

2. VOLUMETRY (TITRIMETRY)

Volumetry is an analytical method based on the measurement of solution volume consumed in the reaction of solution with known concentration of solution of substance to be analyzed and another substance capable of reacting with this substance. Because the process is based on titration, it is also called **titrimetry**.

In order for a reaction to be used in volumetric analysis,

1. Reaction should be expressed by a single and simple equation.
2. Reaction should be fast enough.
3. At the point where the reaction called the equilibrium point is completed, the observable physical or chemical change should occur. If this does not occur, the substances that show observable change at equivalent points and that are called indicators should be used.
4. The amount of substance balanced in the equivalent point should be at most 1/1000 of the initial amount.

In titrimetric analysis, the solution with known concentration is called **standard solution**, **adjusted solution or titrant**, the substance that is titrated with the standard solution and the amount is desired to be determined is called **analyte**. The standard solution, which is usually filled in the buret, is added drop by drop to the solution containing the substance to be analyzed in Erlenmeyer. At this time, the Erlenmeyer containing analysis solution is mixed by shaking and the reaction is allowed to take place everywhere. The upper limits of the standard solution in buret are read before process begins and after the reaction is completed. The difference between two levels is found as the volume used for titration (V). Due to the affinity between glass and water molecules, the surface of the solution in the buret is spherical. Volume reading is performed considering the tangent at the lowest point of the spherical surface in colorless solutions and the uppermost part in colored solutions.

To measure the volume of the consumed solution, liter (L) as basic unit of volumetric measurement for liquids or its submultiples (usually milliliter, mL) is used. 1 L is the volume of 1 kg (in the air) consumed water at 4 °C.

Standard solutions at the appropriate dilution and concentration should be used to reduce errors during titration. Depending on the amount of the substance titrated, solutions with concentrations of 1.0 M, 0.1 M, 0.01 M, etc. are usually used. Furthermore, conventional

solutions containing 1 mg/mL analyte and giving the amount of the analyte directly in mg can also be prepared after titration to provide ease calculation.

Standard solutions prepared to be 0.1 M, 0.05 M, 0.01 M etc., cannot be prepared at the exact desired concentration due to reasons such as impurities, weighing errors or decay. Either more concentrated or more diluted solutions than desired are obtained. Therefore, in order to find the actual concentration of the standard solution, the prepared solution should be titrated with the amount of a pure substance (primer standard) weighed sensitively or a specific volume of another solution (secondary standard) with known concentration.

In a volumetric analysis, the process is completed when the standard solution in an amount equivalent to the titrated substance reacts. In order to determine this equivalence point, an indicator appropriate to the medium should be added. At the end of the titration (at the turning point), the amount of standard solution consumed is read from buret. Since the actual concentration of the standard solution is also known, the amount of the substance in it is easily calculated. Since the amount of the standard solution and the amount of the analyte substance are equal in this time, the quantitation of the analyte can be calculated.

Volumetric analyzes are divided into four basic groups, considering the type of reaction occurring during titration:

1) Neutralization Titrations

- a) Acidimetry
- b) Alkalimetry

2) Redox Titrations

A) Oxidimetry (Oxidation-based methods)

- a) Manganometry
- b) Bromometry
- c) Serimetry
- d) Iodometry
- e) Chromometry
- f) Oxidation with iodate

B) Reductimetry (Reduction-based methods)

- a) Titanometry
- b) Iodometry
- c) Reduction with Hipovanadate

d) Reduction with Chromium (II)

3) Precipitation Titrations

4) Complexometric Titrations

2.1. Neutralization Titrations

They include volumetric analyzes, in which the neutralization reactions occur. The determination of the base amount in the sample by titrating with standard acid solution is called “acidimetry”, the determination of the acid amount in the sample with base solution is called “alkalimetry”. The equivalent point of neutralization titrations is determined by the aid of color-changing indicators at a specific pH or potentiometric method.

2.1.1. Acidimetry

Since most of the cations are easily dissolved in water, HCl solution is usually used in the titration. H₂SO₄ solution is used in the presence of chlorine oxidizing agents or it is used when long heating is required.

Preparation of 0.1 M Hydrochloric Acid Solution

Hydrochloric acid is commonly available as a concentrated aqueous solution containing about 37% (w/w) HCl.

Mw: 36.5 g/mol

d_{HCl} = 1.19 g/mL

Mass percentage (w/w): 37%

$$V \text{ mL HCl} = \frac{0.1 \text{ mol HCl}}{1.0 \text{ L HCl}} \cdot \frac{36.5 \text{ g HCl}}{1 \text{ mol HCl}} \cdot \frac{100 \text{ g}}{37 \text{ g}} \cdot \frac{1 \text{ mL}}{1.19 \text{ g}} = 8.29 \text{ mL}$$

II. Solution Route:

While,

1 mole HCl is 36.5 g

0.1 mole HCl is X g

X = 3.65 g HCl

100 g of HCl solution have 37 g HCl, then

X g of HCl solution have 3.65 g HCl

X = 9.86 g of HCl solution is required.

1 mL of HCl solution	is 1.19 g
<u>X mL of solution</u>	<u>is 9.86 g</u>

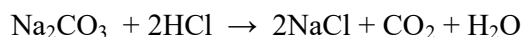
X= 8.29 mL

HCl acid volume calculated is transferred into a volumetric flask, then diluted until 1.0 L with distilled water and mix well.

