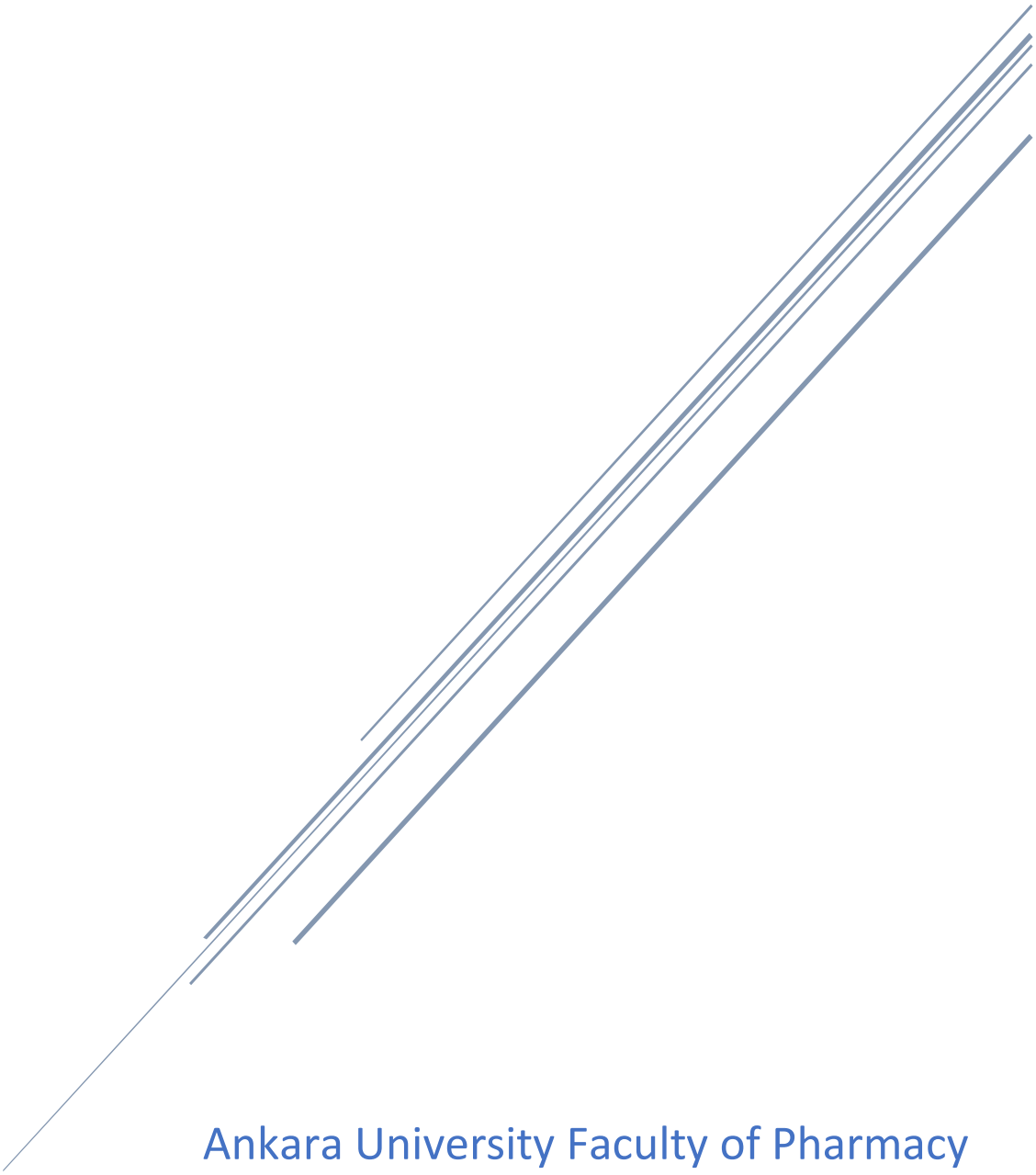
ANALYTICAL CHEMISTRY LABORATORY MANUAL 2



Ankara University Faculty of Pharmacy
Department of Analytical Chemistry
Analytical Chemistry Practices

Contents

INTRODUCTION TO QUANTITATIVE ANALYSIS

Quantitative analytical chemistry is related with the quantitative determinations of the substances. Today, many methods for quantification are exist. In practice, some factors such as the structural properties of a material, sensitivity, accuracy, reliability, ease of implementation and cost-effectiveness of methods are considered for selecting a proper method. In our lab, volumetric and instrumental analysis will be used for quantitative analysis.

Qualitative Analysis	**Quantitative Analysis**
Analysis for identification of species in a sample.	Analysis for determination of the quantities of species in a sample.

Quantitative Analytical Methods	
Classical Methods	Instrumental Methods
If the analysis is carried out solely using solutions of chemical substances, this is called as classical analysis. - Gravimetric analysis - Volumetric analysis	If the analysis is performed using a device, then it is called instrumental analysis. - Spectroscopic analysis - Electrochemical analysis - Chromatographic analysis

VOLUMETRIC ANALYSIS

Volumetric analysis is a quantitative analysis based on the measurement of the volume of solutions that gives reaction. Here, the concentration of analyte can be found by reacting it with a standard solution with a known concentration.

The volumetric analysis is based on the stoichiometry between reactive species. For example;

$$A + B \rightarrow AB$$

according to the above reaction, the stoichiometry between A and B is 1:1. It means 1 mol of A reacts with 1 mol of B to give 1 mol of AB.

$$C + 2D \rightarrow CD_2$$

On the other hand, for the above reaction, the stoichiometry between C and D is 1:2. It means 1 mol of C reacts with 2 moles of D to give 1 mol of CD_2.

Volumetric Analysis Calculations

$$A + B \rightarrow AB$$

The concentration of a sample A can be found by reaction with a substance B with exactly known concentration (standard solution). Since they reacted 1:1 ratio, their moles will be equal at the end of reaction (equivalence point):

$$n_A = n_B$$

$$M_A \times V_A = M_B \times V_B$$

Here, V_A and V_B are the volumes of A and B, and M_B is the molarity of B. By using this equation, the molarity of A (M_A) can be calculated.

