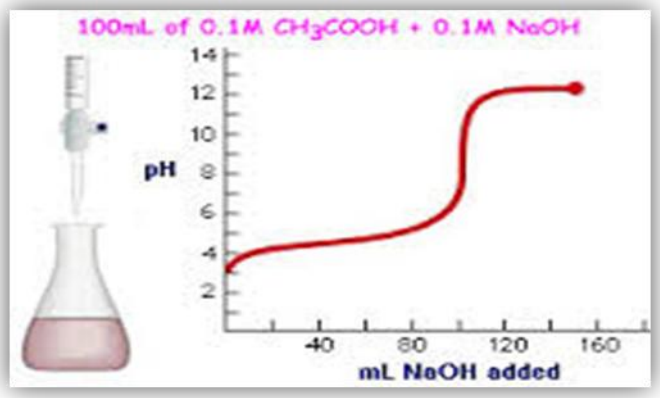


Practical Analytical 1 Chemistry





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Chemical Analysis

Chemical analysis is divided into two main classes:

I- Quantitative Analysis:

The object of quantitative analysis is to determine the actual amounts of the constituents of a compound, and also the amount of material dissolved in solutions. Depending upon the tools used , or the procedures followed to perform the analysis, it can be classified into 3 main classes:

a) Volumetric analysis :

i.e., determination of the constituents by titration.

b) Gravimetric analysis :

i.e., determination of the constituents by pptn.

c) Instrumental analysis :

i.e., determination of the constituents by the use of instruments and apparatus.

II - Qualitative Analysis:

This type of analysis involves the investigation and identification of substances in its simplest or complicated forms.

I- Quantitative Analysis:

a) Volumetric analysis

Experimental 1:

I- Standardization of HCl using standard solution of Na_2CO_3

II-Determination of concentration of NaOH and Na_2CO_3 in a mixture

1- Standardization of HCl using standard solution of Na_2CO_3

Principle

Sodium carbonate reacts with hydrochloric acid according to the following equation:

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

In other words, to neutralize all the carbonate, two equivalent of HCl should be used and as such the equivalent weight of sodium carbonate = M.wt/2 =53 When one equivalent of HCl is added to the carbonate it is transformed into bicarbonates.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \qquad \text{ph.ph.}$$

And the pH of the solution changes form 11.5 (alkaline) to 8.3. When phenolphthalein is used, it changes to colorless at the end of this stage as its color range falls within the same zone. ph.ph (8.3-10).

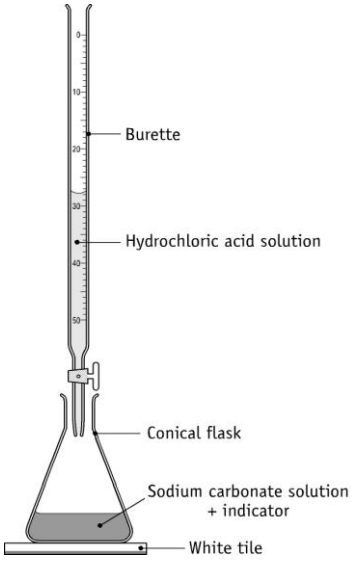
When another equivalent of HCl is added to the solution of bicarbonate, complete neutralization takes place and it is transformed into sodium chloride and CO_2 gas is evolved.

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2 \qquad \text{M.O.}$$

The pH of solution changes from 8.3 to 3.8, which is near enough to the color range of M.O. (3.1-4.4). If methyl is used at this stage, the color of the solution changes from yellow to red. It thus follows that ph.ph. is used in the neutralization of HCl with sodium carbonate, the volume of acid used will be equivalent to half of the carbonate, when methyl orange is used in this titration the volume of acid used will be equivalent to all carbonate. Methyl orange is generally used in this as ph.ph. is sensitive to carbon dioxide.

Chemicals and tools:

- 50-mL Burette
- 250-mL conical flasks
- Burette funnel
- Two 250-mL beaker
- 10-mL pipette
- Pipette pump.
- HCl(aq)
- Na_2CO_3(aq)
- M.O
- Distilled water



Preparation of standard solution of Na_2CO_3 (0.1 N):

1- Weigh out accurately 1.325 gm of A.R. Na_2CO_3.

2- Dissolve in small quantity of distilled water and transfer quantitatively to 250 ml measuring flask.

3- Complete to the mark and shake well.

4- Calculate the exact normality of Na_2CO_3 solution.

Weight required = Normality x eq.wt. x volume in liter.

Procedure:

1- Wash the tools.

2- Add the acid solution to the burette.

3- Draw 10 mL of the base solution into the volumetric pipette and transfer this solution into an Erlenmeyer flask. Add 2-3 drops of M.O to the base solution in the flask.

4- Place the flask under the burette and start adding the acid solution to the Erlenmeyer flask, until the color change from yellow to red-orange.

5- Record the final reading of the burette. Wash the contents of the flask down the drain with water.

7. Calculate the concentration of HCl.

Calculation

M.O

Suppose that the volume of HCl is V_1 and its normality is N_1 while V_2 is the volume taken from sodium carbonate and N_2 is its normality.

The volume of HCl (from burette) ≡ all carbonate = V_1

$$\mathbf{(N_1 \times V_1)}\ HCl = \mathbf{(N_2 \times V_2)}\ Na_2CO_3$$

$$\mathbf{N_1}\ HCl = \frac{\mathbf{(N_2 \times V_2)}\ Na_2CO_3}{\mathbf{V_1}\ HCl} = N$$

ph.ph.

The volume of HCl (from burette) ≡ 1/2 carbonate

The volume of HCl ≡ all carbonate = $2V_1$

$$\mathbf{(N_1 \times 2V_1)}\ HCl = \mathbf{(N_2 \times V_2)}\ Na_2CO_3$$

$$\mathbf{N_1}\ HCl = \frac{\mathbf{(N_2 \times V_2)}\ Na_2CO_3}{\mathbf{2V_1}\ HCl} = N$$

strength in gm/L = normality x eq. wt.

Strength of HCI = N_1 x 36.5 g/L

2- Determination of concentration of NaOH and Na_2CO_3 in mixture

Principle:

1- When a known volume of the mixture is titrated with HCl in presence of ph. ph., the acid reacts with all the sodium hydroxide and with only half of the carbonate.