Standardization of 0.1 M HCl Solution

Since the exact concentration of the concentrated HCl reagent solution cannot be reliably known (the gas fumes out of the solution all the time), the exact concentration of HCl solution is determined by titration with primary or secondary standard chemicals. This solution is to be standardized using anhydrous Na₂CO₃, NaHCO₃, Na₂B₄O₇, HgO or tiosulphate solutions.

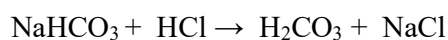
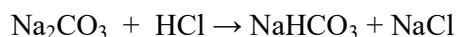
Sodium carbonate is frequently used as a standard material for acid solutions.



Accurately weigh out three 0.1 g samples of dried, anhydrous Na₂CO₃ directly into separate, clean and dry 250 mL conical flasks. Add 50 mL of distilled water to dissolve the carbonate. Rinse 50 mL buret with small portions of your HCl solution and then fill it with the acid solution (record the initial reading). Add 3-5 drops of methyl orange as an indicator to the flask. Carry out a titration by adding the HCl solution prepared from the burette to the conical flask, swirling the flask constantly, until the solution just changes its color from yellow to red. Repeat the titration three times and find the average of volumes. Calculate the real concentration of the HCl solution and write its molar concentration founded on label.

Calculations:

Two end points are observed in the titration of sodium carbonate:



Specimen results:

Average of accurate titres: 10.0 mL

Weight of Na₂CO₃= 0.0500 g

$$0.0500 \text{ g Na}_2\text{CO}_3 = 10.0 \text{ mL HCl} \cdot \frac{\text{X mol HCl}}{1000 \text{ mL HCl}} \cdot \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol HCl}} \cdot \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3}$$

X = 0.0943 M HCl, real concentration of hydrochloric acid solution.

II. Solution Route:

106 g Na₂CO₃ is 1 mole

0.0500 g is X mole.

$$X = 4.72 \times 10^{-4} \text{ mole Na}_2\text{CO}_3$$

According to the reaction above;

1 mole Na₂CO₃ react with 2 mole HCl

4.72x10⁻⁴ mole Na₂CO₃ react with X mole HCl.

$$X = 9.43 \times 10^{-4} \text{ mol HCl}$$

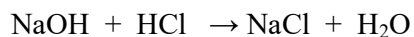
10.0 mL of HCl solution contain 9.43x10⁻⁴ mole HCl, so

1000 mL of HCl solution contain X mole HCl.

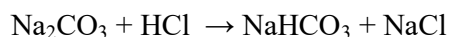
$$X = 0.0943 \text{ mol/L HCl}$$

2.1.1.1. Determination of Sodium Hydroxide-Sodium Carbonate

A. Take your sample which is provided in a 100 mL volumetric flask and add distilled water till the its mark. Shake the solution well and transfer duplicate 25.0 mL samples with pipette into two separate conical flasks. Dilute the samples to 75-100 mL with distilled water. Add 3-5 drops of phenolphthalein indicator (pink color occurs, pH: 8.3). Titrate with standardized HCl solution until the indicator turns colorless. Record the titrant volume where the indicator changes color (V₁).



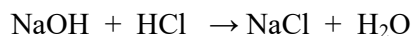
if the volume of HCl solution used in this titration; X mL and



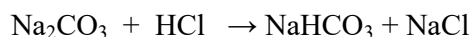
the volume of HCl solution used in this titration; Y mL, then

$$V_1 = X + Y$$

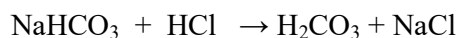
Take another sample containing 25.0 mL of the unknown solution, add 3-5 drops of methyl orange indicator (yellow-orange color, pH: 3.1 - 4.7) and carry the titration until the color turns into red. Boil the solution gently and drive off CO₂. Cool the solution to room temperature under the tap water and carry on the titration till you reach the red end-point. Record again the titrant volume where the indicator changes color (V₂).



if the volume of HCl solution used in this titration; X mL,



the volume of HCl solution used in this titration; Y mL and



again the volume of HCl solution used in this titration; Y mL. Because the mole number of Na₂CO₃ equals to the mole number of NaHCO₃, they require the same volume of HCl solution. If so;

$$V_2 = X + Y + Y$$

Calculations:

In order to titrate NaOH and Na₂CO₃, volumes of standardized HCl solution required:

$$V_{\text{NaOH}} = V_1 - (V_2 - V_1) \quad \text{mL} \quad \{ V_{\text{NaOH}} = (X + Y) - [(X + Y + Y) - (X + Y)] \}$$

$$V_{\text{NaOH}} = X \text{ mL}$$

and

$$V_{\text{Na}_2\text{CO}_3} = 2 \times (V_2 - V_1) \quad \text{mL} \quad \{ V_{\text{Na}_2\text{CO}_3} = 2 \times [(X + Y + Y) - (X + Y)] \}$$

$$V_{\text{Na}_2\text{CO}_3} = 2Y \text{ mL}$$

$$M_{\text{HCl}} = 0.1000 \text{ M}$$

$$M_{\text{WNaOH}} = 40 \text{ g/mol}$$

$$M_{\text{WNa}_2\text{CO}_3} = 106 \text{ g/mol}$$

$$\text{? m NaOH} = X \text{ mL HCl} \cdot \frac{0.1000 \text{ mol HCl}}{1000 \text{ mL HCl}} \cdot \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \cdot \frac{40 \text{ g NaOH}}{1 \text{ mol NaOH}} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

$$? \text{ m Na}_2\text{CO}_3 = 2Y \text{ mL HCl} \cdot \frac{0.1000 \text{ mol HCl}}{1000 \text{ mL HCl}} \cdot \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol HCl}} \cdot \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

II. Solution Route:

The mole number of NaOH:

$$n_{\text{HCl}} = M_{\text{HCl}} \cdot V_{\text{HCl}} = 0.1000 \cdot X = A \text{ mmol HCl}$$

At the end-point, the mole number of HCl equals to the mole number of NaOH; A mmol.