For calculation of concentration in g/L, molarity of A can be multiplied with molecular weight of A:

$$C\ (g/L) = M_A \times MW_A$$

If the mol ratio is different than 1:1, then this must be taken into account. For example, the concentration of an analyte C can be found by reacting it with a standardized solution of D with a mol ratio of 1:2. It means 1 mol of C reacts with 2 moles of D.

$$C + 2D \rightarrow CD_2$$

In this case, firstly the mol of D should be calculated. If the D is an aqueous solution, then use volume and molarity of it:

$$n_D = M_D \times V_D$$

If the D is solid then use the amount and molecular weight of it.

$$n_D = \frac{m_D}{MA_D}$$

Then calculate the mol of C that reacts with:

2 moles of D reacts with 1 mol of C

n_D mol D reacts with x mol of C.

Calculate x which is the mol of C and using x calculate molarity of C:

$$M_C = \frac{x}{V_C}$$

Finally, for calculation of concentration in g/L, molarity of C can be multiplied with molecular weight of C:

$$C\ (g/L) = M_C \times MW_C$$

Dilution Factor

Samples are (not necessarily but generally) diluted before analysis. The reason for dilution might be the reduction of reagent use in the analysis or increase of the volume of the sample so that analysis can be repeated when needed. Dilution must be accounted in calculations:

Dilution ratio = amount before dilution / amount after dilution

Dilution factor (DF) = amount after dilution / amount before dilution

For example, if 90 mL of distilled water is added onto 10 mL sample, the total volume after dilution will be 100 mL. It means that the sample is diluted 10/100 ratio (or 1/10 ratio). The dilution factor in this case:

$$DF = 100/10 = 10$$

After the titration, the concentration of the diluted sample can be calculated using titration results. Then the concentration of the real sample can be calculated by multiplying the concentration of diluted sample with DF.

Example:

A concentrated sample of 20 mL HCl is diluted to 100 mL with distilled water. Then 25 mL of the diluted sample is titrated with 0.1 M 12.5 mL NaOH. Calculate the molarity of the sample?

$HCl + NaOH \rightarrow NaCl + H_2O$ (mol ratio 1:1)

The moles of NaOH consumed during titration can be calculated from the following equation using the volume of NaOH that is consumed in the titration and the molarity of the NaOH.

$$n_{NaOH} = M_{NaOH} \times V_{NaOH}$$

According to the reaction equation:

If	1 mol NaOH reacts with	1 mol HCl
	n_{NaOH} mol reacts with	x mol HCl

From this ratio, the moles of HCl ($x = n_{HCl}$) is calculated and the molarity of diluted HCl is calculated from *x*.

$$M_{HCl} = \frac{x}{V_{HCl}}$$

The molarity of the original sample (M_{sample}) then can be calculated by multiplying the molarity of the diluted sample by the dilution factor.

$$\text{Dilution factor} = 100 / 20 = 5$$

$$M_{sample} = M_{HCl} \times DF$$

$$M_{sample} = 0.05 \times 5$$

$$M_{sample} = 0.25\ M$$

Standard Solutions

Standard solutions are solutions that have exactly known concentration and react with analytes.

For example, if concentration of a base solution is to be determined, an acid solution with known concentration can be used as standard solution.

The standard solution can be prepared by precisely weighing the required amount of reagent. Then, the precise concentration of the standard solution can be found by the reaction with special substances called primary standards.

Primary standard

A primary standard is a highly pure compound that serves as a reference material in volumetric and mass titrimetric methods. The accuracy of a method is critically dependent on the properties of this compound. Important requirements for a primary standard are the following:

1. Highly pure or exact purity must be known.

2. Atmospheric stability.

3. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.

4. Modest cost.

5. Reasonable solubility in the titration medium.

6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

Primary standards for acid standardization:

$KHCO_3$, $TlCO_3$ Na_2CO_3

Primary standards for base standardization:

$KHC_8H_4O_4$, $H_2C_2O_4.2H_2O$, $HC_7H_5O_2$ …..

Characteristics of Quantitative Reaction

1) Reaction must be specific and unique

2) Reaction must be in one direction

3) The reaction must be fast

4) The end of the reaction can be detected easily

5) The reaction must be repeatable yielding same results every time.

Preparation of 1 L 0.1 M HCl Solution

From HCl stock solution, 37% purity, d= 1.19 g/cm^3

m=d xV

The weight of concentrated HCl of 1000 mL is

m= 1.19 x1000= 1190 gr.

In 100 g 37 g HCl is pure

In 1190 g x x= 440.3 g pure HCl

1 M 1 L HCl 36.5 g HCl required

0.1 M 1 L 3.65 g HCl requires.

1000 mL 440.3 g pure HCl

x 3.65 g HCl x=8.3 mL

Therefore, if you take 8.3 mL acid and dilute it to 1000 mL it will be 1 L, 0.1 M HCl. Do not forget, never add acid to water*****, put some water to volumetric flask first, then add 8.3 mL of HCl. And mix it well, finally complete it to 1000 mL till the line.

*****If you add water onto acid, then high amount of heat is produced and it may explode**!**

Preparation of 1 L 0.1 M NaOH Solution

1 L 1 M NaOH solution 40 g NaOH required

2.5 L 0.1 M 10 g NaOH requires.

10 g of NaOH is weighed in watch glasses******. Then it is transferred to a beaker and dissolved in nearly 400 mL of distilled water. Transfer it to the volumetric flask, complete it until 1 L. Then transfer it to 2.5 L of bottle. Add more 1.5 L distilled water to this bottle and mix well. Do not forget labelling.

******Be careful! NaOH is a strong irritant. In case of contact, please wash the affected area with copious amount of water.

NEUTRALIZATION TITRATIONS

The reaction between an acid and a base is called as **neutralization reaction**.

