B.Sc. CHEMISTRY LAB MANUAL

3rd Semester

Prepared By

Pure & Applied Science Dept.

Chemistry

MIDNAPORE CITY COLLEGE

CHEMISTRY HONOURS
[Choice Based Credit System]
(Semester Programme)
SEMESTER-III

C5P: Physical Chemistry Lab

Experiment 1: Study of viscosity of unknown liquid (glycerol, sugar) with respect to water

Theory:

From the literature value of viscosity coefficient of water (η_w) at the experimental temperature and the measured specific gravity of solutions of different concentrations we can determine the value of absolute viscosity coefficients of experimental solution of different concentrations. Thus we can study the variation of viscosity coefficient with concentration by plotting a graph of viscosity coefficient vs. concentration. We can also determine concentration of a solution of unknown concentration from the calibration curve.

Apparatus Required:

1) 100ml beaker -2
2) 250ml volumetric flask -1
3) 50ml volumetric flask -4
4) 10ml sp. Gravity bottle -1
5) Viscometer (Time of flow of 10ml of water should be at least 80 secs)
6) 10ml pipette -1
7) Stop watch.

Chemical required:

Sucrose/ Glycerol

Procedure:

1) Prepare a stock solution of 15% (v/v) Glycerol in a 250ml volumetric flask. Then prepare 12%, 9%, 6%, 3% Glycerol solution each of 50ml from the stock solution by exact dilution.
2) Clean the viscometer with chromic acid and wash thoroughly with deionized water. Remove the water completely. Add 10 ml water in the wider limb using a 10ml pipette. Suck up the water in the other limb and allow it to run between two specified marks. Note the time of flow. Remove the water completely. Rinse the viscometer with experimental liquid (start with lowest concentration of experimental solution and then with increasing concentrations] and discard the rinsing. Add 10ml of experimental liquid with pipette , repeat the procedure and note the time

of flow. Note the time of flow for each of the liquid (water, experimental liquids) at least twice.

3) Use a clean dry 10ml specific gravity bottle to determine the specific gravity of the experimental liquids at room temperature. Record the temperature.

Experimental Result :

1) Room temperature:
2) Preparation of Glycerol solution of different concentration from the stock (15%) solution.

Concentration of the prepared solution (%)	Volume of 15% Glycerol solution(ml)	Volume of water(ml)
3	10	40
6	20	30
9	30	20
12	40	10

3) Determination of specific gravity of experimental liquid:

Weight of empty sp. Gravity bottle (w_1g)	Weight of sp. Gravity bottle+ water (w_2g)	Weight of sp. Gravity bottle+ expt. Solution(w_xg)	Sp. Gravity of the experimental solution $S_x=(w_x-w_1)/(w_2-w_1)$
		w_3=	S_3=
		W_6 =	S_6=
		W_9=	S_9=
		W_{12}=	S_{12}=
		W_{15}	S_{15}=

4) Determination of viscosity coefficient of experimental liquids:

Sl. No	Time of flow for fixed volume of liquid (sec.)					
	Water	Glycerol solution				
		3%	6%	9%	12%	15%
(i) (ii)						
Average time of flow	t_w =	$\mathbf{t_3}$ =	$\mathbf{t_6}$ =	$\mathbf{t_9}$=	$\mathbf{t_{12}}$ =	$\mathbf{t_{15}}$=

Calculation :

From the literature value of (η_w) at experimental temperature, absolute value of viscosity coefficient of experimental liquids can be determined ,

$$\eta_x = \eta_w S_x \, . \, t_L/t_w \; = [X= 3,6,9,12,15]$$

Graph Plotting

Coefficient of viscosity (poise)					
Concentration of Glycerol solution	3%	6%	9%	12%	15%

Plotting a graph of viscosity coefficient vs. concentration gives a calibration curve from which unknown concentration of glycerol solution can be obtained.

Experiment 2: Determination of partition coefficient for the distribution of I_2 between water and CCl_4.