V_1 = all hydroxide + 1/2 the carbonate

2- When a known volume of the mixture is titrated with HCl in presence of M.O., the acid reacts with all the hydroxide and all the carbonate.

V_2 = all hydroxide + all carbonate

Volume of HCl = 1/2 carbonate = $V_2 - V_1$ = V ml

Volume of HCl = all carbonate = 2V ml

Volume of HCl = NaOH = V_2 - 2V ml or $2V_1 - V_2$ ml

Chemicals and tools:

- 50-mL Burette
- 250-mL conical flasks
- Burette funnel
- Two 250-mL beaker
- 10-mL pipette
- Pipette pump.
- HCL(aq)
- Na_2CO_3(aq)
- NaOH (aq)
- M.O
- Ph.ph
- Distilled water

Procedure

1- Transfer with a pipette 10 ml of the mixture to a conical flask, and add one or two drops of ph. ph.

2- Add the acid from the burette till the solution becomes colorless.

3- Repeat the experiment twice or three times and tabulate your results.

4- Repeat the experiment with methyl orange until the color of the solution is changed to red -orange.

5- Repeat the experiment twice or three times and tabulate your results.

6- Calculate the strength of the sodium hydroxide and the sodium carbonate in the mixture.

Calculations

In the case of Na_2CO_3:

$$N \times 2V = N\ (Na_2CO_3) \times 10$$

$$\text{Strength } Na_2CO_3 = N\ (Na_2CO_3) \times 53\ g/L$$

In the case of NaOH:

$$N \times (V_2 - 2V) = N\ (NaOH) \times 10$$

$$\text{Strength NaOH} = N\ (NaOH) \times 40\ g/L$$

Experimental 2:

1- Standardization of NaOH using standard solution of potassium hydrogen phthalte
2- Determination of % acetic acid in a vinegar solution

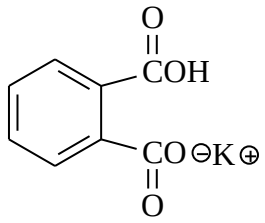
1- Standardization of a Solution of Sodium Hydroxide

Objectives:

You will determine the concentration (standardize) of an unknown solution of NaOH using the primary standard, potassium hydrogen phthalate.

Principle

Sodium hydroxide is hygroscopic and absorbs water from the air when you place it on the balance for massing. This water will prevent you from being able to find the exact mass of sodium hydroxide. In order to determine the exact concentration of a sodium hydroxide solution you must standardize it by titrating with a solid acid that is not hygroscopic. Potassium hydrogen phthalate, $KHC_8H_4O_4$ (abbreviated KHP), is a non-hygroscopic, crystalline, solid that behaves as a monoprotic acid. It is water soluble and available in high purity. Because of its high purity, you can determine the number of moles of KHP directly from its mass and it is referred to as a primary standard. You will use this primary standard to determine the concentration of a sodium hydroxide solution. The structure of KHP is shown below:



When KHP and a base a reacted, a neutralization reaction occurs that is represented by the following equation:

$$KHC_8H_4O_{4\,(aq)} + NaOH_{(aq)} \rightarrow KNaC_8H_4O_{4\,(aq)} + H_2O_{(l)}$$

The net ionic equation is:

$$HC_8H_4O_4^{-1}{}_{(aq)} + OH^-_{(aq)} \rightarrow C_8H_4O_4^{-2}{}_{(aq)} + H_2O_{(l)}$$

Chemicals and tools:

- 50-mL Burette
- 250-mL conical flasks
- Burette funnel
- Two 250-mL beaker
- 10-mL pipette
- Pipette pump.
- KHP NaOH(aq)
- ph.ph
- Distilled water

Preparation of standard solution of KHP (o.lN):

1- Weigh out accurately 2.042 gm of A.R. KHP

2- Dissolve in small quantity of distilled water and transfer quantitatively to 100 ml measuring flask.

3- Complete to the mark and shake well.

4- Calculate the exact normality of KHP solution.

- Weight required = Normality x eq.wt. x volume in liter.

Procedure

1) Clean all tools.

2) With the aid of a 10 ml pipette measure out exactly 10 ml of the 0.1N KHP and transfer it into a clean conical flask.

8) Add 2-3 drops of Phenolphthalein indicator.

9) Rinse your buret with distilled water and then several times with small (5-10 mL) portions of the NaOH solution you have prepared, draining off the solution through the buret tip. Fill the buret nearly to the top of the graduated portion with the NaOH solution and make sure that the buret tip is full of solution. With a piece of paper towel, remove

any drop of NaOH hanging from the tip. See your instructor if your buret does not drain properly, if there are air bubbles trapped in the tip, or if it leaks.

10) Make a preliminary titration to learn approximately how the titration proceeds. Place a sheet of white paper under the flask so that the color of the solution is easily observed.

11) Repeat the experiment three times and tabulate your results.

12) Calculate the concentration and strength of the sodium hydroxide.

Calculation

$$(\mathbf{N_1 \times V_1}) \text{ KHP} = (\mathbf{N_2 \times V_2}) \text{ NaOH}$$

$$\mathbf{N_2} \text{ NaOH} = \frac{(\mathbf{N_1 \times V_1}) \text{ KHP}}{\mathbf{V_2} \text{ NaOH}} = \text{N}$$

Strength NaOH $= N_2$ (NaOH) x 40 g/L

2-Determination of % acetic acid in a vinegar solution

Purpose

The goal of this experiment is to determine accurately the concentration of acetic acid in vinegar *via* volumetric analysis, making use of the reaction of acetic acid with a strong base, sodium hydroxide.

Principle

Acetic acid is a weak acid having a K_a of 1.76×10^{-5}. It is widely used in industrial chemistry as acetic acid (it has a specific gravity of 1.053 and is 99.8% w/w) or in solution of varying concentration. In the food industry it is used as vinegar, a dilute solution of glacial acetic acid. The stochiometry of the titration is given by:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

In this experiment, a standardized sodium hydroxide solution (NaOH) will be used. Using basic stoichiometry, the moles of acetic acid (CH_3COOH) in the vinegar solution can be determined from the moles of NaOH added to the reaction.