While,

1 mmol NaOH	is 40 mg	If 25 mL of sample	contain 40A mg of NaOH,
A mmol NaOH	is 40A mg.	100 mL of sample	contain 160A mg of NaOH.

The mole number of Na₂CO₃:

$$n_{\text{HCl}} = M_{\text{HCl}} \cdot V_{\text{HCl}} = 0.1000 \cdot 2Y = B \text{ mmol}$$

At the end-point, for B mmol HCl, there is B/2 mmol Na₂CO₃. Because 2 mol HCl react with 1 mol Na₂CO₃ according to the neutralization reaction.

1 mmol Na ₂ CO ₃	is 106 mg	If 25 mL of sample	contain 53B mg of Na ₂ CO ₃ ,
B/2 mmol Na ₂ CO ₃	is 53B mg.	100 mL of sample	contain 4 x 53B mg of Na ₂ CO ₃ .

Report the results in terms of mg of analyte per 100 mL of sample.

B. Only one sample can be used for the titration of these analytes. Take a 25 mL portion of sample, add 3-5 drops of phenolphthalein indicator and titrate the sample with standard HCl until the indicator turns colorless. Record the titrant volume where the indicator changes color (V₁). Afterwards, add 3-5 drops of methyl orange indicator and perform the titration until the color turns into red. Again, note the HCl volume where methyl orange indicator changes color (V₂).

The volumes of HCl solution required for analytes can be calculated as showed below:

$$V_{\text{NaOH}} = V_1 - V_2 \quad \text{mL} \quad \{ V_{\text{NaOH}} = (X + Y) - (Y) \}$$

$$V_{\text{NaOH}} = X \quad \text{mL} \quad \text{and}$$

$$V_{\text{Na}_2\text{CO}_3} = 2 \times V_2 \quad \text{mL} \quad \{ V_{\text{Na}_2\text{CO}_3} = 2 \times Y \}$$

$$V_{\text{Na}_2\text{CO}_3} = 2Y \quad \text{mL}$$

Similarly, the amounts of the analytes can be calculated as described above.

2.1.2. Alkalimetry

Standard base solutions are prepared using NaOH, KOH or Ba(OH)₂. Because it is cheap, the most used base solution is NaOH. However, due to its dissolution in alcohol, KOH is used for titration in alcoholic medium and Ba(OH)₂ solution is used for titration of organic acids.

Preparation of 0.1 M Sodium Hydroxide Solution

Solid NaOH is highly hygroscopic (it absorbs water from the air) and thus it cannot be accurately weighed. It also absorbs carbon dioxide from the air, forming sodium carbonate and thereby reducing the amount of sodium hydroxide present. This means that a NaOH solution of known molarity cannot be directly prepared without resorting to an air-and-water-free environment. In cases like this we need to use an acid as the primary standard (potassium hydrogen phthalate) or an acid solution as the secondary standard (standardized HCl solution) to determine the exact concentration of the NaOH solution.

NaOH quantity (m_{NaOH} , g), which is required to prepare 1.0 L 0.1 M solution, is calculated as follows:

$$m_{\text{NaOH}} = \frac{0.1 \text{ mol NaOH}}{1 \text{ mol NaOH}} \cdot 40 \text{ g NaOH}$$

$$m_{\text{NaOH}} = 4 \text{ g NaOH}$$

Weigh out 4 g NaOH and dissolve the base in some distilled water. Then transfer the solution to 1.0 L volumetric flask and make up the volume to 1.0 L with distilled water.

Standardization of 0.1 M NaOH Solution using a Standard Solution of HCl

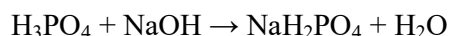
Pipette 10.0 mL of standardized HCl solution into a flask and add 3-4 drops of methyl orange or phenolphthalein indicator. Fill the burette with NaOH solution prepared and the titrant is slowly added to the solution being titrated until the indicator changes color. Repeat the titration with at least three samples, record the average off all titrations and calculate the real molarity of the NaOH solution as stated below. Record the value on the bottle label.

$$M_{\text{HCl}} \cdot V_{\text{HCl}} = M_{\text{NaOH}} \cdot V_{\text{NaOH}}$$

2.1.2.1. Determination of Phosphoric Acid-Disodium Hydrogen Phosphate

Although phosphoric acid often listed together with strong mineral acids (hydrochloric, nitric and sulfuric) it is relatively weak, with $pK_{a1}=2.15$, $pK_{a2}=7.20$ and $pK_{a3}=12.35$. That means titration curve contains only two inflection points and phosphoric acid can be titrated either as a monoprotic acid or as a diprotic acid. In the first case acid has to be titrated against indicator changing color around pH 4.7 (for example methyl orange), in the second case - against indicator changing color around pH 9.6 (for example thymolphthalein). Phenolphthalein can't be used for only H_3PO_4 , as it starts to change color around pH 8.2, when phosphoric acid is titrated in about 95%.

