College of science

(التحليل الحجمي)

Department of Chemistry

Volumetric Analysis
(Titration)

المعايرة ومبادئ التحليل الحجمي

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Safety in the laboratory:

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1. Know the location of all fire extinguishers, showers, and eye wash fountains and how to use it.
2. Label all chemicals and solutions that are stored outside their original containers. Include your name and the date of preparation.
3. Tie up long hairs, especially in the presence of open flames.
4. Keep work areas clean and uncluttered.
5. Never begin working until your instructor arrives.
6. Never bring food, drinks, or smoking materials into the laboratory.
7. Never work without an approved laboratory coat or apron and never wear open toed or open-top shoes.
8. Never work without approved eye protection.

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Volumetric Analysis {Titrations}

Titrations are widely used in analytical chemistry to determine acids, basis, oxidants, reductants, metal ions, proteins, and many other species. Titrimetric methods include a large and powerful group of quantitative procedures that are based upon measuring the amount of reagent of known concentration that is consumed by the analyte. Volumetric titrimetry involves measuring the volume of a solution of known concentration that is needed to react essentially completely with the analyte.

Some terms in volumetric titrations:

1. Titration:

Titration is a process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is judged to be complete.

2. Standard solution:

A standard solution is a reagent of exactly known concentration that is used in a titremetric analysis

3. Back-Titration:

A back-titration is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution.

4. The equivalence point :

The equivalence point is the point in a titration when the amount of added standard reagent(titrant) is exactly equivalent to the amount of analyte.

5. The end point :

The end point is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

6. Indicators:

Indicators are reagents often added to the analyte solution to produce an observable physical change (e.g, color) at or near the equivalence point.

7. Titation error :

Is the very small difference in volume or mass between the equivalence point and the end point.

$$E_t = V_{ep} - V_{eq}$$

V_{ep} is the actual volume of reagent is required to reach the end point
V_{eq} is the theoretical volume to reach the equivalence point.

8: Primary standards:

A primary standard is an ultra pure compound that serves as the reference material for a titremetric methods of analysis. The important requirements for a primary standards are the followings:

The substance should be readily purified.
It should not be hygroscopic.
It should not be contain hydrate water.
It should be readily soluble.
It should have a relatively high equivalent weight.
It should be available and not too expensive.
It should be stable toward air.
It should be stable on storage.
It should not undergo any side-reaction.

Examples: Na_2CO_3 , pure metals (Zn,Cu,Mg)salts , Ag , $AgNO_3$, NaCl , $K_2Cr_2O_7$, $Na_2C_2O_4$.

Very few compounds meet or even approach these criteria and only a limited number of primary standard substances are available commercially, as consequences less pure compounds must sometimes be used in place of a primary standard.

The purity of such a **secondary standard** must be established by careful analysis.

The properties of secondary standards substances is :a. volatile (HCl, H_2SO_4 , HNO_3).b. hydrated or hygroscopic (NaOH , KOH). c.effected by atmosphere ($KMnO_4$).

9. Standard solutions:

Standard solution play a central role in all titrimetric methods of analysis. The ideal standard solution for a titrimetric method well:

1. be sufficiently stable.
2. react rapidly with the analyte.
3. react more or less completely with the analyte.
4. undergo a selective reaction with the analyte that can be described by a balanced chemical equation.

Few reagents meet all these ideals perfectly. **Two** basic methods are used to establish the concentration of such solutions:

1. Direct method: primary standard dissolved in known volume.
2. Standardization : in standardization, the concentration of a volumetric solution is determined by titrating it against carefully measured quantity of a primary or secondary standard or an exactly known volume of another standard solution.

Requirements of titration process:

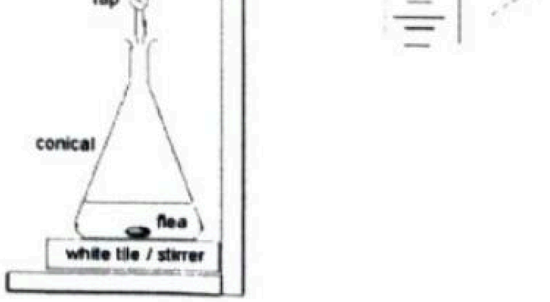
1. It should have well defined equation reaction.
2. The reaction should be rapid.
3. There should be no side reactions.
4. There should be a marked change in some properties of the solution when the reaction is complete.
5. The reaction should be quantitative.

Apparatus for precisely measuring volume:

Volume may be measured with a pipet , buret , and volumetric flasks. Volumetric equipment is marked by the manufacturer to indicate not only the manner of calibration, but also the temperature at which the calibration strictly applies.

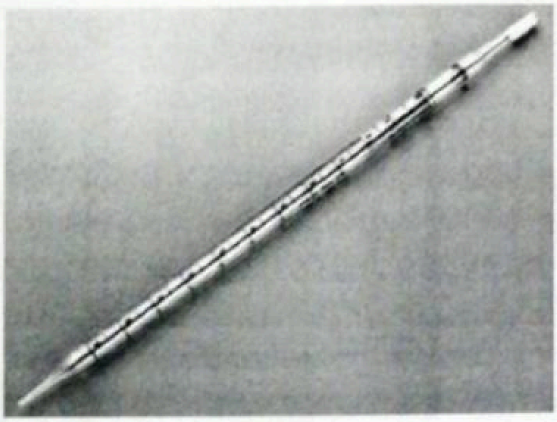
The Buret:

The only essential piece of equipment for delivering the titrant to the solution containing the analyte. The most common method for delivering the titrant is a **buret** . A buret is a long, narrow tube with graduated markings, and a stopcock for dispensing the titrant. Using a buret with a small internal diameter provides a better defined meniscus, making it easier to read the buret's volume precisely.