Theory:

If a solute (soluble in both the solvents) is added to a pair of immiscible solvents then it will distribute itself between the two solvents in a constant temperature and pressure. This is Nernst distribution law. Let C and C be the molar concentration of the dissolved substance (solute) in solvent I and II respectively.Then according to the above law

$$\frac{C_1}{C_2} = K, \text{ at constant temperature and pressure}$$

Where K is a constant, called distribution or partition co-efficient of the dissolved substance between the solvent I and II.

The thermodynamic criterion for the equilibrium of the above system is that the chemical potential, μ_1 of the dissolved substance in solvent I must be equal to its chemical potential μ_2 in solvent II, i.e.,

$$\mu_1 = \mu_2$$

$$\text{or, } \mu_1^*(T,P) + RT\ln a_1 = \mu_2^*(T,P) + RT\ln a_2$$

Where a_1 and a_2 are activities of the dissolved substance in solvent I and II respectively and μ_1^* & μ_2^* are constant temperature and pressure. Then it follows from the relation that

$$\frac{a_1}{a_2} = \text{Constant, at constant temperature and pressure}$$

If the two solutions behave ideally then the activities will be equal to the respective mole fraction (x), so that

$$\frac{a_1}{a_2} = \frac{x_1}{x_2} \approx \frac{C_1}{C_2} \quad \text{,if the solutions are dilute.}$$

Then, $\frac{C_1}{C_2}$ = K, at constant temperature and pressure provided the solutions are ideal and dilute and the dissolved substance exists in the same molecular form in the two solvents (and of course the two solvents must be immiscible, otherwise μ_1^* & μ_2^* will depend on the chemical nature of the solvent).

For example if iodine is added to a mixture of water and carbon tetrachloride and is shaken vigorously, at equilibrium, it will distribute itself between the two solvents in a constant ratio of concentration. Concentration of Iodine in each layer is determined by titrating against sodium thiosulphate solution using starch as indicator.

Apparatus required:

1) 250 ml stoppered glass bottles -2
2) 5 ml pipette – 1
3) 25 ml pipette – 1
4) Burette – 1
5) 500 ml glass bottle – 1
6) 250 ml volumetric flask – 1
7) 250 ml conical flask – 2

Chemicals required:

i)Saturated I_2 solution in CCl_4, ii) Pure CCl_4, iii) 10% KI, iv) 1% starch solution, v) $Na_2S_2O_3$.

Procedure:

1) Prepare 250 ml ~ (N/20) $Na_2S_2O_3$ solution.
2) Prepare 250 ml ~ (N/100) $Na_2S_2O_3$ solution by pipetting out 50 ml ~ (N/20) $Na_2S_2O_3$ solution in a 250 ml volumetric flask followed by dilution up to the mark with deionized water.
3) Prepare two sets in 250ml stoppered glass bottle as follows :

Set	**Volume of saturated I_2 solution in CCl_4**	**Volume of CCl_4(ml)**	**Volume of water(ml)**	**Total volume(ml)**
1	35	15	100	150
2	15	35	100	150

After mixing stopper the bottles properly and shake vigorously for an hour. Allow to settle for 10 minutes so that two layers become clearly separated.

4) Pipette out 25 ml of the aqueous layer carefully from each set (so that no organic layer is taken out) and titrate with ~ (N/100) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time.
5) Pipette out 5 ml of the organic layer carefully from each set (so that no aqueous layer is taken out) in a 250 ml conical flask. Add 25ml water and 10 ml 10% KI solution to it. Shake well by swirling motion and titrate with ~ (N/20) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time.

Experimental result:

1) Room temperature:
2) Preparation of 250ml ~ (N/20) $Na_2S_2O_3$ solution

3) Prepare 250ml ~ (N/100) $Na_2S_2O_3$ solution from ~ (N/20) $Na_2S_2O_3$ solution:
4) Table 1:Titration of solvent layers

Set	Organic layer				Aqueous layer			
	No. of obs.	**Vol. of organic layer(ml)**	**Vol. of ~ (N/20) $Na_2S_2O_3$ solution (ml)**	**Mean vol.of ~ (N/20) $Na_2S_2O_3$ solution (ml)**	**No. of obs.**	**Vol. of aqueous layer**	**Vol. of ~ (N/100) $Na_2S_2O_3$ solution (ml)**	**Mean vol. of ~ (N/100) $Na_2S_2O_3$ solution(ml)**
1	i.	5			i.	25		
	ii.	5			ii.	25		
2	i.	5			i.	25		
	ii.	5			ii.	25		