Titration is a laboratory technique that measures the concentration of an analyte using reaction between analyte and standard solution (solution of known concentration).

Acid-base titrations is also called **neutralization titrations**.

Acidimetry is the determination of concentration of basic substances by titration with a standard acid solution, and **alkalimetry** is the measurement of concentration of acid substances by titration with a standard base solution.

The **end-point** (equivalence point) of acid-base reactions are observed by using **indicators** which are substances that changes colors near their pKa. Therefore, a suitable indicator should be selected for acids and bases that are reacted.

A **titration curve** is a plot of pH *vs*. the amount of titrant added. Shape of titration curves differ for weak and strong acid-bases or for polyprotic acids and bases.

Tips for Titrations

1) Solutions must be shaken well before starting.
2) First, a known volume of the analyte is placed in an erlenmeyer flask, and a few drops of an acid-base indicator, such as phenolphthalein, are added.
3) Next, the standard solution is placed into a burette. This solution is also called as **titrant**.
4) Then, the titrant is added drop by drop to the analyte while swirling the erlenmeyer flask. Titration must be performed slowly and always hold stopcock one hand while swirling the flask with other hand.

STANDARDIZATION OF 0.1 N NaOH SOLUTION

Experimental procedure:

Carefully weigh 0.1-0.2 gram of oxalic acid ($H_2C_2O_4.2H_2O$) and note the exact amount. This should be done by taking required amount of oxalic acid from the stock of oxalic acid on the balance and transferring it to an erlenmeyer flask.

Dissolve oxalic acid by adding 50 mL of water into the erlenmeyer flask.

Add 1-2 drops of phenolphthalein to the erlenmeyer flask.

Fill a burette with NaOH solution that you want to standardize. Check for leak and bubbles. Read the *bottom* of the meniscus.

Deliver solution drop by drop to the erlenmeyer flask by turning the stopcock while swirling the flask. Continue to the titration until the color of the solution in the flask turns to light pink.

Reaction equation:

$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$ (mol ratio in reaction 1:2)

Calculations:

Firstly, mol of oxalic acid is calculated using weighted oxalic acid.

($MW_{H_2C_2O_4.2H_2O} = 126.1$ g/mol)

$$n_{C_2H_2O_4.2H_2O} = \frac{m_{H_2C_2O_4.2H_2O}}{126.1}$$

According to the reaction equation:

If 1 mol $C_2H_2O_4.2H_2O$ reacts with 2 moles NaOH

$n_{C_2H_2O_4.2H_2O}$ mol $C_2H_2O_4.2H_2O$ reacts with *x* mol NaOH

From this ratio, the moles of NaOH ($x = n_{NaOH}$) is calculated and the molarity NaOH is calculated from *x*.

$$M_{NaOH} = \frac{x}{V_{NaOH}}$$

Weighing oxalic acid:

Take the crucible having oxalic acid in it from desiccator and put it onto a balance.

Take a note of the amount on the screen (For example 30.100 g).

For taking 0.1 - 0.2 g of oxalic acid

30.100 – 0.2 = 29.900

30.100 – 0.1 = 30.000

We need to take an amount of oxalic acid that the remaining amount must be in between 29.900 g – 30.000 g.

If the final amount of remaining oxalic acid is 29,980 then we took

30.100 – 29.980 = 0.120 gram

Then, by using a spatula, take required amount of oxalic acid and transfer it to the erlenmeyer flask and keep the spatula in the flask for flushing the oxalic acid sticked on the surface of the spatula.

STANDARDIZATION OF 0.1 M HCl SOLUTION

Experimental:

Pour 10 mL HCl into an erlenmeyer flask and add 1-2 drops of phenolphthalein.

Fill a burette with NaOH solution that you already standardized.

Titrate until light pink color.

Reaction equation:

$HCl + NaOH \rightarrow NaCl + H_2O$ (reaction mol ratio 1:1)

Calculations:

First, the moles of NaOH consumed during titration can be calculated from the following equation using the volume of NaOH that is consumed in the titration and the molarity of the NaOH.

$$n_{NaOH} = M_{NaOH} \times V_{NaOH}$$

According to the reaction equation:

If	1 mol NaOH reacts with	1 mol HCl
	n_{NaOH} mol reacts with	x mol HCl

From this ratio, the moles of HCl ($x = n_{HCl}$) is calculated and the molarity HCl is calculated from *x*.

$$M_{HCl} = \frac{x}{V_{HCl}}$$

DETERMINATION OF BORIC ACID (H_3BO_3)

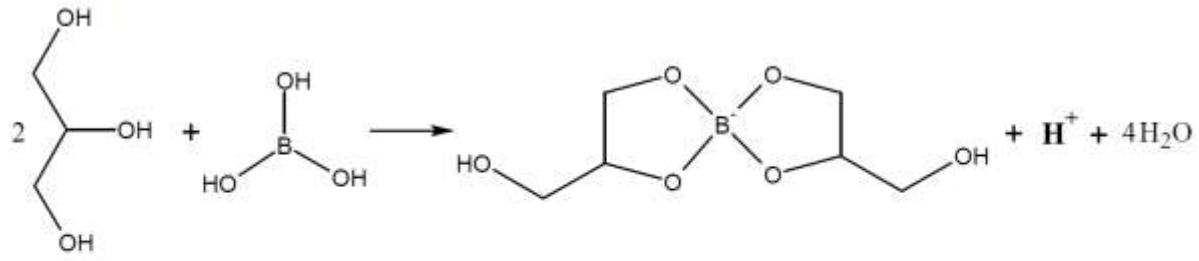
Experimental procedure:

Each student receives 5 mL of boric acid solution with different concentrations in a 100 mL volumetric flask.

Complete the sample in the flask to 100 mL with distilled water. Take a portion of it into an erlenmeyer flask with your single volume pipette. Add 10 mL glycerol solution (1:1 diluted and neutralized) to the erlenmeyer flask. (The glycerol solution prepared by the lab personnel will be ready to use.)