Note the molar relationship. For every one mole of acetic acid, it would take one mole of NaOH to completely react it. For every one mole of NaOH, it takes one mole of acetic acid to react with it.

moles of NaOH = moles of acetic acid

Chemicals and tools:

- 50-mL Burette
- 250-mL conical flasks
- Burette funnel
- Two 250-mL beaker
- 10-mL pipette
- Pipette pump.
- vinger
- NaOH(aq)

- ph.ph
- Distilled water
-

Procedures

1) Clean all tools with D.I.water .
2) Pipet 10 ml of the vinegar solution into a clean 100 ml measuring flask and complete to the mark with water.
3) Shake the volumetric flask thoroughly to make sure the solution is homogeneous.
4) Rinse the buret with 5 ml portions of the diluted vinegar solution. Make sure you drain the diluted vinegar solution through the tip of the burette.
5) Using a funnel, fill the burette with the diluted vinegar solution. Make sure that the tip is also filled and there are no air bubbles in the tip.
6) With the aid of a 10 ml pipette measure out exactly 10 ml of the standardized NaOH and transfer it into a clean conical flask.
7) Add two drops of phenolphthalein indicator.
8) Place a white background underneath the flask with the NaOH solution.
9) Slowly add with constant swirling the diluted vinegar solution drop wise to the NaOH solution.
10) Continue adding drop wise to the NaOH solution until the NaOH solution turns to colorless. This is called your endpoint.
11) Calculate the % of acetic acid in the vinegar solution.

Calculation

I. After dilution

(N x V) $NaOH$ = **(N` x V `)** CH_3COOH

$$\mathbf{N`}\ CH_3COOH = \frac{\mathbf{(N \times V)}\ NaOH}{\mathbf{V`}\ CH_3COOH} = N$$

I. Before dilution

(N x V) CH_3COOH = **(N` x V `)** CH_3COOH

$$\mathbf{N`}\ CH_3COOH = \frac{\mathbf{(N \times V)}\ CH_3COOH}{\mathbf{V`}\ CH_3COOH} = N$$

Strength of CH_3COOH =N (CH_3COOH) x 60

= g/L

Volume =mass/density

Density (CH_3COOH) = 1.049 g/ml

g ⟶ 1L (1000ml)

Volume percent (%v/v) is defined as $\%v/v = \frac{V_{solute}}{V_{solution}} \times 100$

Experimental 3:

Oxidation reduction reaction

(I)Standardization of potassium permanganate with oxalic acid
II) Analysis of a mixture of oxalic acid and sodium oxalate

(I)Standardization of potassium permanganate with oxalic acid

Principle

Potassium permanganate, $KMnO_4$, 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 faint pink color 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, $C_2O_4^{2-}$ in acidic conditions. Oxalate reacts very slowly at room temperature so the solutions are titrated hot to make the procedure practical. The unbalance redox reaction is shown below.

$$2KMnO_4 + 3H_2S0_4 + 5H_2C_2O_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

In this experiment, a potassium permanganate solution will be standardized against a sample of potassium oxalate. Once the exact normality (eq/L) of the permanganate solution is determined, it can be used as a standard oxidizing solution.

Chemicals and tools:

$KMnO_4$
$H_2C_2O_4$
6 N H_2SO_4
pipet bulb

Procedure

1. Rinse and fill the buret with the $KMnO_4$ solution.
2. Add 20 mL of 6 N H_2SO_4 to the oxalate sample in the Erlenmeyer flask.
3. Heat the acidified oxalate solution to about 85 °C. Do not boil the solution.

4. Record the initial buret reading. Because the $KMnO_4$ solution is strongly colored, the top of the meniscus may be read instead of the bottom.

5. Titrate the hot oxalate solution with the $KMnO_4$ solution until the appearance of a faint pink color.

6. Record the final buret reading and calculate the volume of $KMnO_4$ used in the titration.

7. Discard the titration mixture down the drain and repeat the titration with a new sample of oxalate for a total of 2 trials.

Calculations

$$C_2O_4^{-2} \rightarrow 2CO_2 + 2e^-$$

eq.wt. of oxalic acid $= \frac{M.wt.}{2} = 63$

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$$

eq.wt. of $KMnO_4$ =Mwt/5 = 31.6

$$\mathbf{(N \times V)}_{H_2C_2O_4} = \mathbf{(N` \times V `)}_{KMnO_4}$$

$$\mathbf{N`}_{KMno_4} = \frac{\mathbf{(N \times V)}_{H_2C_2O_4}}{\mathbf{V `}_{KMno_4}} = \quad N$$

$$C_{g/L} = N \times Eq$$

$$N \times \frac{M._{Wt}}{valence} = \quad g/L$$

(II) Analysis of a mixture of oxalic acid and sodium oxalate

Principle:

The strength of oxalic acid is determined by titration with NaOH solution and the amount of oxalate ions is determined by titration with potassium permanganate.

$$H_2C_2O_4 + 2NaOH \longrightarrow 2H_2O + Na_2C_2O_4$$

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

Chemicals:

Potassium permanganate solution 0.1N

Sodium hydroxide solution 0.1N

A mixture of oxalic acid and sodium oxalate solution of unknown strength Dilute sulphuric acid (2N)

Procedure:

1- Transfer 10mL of the mixture to a conical flask, and add two drops of ph.ph.
2- titrate against sodium hydroxide solution. Calculate the strength of oxalic acid in solution in gm/L.
3- Transfer 10 ml of the mixture to a conical flask, add an equal amount of dilute sulfuric acid, heat to 60-90 °C then titrate against permanganate solution till pale rose in color.

Calculation

In the first titration:

Suppose that V_1 ml of 0.1N NaOH solution was taken in the titration

$$V_1 \text{ ml of } 0.1N \text{ NaOH} \equiv \text{oxalic acid in the solution} \equiv$$

From the relation:

$$N_1 \times V_1 \text{ (NaOH)} = N_2 \times V_2 \text{ (oxalic acid)}$$

We can deduce the normality of oxalic acid and calculate its strength in g/L.

In the second titration:

Suppose that V_2 ml of 0.1N $KMnO_4$ was used up in the titration of the total oxalate.

$$\text{Volume of } KMnO_4 \equiv \text{sodium oxalate} = V_2 - V_1 = V_3 \text{ ml}$$

and from the relation:

$$N \times V_3(KMnO_4) = N' \times V' \text{ (sod. Oxalate)}$$

We can deduce the normality of sodium oxlate and from the relation:

$$\text{strength} = N \times \text{eq. wt.} \quad g/L$$

we can deduce the strength of sodium oxalate.