Calculation:

If V_1 ml of 250ml ~ (N/20) $Na_2S_2O_3$ solution is required for 5 ml of organic layer and V_2 ml of ~ (N/100) $Na_2S_2O_3$ solution is required for 25 ml of aqueous layer then partition co-efficient K is given by

$$K=\frac{C_1}{C_2}=\frac{\frac{V_1\times(\frac{N}{20})}{5}}{\frac{V_2\times(\frac{N}{100})}{25}}=25(\frac{V_1}{V_2})$$

Set	Mean vol. of ~ (N/20) $Na_2S_2O_3$ solution(ml) (V_1)	Mean vol. of ~ (N/100) $Na_2S_2O_3$ solution(ml) (V_2)	K=25(V_1/V_2)	Mean K
I.				
II.				

Precautions and suggestions:

Care should be taken during pipetting out different layers so that no mixing occurs. Use bulb pipetizer instead of mouth sucking during pipetting out layers.

Experiment 3: Determination of Keq for KI + I_2 = KI_3, using partition coefficient between water and CCl_4

Theory:

In aqueous solution I_2 and KI from complex as below

$$KI + I_2 = KI_3$$

For which equilibrium constant (K_{eq}) is given by

$$K_{eq} = \frac{[KI_3]_{aq}}{[I_2]_{aq,free}[KI]_{aq,free}} \quad \text{..... (i) , for dilute solution}$$

This equilibrium constant can be determined by applying Nernst distribution law if the second immiscible organic solvent is so chosen that only one of the reactants or products can be distributed between two layers. In this case CCl_4 is chosen as second solvent in which I_2 is soluble. If distribution or partition coefficient (K_d)of I_2 in CCl_4 and water at a particular temperature is given by

$$\frac{[I_2]_{CCl_4}}{[I_2]_{water}} = K_d$$

Then at equilibrium, concentration of free iodine in aqueous layer,

$$[I_2]_{aq,\ free} = \frac{[I_2]_{CCl_4}}{K_d}$$

$[KI_3]_{aq}$= Total I_2 in aqueous layer $-[I_2]_{aq\ ,\ free}$

$$= [I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}$$

Concentration of free KI in aqueous solution,

$[KI]_{aq,free}$= Total concentration of KI-$[KI_3]_{aq}$

$$= [KI]_{aq,\ total} - \{[I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d} \}$$

Therefore, $K_{eq} = \frac{[KI_3]_{aq}}{[I_2]_{aq,free}[KI]_{aq,free}} = \frac{[I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}}{\left(\frac{[I_2]_{CCl_4}}{K_d}\right)([KI]_{aq,total} - \{[I2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}\})}$

Thus from the knowledge of $[I_2]_{aq,\ total}$, $[I_2]_{CCl4}$, $[KI]_{aq,\ total}$ and K_d, the value of K_{eq} can be determined.

Apparatus required:

1) 250 ml volumetric flask -2
2) Glass bottle -1
3) Burette -1

4) 25 ml pipette -1
5) 10 ml pipette -1
6) 250 ml stoppered glass bottle -2
7) 500 ml conical flask -1
8) 250 ml conical flask -2
9) Watch glass -1

Chemicals required: $K_2Cr_2O_7$, $Na_2S_2O_3$, KI, I_2 solution in CCl_4, 4(N) H_2SO_4, Starch.

Procedure:

1) Prepare 250ml of standard (N/20) $K_2Cr_2O_7$ solution and 250ml of standard (N/20) KI solution by accurate weighing.
2) Prepare 500ml ~ (N/20) $Na_2S_2O_3$ solution.
3) Standardize the (N/20) sodium thiosulphate solution idometrically using starch solution as indicator. Take 25ml of standard (N/20) $K_2Cr_2O_7$ solution in a 500 ml conical flask. Add about 10ml (one test tube) of 10% KI solution and 25ml of 4(N) H_2SO_4 solution. Cover the conical flask with watch glass and keep in dark for about 5 minutes. Add 150ml of distilled water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator.
4) Prepare two sets in dry, clean 250ml stoppered glass (leak proof) bottles:

Set	Volume of (N/20) KI solution(ml)	Volume of I_2 solution in CCl_4(ml)	Volume of water(ml)
I	10	~40	90
II	20	~40	80

Stopper the bottles properly and shake the mixtures thoroughly for 45 minutes and allow to stand till complete separation of layers.