Add 2 drops of phenolphthalein to the erlenmeyer flask and titrate with standardized NaOH solution until the pink color is observed.

Reaction equation:



$$H^+ + NaOH \longrightarrow Na^+ + H_2O$$

Calculations:

Boric acid concentration of the original sample is calculated as g/L and w/v %.

($MW_{H_3BO_3} = 61.82$ g/mol)

First, the moles of NaOH consumed during titration can be calculated from the following equation using the volume of NaOH that is consumed in the titration and the molarity of the NaOH.

$$n_{NaOH} = M_{NaOH} \times V_{NaOH}$$

According to reaction equation:

If 1 mol NaOH reacts with 1 mol H_3BO_3

n_{NaOH} reacts with *x* mol H_3BO_3

From this ratio, the moles of H_3BO_3 in the diluted sample ($x = n_{H_3BO_3}$) is calculated. Then the molarity of the diluted sample is calculated from *x*.

$$\mathrm{M}_{\mathrm{H_3BO_3}} = \frac{x}{\mathrm{V}_{\mathrm{H_3BO_3}}}$$

The molarity of the original sample (M_{sample}) then can be calculated by multiplying the molarity of the diluted sample by the dilution factor.

$$\mathrm{M}_{sample} = \mathrm{M}_{\mathrm{H_3BO_3}} \times \mathrm{DF}$$

The molarity is multiplied by the molecular weight to convert the concentration of the original sample to g/L:

$$\mathrm{C(g/L)} = \mathrm{M}_{sample} \times 61.82$$

Concentration of the original sample is calculated as w/v %.

$$\text{(w/v) \%} = \frac{\mathrm{g}}{100\ \mathrm{mL}}$$

$$\mathrm{C(g/L)} = \frac{\mathrm{g}}{1000\ \mathrm{mL}}$$

$$\text{(w/v) \%} = \mathrm{C(g/L)} \times 10$$

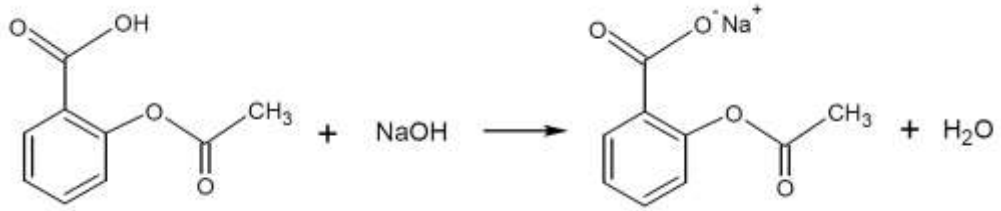
In your report, explain how to prepare 100 mL of 2 % (w/v) boric acid solution by using the original sample you have received with dilution calculations.

PERCENT PURITY DETERMINATION OF ASPIRIN SAMPLES

Experimental procedure:

Carefully weigh 0.1-0.2 gram of solid aspirin sample into an erlenmeyer flask and note the exact amount. Dissolve it in 25 mL 60 % (v/v) ethanol. (Since the solubility of aspirin is very low in water, ethanol solution is used.) Add 1-2 drops of phenolphthalein and titrate with standardized NaOH until the pink color is observed.

Reaction equation:



Calculation:

Percent amount of the pure aspirin will be calculated. ($MW_{aspirin} = 180$ g/mol)

First, the moles of NaOH consumed during titration can be calculated from the following equation using the volume of NaOH that is consumed in the titration and the molarity of the NaOH.

$$n_{NaOH} = M_{NaOH} \times V_{NaOH}$$

According to reaction equation:

If 1 mol NaOH reacts with 1 mol Aspirin

n_{NaOH} x mol Aspirin

From this ratio, the moles of aspirin in the reaction ($x = n_{aspirin}$) is the moles of aspirin in the weighed amount. Using this mol (x), the mass of aspirin in the weighed sample can be calculated.

$$m_{aspirin} = x \times MW_{aspirin}$$

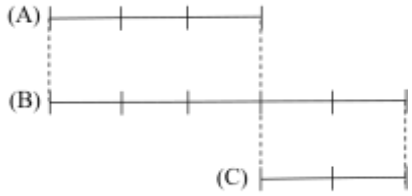
The amount of pure aspirin is calculated as the % of the sample weighed.

$$\%\, purity = \frac{m_{aspirin}}{m_{weighed}} \times 100$$

$CaCO_3$ PURITY DETERMINATION

Calcium carbonate ($CaCO_3$) cannot be directly titrated since it's not soluble in water. At this point, it can be analyzed using the back titration method.

In back titration, a sample solution (A) reacts with excess amount of standard solution "B". As a result of the reaction, a portion of the solution B remains in the erlenmeyer flask in excess. A titration is then performed with a titrant (standard solution) "C" to react with the remaining B solution. This whole process is called as "*Back titration*".



Experimental procedure:

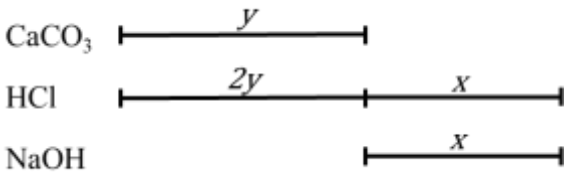
Carefully weigh 0.1-0.2 g of solid $CaCO_3$ sample into an erlenmeyer flask and note the exact amount. Add 50 mL of standard HCl solution from a burette into the erlenmeyer flask. A portion of the added acid reacts with $CaCO_3$. Heat the erlenmeyer on wire gauze for 2-3 minutes in order to remove the CO_2. Add 1-2 drops of phenolphthalein and titrate the remaining acid in the erlenmeyer flask with standard NaOH until a permanent pink color is observed.

Reaction equation:

$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

$HCl + NaOH \longrightarrow NaCl + H_2O$

Calculations:



Percent amount of $CaCO_3$ will be calculated.

