

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

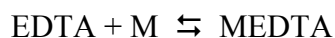
This experiment is an example of a classic *titrimetric analysis*. *Classical* methods of analysis such as titrimetric and gravimetric analyses are usually capable of very high precision and accuracy – typically on the order of $\pm 0.1\%$ or even better if done properly. However, there is always a tradeoff. 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 $Na_2H_4Y \cdot 2H_2O$ (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. Obtain approximately 1 g of predried analytical-reagent-grade CaCO₃. *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,

the titration volume will be in error. Squirt down the insides of the burette a couple of times with a mL or two of the EDTA solution with a medicine dropper to rinse any remaining deionized water out of the burette.

3. Now close the burette valve and over-fill the burette with your standard EDTA solution. Check to see if any air bubbles are trapped in the tip of the burette. If so, open and close the valve quickly as though you were “squirting” reagent from the burette into the waste beaker until the bubbles have cleared from the tip. Carefully bring the reagent level to somewhere between the 0- and 1-mL marks. **Do not try to bring the level exactly to the 0.00-mL mark.** This is a waste of time. Rinse the burette tip off with a squirt of deionized water, let it drain, and then touch the tip to the side of the waste beaker to remove excess water.
4. Pipet 25.00-mL aliquots of your standard Ca^{2+} solution into each of three or four 250-mL Erlenmeyer flasks. Each aliquot will thus contain one-tenth of the total CaCO_3 that was weighed out to prepare the standard solution.
5. *Take each sample to completion before starting the next sample.* Read the initial volume on the burette at least twice. Add 7-8 mL of pH 10 buffer from the Repipet® dispenser, 15 mL of deionized water, and **3 drops** of Eriochrome Black T indicator, **immediately prior** to titrating a sample. The solution should be a pale pink. Do **not** add more indicator to make the solution darker as this can cause problems with the endpoint. Titrate the solution immediately with EDTA against a white background until the LIGHT PINK solution turns a LIGHT SKY BLUE. Read the final volume at least twice.

Titration must be performed swiftly (but carefully) because the NH_3 will evaporate to some degree and thus the pH of the solution will change. In general, the faster the titration is performed the better the results will be, as long as the endpoint is not overshot due to excessive haste.

It is advantageous to perform a trial titration to locate the approximate endpoint and to observe the color change. In succeeding titrations, titrate very rapidly to within about 1 or 2 mL of the endpoint, and then titrate very carefully, a drop or half-drop at a time, to the endpoint. Near the endpoint, periodically squirt the sides of the flask and the burette tip and swirl the flask to ensure all the titrant has gotten into the solution in the flask.

The endpoint color change is rather subtle, and sometimes it is slow, so you need to be careful at the end. If you are having trouble with the endpoint color change, see Note 1 at the end of the report for the preparation of “before” and “after” flasks.

Calculate the molarity of the EDTA solution from the volume of EDTA used in the titration of each aliquot. The values (M_{EDTA} and titration volumes) should all agree very closely, to within about $\pm 0.2\%$ relative standard deviation. If not, titrate additional aliquots until better agreement is reached.

Outlying values can always be rejected *for cause* or **one** outlying value by using the Q -test.

Analysis of the Zinc Unknown

1. Carefully dilute your unknown sample in the 250-mL volumetric flask to the mark with deionized water. Mix thoroughly.
2. Pipet 25.00-mL aliquots into each of three or four 250-mL erlenmeyer flasks. Add 15 mL of deionized water, 9-10 mL of pH 10 buffer, and 3 drops of Eriochrome Black T immediately prior to titrating a sample.
3. Titrate with standardized EDTA until the pink solution turns light blue.

Calculate the milligrams of zinc in the *total* sample. Remember that each aliquot represents one-tenth of the total sample volume – a 25-mL aliquot titrated out of 250 mL total volume.