Experimental 4:

Iodimetry and iodometry

I- Standardization of sodium thiosulphate solution with potassium iodate

II-Determination of copper in copper sulphate ($CuSO_4.5H_2O$)

I-Standardization of sodium thiosulphate solution with potassium iodate

Principle:

potassium iodide reacts in acid medium with potassium iodate with the liberation of Iodine:

$$KIO_3 + 3H_2SO_4 + 5KI \rightarrow 3K_2SO_4 + 3I_2 \uparrow + 3H_2O$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Procedure:

1- Transfer 10 ml of 0.1 N potassium iodate solution to a conical flask.
2- Add 1 gm of potassium iodide then add 2 ml of dilute sulphuric acid.
3- Dilute the solution with distilled water then titrate the liberated iodine against sodium thiosulphate solution till the color becomes pale yellow.
4- Add 1 ml of starch solution and continue titration with thiosulphate solution till the color change from blue to colorless.

Calculation

Equivalent weight of $Na_2S_2O_3.5H_2O$ = *M. wt.*

Calculate normality from the relation:

$$N_1 \cdot V_1 (Na_2S_2O_3) = N_2 \cdot V_2 (KIO_3)$$

(II) Determination of copper in copper sulphate ($CuSO_4.5H_2O$)

Principle:

Copper sulphate reacts with potassium iodide according to the following equation:

$$2CuSO_4 + 4KI \rightarrow Cu_2I_2 + I_2\uparrow + 2K_2SO_4$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

i.e. $$2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3$$

The equivalent weight of copper sulphate = M. wt.

The equivalent weight of copper = atomic wt. = 63.5

Procedure:

1- Transfer 10 ml of copper sulphate solution to a conical flask, and then add 10 ml of potassium iodide solution (10%).

2- Titrate the liberated iodine with 0.1N thiosulphate solution till the color becomes pale yellow.

3- Add 1 ml of starch solution and continue adding the thiosulphate solution till the blue color is discharged (a white ppt. of cuprous iodide remains).

4- Repeat the experiment twice.

Calculation:

$$1\ ml\ 0.1N\ Na_2S_2O_3\ solution \equiv \frac{0.1 \times 63.5}{1000} \equiv 0.00635\ gm\ Cu$$

$$wt.\ of\ Cu = V(S_2O_3^{-2}) \times 0.00635\ gm / 10\ ml$$

or:

$$N\ .\ V\ (S_2O_3^{-2}) = N\ .\ V\ (Cu)$$

$$N\ .\ V\ (S_2O_3^{-2}) = \frac{wt.of\ Cu}{eq.wt} \times 1000$$

$$\therefore wt.\ of\ Cu\ (gm) = \frac{N.V(S_2O_3^{-2}) \times eq.wt.}{1000}$$

Experimental 5:

Complexometric Titration using EDTA

(I)Preparation and Standardization of EDTA Solution

(II) Determination of ferric iron with EDTA

Principle

EDTA solutions are usually prepared by weighing the dehydrated disodium salt of ethylene diamine tetra acetic acid.

Preparation of 0.1M Solution of EDTA:

Dissolve 37.225 gm of analytical reagent (A.R.) disodium dihydrogen ethylene diamine tetra acetate dihydrate in water and dilute to one liter.

Metal ion indicators used in these titrations:

The requisites of a metal ion indicator for use in the visual detection of end points include:

1- The color detection must be such that before the end point when nearly all the metal ion is complexed with EDTA, the solution is strongly colored.

2- The color reaction should be specific or at least selective .

3- The metal-indicator complex must be less stable than the metal -EDTA complex to ensure that at the end point, EDT A removes metal ions from the metal indicator complex. The change in equilibrium from the metal indicator complex to metal EDTA complex should be sharp and rapid.

4- The color contrast between then free indicator and the metal indicator complex should be such as to be readily observed.

5- The indicator must be very sensitive to metal ions so that the color change occurs as near to the equivalence point as possible.

Preparation of buffer (pH = 10):

Put 142 m1 of concentrated ammonia solution + 17.5 gm of A.R. NH_4Cl and dilute to 250 m1 with distilled water.

Preparation of standard 0.01 M $MgSO_4$ .7 H_2O:

Dissolve 2.4632 gm in one liter.

Preparation of 0.01 M EDTA solution:

Dissolve 3.7225 gm in one liter.

I-Standardization of EDTA solution against $MgSO_4$ .7H_2O

Procedure:

1- Pipette 10 m1 of the $MgSO_4$ solution into a 250 ml conical flask, then add 50-60 ml of distilled H_2O and 3 ml of buffer (pH=10) .

2- Add about 3 or 4 pieces of Eriochrome black T indicator and titrate with the EDTA solution until the wine red color changes to clear blue.

Calculations:

Calculate the molarity of EDTA

$$M \,.V\,(MgSO_4) = M'\,.V'\,(EDTA)$$

$0.01 \quad x\ 10 = M'\,.V'$ (Volume taken from burette)

(II) Determination of ferric iron with EDTA

Principle

Salicylic acid and ferric ions form a deep-colored complex with a maximum absorption (λ_{max}) at about 525 nm; this complex is used as the basis for the photometric titration of ferric ion with standard EDTA solution. At a pH of 2.4 the EDTA-iron complex is much more stable (higher formation constant) than the iron-salicylic acid complex. In the titration of an iron-salicylic acid solution with EDTA the iron-salicylic acid color will therefore gradually disappear as the end point is approached.

Reagents:

1- EDTA solution 0.1 M.

2- Ferric iron solution 0.05 M (Dissolve about 12.0gm, accurately weighed, of A.R. ferric chloride in water to which a little dilute H_2SO_4 is added, and dilute the resulting solution to 500ml in a volumetric flask).

3- Sodium acetate-acetic acid buffer (Prepare a solution which is 0.2 M in sodium acetate and 0.8 M in acetic acid. The pH is 4.0) .

4- Salicylic acid solution (Prepare a 6% solution of A.R. salicylic acid in A.R. acetone).

Procedure:

1- Transfer 10 ml of ferric iron solution to the conical Flask, add about 10 ml of the buffer solution of pH = 4 and about 120 ml of dist. H_2O.

2- Add 1.0 ml of salicylic acid solution.

3- Add the EDTA solution slowly until the color will decrease, then introduce the EDTA solution in 0.1 ml aliquots until the color disappear.

