

COMPLEXOMETRIC TITRATION OF CALCIUM

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OBJECTIVE: To determine the calcium content of an unknown mixture by complexometric titration, and also the content of a calcium pill.

CONCEPTS:

End/Equivalence Point
Ligands (complexers) Polydentate Ligands
Complex Formation Stability of Complexes
Selective Complexation Buffers for pH control

TECHNIQUES:

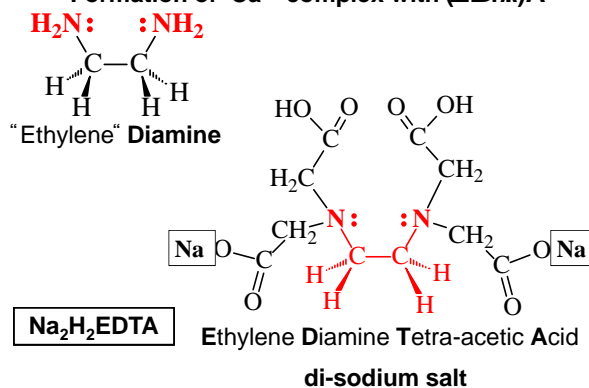
Weighing by Difference Titration

EQUIPMENT:

Buret

TECHNIQUE

Formation of Ca^{+2} complex with (EDTA)



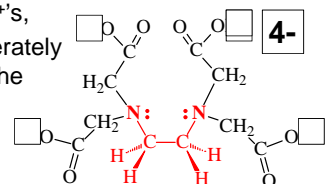
EFFECT OF pH

$\text{Na}_2\text{H}_2\text{EDTA}$ dissolves in neutral solutions to give $2 \text{Na}^+ + \text{H}_2\text{EDTA}^{2-}$ anions

However, the most effective complexing form is EDTA^{4-}

To neutralize last two H^+ 's, we will maintain a moderately **basic** environment for the titration by adding a

pH = 10 buffer



Complex between EDTA and Ca^{+2} is 1 : 1

i.e.,
 1 EDTA^{4-} reacts with 1 Ca^{+2}
 $\text{Ca}^{+2} + \text{EDTA}^{4-} \rightarrow \text{Ca}(\text{EDTA})^{2-}$

<http://www.ic.sunysb.edu/Class/che134/temp/mgedtaxvz.html>

EQUIVALENCE (END) POINT = when all Ca^{+2} has reacted with EDTA

But, neither EDTA^{4-} , nor Ca^{+2} nor its COMPLEX with Ca^{+2} IS COLORED

How will we know when **EQUIVALENCE (End) POINT** has been reached?

USE **INDICATOR**

ERIOCHROME BLACK T (EBT)

- a **BLUE** dye - to detect Ca^{+2}

EBT also forms a 1 : 1 complex with Ca^{+2}

The complex is **RED**, but,

Ca-EBT complex is **MUCH LESS STABLE** than **Ca-EDTA complex**

Therefore, the **Ca-EBT complex** can only exist when there is **free** Ca^{+2} .

If all Ca^{+2} is tied up as the EDTA complex, the **Ca-EBT complex** cannot form. **Free EBT is BLUE**.

WHAT'S IN THE SOLUTION WHEN

Suppose we start with **2.00** mmol of Ca^{+2} to which we add 5 mg (~ **0.01** mmol) of **EBT**.

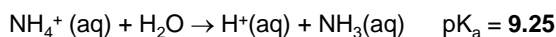
	mmol EDTA ADDED			
	0.00	1.99	2.00*	2.01
Ca^{+2}	1.99	0.00	0.00	0.00
Ca⁺²(EBT)	0.01	0.01	0.00	0.00
$\text{Ca}^{+2}(\text{EDTA})$	0.00	1.99	2.00	2.00
EBT	0.00	0.00	0.01	0.01
EDTA	0.00	0.00	0.00	0.01

* **END POINT**

[Titration is conducted in moderately **basic** solution, **pH = 10** to enhance formation of EDTA^{-4} ion]

THE pH = 10 BUFFER

A **pH = 10** buffer can be made from an NH_4^+ salt and $\text{NH}_3(\text{aq})$



$$K_a = \frac{[\text{H}^+][\text{NH}_3(\text{aq})]}{[\text{NH}_4^+]} = 10^{-9.25} = 5.6 \times 10^{-10}$$

$$[1.0 \times 10^{-10}][\text{NH}_3(\text{aq})] / [\text{NH}_4^+] = 5.6 \times 10^{-10}$$

$$[\text{NH}_3(\text{aq})] / [\text{NH}_4^+] = 5.6$$

Solutions of aqueous ammonia ($\text{NH}_3(\text{aq})$) smell like ammonia.

When you dispose of solutions after titration, please do so in the drains in hoods

PROCEDURE

[0. **PREPARE SAMPLE** (if necessary)

Grind Pill to uniform composition]

1. **WEIGH SAMPLE** accurately, by difference

2. **DISSOLVE** in acid (5 mL 6M HCl)

3. **ADJUST pH** (to insure basic solution)

25 mL water + 10 mL pH 10 buffer

4. **ADD INDICATOR (EBT)** – **RED Color**

5. **TITRATE WITH EDTA** to **BLUE end point** –

Hold up to light – No trace of **RED**

6. **REPEAT PROCEDURE** –

Once more with pill

Trial run + 2 or more times with unknown

HOW MUCH OF A TABLET SHOULD YOU WEIGH?