CALCULATIONS

The molarity of the Ca^{2+} standard solution (M_{Ca}) is calculated in normal fashion using the molar mass of calcium carbonate (MM CaCO_3) weighed out and the total volume in liters of the standard solution prepared.

$$M_{\text{Ca}} = \text{mol Ca} / \text{L solution} = (m_{\text{Ca}} / \text{MM CaCO}_3) / \text{L solution}$$

Calculate the molarity of the EDTA from the volume of EDTA used in the titration of each aliquot of the Ca^{2+} standard solution and the known 1:1 stoichiometry between Ca and EDTA in the reaction. If the reaction has 1:1 stoichiometry, then

$$\text{mmol}_{\text{EDTA}} = \text{mmol}_{\text{Ca}}$$

The mmol of each constituent is obtained by multiplying the molarity of each of the two solutions times the volume in mL of each solution used to reach the endpoint, ep:

$$M_{\text{EDTA}} \times V_{\text{EDTA}} = M_{\text{Ca}} \times V_{\text{Ca}}$$

The volume of the Ca standard solution originally taken was 25.00 mL and the volume of EDTA used is the volume used to reach the endpoint, $V_{\text{ep}} = V_{\text{EDTA}}$, in mL. Therefore,

$$M_{\text{EDTA}} = (M_{\text{Ca}} \times V_{\text{Ca}}) / V_{\text{EDTA}} = 25.00 \times M_{\text{Ca}} / V_{\text{EDTA}}$$

The mmol of zinc determined in an individual titration uses the same 1:1 reaction stoichiometry as for calcium above. Substituting molarity times the volume of EDTA used in each titration of the Zn unknown produces:

$$\text{mmol}_{\text{Zn}} = \text{mmol}_{\text{EDTA}} = \text{mmol}_{\text{EDTA}} \times V_{\text{EDTA}} = \text{mmol}_{\text{EDTA}} \times V_{\text{ep}}$$

The mass of Zn obtained in a single titration, in mg, is equal to the number of mmol of Zn times its molar mass (MM):

$$\text{mg}_{\text{Zn}} = \text{mmol}_{\text{Zn}} \times \text{MM}_{\text{Zn}} = \text{mmol}_{\text{Zn}} \times 65.38 \text{ mg/mmol}$$

And the total mass of Zn in the original 250-mL sample is therefore 10 times this amount.

HAZARDOUS WASTE DISPOSAL

Empty all the Ca and Zn solutions that were titrated into the proper Hazardous Waste Bottle for this experiment. If you are unsure of the proper container, ASK.

*When you are **completely** done with the experiment, including having received your grade, mix any remaining EDTA titrant, Ca standard stock solution, and Zn unknown solution together in a large beaker. Pour down the drain with copious amounts of cold tap water flowing. The first two solutions are slightly basic and slightly acidic, respectively. When mixed, they will be near neutral. In addition, EDTA, Ca, and Zn are not toxic and in very low concentrations, so disposal directly down the drain is permitted and environmentally safe.*

NOTE

1. Eriochrome Black T Indicator. The color change of Eriochrome black T at the endpoint is rather subtle. It is not an abrupt change from deep red to a dark blue; but rather it is from a light red (or pink) to a pale blue. At least one trial titration is recommended. (You can always discard a “bad” value when you know there is a definite reason for its being bad. Make sure you indicate a possible problem in your notebook at the time you observe it.)

If you have trouble distinguishing the endpoint, a “before” and an “after” flask are recommended. Prepare two 250-mL flasks in a similar manner as were the samples – except do not add the 25 mL of Ca solution. Instead, add a total of about 80-90 mL of deionized water to approximate the volume of the sample aliquot (25 mL), the volume of EDTA titrant that would have been titrated into the flask, and the 15 mL of deionized water. Add the indicator and the ammonia buffer. To one flask (the “before” the endpoint flask) add a few drops of the Ca solution; to the other flask (the “after” flask) add a small amount of EDTA solution to get just past the color change at the endpoint. Stopper the flasks and keep them nearby for comparison of the colors. Titrate against a white background for better discrimination of colors.

Sometimes the Eriochrome black T solution goes bad because of air oxidation. If the endpoints seem very indistinct or slow to you, try a fresh bottle of indicator. Alternatively, try adding a small amount of solid Eriochrome black T mixture (1 g indicator ground with 100 g NaCl). A small amount on the end of a spatula is sufficient.

REFERENCES

D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Analytical Chemistry: An Introduction*, 7th ed., Chapter 15, pp. 345-381.

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