First, the moles of NaOH consumed during titration can be calculated from the following equation using the volume of NaOH that is consumed in the titration and the molarity of the NaOH.

$$n_{NaOH} = M_{NaOH} \times V_{NaOH}$$

According to the reaction equation; $HCl + NaOH \longrightarrow NaCl + H_2O$

If	1 mol NaOH reacts with	1 mol HCl
	n_{NaOH} mol NaOH reacts with	*x* mol HCl

In this reaction, since the mol ratio of NaOH and HCl is 1:1, the moles of HCl (*x*), which reacts with NaOH, equals to the moles of consumed NaOH.

Then the total moles of HCl, added into the erlenmeyer flask, is calculated as below:

$$n_{HCl(total)} = M_{HCl} \times V_{HCl}$$

When we subtract the moles of HCl, which neutralized the NaOH, from the total moles of HCl, we find the moles of HCl, which reacted with $CaCO_3$.

$$\text{moles of HCl, which reacts with } CaCO_3 = n_{HCl(total)} - x$$

According to the reaction equation; $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

If	2 moles HCl react with	1 mol $CaCO_3$
	$n_{HCl(total)} - x$ mol HCl reacts with	*y* mol $CaCO_3$

The moles of $CaCO_3$ found from this ratio (*y*) is the moles of $CaCO_3$ in the erlenmeyer flask, which means the moles of $CaCO_3$ in the weighed solid. The mass of $CaCO_3$ in the weighed sample can be calculated using *y*. ($MW_{CaCO_3} = 100$ g/mol)

$$m_{CaCO_3} = y \times MW_{CaCO_3}$$

The amount of pure $CaCO_3$ is calculated as the % of the sample weighed.

$$\%\, purity = \frac{m_{CaCO_3}}{m_{weighed}} \times 100$$

H_3PO_4 (PHOSPHORIC ACID) DETERMINATION

Polyprotic acids contain more than one mol ionizable hydronium ions per mol of acids, for example phosphoric acid (H_3PO_4), carbonic acid (H_2CO_3) sulfuric acid (H_2SO_4), oxalic acid ($H_2C_2O_4$). They ionize to give more than one H^+ ions per molecule. Phosphoric acid contains 3 protons has three acidities different from each other.

Polyprotic acids ionize to three steps. Each step gives one proton and for each step the effect value is 1. Thus, total effect value is three.

It is difficult to titrate 3rd proton of phosphoric acid as it is very weak ($K_{a3} = 4.20x10^{-13}$).

Experimental procedure:

Dilute the given sample (20 mL) to 100 mL with distilled water. Transfer 25 mL of sample to an erlenmeyer flask.

Add 2 drops of bromocresol green and phenolphthalein.

Titrate with 0.1 M NaOH until blue-green color and note the volume of titrant used (V_1). Continue titration until violet color and note the volume of titrant used for second part (V_2).

Reaction equation:

$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$ $K_{a1} = 7.11x10^{-3}$
(End point of bromocresol green)

$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$ $K_{a2} = 6.34x10^{-8}$
(End point of phenolphthalein)

$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$ Total acidity

Calculations:

The concentration of phosphoric acid in the sample is calculated in g / L. ($MW_{H_3PO_4} = 98$ g/mol)

Determination of 1st proton (1st acidity)

First, the moles of NaOH consumed during titration can be calculated from the following equation using the volume of NaOH that is consumed in the titration and the molarity of the NaOH.

$$n_{NaOH} = M_{NaOH} \times V_1$$

According to reaction equation:

If 1 mol NaOH reacts with 1 mol H_3PO_4
n_{NaOH} mol NaOH reacts with *x* mol H_3PO_4

From this ratio, the moles of H_3PO_4 in the diluted sample ($x = n_{H_3PO_4}$) is calculated and the molarity of the diluted sample is calculated from *x*.

$$M_{H_3PO_4} = \frac{x}{V_{H3PO4}}$$

The molarity of the original sample (M_{sample}) can then be calculated by multiplying the molarity of the diluted sample by the dilution factor.

$$M_{sample} = M_{H_3PO_4} \times DF$$

Finally, the molarity is multiplied by the molecular weight to convert the concentration of the original sample to g/L:

$$C(g/L) = M_{sample} \times 98$$

Determination of 2nd proton (2nd acidity):

First, the moles of NaOH consumed during titration can be calculated from the following equation using the volume of NaOH that is consumed in the titration and the molarity of the NaOH.

According to reaction equation:

$$n_{NaOH} = M_{NaOH} \times V_2$$

If 1 mol NaOH reacts with 1 mol H_3PO_4
n_{NaOH} mol NaOH reacts with *x* mol H_3PO_4

From this ratio, the moles of H_3PO_4 in the diluted sample ($x = n_{H_3PO_4}$) is calculated and the molarity of the diluted sample is calculated from *x*.

$$M_{H_3PO_4} = \frac{x}{V_{H3PO4}}$$

The molarity of the original sample (M_{sample}) can then be calculated by multiplying the molarity of the diluted sample by the dilution factor.

$$M_{sample} = M_{H_3PO_4} \times DF$$

Finally, the molarity is multiplied by the molecular weight to convert the concentration of the original sample to g/L:

$$\mathrm{C(g/L)} = \mathrm{M}_{sample} \times 98$$

Determination of total acidity:

Transfer 25 mL of sample to an erlenmeyer flask.

Add 2 drops of phenolphthalein.