5) Pipette out 10 ml of the organic layer carefully from each set (so that no aqueous layer is taken out) in a 250ml conical flask. Add 25 ml water and 10ml 10% KI solution to it. Shaken well by swirling motion and titrate with standard (N/20) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time. Calculate concentration of I_2 in organic layer.
6) Pipette out 10ml of the aqueous layer carefully from each set (so that no organic layer is taken out), add ~ 40ml water and titrate with standard (N/20) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time. Calculate total concentration of I_2 in aqueous layer.
7) Calculate the value of K_{eq} using the supplied value of K_d.

Experimental result:

1) Room temperature.
2) Preparation of 500ml ~ (N/20) $Na_2S_2O_3$ solution.
3) Preparation of 250ml standard (N/20) $K_2Cr_2O_7$ solution.
4) Preparation of 250ml standard (N/20)KI solution.
5) Standardization of the prepared $Na_2S_2O_3$ solution:

Vol. of (N/20) $K_2Cr_2O_7$ solution (ml)	Burette reading		Vol. of $Na_2S_2O_3$ used (ml)	Average vol. of $Na_2S_2O_3$ (ml)
	Initial(ml)	Final(ml)		
25ml				
25ml				

Strength of $Na_2S_2O_3$:

6) Preparation of sets:

Set	Volume of (N/20) KI solution (ml)	Volume of I_2 solution in CCl_4 (ml)	Volume of water (ml)	$[KI]_{aq,total}$

7) Titration of solvent layers:

Set	Organic Layer				Aqueous Layer			
	No. of Obs.	Vol. of organic layer (ml)	Vol. of standard (N/20) $Na_2S_2O_3$ solution (ml)	Mean vol. of standard (N/20) $Na_2S_2O_3$ solution [v_{org}(ml)]	No. of Obs.	Vol. of aqueous layer (ml)	Vol. of standard (N/20) $Na_2S_2O_3$ solution (ml)	Mean vol. of standard (N/20) $Na_2S_2O_3$ solution [v_{aq}(ml)]
I	i	10			i	10		
	ii	10			ii	10		
II	i	10			i	10		
	ii	10			ii	10		

Calculation:

For Set I :

Concentration of I_2 in organic layer, $[I_2]_{CCl_4} = \frac{Mean\ vol.of\ Na_2S_2O_3(V_{org}) \times \text{its strength}}{10}$

Total concentration of I_2 in aqueous layer, $[I_2]_{aq,\ total} = \frac{Mean\ vol.of\ Na_2S_2O_3(Vaq) \times \text{its strength}}{10}$

Similarly for set II calculate $[I_2]_{CCl_4}$ and $[I_2]_{aq,\ total}$.

Calculate k_{eq} for set I and set II using the relation,

$$K_{eq} = \frac{[I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}}{\left(\frac{[I_2]_{CCl_4}}{K_d}\right)\left([KI]_{aq,total} - \left\{\left[I_2\right]_{aq,total}\frac{[I_2]_{CCl_4}}{K_d}\right\}\right)}$$

Experiment 4: Conductometric titration of an acid (strong, weak/ monobasic, dibasic) against base strong.

Theory:

The conductance of an electrolyte solution depends on the mobility and concentration of each type of ions present in the solution. Any reaction which is associated either with replacement of one kind of ion by another of different mobility or with a charge I ionic concentration will be associated with a change in conductance of the reaction mixture. For such reaction gradual addition of one of the reactant to the other will result in a change of conductance in particular manner (depending on the nature of the reaction) up to equivalence point and in different manner after equivalence point. Then equivalence point corresponds to the break in titration curve obtained on plotting the conductance against the volume of the added substance (titrant).The conductance should be measured in a conductivity cell placed in a thermostat (to avoid change in conductance due to change in temperature). The titrant used should be many times stronger than the solution to be titrated to avoid change in conductance due to dilution .To avoid change in conductance due to change of electrolyte concentration resulting from electrolysis with direct current, measurement of conductance should be done using Alternating current based on Wheatstone Bridge principle. The electrodes used must be platinized (to avoid polarization).