4- Calculate the concentration of Ferric iron.

Calculations:

$$M.V\,(EDTA) = M'.V'\,(Fe^{+3})$$

$$wt.\ of\ Fe^{+3} = \frac{M.V\,(EDTA) \times atm.wt.Fe^{+3}}{1000} = \ gm/10ml$$

Experimental 6:

Precipitation Titration
Standardization of Silver Nitrate against Sodium Chloride
(I) By the use of potassium chromate as indicator (Mohr's method):

I-Silver nitrate titration by using Mohr's method

Principle

This method determines the chloride ion concentration of a solution by titration with silver nitrate. As the silver nitrate solution is slowly added, a precipitate of silver chloride forms.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

The end point of the titration occurs when all the chloride ions are precipitated. Then additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.

$$2\ Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$$

The Mohr titration should be carried out under conditions of pH 6.5 – 10. At higher pH silver ions may be removed by precipitation with hydroxide ions, and at low pH chromate ions may be removed by an acid-base reaction to form hydrogen chromate ions or dichromate ions, affecting the accuracy of th end point. If the solutions are acidic, the gravimetric method or Volhard's method should be used.

Chemicals and tools:

burette and stand

10 and 20 mL pipettes

250 mL conical flasks

10 mL and 100 mL measuring cylinders

0.1 N NaCl

0.1N silver nitrate solution

Chromate indicator

Procedure

1. Pipette a 10 mL of NaCl into a conical flask and add 1 mL of chromate indicator.
2. Titrate the sample with 0.1 mol L^{-1} silver nitrate solution. Although the silver chloride that forms is a white precipitate, the chromate indicator initially gives the cloudy solution a faint lemon-yellow colour (figure 1).
3. Repeat the titration until concordant results (titres agreeing within 0.1 mL) are obtained.
5. Calculate the concentration of chloride ions.

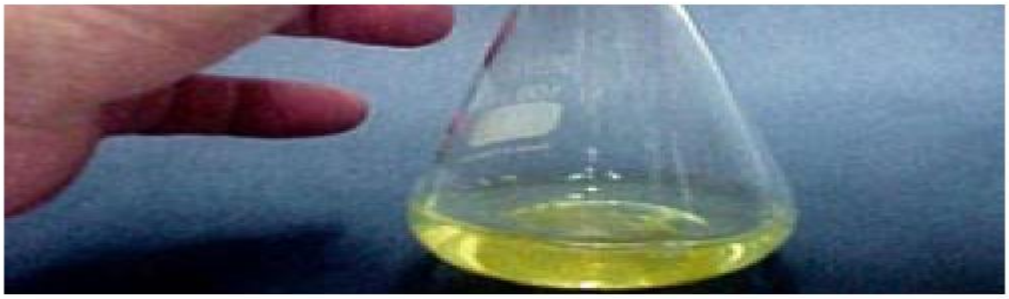


Figure 1 before the addition of any silver nitrate the chromate indicator gives the clear solution a lemon-yellow colour

The endpoint of the titration is identified as the first appearance of a red-brown colour of silver chromate (figure 2).



Figure 2 Left flask: before the titration endpoint, addition of Ag+ ions leads to formation of silver chloride precipitate, making the solution cloudy. The chromate indicator gives a faint lemon-yellow colour. Centre flask: at the endpoint, all the Cl^- ions have precipitated. The slightest excess of Ag+ precipitates with the chromate indicator giving a slight red-brown colouration. Right flask: If addition of Ag+ is continued past the

endpoint, further silver chromate precipitate is formed and a stronger red-brown colour results.

Calculation

$$\textbf{(N x V)}\ AgNO_3 = \textbf{(N` x V `)}\ NaCl$$

$$\textbf{N`}\ NaCl = \frac{\textbf{(N x V)}\ AgNO_3}{\textbf{V `}\ NaCl} = N$$

Strength NaCl =N (NaCl) x 58.5

= g/L

II- Silver nitrate titration by using volhard's method

Principle

It is not always possible to use Mohr method to determine concentration of chlorides. For example, Mohr method requires neutral solution, but in many cases solution has to be acidic, to prevent precipitation of metal hydroxides (like in the presence of Fe^{3+}). In such cases we can use Volhard method, which is not sensitive to low pH.

In the Volhard method chlorides are first precipitated with excess silver nitrate, then excess silver is titrated with potassium (or sodium) thiocyanate. To detect end point we use Fe^{3+} cations, which easily react with the thiocyanate, creating distinct wine red complex.

There is a problem though. Silver thiocyanate solutility is slightly lower than solubility of silver chloride, and during titration thiocyanate can replace chlorides in the existing precipitate:

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

To avoid problems we can filtrate precipitated AgCl before titration. However, there exist much simpler and easier procedure that gives the same result. Before titration we add some small volume of a heavy organic liquid that is not miscible with water (like nitrobenzene, chloroform or carbon tetrachloride). These liquids are better at wetting precipitate than water. Once the precipitate is covered with non polar liquid, it is separated from the water and unable to dissolve.

Precipitate solubility is not a problem during determination of I^- and Br^-, as both AgBr and AgI have much lower solubilities than AgSCN.

There are two reactions, as this is a back titration. First, we precipitate chlorides from the solution:

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$

Then, during titration, reaction taking place is:

$$Ag^+ + SCN^- \rightarrow AgSCN(s)$$

Note, that silver nitrate can be added not using single volume pipette, but from burette. If the amount of chlorides is approximately known, this way it is possible to control excess of silver nitrate and volume of the thiocyanate titrant.

End point is detected with the use of iron (III) thiocyanate complex, which have very distinct and strong wine color.

Chemicals

0.1 M silver nitrate solution

0.1 M potassium thiocyanate solution

nitric acid (1+1) to acidify solution

ammonium ferric sulfate solution

nitrobenzene

distilled water

Procedures

1. Pipette 10 ml of chlorides solution into 250 mL Erlenmeyer flask.
2. Add 5 mL of 1+1 nitric acid.
3. Add 20 mL of 0.1M silver nitrate solution.
4. Add 3 mL of nitrobenzene or chloroform.
5. Add 1 mL of iron alum solution.
6. Shake the content for about 1 minute to flocullate the precipitate.
7. Titrate with thiocyanate solution till the first color change.