Titrate with 0.1 M NaOH until pink color and note the volume of titrant.

$$\mathrm{n_{NaOH}} = \mathrm{M_{NaOH}} \times \mathrm{V_{NaOH}}$$

According to reaction equation:

If 2 mol NaOH reacts with 1 mol H_3PO_4

$\mathrm{n_{NaOH}}$ mol NaOH reacts with *x* mol H_3PO_4

From this ratio, the moles of H_3PO_4 in the diluted sample ($x = \mathrm{n_{H_3PO_4}}$) is calculated and the molarity of the diluted sample is calculated from *x*.

$$\mathrm{M_{H_3PO_4}} = \frac{x}{\mathrm{V_{H3PO4}}}$$

The molarity of the original sample (M_{sample}) can then be calculated by multiplying the molarity of the diluted sample by the dilution factor.

$$\mathrm{M}_{sample} = \mathrm{M_{H_3PO_4}} \times \mathrm{DF}$$

Finally, the molarity is multiplied by the molecular weight to convert the concentration of the original sample to g/L:

$$\mathrm{C(g/L)} = \mathrm{M}_{sample} \times 98$$

REDOX TITRATIONS

Redox titration is a titration based on the oxidation-reduction reaction between analyte and titrant.

PERMANGANOMETRY

Titration in which potassium permanganate ($KMnO_4$) is used as a standard solution is called permanganometry. The half reaction of permanganate (MnO_4^-) is different in acidic and basic medium.

Acidic medium: $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$

Alkali medium: $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$

In this laboratory, the permanganometric titrations will be performed in acidic medium.

In permanganometric titrations indicator is not used. MnO_4^- solution has a purple color whereas its reduction product Mn^{+2} is colorless. When all the species that reduces MnO_4^- to Mn^{+2} are consumed, the colorless solution in the erlenmeyer flask becomes pink-purple with the addition of 1 excess drop of $KMnO_4$. The occurrence of pink-purple color indicates the end point of the titration. That is why, $KMnO_4$ is an "auto indicator".

Preparation of 0.02 M 1 L $KMnO_4$ Solution

Weight around 3.2605-3.3605 g of $KMnO_4$ into a beaker. This amount is 0.1-0.2 g more than 0.02 mol $KMnO_4$. (Molar mass of $KMnO_4$: 158.032 g/mol)

Add 400-500 mL distilled water to the beaker and dissolve the solid $KMnO_4$ by mixing with a glass-rod. Transfer the solution to a 1 L volumetric flask. In order to dissolve the remaining solid $KMnO_4$, add 100-200 mL of distilled water to the beaker and mix it with the glass-rod. Transfer the solution into the same flask. Repeat this step until all the solid $KMnO_4$ in the beaker is dissolved. (***Be careful! Do not add more water than 1 L in total***). Fill the flask up to the 1 L mark with distilled water. Shake the volumetric flask to make sure all the $KMnO_4$ is dissolved in the flask. Put the solution into an amber-color bottle and keep it in dark for 1 week.

After waiting 1 week, filter the solution by glass fibers into a clean amber glass bottle. The final solution is kept in dark.

Standardization of $KMnO_4$ Solution

Experimental procedure:

Weight 0.1-0.2 g (take a note of exact amount) of oxalic acid ($H_2C_2O_4.H_2O$) and dissolve it in around 100 mL of distilled water in an erlenmeyer flask. Add 10 mL of ½ diluted H_2SO_4. (The acid solution will be ready to use). Heat up the erlenmeyer flask on a bunsen burner for 3-4 minutes (*should not be boiled!*) and then cool it down until it is cool enough to touch.

Titrate the solution with $KMnO_4$ solution until permanent pink color.

After each student calculates the molarity of the $KMnO_4$ solution, the results will be evaluated with the assistant and the average molarity will be reported for each lab bench.

Reaction equation:

$$2/ \quad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$$

$$5/ \quad C_2O_4^{-2} \longrightarrow 2CO_2 + 2e^-$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{-2} \longrightarrow 2Mn^{+2} + 8H_2O + 10CO_2$$

Calculations:

First, the moles of oxalic acid consumed during titration can be calculated from the following equation using the mass of oxalic acid that is weighed and the molecular weight of the oxalic acid. (MW: $H_2C_2O_4.H_2O$: 126.07 g/mol)

$$n_{H_2C_2O_4.H_2O} = \frac{m_{H_2C_2O_4.H_2O}}{MWt_{\ H_2C_2O_4.H_2O}}$$

$$n_{H_2C_2O_4.H_2O} = n_{H_2C_2O_4}$$

According to reaction equation:

If 5 moles oxalic acid reacts with 2 moles $KMnO_4$

$n_{H_2C_2O_4}$ moles oxalic acid reacts with *x* moles $KMnO_4$

Then, the molarity of $KMnO_4$ is calculated from the following equation using the volume of $KMnO_4$ that is consumed in the titration and the mol of the $KMnO_4$ $(x = n_{KMnO_4})$, which was calculated from the above ratio.

$$M_{KMnO_4} = \frac{x}{V_{KMnO_4}}$$

$FeSO_4$ DETERMINATION

Experimental procedure:

Fe^{2+} is oxidized to Fe^{3+} in acidic medium by MnO_4^- Dilute the 20 mL $FeSO_4$ sample in the volumetric flask to 100 mL with distilled water and mix it well. Transfer a portion of 25 mL diluted sample to an erlenmeyer flask and add 10 mL ½ diluted H_2SO_4. Add 50-100 mL distilled water and titrate with standardized $KMnO_4$ solution until pink color.

Reaction equation:

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Calculations:

Calculate the concentration of the iron (II) sulfate of the sample in g/L

(MW_{FeSO_4} = 152 g/mol)

Firstly, calculate the moles of reacted $KMnO_4$ using the molarity of $KMnO_4$ and the volume of $KMnO_4$ used in the titration:

$$n_{KMnO_4} = M_{KMnO_4} \times V_{KMnO_4}$$

According to the reaction:

If 1 mol $KMnO_4$ reacts with 5 mol $FeSO_4$

n_{KMnO_4} mol $KMnO_4$ reacts with *x* mol $FeSO_4$

Calculate the moles of diluted $FeSO_4$ ($x = n_{FeSO_4}$) is using above proportion. Using *x*, calculate the molarity of diluted $FeSO_4$:

$$M_{FeSO_4} = \frac{x}{V_{FeSO_4}}$$

Calculate the molarity of sample by multiplying the molarity of diluted sample with dilution factor:

$$M_{sample} = M_{FeSO_4} \times DF$$

Finally, convert the molarity of sample to concentration in g/L:

$$C(g/L) = M_{sample} \times 152$$

IODIMETRY AND IODOMETRY

TITRATION WITH IODINE

Iodine is a good oxidizing agent. Since Iodine/Iodide ((I_2/I^-) has a standard redox potential between strong oxidizing agent and strong reducing agent, it has a wide range of applications.