Pipet:

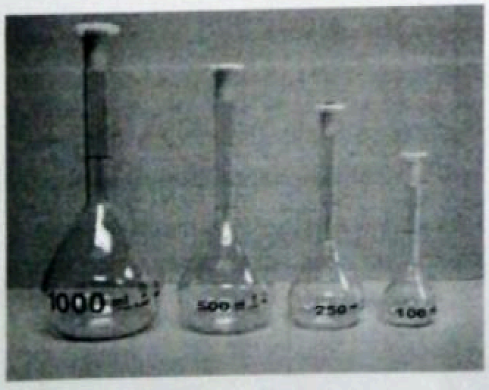
A **pipet** is used to deliver a specified volume of solution. several different styles of pipets are available. transfer pipet and graduated pipet .Transfer pipets provide the most accurate means for delivering a known volume of solution.



Volumetric flask:

Volumetric flask is a vessel with a long narrow neck , a thin line etched around the neck indicates the volume. Pipets and volumetric flasks provide more accurate means for measuring volume.

When filled to its calibration mark, a **volumetric flask** is designed to contain a specified volume of solution at a stated temperature,usually 20 °C.



Classification of reactions in titrimetric analysis:

There are four types of reactions in titrimetric analysis :

1. **Neutralization reactions** , or acid-base titration or acidimetry and alkalimetry : these reactions involve the combination of hydrogen and hydroxide ions to form water.

2. **Precipitation reactions**: these reactions depend upon the combination of ions to form a slightly soluble precipitate.

3. **Complex formation reactions** or **complexometric reactions**: these reactions depend upon the combination of metal ion which is an electron acceptor with a ligand which is an electron donor, to form a soluble and stable complex.

4. **Oxidation – Reduction reactions (Redox):** these reactions involves transfer of electrons between reactants, therefore it involves a change of oxidation number.(no change in oxidation number in above reactions).

Methods of expressing concentration:

1. Molarity (M) of solids :

Molarity is a number of moles of solute in one liter of solution:

M = moles of solute / volume of solution (L)

= (wt(g) / F.wt) / (v (mL)/ 1000)

= (wt (g) x 1000) / (F.wt x V(mL))

F.wt = formula weight

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2. Normality (N) of solids :

Normality is a number of equivalents of solute in one liter of solution.

N = no. of equivalents of solute / volume of solution (L)

= (wt(g) / Eq.wt) / (v (mL)/ 1000)

= (wt (g) x 1000) / Eq.wt x V(mL)

= (wt (g) x 1000) / Eq.wt x V(mL)

Eq.wt = equivalent weight

The Eq. wt (Equivalent weight) of a substance is not a constant quantity but its value depend upon the reaction in which it is taken part.

Eq.wt = M.wt / n

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3. Molarity of liquids :

M = (sp. gr. x % x 1000) /F.wt

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4. Normality of liquids :

N = (sp. gr. x % x 1000 / Eq.wt)

Sp. gr. = specific gravity = density of substance / density of water

since the density of water = 1.0 g / mL

So sp. gr. = density

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5. Percentage concentration:-
   a) mass or weight percent w / w :-
      No. of grams solute in 100 g solution.
      w /w % = (mass of solute (g) / mass of solution (g)) x 100

   b) mass / volume percent m / v or wt / v
      No. of grams solute in 100 mL solution
      m / v % = (mass of solute (g) / volume of solution (mL)) x 100

   c) Volume percent v /v % :-
      No. of mL solute in 100 mL solution.
      v / v % = (volume of solute / volume of solution (mL)) x 100

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6. ppm = part per million
   = Number of mg solute in 1 Kg solution or
   Number of mg solute in 1 L solution (aq.)

ppm = (mass of solute (g) / mass of solution (g)) x 10^6 or
ppm = (mass of solute (g) / volume of solution (mL)) x 10^6

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7. g/L = gram per liter
   = M x M.wt

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8. Dilution law: the number of moles of both diluted and concentrated solutions must be equal.

That is mean: $M_1 \times V_1 = M_2 \times V_2$

Neutralization Reactions (acid – base)

A wide variety of acidic and basic substances , both organic and inorganic , can be determined by an acid – base titration. There are also many examples in which the analyte can be converted chemically into an acid or base and then determined by titration.

Types of neutralization reaction

- Strong Acid + Strong Base = Salt + Water
- HCl + NaOH = NaCl + H2O

- Strong Acid + Weak Base = Salt + Water
- HCl + NH_4OH = $NH_4Cl + H_2O$

- Weak Acid + Strong Base = Salt + Water
- CH_3COOH + NaOH = $CH_3COONa + H_2O$

- Weak Acid + Weak Base = Salt + Water (*)
- CH_3COOH + NH_4OH = $CH_3COONH_4 + H_2O$

(*) For neutralization titrations, usually weak electrolyte (acid or base) is titrated with strong electrolyte in order to observe sharp end point.