Calculation

V1= volume of KSCN

V2= volume of total AgNO3

V3= volume of $AgNO_3$ react with NaCl

(N x V3) $AgNO_3$ **= (N` x V `)** NaCl

$$\textbf{N`}\ NaCl = \frac{\textbf{(N x V)}\ AgNO_3}{\textbf{V `}\ NaCl} = N$$

Strength NaCl =N (NaCl) x 58.5

= g/L

b) Gravimetric analysis

Technique of gravimetric analysis

The operation of gravimetric analysis may be summarized under the headings:

a) Precipitation. b) filtration. c) the washing of the ppt .

d) the drying, ignition and weighing of the ppt. e) the calculations.

Precipitation:

Precipitations are usually carried out in resistance-glass beakers, and the solution of the precipitant is added slowly (by means of a pipette, burette or tap funnel) and with efficient stirring of the suitably diluted solution. The addition must always be made without splashing, this is the best achieved by allowing the solution of the reagent to flow down the side of the beaker or precipitating vessel. Only a moderate excess of the reagent is generally required, a very large excess may lead to increasing solubility or contamination of the ppt. After the ppt has settled a few drops of the precipitant should always be added to determine whether further precipitation occurs. As a general rule, precipitates are not filtered off immediately after they have been formed , most ppt, with the exception of those which are definitely colloidal , such as ferric hydroxide, require more or less digestion to complete the precipitation and make all particles of filterable size.

The purity of the precipitate:

When ppt separates from a solution, it is not always perfectly pure. It may contain varying amounts of impurities dependent upon the nature of the ppt and the conditions of precipitation. The contamination of the ppt by substances which are normally soluble in the mother liquor is called co-precipitatin.

Digestion:

It is usually carried out by allowing the ppt to stand for 12-24 hours at room temperature, or sometimes by warming the ppt for some time in contact with the liquid from which it was formed : the object is, of course to obtain complete precipitation in a form which can be readily filtered.

Crucibles fitted with permanent porous plates:

These possess an advantage over Gooch crucibles in so far that no preparation of a filter-mat is necessary. The best known are the sintered-glass crucibles.

The advantages of sintered-glass crucibles are:

1- They are made entirely of glass, which is resistant to most chemical reagents with the exception of hydrofluoric acid and hot, concentrated alkalis.
2- They can by dried to constant weight at 100-150°C .
3- They are readily cleaned.
4- It is ideal for work requiring temperature less than about 300°C

Experimental 7:

Determination of Water of crystallisation in barium chloride

Objectives

To calculate the water of crystallization in barium chloride

Principle

A hydrate salt is composed of anions (negative ions) and cations (positive ions) which are surrounded by and weakly bonded water molecules. Each hydrate salt has a fixed number of water molecules associated with it, called waters of hydration or water of crystallization. When a salt holds waters of hydration, we call it a hydrated salt or a hydrate (hydrate from *hydor*, the Greek word for water).

Barium chloride dihydrate, $BaCl_2 \bullet 2H_2O$, has two waters of crystallization, or two waters of hydration. Other hydrates have waters of hydration ranging from one to twelve. Upon heating, a hydrate decomposes and produces an anhydrous salt and water (in the form of steam).

$$BaCl_2 \bullet 2H_2O_{(s)} \xrightarrow{\Delta} BaCl_{2\,(s)} + 2\,H_2O_{(g)}$$

Procedure

1. Obtain a porcelain crucible from the stockroom, rinse with water, and heat in an oven for 10 minutes to remove any surface moisture. Use crucible tongs when handling hot crucibles.

2. Weigh the cool, dry crucible and lid. Record the weight on the data sheet.

3. Place between 1.0 and 1.5 g of $BaCl_2 \bullet 2H_2O$ in the crucible and reweigh the crucible, lid and contents. Record the mass on the data sheet. Calculate the weight of the hydrate. Record the mass of the hydrate on the data sheet.

4. Place the crucible back on the clay triangle with the lid almost covering the crucible. Heat in an oven for 60 minutes. Allow the crucible to cool until it is cool to the touch. Weigh the crucible and lid and record the mass on the data sheet.

5. Complete the calculations to determine the percent water in the compound. Show the calculations on the data sheet.

6. Dispose of the $BaCl_2 \bullet 2H_2O$. Repeat the procedure as Trial 2 on the data sheet.

Result sheet



A. Percentage of Water in Barium Chloride Dihydrate

Trial 1

(1) Mass of crucible and lid _____g

(2) Mass of crucible, lid and hydrate _____g

(3) Mass of hydrate (2) – (1) _____g

(4) Mass of crucible, lid and _____ g

anhydrous salt (after heating)

(5) Mass of water _____ g

Calculations



The **experimental percentage** of water in a hydrate is found by comparing the mass of water driven off to the total mass of the compound, expressed as a percentage.

A 1.250 g sample of barium chloride dihydrate has a mass of 1.060 g after heating. Calculate the experimental percentage of water.

Solution: The mass of water lost is found by difference:

1.250 g – 1.060 g = 0.190 g

hydrate anhydrous water salt

The experimental percentage of water is

$$\frac{\text{mass of water}}{\text{mass of hydrate}} \times 100 = \% \text{ of water}$$

$$\frac{0.190\text{ g}}{1.250\text{ g}} \times 100 = 15.2\% \text{ water}$$

Problem 3 – Water of crystallization

Calculate the water of crystallization for an unknown hydrate that is found to contain 30.6 % water. The formula mass of the anhydrous salt (AS) is 245 amu.

Solution: The unknown hydrate is 30.6 % water. subtracting from 100 %, the hydrate must be 69.4 % anhydrous salt. If we make the sample 100 g, the mass of water is 30.6 g and the anhydrous salt 69.4 g. to calculate the moles of water and the anhydrous salt (AS)

$$30.6 \text{ g } H_2O \times \frac{1 \text{ mole } H_2O}{18.0 \text{ g } H_2O} = 1.70 \text{ moles } H_2O$$

$$69.4 \text{ g AS} \times \frac{1 \text{ mole AS}}{245 \text{ g AS}} = 0.283 \text{ mole AS}$$

To find the water of crystallization, simply divide the mole ratio of water to anhydrous salt.

$$\frac{1.70 \text{ moles } H_2O}{0.283 \text{ mole AS}} = 6.01 \approx 6$$

The water of crystallization is always a whole number, therefor the formula for the unknown hydrate is $AS \bullet 6H_2O$

Experimental 8:

Determination of Lead as Chromate

Principle:

The lead is precipitated as lead chromate by treating a hot acidic solution of lead salt with potassium chromate solution.

$$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2KNO_3$$

Procedure:

1- Weigh out 0.3 gm of the Lead Nitrate and dissolve it in 150 ml of distilled water.
2- Add two drops of conc. acetic acid to the solution until it is distinctly acidic [use litmus paper].
3- Heat to boiling then add from a pipette 10ml of 4% potassium chromate solution.
4- Boil gently for 5- 10 minutes [or until the precipitate settles], the supernatant liquid must be colored slightly yellow.
5- Filter through a clean and weighed sintered glass crucible.
6- Wash thoroughly with hot water.
7- Dry at 120° C to constant weight.
8- Weigh as $PbCrO_4$, and calculate the weight of Pb in the sample.