Different cases of Conductometric titration:

1) Strong acid vs. strong base:

Let us consider a strong acid (e.g.HCl) is titrated by a strong base (e.g. NaOH). Here the reaction involved is

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

In this reaction H^+ ions are replaced by Na^+ ions of lower mobility. Therefore conductance of the reaction mixture will gradually decrease linearly up to equivalence point and after equivalence point the conductance will increase linearly due to excess of added electrolyte (NaOH) . The nature plot conductance vs volume of NaOH added is shown in the Figure-7.1, where intersection of two straight lines (say O) represents the equivalence point.

2) **Weak acid (monobasic, dibasic) vs. strong base:**

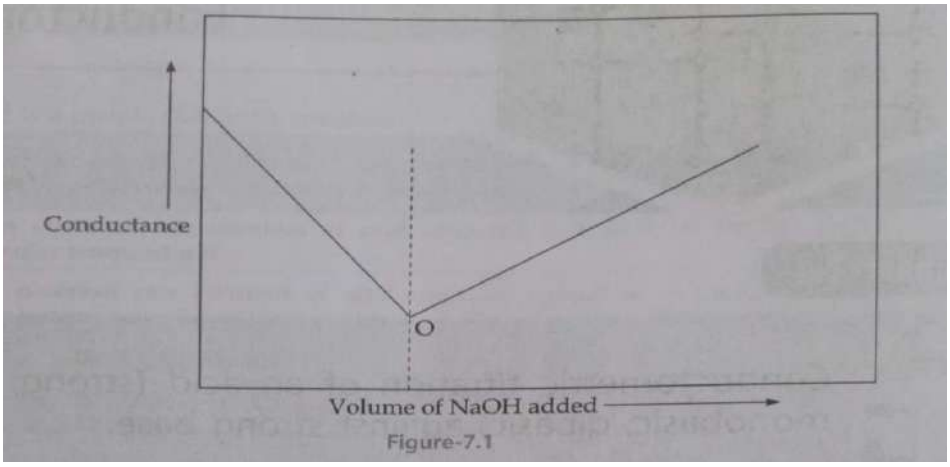


Figure-7.1

a) Titration of weak monobasic acid (CH_3COOH) by strong base (NaOH):

Here the reaction involved is

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ + Na^+ + OH^- \rightarrow Na^+ + CH_3COO^- + H_2O$

Initially H^+ ions (resulting from slight dissociation of CH_3COOH) are replaced by Na^+ ions of lower mobility. Due to this and also suppression of dissociation, conductance of reaction mixture initially slightly decreases. After appreciable addition of NaOH the conductance of reaction mixture will gradually increase up to equivalence point due to formation of highly ionized $CH_3COO^-Na^+$. After equivalence point the conductance will further increase at a different rate. The break in titration curve (Figure7.2) indicates the equivalence point.