While strong oxidizing agent oxidize iodide (I^-) to iodine (I_2), strong reducing agents reduce iodine to iodide.

Since solubility of iodine in water is very low, KI is added to dissolve it by formation of I_3^- (triiodide) complex:

$I_2 + I^- \rightarrow I_3^-$

Since triiodide/iodide (I_3^-/I^-) pair has same reduction potential with iodine/iodide (I_2/I^-) pair (0.54 V), I_2 can be written instead of I_3^- for avoiding confusion.
There are two type of iodine titrations:
Iodimetry (Direct method)
Iodometry (Indirect method)
Iodimetry (Direct method): In this method, a reducing agent is titrated with a standard iodine solution. Reaction medium either neutral or mild acidic. The analytes having standard reduction potentials lower than iodine/iodide pair are oxidized by iodine.

Iodometry (Indirect method): In this method, excess of iodide (I^-) is added on an oxidizing agent (analyte) and iodine (I_2) is produced depending on the amount of analyte. Then produced iodine is titrated with standard thiosulfate ($S_2O_3^{-2}$) solution. The advantage of this method is that even small amount of iodine can be easily observed because of the color of iodine.

Iodine reactions are not favored in alkali medium because internal redox reaction (the oxidized and reduced elements originate in the same compound) can be observed in alkali medium.

Starch is the indicator in iodine titrations. Starch and iodine form a complex having strong blue color. In iodimetry, end point is observed by blue color formation which is the result of starch-iodine complex after all analyte is consumed and unreduced iodine exist in the medium. On the other hand, in iodometry, since at the beginning of the titration there is iodine in the medium, blue color is observed at first. Then at the end point, since all iodine is reduced, blue color disappears.

Standardization of iodine

Iodine solution is standardized with arsenite (AsO_3^{-3})
Transfer 10 mL of arsenite with known concentration to an erlenmeyer flask.
Add 1g of $NaHCO_3$.
Titrate with iodine and add 1 mL of starch solution approaching the end point (ask your TA). continue to titrate until blue.

METAMIZOLE SODIUM DETERMINATION

Since metamizole sodium is unstable in water, a small amount of water is used for dissolving metamizole sodium and the titration is performed quickly. The reaction between metamizole sodium and iodine is an addition reaction.

Experimental procedure:

Weight ten tablets that were given to your group and calculate the amount equivalent to one tablet.

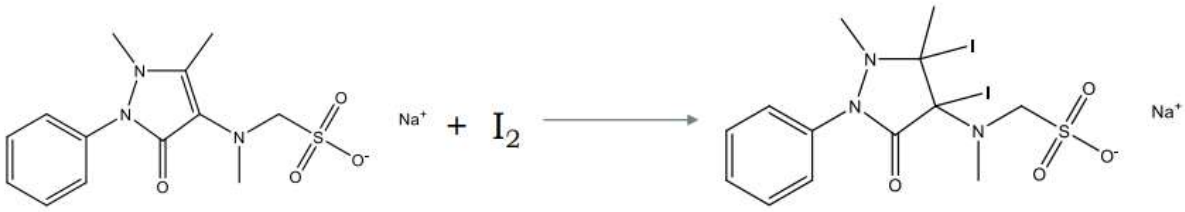
Ground ten tablets in a mortar and transfer the amount equivalent to one tablet to an erlenmeyer flask.

Add 5 mL of distilled water and 5 mL of 0.02 M HNO_3 and begin titration with iodine solution without waiting.

Approaching to the end point (ask your TA), add 1 mL of starch solution.

Continue titration until 2 min stable violet color is obtained.

Reaction equation:



Calculations:

The amount (mg) of metamizole sodium in one tablet will be calculated ($MW_{metamizole\ sodium} = 352$ g/mol)

First, the moles of iodine consumed during titration can be calculated from the following equation using the volume of iodine that is consumed in the titration and the molarity of the iodine.

$$n_{iodine} = M_{iodine} \times V_{iodine}$$

According to reaction equation:

If 1 mol iodine reacts with 1 mol metamizole sodium

n_{iodine} x mol metamizole sodium

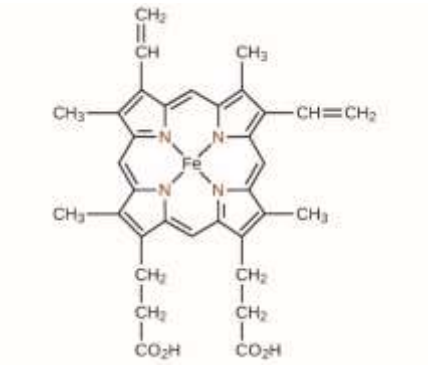
From this ratio, the mol of metamizole sodium in the reaction ($x = n_{metamizole\ sodium}$) is the mol of pure metamizole sodium in the weighed amount. Using this mol (x), the mass of metamizole sodium in the weighed sample (one tablet amount) can be calculated.

$$m_{metamizole\ sodium} = x \times MW_{metamizole\ sodium}$$

COMPLEXOMETRIC TITRATIONS

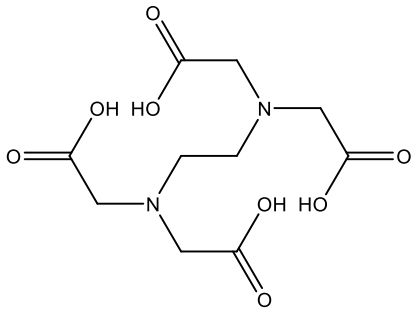
Complex is an ensemble of one or more central atom (usually metals) and ligands that surround the central atom. They are called as mononuclear complex (one central atom) or polynuclear complex (more than one central atom) depending on the number of central atoms.