Experiment No.1 :

Standardization of the approximately 0.1 N HCl

Principle:

Hydrochloric and sulphuric acids are secondary standards because of their volatility , so it should be standardized with a primary standard base using a suitable indicator.

Procedure:

A. Preparation of ~ 0.1 N Hydrochloric acid(HCl) solution.
Transfer 1mL of concentrated HCl in a 100 mL volumetric flask, dilute wih distilled water to the mark ,shake well (about 10 times).

B. Preparation of 0.1 N Sodium carbonate (Na_2CO_3) solution.
Weigh accurately 0.53 g. of dried (at 104°C) sodium carbonate (purity$\geq$ 99.9%), dissolve it with enough amount of distilled water (D.W.), transfer the solution to a 100mL volumetric flask, complete the volume to the mark with D.W.

C. Titration process:

1. Rinse and fill the burette to the top indicator with **Na_2CO_3** solution (prepared in B).
2. Transfer 5mL of HCl (prepared in A) using a pipette (for accurate results), then release it into a conical flask.
3. Add 2-4 drops methyl orange indicator (M.O.), the solution color will be red.
4. Put the conical flask on top of a white tile, this makes it easier to notice any color change. Open the burette so the **Na_2CO_3** slowly flows/drops into the conical flask.
5. Swirl the conical flask during titration, continue titration by adding **Na_2CO_3 dropwise**.Turn off the burette as soon as the yellow color is

appeared (end point).

6. Record the volume of **Na_2CO_3** (V_2 mL).
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

$$N_1V1 = N_2V_2$$

HCl **Na_2CO_3**

N_1 x 5 = 0.1 x V_2 (average volume)

N_1 = (   ) N the exact normality of HCl.

Experiment No.2:

Determination of sodium hydroxide (NaOH) by titration with standardized HCl.

Principle:

There are two common ways for the determination of NaOH volumetrically:

1. Titration with primary standard substance (acid) such as potassium hydrogen phthalate ($KHC_8H_4O_4$).
2. Titration with standardized HCl.

Procedure:

1. Rinse and fill the burette to the top indicator with hydrochloric acid solution (standardized).
2. Transfer 5mL of sodium hydroxide (using a pipette) into a conical flask.
3. Add 2-3 drops of phenolphthalene (ph. ph.) indicator (color will be dark pink).
4. Put the conical flask on top of a white tile, this makes it easier to notice any colour change. Open the burette so the HCl slowly flows/drops into the conical flask.
5. Swirl the conical flask and titrate until the solution turns colorless which is indication of the e.p.
6. Record the volume of HCl (V_1) .
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

$$\underset{\textbf{HCl}}{N_1V_1} = \underset{\textbf{NaOH}}{N_2V_2}$$

N_1 = (   ) N the exact normality of NaOH

Experiment No. 3 :

Determination of a mixture solution of carbonate and hydroxide.

Principle:

If sodium carbonate is titrated with hydrochloric acid using methyl orange as an indicator, the titre is twice what it is if phenolphthalein is used as an indicator. The reason is that the two indicators do not change color at the same pH.

Methyl orange changes at about pH 3 - 4; this corresponds to the complete neutralisation of sodium carbonate with two moles of hydrochloric acid:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

On the other hand phenolphthalein color changes at pH 8.5 – 10; this colour change corresponds to one mole of hydrochloric acid reacting with sodium carbonate:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

Sodium carbonate is used as a primary standard for the determination of HCl. Usually, samples containing carbonates only are neutralized to the methyl orange point. Mixtures of carbonate and hydroxide, can be titrated with standard HCl to two end points using two indicators ; phenolphthaline (ph. ph) and methyl orange (M.O). at the phenolpthaline end point , sodium carbonate(Na_2CO_3) is half-neutralized to form $NaHCO_3$; and bicarbonate has not yet reacted , while hydroxide(OH) is reacted completely. From the ph. ph to M.O end point , bicarbonate is being neutralized.

There are tow ways to determine this mixture:-

I. Titration of two mixture solutions by using two different indicators

II. Titration of one mixture solution by using two different indicators sequently.

I.Titration of two mixture solutions by using two different indicators.

Step: 1. Titration of the mixture of sodium carbonate & hydroxide against standard HCl, using methyl orange as indicator.

Procedure:

1. Rinse and fill the burette to the top indicator with standard hydrochloric acid solution.
2. Transfer 5mL of the mixture solution (using a pipette) into a conical flask.
3. Add 2-3 drops of of M.O (solution color will be yellow).
4. Titrate with standard HCl.
5. Swirl the conical flask, when adding the HCl **dropwise**. turn off the burette as soon as the orange red color is appeared.
6. Record the volume of HCl (X mL).
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL.