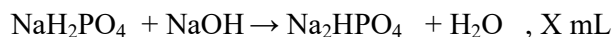
Transfer 25.0 mL sample with pipette into a conical flask. Dilute the sample to 75-100 mL with distilled water. Add 3-4 drops of methyl orange indicator. Titrate with standardized NaOH solution till the first color change. Record the titrant volume where the indicator changes color (V_1).



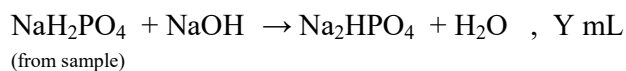
if the volume of NaOH solution used in this titration; X mL, then

$$V_1 = X \text{ mL}$$

Take another sample containing 25 mL of the sample solution, add 3-4 drops of phenolphthalein indicator and carry out the titration until the color turns into pink. Record again the titrant volume where the indicator changes color (V_2).



$$V_{H_3PO_4} = X + X = 2X \text{ mL},$$



$$V_{NaH_2PO_4} = Y \text{ mL}$$

$$V_2 = V_{H_3PO_4} + V_{NaH_2PO_4}$$

$$V_2 = 2X + Y$$

Calculations:

In order to titrate H_3PO_4 and NaH_2PO_4 , volumes of standard NaOH solution required:

$$V_{\text{H}_3\text{PO}_4} = 2V_1 = 2X \text{ mL},$$

$$V_{\text{NaH}_2\text{PO}_4} = V_2 - 2V_1 = (2X + Y) - 2X = Y \text{ mL}$$

The amounts of the analytes can be calculated as follows:

$$M_{\text{NaOH}} = 0.1000 \text{ M}$$

$$M_{\text{H}_3\text{PO}_4} = 98 \text{ g/mol}$$

$$M_{\text{NaH}_2\text{PO}_4} = 120 \text{ g/mol}$$

$$\text{? m H}_3\text{PO}_4 = 2X \text{ mL NaOH} \cdot \frac{0.1000 \text{ mol NaOH}}{1000 \text{ mL NaOH}} \cdot \frac{1 \text{ mol H}_3\text{PO}_4}{2 \text{ mol NaOH}} \cdot \frac{98 \text{ g H}_3\text{PO}_4}{1 \text{ mol H}_3\text{PO}_4} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

$$\text{? m NaH}_2\text{PO}_4 = Y \text{ mL NaOH} \cdot \frac{0.1000 \text{ mol NaOH}}{1000 \text{ mL NaOH}} \cdot \frac{1 \text{ mol NaH}_2\text{PO}_4}{1 \text{ mol NaOH}} \cdot \frac{120 \text{ g NaH}_2\text{PO}_4}{1 \text{ mol NaH}_2\text{PO}_4} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

II. Solution Route:

The mole number of H_3PO_4 :

$$n_{\text{NaOH}} = M_{\text{NaOH}} \cdot V_{\text{NaOH}} = 0.1000 \cdot 2X = A \text{ mmol NaOH}$$

At the end-point, for A mmol NaOH, there is A/2 mmol H_3PO_4 .

1 mmol H_3PO_4	is 98 mg	If 25 mL of sample	contain 49A mg H_3PO_4 ,
A/2 mmol H_3PO_4	is 49A mg.	100 mL of sample	contain 4 x 49A mg H_3PO_4 .

The mole number of NaH_2PO_4 :

$$n_{\text{NaOH}} = M_{\text{NaOH}} \cdot V_{\text{NaOH}} = 0.1000 \cdot Y = B \text{ mmol NaOH}$$

At the end-point, the mole number of NaOH equals to the mole number of NaH_2PO_4 ; B mmol.

While,

1 mmol NaH_2PO_4	is 120 mg	If 25 mL of sample	contain 120B NaH_2PO_4 ,
B mmol NaH_2PO_4	is 120B mg.	100 mL of sample	contain 4 x 120B mg NaH_2PO_4 .

Report the results in terms of mg of analyte per 100 mL of sample.

2.2. Redox Titrations

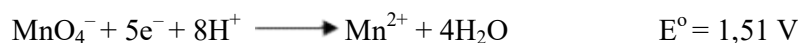
When electrons are transferred from one atom to another in the substances reacting during a reaction, such reactions are called redox reactions. In a redox reaction, the element-losing electron is oxidized, while the element-gaining electron is reduced. The substances containing an element that losses electron are defined as reducing agent, the substances containing an element that gains electron are defined as oxidizing agent. A substance in the low oxidation step in the solution is converted to the compound in the higher oxidation step by reacting with an oxidizing agent. The amount of reducing agent is calculated using the concentration of the oxidizing agent solution and the volume consumed in the titration. Similar calculations apply for the amount of oxidizing agent.

Titration performed by oxidation and reduction reactions are called redox titration. If the solution used in the titration is an oxidizing agent solution, the analytical method is called oxidimetry, if the solution used in the titration is a reducing agent solution, the analytical method is called reductimetry.