If a ligand contains more than one electron donating group, those groups can coordinate with same central atom and this type of complexes are called chelate complexes. For example, protoporphyrin – Fe^{+2} is a chelate complex. This complex is also called «heme» and it forms hemoglobin with globin.



Heme complex

EDTA TITRATIONS



EDTA (Ethylene Diamine Tetra Acetic Acid)

EDTA coordinate with +2 and +3 charged cations with a 1:1 mol ratio. EDTA forms hexadentate complexes using its six unpaired electrons (two on nitrogens and four on carboxyls).

EDTA is commercially sold as water-soluble sodium salt ($Na_2H_2Y.2H_2O$). Regardless of the charge of central atoms, $2H^+$ is produced in EDTA coordination:

$$M^{+2} + H_2Y^{-2} \leftrightarrow MY^{-2} + 2H^+$$

$$M^{+3} + H_2Y^{-2} \leftrightarrow MY^{-} + 2H^+$$

Metal titration indicators are used in EDTA titrations. Color of the metal titration indicators depend on the existence of free metal in the medium. Eriochrome black T, murexide, pyrocatechol violet, variamine blue, xylenol orange and fast sulfone black can be given as examples for metal titration indicators.

Ca^{2+} EDTA TITRATION

Experimental procedure:

Dilute the sample to 100 mL with distilled water and transfer 20 mL of diluted sample to erlenmeyer flask.

Add 10 mL of pH 10 buffer in erlenmeyer flask followed by 50 mL distilled water.

Add 2 drops of Eriochrome black T indicator. Eriochrome black T forms a red colored complex with free calcium in the erlenmeyer flask.

Titrate with EDTA until blue color occures. Blue color formation shows that all calcium forms complex with EDTA and free eriochrome black T gives its blue color to the solution.

Calculations:

Calculate the concentration of the Ca^{2+} of the sample in g/L. ($MW_{Ca^{2+}}$= 40 g/mol)

Firstly, calculate the moles of reacted EDTA using the molarity of EDTA and the volume of EDTA used in the titration:

$$n_{EDTA} = M_{EDTA} \times V_{EDTA}$$

According to the reaction:

If 1 mol EDTA reacts with 1 mol Ca^{2+}

n_{EDTA} mol EDTA reacts with *x* mol Ca^{2+}

Calculate the moles of diluted Ca^{2+} ($x = n_{Ca^{2+}}$) is using above proportion. Using *x*, calculate the molarity of diluted Ca^{2+}:

$$M_{Ca^{2+}} = \frac{x}{V_{Ca^{2+}}}$$

Calculate the molarity of sample by multiplying the molarity of diluted sample with dilution factor:

$$M_{sample} = M_{Ca^{+2}} \times DF$$

Finally, convert the molarity of sample to concentration in g/L:

$$C(g/L) = M_{sample} \times 40$$

PRECIPITATION TITRATIONS

A titration in which the analyte and titrant form an insoluble precipitate called precipitation titration.

ARGENTOMETRIC Cl^- DETERMINATION

The most used technique for the determination of chloride is argentometry. There are three different types of indicator in argentometric titrations. Depending on these indicators the methods can be named as: Mohr, Volhard, Fajans. The most useful one is Mohr method which is based on the precipitation of chloride ions are with silver ions.

Experimental procedure:

Add 20 mL of distilled water and 2 drops of 10% K_2CrO_4 to the 20 mL sample solution. Add pinches of spatula from $NaHCO_3$ and wait until the gas outlet is finished. Put 0.1 M standardized $AgNO_3$ to the burette. Achieve titration till the pink color is observe.

Since the silver chromate solubility product is smaller than the silver chloride solubility product, all chromates are precipitated as silver chloride, provided that the chromate concentration is kept small, then the silver chromate precipitates. (Ag_2CrO_4 for $K_{sp}= 2x10^{-12}$, AgCI for $K_{sp} = 1.56x10^{-10}$)

After precipitating all the Cl^- ions in the medium with Ag^+ ions as AgCl, the Ag^+ ions in the medium are combined with CrO_4^{-2} to form a red-brown color silver chromate ($AgCrO_4$).

$$2AgNO_3 + K_2CrO_4 \longrightarrow Ag_2CrO_4 + 2KNO_3 \text{ (Indicator reaction)}$$

Titration should be done at room temperature as the solubility of Ag_2CrO_4 increases rapidly in the hot. The pH of the medium is also important in this experiment. In acidic solutions, the chromate is converted into bichromate.

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

Reaction equation:

$$AgNO_3 + NaCl \longrightarrow AgCI + NaNO_3$$

Calculations:

The sodium chloride concentration in the original sample will be calculated in g/L. ($MW_{NaCl} = 58.5$ g/mol)

First, the moles of $AgNO_3$ consumed during titration can be calculated from the following equation using the volume of $AgNO_3$ that is consumed in the titration and the molarity of the $AgNO_3$.

$$n_{AgNO_3} = M_{AgNO_3} \times V_{AgNO_3}$$

According to reaction equation:

If 1 mol $AgNO_3$ is reacted with 1 mol NaCl

n_{AgNO_3} x mol NaCl

From this ratio, the moles of NaCl in the diluted sample ($x = n_{NaCl}$) is calculated and the molarity of the diluted sample is calculated from *x*.

$$M_{NaCl} = \frac{x}{V_{NaCl}}$$

The molarity of the original sample (M_{sample}) can then be calculated by multiplying the molarity of the diluted sample by the dilution factor.

$$M_{sample} = M_{NaCl} \times DF$$

Finally, the molarity is multiplied by the molecular weight to convert the concentration of the original sample to g/L:

$$C(g/L) = M_{sample} \times 58.5$$