(X) represents the volume of HCl ≡ all OH^- + all $CO_3^=$

Step: 2. Titration of the mixture of sodium carbonate & hydroxide against standardized HCl , using phenolpthaline(ph. ph) as an indicator

Procedure:

1. Transfer 5mL the of mixture solution (using a pipette) into a conical flask.
2. Add 2-3 drops of phenolphthalene (ph. Ph.) indicator (color solution will be dark pink)
3. Titrate with standard HCl .
4. Swirl the conical flask, when adding the HCl **dropwise**. turn off the burette as soon as the solution becomes colorless.
5. Record the volume of HCl (Y mL).
6. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

(Y) represents the volume of HCl ≡ all OH^- + ½ $CO_3^=$

Calculations:-

$$\text{If} \quad \begin{aligned} X &= OH^- + CO_3^= \\ Y &= OH^- + 1/2\, CO_3^= \end{aligned}$$

$$X\text{-}Y = \tfrac{1}{2} CO_3^= = R(\text{volume of HCl} \equiv \tfrac{1}{2} CO_3^=)$$

$$\text{So ; } 2R = \text{volume of HCl} \equiv \text{all } CO_3^=$$

$$X\text{-} 2R = \text{volume of HCl} \equiv \text{all } OH^-$$

1. Concentration of carbonate:

$$\underset{HCl}{N_1V_1} = \underset{Na_2CO_3}{N_2V_2}$$

$$V_1 = 2R \text{ mL}$$

2. Concentration of hydroxide:

$$\underset{HCl}{N_1V_1} = \underset{NaOH}{N_2V_2}$$

$$V_1 = X - 2R$$

II. **Titration of one solution mixture by using two different indicators sequently.**

Procedure:

1. Rinse and fill the burette to the top indicator with standard HCl solution.
2. Transfer 5mL of the mixture solution (using a pipette)into a conical flask.
3. Add 2-3 drops of phenolphthalene (ph. ph.) indicator (color solution will be dark pink)
4. Titrate with standard HCl, Swirl the conical flask, when adding the HCl **dropwise**. Turn off the burette as soon as the solution becomes colorless, record the volume of HCl (V_{ph})
5. Add directly 2drops of M.O (solution color will be yellow) continue titrating until color changes to orange-red.
6. Record the volume of HCl (V_m mL).
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

V_{ph} = **volume of HCl** ≡ all OH^- + ½ $CO_3^=$

V_m = volume of HCl ≡ ½ $CO_3^=$

So: 2 x V_m = volume of HCl ≡ all $CO_3^=$

V_{ph} - V_m = **volume of HCl** ≡ all OH^-

Calculate the normality of each component using dilution law.

Precipitation Titrations

The formation of a precipitate can be used as the basic of a titration. Volumetric method based on the formation of a slightly soluble product are Precipitation Titrations.

Because of the slow rate of formation of most precipitate, however there are only a few precipitating agents that can be used in titremetry, by far the most widely used and most important agents is silver nitrate; which is used for the determination of the halides, the halide-like anions (SCN^- , CN^-, CNO^-), mercaptanes, fatty acids, and several divalent and trivalent inorganic anions. this methods are sometimes called **argentometric methods.**

Classification of Precipitation Titrations

1. Direct methods such as Mohr method and Fajan method.

2. Indirect method (back titration) such as Volhard Method.

Indicators:

1. Chromate ion: The Mohr method.

Potassium chromate can serve as an indicator for the **argentometric determination** of, Cl^- , Br^-, and CN^- by reacting with silver ion to form a brick-red of silver chromate precipitate in the end point.

2. Adsorption indicator: The Fajan method

An adsorption indicator is an organic compound that tends to be adsorbed onto the surface of the solid in a precipitation titration, ex. Fluorescein.

3. Iron(III): The Volhard method

Iron (III) serves as the indicator in Volhard method, the solution color turns brick red with the first slight excess of thiocyanate ion.

The Mohr method

Principle:

This is the one of the oldest titrations methods in existence, described by Mohr in 1856. the method is summarized as follows:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

standard unknown white

Suppose that some K_2CrO_4 is added to a solution of NaCl that is to be titrated with standard $AgNO_3$. since Ag_2CrO_4 is more soluble than AgCl, the added Ag^+ reacts with Cl^- rather than $CrO_4^=$ up to the equivalence point. After the Cl^- is precipitated quantitatively as AgCl. The first slight excess of Ag^+ added beyond the equivalence point precipitates $CrO_4^=$ as intensely brownish red precipitate (Ag_2CrO_4), giving the end point.

$$2Ag^+ + CrO_4^= \rightarrow Ag_2CrO_4\downarrow$$

slight excess yellow indicator brownish red precipitate

Factors affecting the titration using Mohr method

1. pH of the medium:-

Because $CrO_4^=$ is a weak base, the solution usually is maintained at a slightly alkaline pH. If the pH is too acidic, chromate is present as $HCrO_4^-$, and the Ag_2CrO_4 end point will be in significant error. The pH also must be kept below a level of 10 to avoid precipitating silver hydroxide (Ref. 3).

$$2CrO_4^= + 2H_3O^+ \rightarrow 2HCrO_4^- + 2H_2O$$

2. Indicator concentration:-

The $[CrO_4^{=}]$ should be about 0.002 M (5%). If the concentration is much higher than this, the yellow color interferes with the end point, whereas if it is much lower, the end point coloration is faint and may not appears until well past the equivalence point.