2.2.1. Manganometry

Redox titrations using potassium permanganate are called manganometry. Potassium permanganate is a strong oxidizing. Depending on pH of the medium, the reactions can be as follows:

a) In strong acidic mediums



b) In weak acidic, weak basic and neutral mediums



c) In strong basic mediums



The permanganate solution is one of the most preferred solutions for redox titrations, due to the reasons such as the ability to oxidize even weaker reducing agents and no need for an indicator to show the turning point during titration.

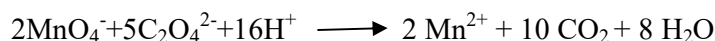
Preparation of 0.02 M Potassium Permanganate Solution

Weigh out 3.16 g of KMnO_4 (Mw: 158 g/mol) and dissolve it in 1.0 L of distilled water. Heat to boiling and keep hot for about 15-30 min. After cooling, filter the solution through a fine-porosity filtering crucible. Transfer the solution to a clean glass-stoppered dark bottle and keep away from sunlight.

Standardization of 0.02 M KMnO_4 Solution with Sodium Oxalate

As_2O_3 , KI, iron wire, $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, $\text{Na}_2\text{C}_2\text{O}_4$ or $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ can be used to determine the exact concentration of the KMnO_4 solution.

Dry $\text{Na}_2\text{C}_2\text{O}_4$ for at least 1 h at $105\text{--}110^\circ\text{C}$ and cool in a desiccator. Dissolve 0.1 g of the dried $\text{Na}_2\text{C}_2\text{O}_4$ in 50 mL of distilled water in a conical flask. Transfer 10.0 mL of 1.0 M H_2SO_4 solution and heat the content of the flask up to $80\text{--}90^\circ\text{C}$. Titrate until the single drop of potassium permanganate is enough for the solution to get purple. If the amount of acid is not enough, brown precipitate of MnO_2 can be formed. Repeat the titration with at least three samples, record the average off all titrations and calculate the real molarity of the KMnO_4 solution as stated below. Record the value on the bottle label.



Calculations:

Chemical reaction above is observed in the titration of $\text{Na}_2\text{C}_2\text{O}_4$ with KMnO_4 under acidic conditions.

Specimen results:

Average of accurate titres (V_{KMnO_4}): 15.0 mL

Weight of $\text{Na}_2\text{C}_2\text{O}_4$ = 0.1000 g

$$0.1000 \text{ g Na}_2\text{C}_2\text{O}_4 = 15.0 \text{ mL KMnO}_4 \cdot \frac{X \text{ mol KMnO}_4}{1000 \text{ mL KMnO}_4} \cdot \frac{5 \text{ mol Na}_2\text{C}_2\text{O}_4}{2 \text{ mol KMnO}_4} \cdot \frac{134 \text{ g Na}_2\text{C}_2\text{O}_4}{1 \text{ mol Na}_2\text{C}_2\text{O}_4}$$

X = 0.0198 M KMnO_4 , real concentration of the solution.

II. Solution Route:

While,

134 g $\text{Na}_2\text{C}_2\text{O}_4$ is 1 mol

0.1000 g is X mol.

$$X = 7.46 \times 10^{-4} \text{ mol Na}_2\text{C}_2\text{O}_4$$

According to the reaction above;

$$\begin{array}{ll} 2 \text{ mol of KMnO}_4 & \text{react with 5 mol of C}_2\text{O}_4^{2-}, \text{ then} \\ \underline{X \text{ mol of KMnO}_4} & \underline{\text{react with } 7.46 \times 10^{-4} \text{ mol C}_2\text{O}_4^{2-}.} \end{array}$$

$X = 2.98 \times 10^{-4} \text{ mol}$ of KMnO_4 is required.

$$\begin{array}{ll} 15.0 \text{ mL of KMnO}_4 \text{ solution} & \text{have } 2.98 \times 10^{-4} \text{ mol of KMnO}_4 \\ \underline{1000 \text{ mL of KMnO}_4 \text{ solution}} & \underline{\text{have } X \text{ mol of KMnO}_4.} \end{array}$$

$$X = 0.0198 \text{ mol/L KMnO}_4 = 0.0198 \text{ M KMnO}_4$$

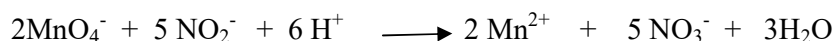
2.2.1.1. Determination of Nitrite Ion

Nitrite ion under acidic conditions transforms as follows:



In order to prevent its transformation, acid solution can be added to the titrant.

Transfer 5.0 mL of standard KMnO_4 solution to a conical flask, dilute it with 50 mL of distilled water and add 5.0 mL of 1.0 M H_2SO_4 solution. Fill the burette with nitrite sample and titrate the KMnO_4 solution with sample solution until the solution changes its color from purple to colorless. Repeat the titration at least three times and record the average of the sample volumes consumed.



Calculations:

Calculate the amount of nitrite according to chemical reaction above.