Calculation:

$PbCrO_4$ ------- Pb

323 207

1gm ---------- X

Gravimetric factor of Pb in $PbCrO_4$ =207/323 = 0.64 gm

$$\% Pb = \frac{wt.of\ ptt.}{wt.of\ sample} \text{x } 0.64 \text{ x } 100$$

II-Qualitative Analysis

Introduction:

When an acid, e.g. HCl is made to react with a base, e.g. NaOH, salt, NaCl, and water are formed according to the following equation :

$$HCl + NaOH = NaCl + H_2O$$

acid base salt water

The part of the salt which is derived from the base, Na^+, is called the" basic radical",where as the other part which is derived from the acid is termed the" acidic radical".

In the following labs we will describe the schemes of Qualitative Analysis of acid radicals or (anions) and basic radicals or(cations)

Safety Precautions:

In some of the tests you will be required to use fairly concentrated acids and bases. When in contact with skin, most of these chemicals can cause severe burns if not removed promptly. Wear goggles when working with any of the reagents required in this experiment.



Experimental 9:

Part I: Identification of Anions

The common anions are devided into three groups for the purpose of identification:

1) Those which evolve gases with dilute hydrochloric acid :
   a) Carbonate (CO_3^{2-})
   b) Bicarbonate(HCO_3^-)
   c) Nitrite(NO_2^-)
   d) Sulphite(SO_3^{2-})
   e) Thiosulphate($S_2O_3^{2-}$)
   f) Sulphide (S^{2-})

2)Those which do not react with dilute HCl, but which do evolve gases or volatile liquids with concentrated sulphuric acid:

   a) Chloride (Cl^-)
   b) Bromide (Br^-)
   c) Iodide (I^-)
   d) Nitrate (NO_3^-)

3)Those which do not react with either dilute hydrochloric acid or concentrated sulphuric acid:

   a) Phosphate (PO_4^{3-})
   b) Borate ($B_4O_7^{2-}$)
   c) Sulphate (SO_4^{2-})

1) Anions which react with dilute hydrochloric acid

	Carbonates (CO_3^{2-})	**Bicarbonates** (HCO_3^-)	**Thiosulphates** ($S_2O_3^{2-}$)
	All carbonates except those of alkali metals, and ammonium are very slightly or difficulty soluble in water.Accordingly reactions in solution are only carried out in case of the soluble salts.	All bicarbonates are water soluble.	Sodium thiosulphate is readily soluble in water , other thiosulphates are slightly soluble.
Solid salt + dil. HCl	Effervescence and a colourless odourless gas is evolved, gas is carbon dioxide (CO_2), $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$	Effervescence and a colourless odourless gas is evolved, gas is carbon dioxide (CO_2), $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$	Colourless gas with pungent odour , which turns an orange acidified potassium dichreomate paper green and a yellow precipitate appears. Gas is SO_2,green color is chromium sulphate $Cr_2(SO_4)_3$ and ppt is sulphur(S) $Na_2S_2O_3 + 2\ HCl \rightarrow 2\ NaCl + H_2O + SO_2 + S\downarrow$
Salt solution + magnesium sulphate solution or $BaCl_2$	White precipitate is obtained on cold. ppt is magnesium carbonate $Na_2CO_3 + MgSO_4 \rightarrow MgCO_3\downarrow + Na_2SO_4$	No ppt. in the cold , as magnesium bicarbonate is soluble, but on heating, a white ppt.of magnesium carbonate is obtained : $2NaHCO_3 + MgSO_4 \rightarrow Na_2SO_4 + Mg(HCO_3)_2$ $Mg(HCO_3)_2 \xrightarrow[\text{soluble in water}]{\triangle} MgCO_3\downarrow + CO_2 + H_2O$	-

Salt solution + 2 drops of dil. H_2SO_4 + Iodine solution(I_2)	-	--	The brown colour of the iodine solution disappears, because the iodine is reduced to the iodide ion, which is colourless. At the same time, the thiosulphate is oxidized to tetrathionate $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI$
Salt solution + silver nitrate solution ($AgNO_3$)	White precipitate of magnesium carbonate	No ppt. in the cold , but on heating, a white ppt. is obtained .	A white precipitate forms (silver thiosulphate $Ag_2S_2O_3$), which is soluble in excess of the thiosulphate, due to the formation of complex , which is unstable(it changes to yellow, brown and finally to black Ag_2S). $Na_2S_2O_3 + 2\ AgNO_3 \rightarrow Ag_2S_2O_3\downarrow +$ $2\ NaNO_3$ White ppt

2) Anions which react with concentrated sulphuric acid

Note: Do these tests in fuming cuper because the gases which are given off in these tests are extremely irritating, and can cause damage to the sensitive mucous membranes of nose and throat.

	Chlorides (Cl^-)	**Bromides** (Br^-)	**Iodides** (I^-)	**Nitrates** (NO_3^-)
	All chlorides are water soluble except the chlorides of silver, mercurous and cuprous.	Bromides resemble chlorides in their solubility.	Iodides resemble chlorides and bromides in their solubility. However, bismuth iodide is insoluble.	All nitrates are soluble in water except some basic nitrates.
Solid salt +conc. H_2SO_4:	Effervescence with evolution of colourless gas , Hydrogen chloride (HCl), $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl$	Raddish fumes evolve and the solution turns orange due to libertion of bromine (Br_2) $2NaBr + H_2SO_4 \rightarrow 2HBr + Na_2SO_4$ $2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2$	Violet fumes are evolved, (Iodine gas I_2) and a brown or black precipitate is formed in the test tube. $2KI + 2\ H_2SO_4 \rightarrow K_2SO_4 + 2H_2O + SO_2 + I_2$	-ve Dense brown fumes are evolved and the solution turns blue. gas is NO_2 $2NaNO_3 + H_2SO_4 \rightarrow HNO_3 + Na_2SO_4$ $4HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$ *** Brown ring test:** The nitrate solution is mixed with freshly prepared $FeSO_4$ solution, then conc. H_2SO_4 is added and allowed to flow causiously on the side of the test tube. A brown ring $(Fe.NO)SO_4$ is formed at the interface of the two layers. The brown ring disappears on shaking the solution.