3. Stirring:-

Good stirring during the entire addition of $AgNO_3$ is most important in Mohr method. With poor stirring, Ag_2CrO_4 forms locally before the equivalence point and becomes occluded by subsequently formed AgCl, giving an end point that is neither sharp nor reproducible.

Experiment No. 4 :

The Mohr determination of chloride

(A) sodium chloride unknown sample determination.

Procedure:

1. Fill the burette to the top indicator with $AgNO_3$ solution.
2. Transfer 5mL of unknown solution (using a pipet), into a conical flask.
3. Add 1 mL (10drops) of K_2CrO_4 solution(5%) as an indicator (color solution will be yellow)
4. Titrate with $AgNO_3$.
5. Swirl the conical flask, when adding the $AgNO_3$ **dropwise**. Turn off the burette as soon as the color solution becomes brick-red.
6. Record the volume of $AgNO_3$.
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

Calculate the concentration of Cl^- as NaCl in (1) g/L (2) ppm (3) percentage.

(B) chloride determination in tap water& well water :

Procedure:

Use the same procedure in (A) , except i) the volume of sample is 25 mL ii) calculate the concentration of Cl^- ion in g/L, ppm, and percentage.

The Volhard method

Principle:

The most important application of the Volhard method is the indirect determination of halides ions. A measured excess of standard silver nitrate solution is added to the halide sample, some of the $AgNO_3$will react with the halide ion (Cl^-, Br^- , or I^-) and the remaining excess silver is determined by back-titration with a standard thiocyanate solution.

In Volhard method, the silver ions are titrated with a standard solution of thiocyanate ion:

$$\underset{\textbf{known excess}}{Ag^+} + Cl^- \leftrightarrows AgCl\,(s) + \underset{\textbf{remaining}}{Ag^+}$$

$$\underset{\textbf{remaining}}{Ag^+} + \underset{\textbf{standard}}{SCN^-} \leftrightarrows AgSCN\,(s)$$

Iron (III) serves as the indicator. The solution turns red with first slight excess of thiocyanate ion:

$$\underset{\textbf{indicator}}{Fe^{3+}} + \underset{\textbf{slight excess}}{SCN^-} \leftrightarrows \underset{\textbf{red complex}}{Fe(SCN)_3}$$

The titration must be carried out in acidic medium to prevent precipitation of iron(III) as the hydrated oxide.

Since silver chloride is more soluble than silver thiocyanate. As a consequence in chloride determination by the volhard method, the reaction below occurs near the end point of the back-titration of the excess silver ion:

$$AgCl\,(s) + SCN^- \leftrightarrow AgSCN\,(s) + Cl^-$$

So AgCl must be isolated by filtration or by inactivate it with an immiscible organic liquid such as nitrobenzene, this performance only in Cl^- determination (there is no interferences in Br^- determination).

Experiment No. 5 :

The Volhard determination of bromide.

Procedure:

1. Prepare 0.01 N (KSCN) solution, rinse and fill the burette with it.
2. Transfer 5mL of unknown Br^- solution (using a pipet), into a conical flask, add 20 mL of $AgNO_3$ (0.01 N)
3. Add 1 mL (10drops) of Fe^{3+} solution as an indicator into the conical flask.(solution will be colorless)
4. Titrate with KSCN .
5. Swirl the conical flask, when adding the KSCN **dropwise**. Turn off the burette as soon as the color becomes red.
6. Record the volume of KSCN.
7. Repeat the experiment to get **concordant** results, the average of the readings which agree within 0.1mL

Calculation:

$$\overset{AgNO_3}{N_1 \times V_1} = \overset{Br^-}{N_2 \times V_2} + \overset{SCN^-}{N_3 \times V_3}$$

Calculate the concentration of Br^- as 1. KBr in g/500 mL, 2. ppm, 3.percentage.

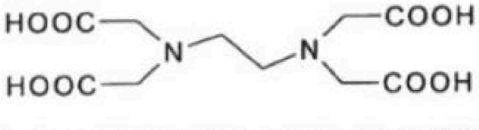
Complex Formation Titrations (Complexometric Titrations)

A complexation reaction involves a reaction between a metal ion (M) and a Ligand (L) containing at least one atom with an unshared pair of electrons. most metals ions react with electron-pair donor to form coordination compounds or complexes. A titration based on complex formation is called a **complexometric titration.**

Metal ions are **Lewis acids,** accepting electron pairs from electron-donating ligands that are **Lewis bases.** Cyanide is called a **monodentate** ligand because it binds to a metal ion through only one atom (the carbon atom). Most transition metal ions bind six ligand atoms. A ligand that attaches to a metal ion through more than one ligand atom is said to be **multidentate** ("many toothed"), or a **chelating ligand** (pronounced KEE-late-ing).

EDTA:

EDTA is a merciful abbreviation for **ethylenediaminetetraacetic acid**, a compound that forms strong 1:1 complexes with most metal ions and finds wide use in quantitative analysis. EDTA plays a larger role as a strong metal-binding agent in industrial processes and in products such as detergents, cleaning agents, and food additives that prevent metal-catalyzed oxidation of food.



