

EXPERIMENT 3

Complexometric Titration of Zn(II) with EDTA

UNKNOWN

Submit a clean, labeled 250-mL volumetric flask to the instructor so that your unknown zinc solution may be issued. Your name, section number, and your locker number should be written legibly on this flask. The flask does not need to be dry on the inside, but needs to have been rinsed with *deionized water* after it has been washed. Note that *the flask must be turned in at least 1 lab period before you plan to do the experiment* so that the Teaching Assistants will have time to prepare the unknown.

*****USE ONLY *DEIONIZED WATER* (NOT DISTILLED WATER!) THROUGHOUT THE ENTIRE EXPERIMENT*****

BACKGROUND

This experiment is an example of a classic *titrimetric analysis*. *Classical* methods of analysis such as titrimetric and gravimetric analyses are usually capable of very high precision and accuracy - typically on the order of $\pm 0.1\%$ or even better if done properly. However, there is always a tradeoff. Usually classical methods are slower and much less sensitive than modern *instrumental* methods of analysis such as atomic absorption spectroscopy, gas and liquid chromatography, and mass spectrometry.

In a titration, an accurately known mass of sample is dissolved in an aqueous solution, often with some sort of chemical treatment such as acid-digestion of solid samples, and diluted with high purity water to an accurately known volume. Then, an accurately known volume of the sample solution, called an *aliquot*, is pipetted into a titration vessel and the analyte of interest is carefully titrated with a standardized solution of an appropriate *titrant* to the *endpoint* or *equivalence point* of the titration. To do this, you need to know when you reach the endpoint. This is often accomplished by means of an *indicator* that undergoes a color change at the endpoint.

From the volume and molarity of the titrant, one can then calculate the number of mols of titrant used. From the known stoichiometry of the reaction between the titrant and the analyte, one can calculate the mols of the analyte and therefore the mass and/or molarity of the analyte. With appropriate calculations, one can then determine the concentration and/or total mass of the analyte in the original sample to complete the analysis.

This titration is known as a *complexometric* or *chelometric* titration because the titrant, a *ligand*, reacts with the analyte, a metal ion, to form a *complex*, more specifically a chelate in this case. A *chelate* is a ligand that has two or more sites that bind to the central ion.

EDTA [ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$, $(HOOCCH_2)_2N-CH_2CH_2-N(CH_2COOH)_2$, MM = 292.24 g/mol, often symbolized by H_4Y] is an excellent chelating agent. It forms very strong 1:1 complexes with almost every divalent and trivalent metal ion depending on solution conditions. Ignoring charges for the moment,



Although it is an equilibrium, the reaction lies very far to the right. The equilibrium formation constants, K_f , are on the order of $10^8 - 10^{25}$ depending on the metal and other conditions.

EDTA itself is a tetraprotic acid; it has 4 ionizable protons with pK_a 's = 1.99, 2.67, 6.16, 10.26. In its fully ionized form, Y^{4-} , the four acetate groups and the lone pairs on the two nitrogens make it a *hexidentate* ligand that wraps itself very tightly around a metal ion. Usually, titrations are performed in basic solution, roughly pH 8-11.

The fully protonated form, H_4Y , is only sparingly soluble in water, so the standard form of EDTA used analytically is usually the disodium salt $Na_2H_2Y \cdot 2H_2O$ (372.24 g/mol), which is much more soluble and available in primary standard purity, except for a small (about 0.3%) amount of adsorbed water.

PROCEDURE

Preparation of Solutions

EDTA, 0.01 M

This solution must be prepared at least one day ahead of time, a week is preferable, to ensure that the solute is completely dissolved. EDTA solutions are prepared at an approximate molarity, and then standardized against a solution of a primary standard such as $CaCO_3$.

1. Dissolve about 3.8 g of the dihydrate of the disodium salt ($Na_2H_2Y \cdot 2H_2O$) and 0.1 g $MgCl_2$ in approximately 1 L of *deionized* water in a large beaker or a 1-L plastic bottle using a magnetic stirrer. A small amount of sodium hydroxide can be added if there is any difficulty in dissolving the EDTA. Try not to exceed 3.8 g of the disodium salt because much more than this dissolves only with difficulty.
2. Before use, the EDTA solution should be filtered using a Buchner funnel and suction filtration. See a teaching assistant for the apparatus. [NOTE: Break the suction *before* you turn off the water flow on the vacuum aspirator.]
3. Store the solution in a clean, labeled 1-L plastic bottle that has been rinsed with deionized water. *Never store reagent solutions in volumetric flasks.*

Ammonia/Ammonium Chloride Buffer Stock Solution, pH 10.

Each titration will require the addition of pH 10 ammonia buffer. The stock buffer solution has been prepared for you, and you should not have to prepare it. The appropriate quantity (7-8 mL) is dispensed directly into your titration flask from the plastic Repipet® repetitive dispenser located in Hood #7. **The buffer should only be added immediately before you titrate an individual sample.** Recipe:

1. Dissolve 64.0 g of ammonium chloride in 600 mL of concentrated ammonia (14.8 M, 28% NH₃).
2. Slowly and carefully add 400 mL deionized water with stirring. This should be sufficient for over 120 titrations.

Calcium Standard Solution.

A CaCO₃ solution is prepared as a primary standard for Ca and used to standardize the 0.01 M EDTA titrant you prepared.

1. Tap out approximately 1 g of predried analytical-reagent-grade CaCO₃ in a weighboat. *Accurately weigh (to within ± 0.1 mg) approximately a 0.25-g sample by difference* into a 150- or 250-mL beaker. **NOTE: NEVER transfer chemicals inside an analytical balance.**
2. Add about 25 mL deionized water and then slowly add concentrated HCl **dropwise** with periodic stirring until the sample dissolves completely. Then add 2 drops more. *Keep the beaker covered during the entire dissolution process.* Mild heating will speed the dissolution. **Do NOT boil; this will spatter the calcium solution and lead to losses.**
3. Transfer the solution quantitatively into a 250-mL volumetric flask. Rinse the beaker thoroughly with deionized water, and carefully dilute to the mark with an eye dropper or with careful use of your wash bottle. Mix thoroughly.

Because this Ca²⁺ standard solution is used to standardize the EDTA titrant, it must be prepared very carefully so that you know its *exact* molarity. Therefore, an exactly known (to ± 0.1 mg) mass of CaCO₃ must be weighed out, dissolved completely, and transferred quantitatively into the 250-mL volumetric flask. ***This is critical.***

Standardization of the EDTA Solution

1. Attach your 50-mL burette to a ringstand, preferably using one with a white ceramic base, and a burette clamp. If the only ringstands available have black bases, cover the base with a completely white sheet of paper before you titrate a sample.
2. Open the burette valve and drain it completely into a "waste" beaker. Squirt down the insides with deionized water a couple of times. ***If any water droplets remain attached to the inside of the burette, you must thoroughly wash the burette with soap and a burette brush to remove them.*** If you leave "reagent spots" in the burette while titrating,