Salt solution + silver nitrate ($AgNO_3$)	A dense white ppt. of silver chloride (AgCl) slowly turns a violet colour when exposed to bright sunligt. $NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$	A yellowish white precipitate of silver bromide(AgBr) is formed. $NaBr + AgNO_3 \rightarrow AgBr\downarrow + NaNO_3$ ppt	A yellow precipitate of silver iodide (AgI) is formed. $KI + AgNO_3 \rightarrow AgI\downarrow + KNO_3$ ppt	-ve
Salt solution + lead acetate	A white precipitate of lead chloride ($PbCl_2$) is formed which is soluble in hot water, and reprecipitates on cooling. $2NaCl + Pb(CH_3COO)_2 \rightarrow PbCl_2\downarrow + 2CH_3COONa$	A white precipitate of lead bromide ($PbBr_2$) appears which is soluble in boiling water and reprecipitates on cooling. $2NaBr + Pb(CH_3COO)_2 \rightarrow$ $PbBr_2\downarrow + 2CH_3COONa$	A yellow precipitate of lead iodide (PbI_2) is formed which dissolves in boiling water and recrystallises on cooling. $2KI + Pb(CH_3COO)_2 \rightarrow PbI_2\downarrow + 2CH_3COOK$	———————

3) Anions which do not react with acids:

	Phosphates (PO_4^{3-})	**Borates** ($B_2O_4^{2-}$)	**Sulphates** (SO_4^{2-})
	Most phosphates are insoluble in water except those of ammonium and alkali metals.	Ammonium and alkali metal borates are water soluble while other borates are slightly soluble in water.	All sulphates are soluble in water except those of some divalent metals e.g. calcium, strontium, barium and lead.
Salt solution + Barium chloride solution ($BaCl_2$)	A white precipitate of barium phosphate ($BaHPO_4$) is produced, soluble in dilute acids e.g. HNO_3 or HCl and insoluble in excess of barium chloride. $Na_2HPO_4 + BaCl_2 \rightarrow BaHPO_4\downarrow + 2NaCl$	A white ppt. of barium borate from concentrated solutions $Ba(BO_2)_2$ is produced, soluble in dilute acids and in excess of barium chloride. $Na_2B_4O_7 + 3H_2O + BaCl_2 \rightarrow$ $Ba(BO_2)_2 + 2H_3BO_3 + 2NaCl$	A white precipitate of barium sulphate ($BaSO_4$) is formed which is insoluble in dilute acids and in excess of barium chloride. $Na_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2NaCl$
Confirmatory tests: Salt solution +($AgNO_3$)	A yellow precipitate of silver phosphate (Ag_3PO_4) is formed, which is readly soluble in dil. HNO_3 and ammonia.	A white ppt. is formed, from concentrated solution, which give brown ppt. after boiling.(also a brown ppt. is formed with diluted solution)	A white ppt. of silver sulphate (Ag_2SO_4) is formed with concentrated solution.
Salt solution + lead acetate:	-ve	-ve	A white precipitate of lead sulphate is formed , which is readily soluble in hot concentrated ammonium acetate or conc.H_2SO_4

Experimental 10:

Part I: Identification of cations

1- First group

Exp	Pb^{+2}
Soln+ dill HCl	White ppt sol in hot water
Soln + dil H_2SO_4	White ppt
Soln+ K_2CrO_4	yellow ppt
Soln + H_2S	Black ppt

2- Second group

Exp	Cu^{+2}	Bi^{+3}	Cd^{+2}
Soln+ dill HCl+ H_2S	Black ppt. sol in dill HNO_3	Brown ppt. sol in dill HNO_3	yellowish or orange ppt. sol in dill HNO_3
Soln + NH_4OH	Bluish ppt. dissolve in excess of ammonia formed soluble blue complex	White ppt. does not soluble in excess of ammonia	Soluble complex

3- Third group

Exp	Al^{+3}	Fe^{+3}
Soln+ NH_4Cl+ NH_4OH	Gel white ppt. sol. In dill acid and base	Gel Reddish brown ppt. sol. In dill HCl
Soln+ NaOH	Gel white ppt	Reddish ppt. sol. In dill HCl
Soln + $K_4[Fe(CN)_6]$	White ppt.	Dark blue ppt.
Soln + KCNS	-ve	Deep red color

4-Fourth group

Exp	Zn^{+2}	Mn^{+2}	Co^{+2}	Ni^{+2}
Soln+ NH_4Cl+ NH_4OH+H_2S	White ppt.	Buff ppt.	Black ppt.	Black ppt.
Soln + NH_4OH	White ppt.	Buff ppt.	Blue color	Greenish ppt.
Soln + DMG	-ve	-ve	-ve	Red ppt.

5-Fifth group

Exp	Ca^{+2}	Ba^{+2}	Sr^{+2}
Soln+ NH_4Cl+ NH_4OH+ $(NH_4)_2CO_3$	White ppt.	White ppt.	White ppt.
Soln+ K_2CrO_4	-ve	Yellow ppt. insoluble in acetic acid	Yellow ppt. soluble in acetic acid
Soln+ $CaSO_4$	-ve	White ppt.	White ppt.after heating
Flame test	Brick red color	Yellowish green color	Crimson red colr

6-Sixth group

Exp	Na^{+2}	K^{+}	NH_4^{+}	Mg^{+2}
Sold. Na_2CO_3 +drops of water	-ve	-ve	Gas has a recognized smell is evolved	-ve
Soln+$Na_3[Co(NO_2)_6]$	-ve Yellow solution.	Yellow ppt.	Yellow ppt.	Yellow ppt.
Soln+ NaOH	-ve	-ve	-ve	White ppt.
Flame test	Golden yelloe color	Violet color	-ve	-ve