Ethylenediaminetetraacetic acid (EDTA)

EDTA is, by far, the most widely used chelator in analytical chemistry. By direct titration or through an indirect sequence of reactions, virtually every element of the periodic table can be measured with EDTA.
EDTA is the very simple complexing agent, contains six complexing group. It is tetraprotic acid (H_4Y), standard substance, and water insoluble, but the disodium salt form (Na_2H_2Y) is water soluble.

Advantages of multidentate ligands:

1. They generally react more completely with cations and thus provide sharper end point
2. They react with metal ions in a single step.

Metal Ion (Metalochromic) Indicators:

The most common technique to detect the end point in EDTA titrations is to use a metal ion indicator.

Metal ion indicators are compounds whose color changes when they bind to a metal ion. Because the color of free indicator is pH dependent, most indicators can be used only in certain pH ranges.

A typical titration is illustrated by the reaction of Mg^{2+} with EDTA at pH 10, using Eriochrome black T (E.B. T) as the indicator.

$$\underset{\textbf{Red}}{\text{MgIn}} + \underset{\textbf{Colorless}}{\text{EDTA}} \rightarrow \underset{\textbf{Colorless}}{\text{MgEDTA}} + \underset{\textbf{Blue}}{\text{In}}$$

At the start of the experiment, a small amount of indicator (In) is added to the colorless solution of Mg^{2+} to form a red complex. As EDTA is added, it reacts first with free, colorless Mg^{2+}. When free Mg^{2+} is used up, the last EDTA added before the equivalence point displaces indicator from the red MgIn complex. The change from the red MgIn to blue unbound In signals the end point of the titration.

Titration methods employing EDTA :

1. Direct method.
2. displacement method.
3. indirect method
4. alkalinity titrations.

Requirement of Metallochromic Indicators

1. The metal indicator complex must be less stable than the metal-EDTA complex.
2. The indicator must be very sensitive towards the metal ions.
3. The metal indicator complex must be formed under the same pH as the metal-EDTA complex.

Experiment No.6:

Determination of water hardness by complex formation with EDTA.

Principle:

Hardness is the total concentration of alkaline earth (Group 2) ions, which are mainly exestent in water. Hardness is commonly expressed as the equivalent number of milligrams per liter. Thus, if we would say that the hardness is 100 mg per liter because Water whose hardness is less than 60 mg per liter is considered to be "soft." If the hardness is above 270 mg/L, the water is considered to be "hard."

Water hardness is ordinary determined by an EDTA titration after the sample has been buffered at pH 10. The hardness is due to Ca^{2+} and Mg^{2+} is titrated with standard EDTA using an E.B.T. a standard EDTA solution is prepared from high purity,dried (do not exceed 80°C) $Na_2H_2Y.2H_2O$.

E.B.T is weak acid (H_3In) dissociate in an acidic solution (H_2In^- -red) to (HIn^{2-} - blue).

Equations of the reaction:

In the titration:

$$Mg^{2+} + HIn^{2-} \leftrightarrows \underset{\text{(wine colored)}}{MgIn^-} + H^+$$

$$Ca^{2+} + H_2Y^{2-} \leftrightarrows CaY^{2-} + 2H^+$$
$$Ca^{2+} + MgY^{2-} \leftrightarrows CaY^{2-} + Mg^{2+}$$

At the end point:

$$\underset{\text{(wine colored)}}{MgIn^-} + \underset{\text{(colorless)}}{H2Y^{2-}} \leftrightarrows \underset{\text{(colorless)}}{MgY^{2-}} + \underset{\text{(blue)}}{HIn^{2-}} + H^+ \text{ (pH=10)}$$

Procedure:

1. Prepare 0.01 M solution of disodium salt of EDTA (M.wt=372.24), rinse and fill the burette to the top indicator with it.
2. Transfer 50mL of tap water (using a measuring cylinder) into the conical flask.
3. Add 3 mL of buffer solution (pH10) and a few drops of E.B.T as indicator.(color solution will be wine-colored)
4. Titrate with EDTA.
5. Swirl the conical flask, when adding the EDTA **dropwise**. Turn off the burette as soon as the color becomes blue .
6. Record the volume of EDTA.
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

Calculate total hardness(TH) as $CaCO_3$:-

1L 1M EDTA ≡ 100.09 $CaCO_3$
1ml 1M EDTA ≡ 0.10009 $CaCO_3$

[TH] = (100.09/1000) x M x V x (1000/50)

= ( ) g/L

Experiment No.7:
Determination of nickel by complex formation with EDTA.

Procedure:

1. Prepare 0.01 M solution of disodium salt of EDTA (M.wt=372.24).
2. Transfer 5 mL of nickel ion solution (using a measuring cylinder) into the conical flask.
3. Add 10 mL of EDTA solut ion (prepared in 1) and 3 mL of buffer solution (pH10) and a few drops of E.B.T as indicator.(color solution will be wine-colored)
4. Titrate the excess EDTA with standard 0.01 M magnesium sulphate solution.
5. Swirl the conical flask, when adding the $MgSO_4$ **dropwise**. Turn off the burette as soon as the color becomes red .
6. Record the volume of $MgSO_4$.
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

1L 1M EDTA $\equiv$ 58.71 g Ni^{2+}

Redox titration

Redox reactions or oxidation-reduction reaction, primarily involve the transfer of electrons between two chemical species. The compound that loses an electrons is said to be oxidized (oxidation is the loss of electrons), the one that gain an electrons is said to be reduced(reduction is the gain of electrons). There are also specific terms that describe the specific chemical species. A compound that is oxidized is referred to as a reducing agent, while a compound that is reduced is referred to as the oxidizing agent.