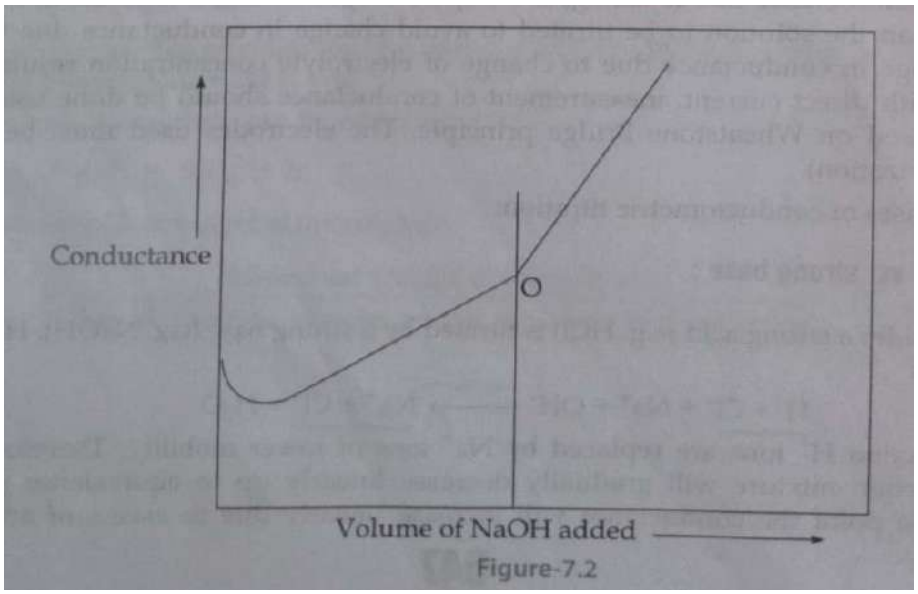
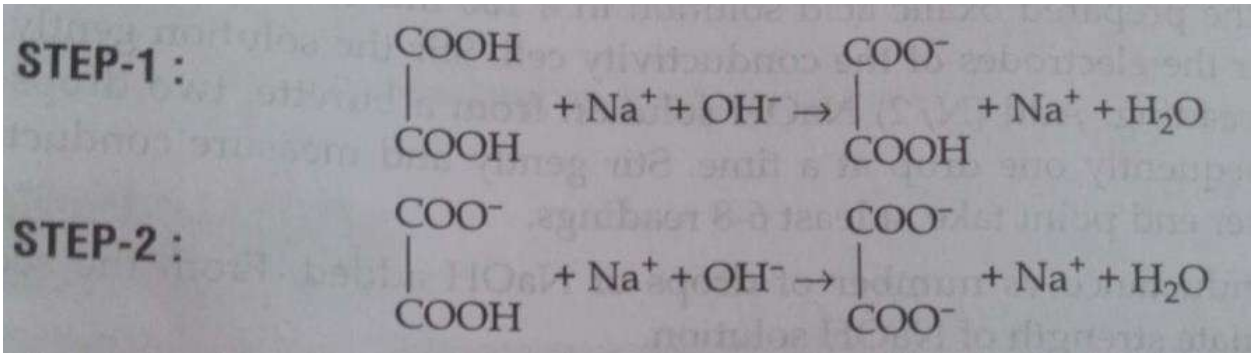


Figure-7.2

b) Titration of weak dibasic acid (Oxalic) by strong base (NaOH):

Here the reaction involved is



Oxalic acid is a dibasic acid and its $pk_2 > pk_1$. Therefore initially up to first equivalence point it will act as a relatively strong acid and conductance of the reaction mixture will gradually decrease linearly up to 1st equivalence point (O) (Figure 7.3) (because H^+ ions are replaced by HC_2O_{4-} ions of lower mobility). Then conductance increases slowly up to 2nd equivalence point due to increase of $C_2O_4^{2-}$ ions with gradual addition of NaOH. After 2nd equivalence point (O_1) conductance will increase rapidly due to excess of added electrolyte(NaOH).