Concentration of EDTA is ~**0.050 M**

Ca^{+2} - EDTA complex is 1 to 1

50 mL of the EDTA solution contain
 $50 \times \sim 0.050 = \sim 2.5$ mmol of EDTA

2.5 mmol of Ca^{+2} weighs
 $2.5 \text{ mmol} \times 40 \text{ mg / mmol} = 100 \text{ mg}$

In order to use less than a **buret-full (50 mL)** of EDTA, you must weigh out a sample which contains

LESS THAN 2.5 mmol = 100 mg of Calcium

But, the contents of antacid pills and calcium supplements are often given as the weight of CaCO_3 , not Ca.

1 mol of CaCO_3 contains 1 mol of Calcium
So, a tablet or sample that contains **100 mg of calcium** would also be described as containing

$$\frac{100 \text{ mg Ca} \times 100 \text{ mg / mmol CaCO}_3}{40 \text{ mg Ca / mmol Ca}} = 250 \text{ mg CaCO}_3$$

This exercise requires you to report the Ca content of the materials you analyze in terms of CaCO_3

Suppose a tablet contains **500 mg of CaCO_3 (200 mg Ca)** and the tablet weighs **1.30 g**

To use **~25 mL of 0.050 M EDTA**, we need to have
~1.25 mmol Ca^{2+} = $1.25 \times 40 = 50 \text{ mg Ca}^{2+}$
or
~1.25 mmol $\text{CaCO}_3 = 1.25 \times 100 = 125 \text{ mg CaCO}_3$

What fraction of the tablet do we need?

$50 / 200 = 125 / 500 = 0.250$ or, about 1/4 of the tablet
which will weigh

$$1/4 \times 1.30 = .325 = \sim 325 \text{ mg}$$

You must repeat this calculation with the actual data on the container in the laboratory.

ITS NEVER TOO LATE
BURETS - SOME DO'S AND DON'TS

DON'T set buret to initial value of 0.00

Burets are made to be **READ**, not **SET**.

DO let initial reading be arbitrary

DON'T record buret readings to 1 decimal and fill in second decimal later

DO read and record buret to nearest $\pm 0.02 \text{ ml}$ (i.e., to **2 decimal places) – always!**

DO rinse buret (including tip) with the reagent that will be delivered

DO make sure there are no bubbles in the tip of the buret

SUSB-017 Data Sheet - 2

Concentration of EDTA solution:	0.04653 M
Init. Mass of vial + sample	14.5432 g
Mass of vial + sample left over	<u>14.4112</u> g
Mass of sample to be titrated	0.1320 g
Final buret reading	25.67 mL
Initial buret reading	<u>3.54</u> mL
Net volume EDTA solution	22.13 mL
mmol EDTA (0.04653×22.13)	1.030
mmol Ca^{2+} in weighed sample	1.030
mmol CaCO_3 in weighed sample	1.030
Mass of CaCO_3 in weighed sample	
$1.030 \times 100.1 = 103.1 \text{ mg}$	0.1031 g
Mass percent CaCO_3 $100 \times 0.1031 / 0.1320$	78.08 %

SUSB-017 Data Sheet - 1

Weight of tablet (g)	0.7710
Init. Mass of container + sample (g)	14.5432
Mass of container + sample left over (g)	<u>14.4112</u>
Mass of sample to be titrated (g)	0.1320
Final buret reading (mL)	25.67
Initial buret reading (mL)	<u>3.54</u>
Net volume EDTA solution (mL)	22.13
mmol EDTA	1.030
mmol Ca^{2+} in weighed sample	1.030
mmol CaCO_3 in weighed sample	1.030
Mass of CaCO_3 in weighed sample (g)	0.1031
Mass of CaCO_3 in tablet (mg)	
$(0.7710 / 0.1320) \times 0.1031 \times 1000 =$	602.2

REVIEW: 3 Results: 5.38, 5.50, 5.41

AVERAGE:

$$\frac{M_1 + M_2 + M_3}{3} = \frac{5.38 + 5.50 + 5.41}{3} = 5.43$$

AVERAGE DEVIATION:

$$\frac{|M_1 - \text{AVG}| + |M_2 - \text{AVG}| + |M_3 - \text{AVG}|}{3}$$

$$\frac{(|5.38 - 5.43| + |5.50 - 5.43| + |5.41 - 5.43|)}{3} = 0.047$$

PERCENT DEVIATION:

$$\frac{100 \times \text{AVG DEV}}{\text{AVG}} = \frac{100 \times 0.047}{5.43} = 0.87\%$$

Why a trial run?

Unknowns contain a ***wide range of CaCO_3***

In any titration, we try to use ***not less than 20 mL*** of titrant to optimize the precision of the buret –

(2 readings, each with an uncertainty of 0.02 mL)

Trial run permits adjustment of weight of unknown which will require about 25 mL

E.g., if in trial run, **117 mg** unknown requires **15 mL** for next titration,

weigh out $\sim 25 \times 117 / 15 = \sim 195$ mg

NEXT WEEK

Kinetics of a Bleaching Reaction

SUSB - 023

Do pre-lab

Check out supplemental information related to this exercise on the WEB