Oxidation and reduction have to happened together. You cannot have oxidation reaction without a corresponding reduction reaction. It is a bit like the idea behind a blood transfusion or an organ transplant.

Because electrons are negatively charged, an increase in electrons decrease in overall charge (the compound becomes more negatively charged). On the other hand, an atom that is oxidized has given up some of those negatively charged electrons, which will increase its overall charge (the compound becomes more positively charged).

Iodimetry and Iodometry:

Oxidation and reduction reactions involving iodine are very useful in the titremetric analysis because iodine can be very conveniently and accurately titrated with standard thiosulphate solution. Titremetric methods involving iodine are two types:-

1. **Iodimetry:** which describes titrations in which a standard iodine solution is used (iodine is a weak oxidant which can be reduced by reductants, such as $SnCl_2$, $Na_2S_2O_3$, H_2SO_3, H_3AsO_3. in this method, a known volume of a solution of the reductant is taken in conical flask, about 1 mL of starch solution is added as an indicator, and a standard solution of iodine is gradually added through a buret, swirling the flask frequently during the titration (solution color change from colorless to blue).
2. **Iodometry:** deals with titrations in which the iodine librated during chemical reactions is titrated. in this method, suppose we have a solution of a strong oxidant, such as $CuSO_4$, KIO_3, $K_2Cr_2O_7$, $KMnO_4$, if to this solution, we add a large excess of KI solution (usually in the presence of acid), the iodide ions are oxidized to iodine as shown by the equation:

$$2I^- + 2e \rightarrow \mathbf{I_2}$$

Experiment No.8:

Determination of Fe^{2+} by titration with $KMnO_4$

Principle:

Potassium permanganate, KMnO4, is a strong *oxidizing agent.* Permanganate, MnO_4^-, is an intense dark purple color. Reduction of purple permanganate ion to the colorless Mn^{2+} ion, the solution will turn from dark purple to a colorless at the equivalence point. No additional indicator is needed for this titration. The reduction of permanganate requires strong acidic conditions.

In this experiment, permanganate will be reduced by oxalate, $C_2O_4^=$ in acidic conditions. Oxalate reacts very slowly at room temperature so the solutions are titrated hot to make the procedure practical. The balance in acidic solution is shown below:

$$\mathbf{2MnO_4^- + 5C_2O_4^= + 16\,H+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

In strongly acidic solutions ($pH \leq 1$), MnO_4^- is reduced to colorless Mn^{2+} (manganous), in neutral or slightly alkaline solution, the product is the brown solid.MnO_2 (manganese dioxide), in strongly alkaline solution (2M NaOH), green manganate ion is produced ($MnO_4^=$).

Part I of this experiment involves the standardization of potassium permanganate ($KMnO_4$) by titrating it against sodium oxalate. Once the exact normality (eq/L) of the permanganate solution is determined, it can be used as a standard oxidizing solution.

In part II of this experiment, the standard permanganate solution will be used to find the concentration of iron(II) in (g/L). The balance is shown below:

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

The titration is conducted in acidic medium using H_2SO_4.

Procedure:

Part I :- Preparation of ~ 0.1 N of potassium permanganate ($KMnO_4$) and 0.1 N of $Na_2C_2O_4$ solutions.

1. Weigh accurately 0.335 g. of $Na_2C_2O_4$ (analytical grade), dissolve in distilled water, transfer to 50 mL volumetric flask and complete to the mark.

2. Weigh 0.316 g. of $KMnO_4$, dissolve in water, transfer to 100 mL volumetric flask and complete to the mark.

Part II : Standardization of $KMnO_4$

1. Rinse and fill the burette to the top indicator with $KMnO_4$ solution (prepared in part I).
2. Transfer 5mL of oxalate solution, into a conical flask, add 3 mL of H_2SO_4 (2 N)
3. Heat the acidified oxalate solution to ~80°C (do not boil)
4. Titrate with $KMnO_4$.
5. Swirl the conical flask, when adding the $KMnO_4$ **dropwise**. turn off the burette as soon as the color becomes light pink(*).
5. Record the volume of $KMnO_4$(**).
6. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

(*) No indicator is needed in this experiment, since one drop of $KMnO_4$ beyond the end point make the solution pink, i.e: $KMnO_4$ is self-indicator.

(**) The top of the meniscus may be read instead of the bottom(because $KMnO_4$ is strongly colored).

Calculation:

Calculate the exact normality of $KMnO_4$:

$$\underset{KMnO_4}{\mathbf{N_1V_1}} = \underset{Na_2C_2O_4}{\mathbf{N_2V_2}}$$

Part III : Determination of ferrous sulphate by titration with $KMnO_4$

1. Rinse and fill the burette to the top indicator with $KMnO_4$ solution (standardized in part II).
2. Transfer 5mL of unknown Fe^{2+} solution into a conical flask.
3. Add 3 mL of H_2SO_4 (2 N)
4. Titrate with $KMnO_4$.
5. Swirl the conical flask, when adding the $KMnO_4$ **dropwise**. Turn off the burette as soon as the color becomes light pink.
6. Record the volume of $KMnO_4$(**).
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

Calculate the concentration in g/L for 1) Fe^{2+}

2) $FeSO_4$

ExperimentNo.9:

Determination of Iron(II) with potassium dichromate ($K_2Cr_2O_7$)

Principle:

$K_2Cr_2O_7$ is a standard oxidizing agent, its solution is primary standard, very stable(can be boiled without decomposition), only a moderately strong oxidizer which does not oxidize chloride(?), inexpensive and readily available commercially.

