when it is removed from the solution to avoid loss of  $\text{Co}^{2+}$ .**
3. Set up a hot plate/stirrer to support your titration solution while titrating and prepare your buret with EDTA solution. Heat the  $\text{Co}^{2+}$  standard solution to approximately  $95^\circ\text{C}$  (DO NOT BOIL!).
4. Adjust the hot plate to maintain the solution temperature in the range of  $85\text{--}95^\circ\text{C}$ . Add 5 drops of xylenol orange indicator (0.2 g/100 mL, 50% alcohol) and a stirring bar to the solution, and titrate **immediately** with EDTA solution. The end point is a sudden color change from violet to yellow-pink, and is rapid only at elevated temperatures.
5. Calculate the molarity of your EDTA titrant using the exact molarity of the  $\text{Co}^{2+}$  standard solution given by the instructor.

#### E. Titration of Unknown Cobalt Solutions

1. Add 10 mL of 4 M sodium acetate to each unknown  $\text{Co}^{2+}$  solution and, using a pH meter, adjust the pH to 5.8 with 3 M sodium hydroxide.
2. Heat the solution to approximately  $95^\circ\text{C}$  using the hot plate/stirrer (DO NOT BOIL!).
3. Add 5 drops of xylenol orange indicator (0.2 g/100 mL, 50% alcohol) and a stirring bar to the solution, and titrate **immediately** with EDTA solution. Maintain the solution temperature in the range of  $85\text{--}95^\circ\text{C}$ . The endpoint is a sudden color change from violet to yellow-pink.

## F. Analysis of Unknown Iron Solutions

You are asked to develop a written, detailed step-by-step procedure for analyzing the solutions that contain iron. You may use either of the two spectrophotometric methods (visible spectrophotometry of  $\text{Fe}(\text{phen})_3^{2+}$  or atomic absorption spectrometry) previously used in this lab. This procedure must be approved by your instructor before you begin analysis of your unknown iron solutions. Please take note of the following as you develop your procedure.

1. After elution from the ion-exchange column, dilute the  $\text{Fe}^{3+}$  solutions to the mark with deionized water.
2. The  $[\text{Fe}^{3+}]$  in the original unknown solution is in the range 0.05 - 0.1 M. Remember to allow for the actual volume delivered by your 2-mL pipet.
3. If you choose to measure the absorbance of  $\text{Fe}(\text{phen})_3^{2+}$  in solution, ensure that an excess of hydroxylamine hydrochloride is added to convert all of the  $\text{Fe}(\text{III})$  to  $\text{Fe}(\text{II})$  before adding the phenanthroline.
4. If you choose to use atomic absorption spectrometry, dilute the unknown and standard solutions to a concentration in the range 0.1 to 3  $\mu\text{g}/\text{mL}$  and measure the absorbance at 248.3 nm.
5. Report the mean  $\text{Fe}^{3+}$  molarity in the original unknown solution and its RMD.

## III. Calculations

Calculate the  $\text{Co}^{2+}$  molarity of your unknown solution for each of the titrations. Remember to allow for the actual volume delivered by your 2-mL pipet.

## IV. Results

Report the mean  $\text{Co}^{2+}$  molarity in the original unknown solution and its RMD.