Specimen results:

Average of the sample volumes consumed: 10.0 mL

$$M_{\text{KMnO}_4} = 0.0200 \text{ M}$$

$$V_{\text{KMnO}_4} = 5.0 \text{ mL}$$

$$M_{\text{WNO}_2} = 46 \text{ g/mol}$$

While,

For 10 mL of nitrite sample are required 5.0 mL of KMnO_4 solution
for 100 mL X mL

X = 50 mL of KMnO_4 solution are required.

$$? m_{\text{NO}_2^-} = 50 \text{ mL } \text{KMnO}_4 \cdot \frac{0.0200 \text{ mol } \text{KMnO}_4}{1000 \text{ mL } \text{KMnO}_4} \cdot \frac{5 \text{ mol } \text{NO}_2^-}{2 \text{ mol } \text{KMnO}_4} \cdot \frac{46 \text{ g } \text{NO}_2^-}{1 \text{ mol } \text{NO}_2^-}$$

$$m_{\text{NO}_2^-} = 115 \text{ mg/100mL}$$

II. Solution Route:

While,

1000 mL of KMnO_4 solution have 0.0200 mol of KMnO_4 ,

50 mL of KMnO_4 solution have X mol of KMnO_4 .

$$X = 1 \times 10^{-3} \text{ mol } \text{KMnO}_4$$

According to the reaction occurred,

2 mol KMnO_4 react with 5 mol NO_2^- , then

$1 \times 10^{-3} \text{ mol } \text{KMnO}_4$ react with X mol NO_2^- .

$$X = 2.5 \times 10^{-3} \text{ mol } \text{NO}_2^-$$

1 mol NO_2^- is 46 g

$2.5 \times 10^{-3} \text{ mol } \text{NO}_2^-$ is X g.

$$X = 0.115 \text{ g} = 115 \text{ mg } \text{NO}_2^- / 100 \text{ mL}$$

2.2.1.2. Determination of Manganese by Volhard's Volumetric Method

Volhard's volumetric method for manganese is based upon the following reaction which takes place in a hot neutral solution.



ZnO , a water-immiscible base, is added for the purpose of providing a neutral solution, since it reacts hydronium ions. Zn^{2+} cation formed is also absorbed by MnO_2 .

Pipette 25.0 mL of sample solution into a conical flask, dilute it with 50 mL of distilled water and add 1 spoon of ZnO . Heat the content of the flask up to 80-90 °C. Fill the burette with KMnO_4 solution and the titrant is slowly added to the sample solution until the solution

changes its color from colorless to purple. Repeat the titration at least three times and record the average of titrant volumes consumed.

Calculations:

Calculate the amount of manganese according to chemical reaction above.

Specimen results:

Average of the titrant volumes consumed (V_{KMnO_4}): 5.0 mL

$M_{\text{KMnO}_4} = 0.0200 \text{ M}$

$M_{\text{W}_{\text{Mn}}} = 55 \text{ g/mol}$

$$? \text{ m}_{\text{Mn}^{2+}} = \frac{5.0 \text{ mL KMnO}_4 \cdot 0.0200 \text{ mol KMnO}_4}{1000 \text{ mL KMnO}_4} \cdot \frac{3 \text{ mol Mn}^{2+}}{\text{mol KMnO}_4} \cdot \frac{55 \text{ g Mn}^{2+}}{1 \text{ mol Mn}^{2+}} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

$$? = 33 \text{ mg Mn}^{2+}/100 \text{ mL}$$

II. Solution Route:

While,

1000 mL of KMnO_4 solution have 0.0200 mol of KMnO_4 ,

5.0 mL of KMnO_4 solution have X mol of KMnO_4 .

$$X = 1 \times 10^{-4} \text{ mol KMnO}_4$$

According to the reaction occurred,

2 mol MnO_4^- react with 3 mol Mn^{2+} , then

$1 \times 10^{-4} \text{ mol MnO}_4^-$ react with X mol Mn^{2+} .

$$X = 1.5 \times 10^{-4} \text{ mol Mn}^{2+}$$

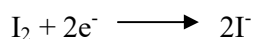
1 mol Mn^{2+} is 55 g 25 mL contain 8.25 mg of Mn^{2+} , then

$1.5 \times 10^{-4} \text{ mol Mn}^{2+}$ is X g. $\frac{100 \text{ mL}}{\text{contain X mg of Mn}^{2+}}$.

$$X = 8.25 \times 10^{-3} \text{ g Mn}^{2+} = 8.25 \text{ mg Mn}^{2+} \quad X = 33 \text{ mg Mn}^{2+}/100 \text{ mL}$$

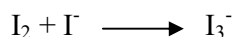
2.2.2. Iodometry

Iodine, which is an oxidizing agent, reduces itself to iodide while oxidizing others in its reactions.

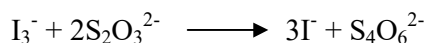


Titration using adjusted iodine solution is called iodimetry, the titration using quantitation of an oxidant performed by titration of iodine, which results from reaction of an oxidizing agent with iodide, with thiosulphate solution is called iodometry.

For quantitation of an oxidizing analyte in iodometric titrations, the medium is first acidified and then excess KI is added. In the presence of the oxidizing agent, iodide is oxidized to iodine. The emerging iodine reacts with excess iodide and forms highly soluble triiodide in water:



When the emerging triiodide/iodine is titrated with the adjusted thiosulfate solution,



Iodine is reduced to iodide according to the reaction, while thiosulfate is oxidized to tetrathionate. The equivalent amount of thiosulfate solution consumed at the end of the titration is equal to the oxidizing analyte and the quantitation is carried out based on this equation.