Dichromate is strong enough to oxidize Fe(II) quantitatively, it is reduced to green chromium(III) ion:-

$$Cr_2O_7^{=} + 14\,H^+ + 6e^- \leftrightarrows 2Cr^{3+} + 7H_2O$$

Dichromate titrations are generally carried out in solutions that are about 1M in HCl or H_2SO_4. The orange color of a dichromate solution is not intense enough for use in end point detection. Diphenylamine sulfonic acid is an excellent indicator for the titrations, with this reagent, however, the oxidized form of the indicator is violet, and it is reduced form is essentially colorless; thus, the color change observed in a direct titrations is from green of chromium(III) to violet.

The principle application of dichromate is the volumetric titration of iron(II) based on the reaction :-

$$Cr_2O_7^{=} + 14\,H^+ + 6Fe^{2+} \leftrightarrows 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Procedure:

1. Prepare 0.05 N ($K_2Cr_2O_7$) solution, rinse and fill the burette to the top indicator with it.
2. Transfer 5mL of unknown Fe^{2+} solution into a conical flask, add 3 mL of 2 N H_2SO_4 and 6 mL of 6M H_3PO_4.
3. Add 4 drops of sod. Diphenylamine sulfonate solution as indicator into the conical flask.(solution will be green-gray)
4. Titrate with $K_2Cr_2O_7$.
5. Swirl the conical flask, when adding the $K_2Cr_2O_7$ **dropwise**. Turn off the burette as soon as the color becomes violet.
6. Record the volume of $K_2Cr_2O_7$.
7. Repeat the experiment to get **concordant** results. Take the average of the readings which agree within 0.1mL

Calculation:

Calculate the concentration of Fe(II) & $FeSO_4$ by g/L.

ExperimentNo.10:

Determination of $CuSO_4$ by iodometric REDOX titration.

Principle:

Iodometric methods have been applied to the determination of a large variety of both organic and inorganic substances.

Metal ion that are easily reduced, such as Cu^{2+} and Fe^{3+} can be determined using the iodometric technique. Iodide reduces Cu^{2+} to Cu^+:

$$2Cu^{2+} + \underset{(\text{excess})}{4I^-} \leftrightarrows 2CuI_{(S)} + I_2$$

$$I_2 + 2S_2O_3^{=} \leftrightarrows 2I^- + S_4O_6^{=}$$

Procedure:

I. Standardization of 0.1 M sodium thiosulphate.

1. Dissolve about 25 g of $Na_2S_2O_3.5H_2O$ in 1 L of distilled water.

2. Dip a 2 in. length of pure copper wire in dilute nitric acid for 5 sec., rinse with water, and wipe dry with a piece of filter paper.

3. Weigh accurately 0.2 – 0.25 g of wire and transfer to 250 mL conical flask. In the hood, add 5 mL of 6M HNO_3 and warm until the copper is dissolved.

4. Dilute with 25 mL of water, add 0.5 g of urea, and boil for 5 min.

5. Add 6M NH_3 until deep blue $Cu(NH_3)_4{}^{2+}$ starts to form. A precipitate of $Cu(OH)_2$ will form and redissolve before the deep blue color appears. Add 5mL of conc. Acetic acid.

6. Add 3 g of KI and titrate the librated iodine immediately with the 0.1 M thiosulphate solution, continuing until the solution is a very pale yellow.

7. Interrupt the titration to add 5 mL of starch indicator, then continue the addition of titrant dropwise until the blue color just disappears with the addition of 1 drop.

8. Interrupt the titration again and add 1.5 g of KSN. The blue color will appear. Continue to add titrant until the color disappears for at least 20 seconds.

9. Calculate the molarity of the titrant.

II. Determination of an unknown $CuSO_4$ sample :-

Pipette out 5 mL of the sample into 250 mL conical flask. Add 10 mL of 10 % KI solution (or 1 g solid). Titrate the liberated I_2 with standard $Na_2S_2O_3$ solution. Repeat the experiment to get concordant results. Take the average of the readings which agree within 0.1mL.

Note :-

There is no need to add acid to $CuSO_4$ solution along with KI as was necessary in the case of KIO_3 and $K_2Cr_2O_7$. the reason is that the reduction does not involve any H^+ ions.

Calculation:

According to the equation of the reaction :-

$$2Cu^{2+} \equiv I_2 \equiv 2Na_2S_2O_3$$

$$\text{or} \quad Na_2S_2O_3 \equiv Cu^{2+} \equiv Cu \text{ (A. wt. 63.54)}$$

$$1 \text{ mL } 0.1 \text{ N } Na_2S_2O_3 = 6.354 \text{ mg Cu}$$

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