Starch is used as an indicator in iodometric titrations. However, as the starch decays in the acidic medium, it should be added to the medium at the end of the titration. When red-brown color resulting from iodine turns into yellow during titration, the starch should be added to the medium and the titration with thiosulfate solution should be continued until the blue color is removed.

Preparation of 0.1 M Sodium Thiosulphate Solution

Weigh about 24.82 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; $M_A=248.19$ g/mol) into a conical flask, dissolve with distilled water, transfer to a 1.0 L volumetric flask and dilute to mark with distilled water and mix well.

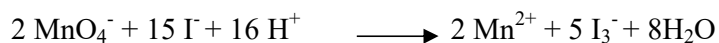
Standardization of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ Solution

$\text{Na}_2\text{S}_2\text{O}_3$ is not a primary standard and thus a freshly prepared solution of this chemical must be standardized. For this purpose, primary standards ($\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , KBrO_3 or pure copper wire) or standardized solutions as the secondary standard (standardized KMnO_4 or iodine solutions) can be used to determine the exact concentration of the $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Weigh about 1 g of KI and transfer to a 250 mL conical flask. Dissolve in 50 mL of distilled water and add 2.0 mL of concentrated HCl solution. Mix well until the KI dissolves. Transfer 5.0 mL of standard KMnO_4 solution to the conical flask. Cover the flask with a watch glass and store in the dark for 10 min in order to complete the reaction.

Fill the burette with $\text{Na}_2\text{S}_2\text{O}_3$ solution prepared and after 10 min, titration is carried out until the single drop of $\text{Na}_2\text{S}_2\text{O}_3$ makes the solution colorless. Repeat the titration at least three times, find the average of titrant volumes and calculate the real molarity of the $\text{Na}_2\text{S}_2\text{O}_3$ solution. Record the value on the bottle label.

Chemical reactions occurred between KMnO_4 and KI and during titration may be represented as:



There is this equation at the end point:

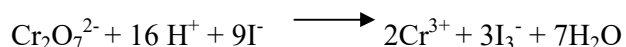
$$M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = M_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3}$$

2.2.2.1. Determination of Dichromate Ion

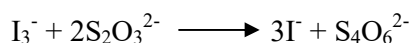
Transfer 10.0 mL of sample solution to a conical flask and dilute with distilled water about 50 mL. Add 1.0 mL of concentrated HCl solution and 1 spoon of KI. The flask is covered with watch glass and allowed to stand for 5 min to allow the reaction to complete in the dark. After 5 min, the solution will turn a dark-brown color and immediately titrate it with the standardized thiosulfate solution. When the color of the solution becomes very pale yellow add 1 mL of starch indicator. Continue the titration until the blue color of the starch complex just disappears. Repeat the titration at least three times and find the average of titrant volumes.

Calculations

Chemical reaction occurred between dichromate ion and iodide;



The following reaction takes place during titration;



Calculate the amount of dichromate ion according to chemical reaction above.

Specimen results:

Average of the titrant volumes consumed ($V_{\text{Na}_2\text{S}_2\text{O}_3}$): 10.0 mL

$M_{\text{Na}_2\text{S}_2\text{O}_3} = 0.1000 \text{ M}$

$M_{\text{Cr}_2\text{O}_7^{2-}} = 216 \text{ g/mol}$

$$? \text{ m Cr}_2\text{O}_7^{2-} = 10.0 \text{ mL Na}_2\text{S}_2\text{O}_3 \cdot \frac{0.1000 \text{ mol Na}_2\text{S}_2\text{O}_3}{1000 \text{ mL Na}_2\text{S}_2\text{O}_3} \cdot \frac{1 \text{ mol Cr}_2\text{O}_7^{2-}}{6 \text{ mol Na}_2\text{S}_2\text{O}_3} \cdot \frac{216 \text{ g Cr}_2\text{O}_7^{2-}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} \cdot 10$$

$$? = 360 \text{ mg Cr}_2\text{O}_7^{2-}/100 \text{ mL}$$

II. Solution Route:

While,

1000 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution have 0.1000 mol of $\text{Na}_2\text{S}_2\text{O}_3$

10.0 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution have X mol.

$$X = 1 \times 10^{-3} \text{ mol Na}_2\text{S}_2\text{O}_3$$

6 mol $\text{S}_2\text{O}_3^{2-}$ react with 1 mol $\text{Cr}_2\text{O}_7^{2-}$, then

$1 \times 10^{-3} \text{ mol S}_2\text{O}_3^{2-}$ react with X mol $\text{Cr}_2\text{O}_7^{2-}$.

$$X = 1.667 \times 10^{-4} \text{ mol Cr}_2\text{O}_7^{2-}$$

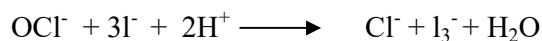
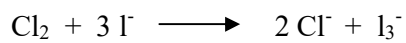
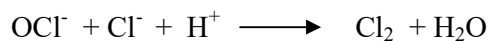
1 mol $\text{Cr}_2\text{O}_7^{2-}$ is 216 g If 10 mL of sample contain 36 mg $\text{Cr}_2\text{O}_7^{2-}$,

$1.667 \times 10^{-4} \text{ mol Cr}_2\text{O}_7^{2-}$ is X g. 100 mL of sample contain X mg $\text{Cr}_2\text{O}_7^{2-}$.

$$X = 3.6 \times 10^{-2} \text{ g Cr}_2\text{O}_7^{2-} = 36 \text{ mg Cr}_2\text{O}_7^{2-} \quad X = 360 \text{ mg Cr}_2\text{O}_7^{2-}/100 \text{ mL}$$

2.2.2.2. Determination of Active Chlorine in Hypochlorite Solution

Chlorine (Cl_2) is a gas, toxic, non-flammable and an economically available oxidizing agent that provides properties desirable in disinfection usage. Chlorine is available in one of three forms: sodium hypochlorite, calcium hypochlorite and liquid chlorine. Sodium hypochlorite, commonly called “liquid bleach”, is commercially available in strengths approximately 15% by weight. Calcium hypochlorite, generally referred to as “powder chlorine”. It contains 70% available chlorine. Liquid chlorine, known also as “chlorine gas”, is chlorine in its elemental form. When comparing elemental chlorine as an oxidizing agent to powder (calcium hypochlorite) or solution (sodium hypochlorite), the oxidizing effect is the same. All of them oxidize iodide to I_2 in acidic media.



The thiosulfate ion reacts with I_3 producing iodide ions:



Take your sample which is provided in a 100 mL volumetric flask and add distilled water till the its mark. Shake the solution well and transfer 25.0 mL of sample with pipette into a conical flask. Add 1.0 mL of 0.1 M HCl solution and 1 spoon of KI. The flask is covered with watch glass and store in the dark for 5-10 min.

Titrate with standardized $\text{Na}_2\text{S}_2\text{O}_3$ solution until the color of the sample solution disappears. Repeat the titration at least three times and find the average of titrant volumes.

Calculations:

Specimen results:

Average of the titrant volumes consumed ($V_{\text{Na}_2\text{S}_2\text{O}_3}$): 10.0 mL

$M_{\text{Na}_2\text{S}_2\text{O}_3} = 0.1000 \text{ M}$

$M_{\text{WCl}_2} = 71 \text{ g/mol}$

? m $\text{Cl}_2 = 10.0 \text{ mL Na}_2\text{S}_2\text{O}_3 \cdot \frac{0.1000 \text{ mol Na}_2\text{S}_2\text{O}_3}{1000 \text{ mL Na}_2\text{S}_2\text{O}_3} \cdot \frac{1 \text{ mol Cl}^-}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} \cdot \frac{71 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$

? = 142 mg $\text{Cl}_2/100 \text{ mL}$

II. Solution Route:

While,

1000 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution have 0.1000 mol of $\text{Na}_2\text{S}_2\text{O}_3$

10.0 mL $\text{Na}_2\text{S}_2\text{O}_3$ solution have X mol.

$X = 1 \times 10^{-3} \text{ mol Na}_2\text{S}_2\text{O}_3$

If 2 mol $\text{S}_2\text{O}_3^{2-}$ react with 1 mol Cl^- ,

$1 \times 10^{-3} \text{ mol S}_2\text{O}_3^{2-}$ react with X mol Cl^- .

$X = 5 \times 10^{-4} \text{ mol Cl}^-$

$$\begin{array}{ll}
 1 \text{ mol Cl}_2 & \text{is 71 g} \\
 5 \times 10^{-4} \text{ mol Cl}_2 & \text{is X g.} \\
 X = 3,55 \times 10^{-2} \text{ g Cl}_2 & = 35,5 \text{ mg Cl}_2
 \end{array}$$

$$\begin{array}{ll}
 \text{If 25 mL} & \text{contain 35.5 mg Cl}_2, \\
 100 \text{ mL} & \text{contain X mg Cl}_2. \\
 X = 142 \text{ mg Cl}_2 / 100 \text{ mL}
 \end{array}$$

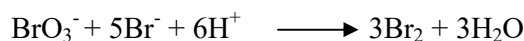
2.2.3. Bromometry

The relatively high standard oxidation strength of a redox couple $\text{BrO}_3^-/\text{Br}^-$ system ($E^0 = +1,44 \text{ V}$) indicates that potassium bromate is a strong oxidizing agent. The bromate is quantitatively reduced to bromine in the direct titration of the reducing agents in sufficient strength with potassium bromate in an acidic medium and the following reaction takes place:

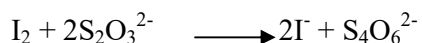
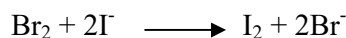


As (III), Sb (III), Sn (II), Tl (I), $\text{Fe}(\text{CN})_6^{4-}$, hydrazine and many other reducing agents can be directly titrated with the bromate solution and they are determined. Direct titrations with KBrO_3 are performed in the presence of indicators such as methyl orange, methyl reds, etc.

Many substances are not directly oxidized with potassium bromate, but react quantitatively with excess elemental bromine. For this purpose, the system is first acidified to form free bromine in the known amount and the excess amount of KBr is added to the medium. Subsequently, a certain amount of KBrO_3 in the form of solid or standard solution is added to the medium and elemental bromine is formed in known quantities.



Without reaction, the excess bromine is reacted with excess KI and the iodine released is titrated with the thiosulfate solution.



Since the consumed thiosulfate solution corresponds to the excess of the standard bromate solution, the difference between the initial solution of bromate and its excess is used to calculate the amount of the analyte. Quantitative determination of many metal ions and some organic compounds such as phenols and aniline can be carried out indirectly by means of potassium bromate solution.