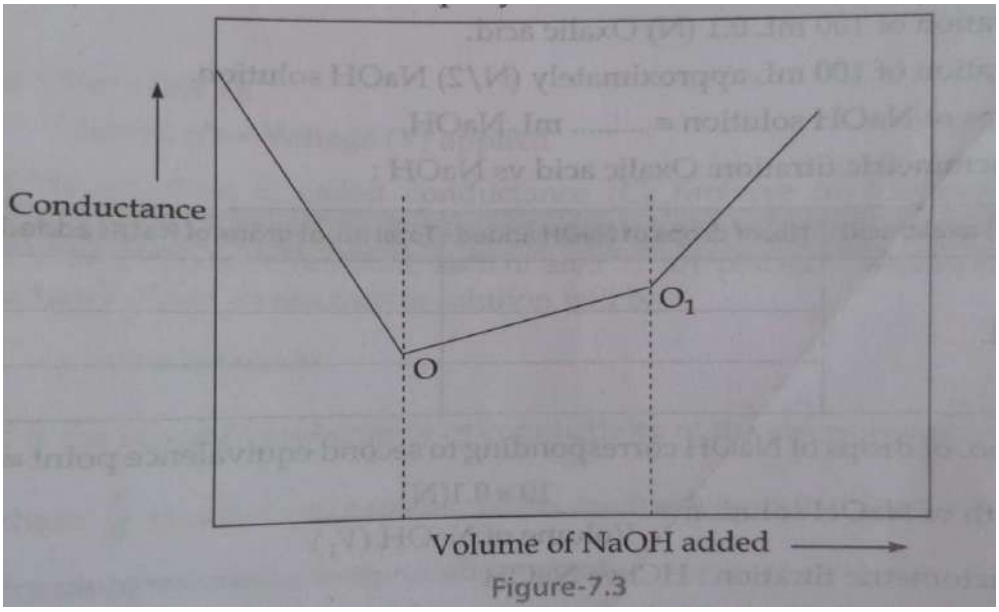


Figure-7.3

Apparatus required:

1) Conductivity meter
2) 100ml beaker
3) Burette (50ml), pipette (10ml) -1
4) 100ml volumetric flask -1
5) 250ml Glass bottle -3

Chemicals required:

Oxalic acid, NaOH, Acetic acid, HCl

Procedure:

1) Prepare 100ml ~(N/2) NaOH solution.
2) Prepare 100ml (N/10) Oxalic acid solution by exact weighing in a volumetric flask.
3) Prepare 100ml ~(N/10) HCl and 100ml ~(N/10) acetic acid solution.
4) Take the NaOH solution in a burette. Determine the volume of 50 drops and calculate the volume of one drop.
5) Standardize the ~(N/2) NaOH solution in the following way. Pipette out 10ml of the prepared oxalic acid solution in a 100ml beaker, add sufficient distilled water

to cover the electrodes of the conductivity cell. Stir the solution gently and take the conductance reading. Add (N/2) NaOH solution from a burette, two drops at a time initially and subsequently one drop at a time. Stir gently and measure conductance after each addition. After end point take at least 6-8 readings.

6) Draw the graph of conductance vs number of drops of NaOH added . From the second equivalence point calculate strength of NaOH solution.
7) Standardize the prepared HCl and acetic acid solution following the procedure of step 5.
8) From the graph of conductance vs number of drops of standard NaOH added, calculate strength of prepared HCl and acetic acid solution.

Experimental result:

1) Room temperature.
2) Preparation of 100ml 0.1(N) Oxalic acid.
3) Preparation of 100ml approximately (N/2) NaOH solution.
4) 50 drops of NaOH solution=…… ml NaOH.
5) Conductometric titration: Oxalic acid vs NaOH:

Volume of (N/10) oxalic acid	No. of drops of NaOH added	Total no, of drops of NaOH added	Conductance (mho)
10ml			

Total no. of drops of NaOH corresponding to second equivalence point≡…..ml NaOH(V_1).

Strength of NaOH solution = $\frac{10\times0.1(N)}{\text{Volume of NaOH}(V1)}$

6) Conductometric titration : HCl vs NaOH

Calculate strength of HCl in a similar way as step 5.

Volume of HCl	No. of drops of NaOH added	Total no. of drops of NaOH added	Conductance(mho)
10ml			

Volume of acetic acid	No. of drops of NaOH added	Total no. of drops of NaOH added	Conductance(mho)
10ml			

7) Conductometric titration: Acetic acid vs NaOH

Calculate strength of Acetic acid in a similar way as step 5

Precautions and Suggestions:

1) Add NaOH solution from a burette, two drops at a time initially and subsequently one drop at a time.
2) Stir gently before taking each conductance reading.

Experiment 5: Study of saponification reaction conductometrically

Theory:

Saponification of ester refers to the aqueous alkaline hydrolysis of any type of ester. As an example saponification of methyl acetate can be represented as

$CH_3COOCH_3 + OH^- \rightarrow CH_3COO^- + CH_3OH$

The rate of the reaction, $R = \frac{d[ester]}{dt} = k[ester][OH^-]$, i.e. the overall kinetic order of the reaction is two.

If 'a' be the initial concentration of ester and 'x' be the concentration of ester reacted at time t then the concentration of unreacted ester is (a-x) . For equal initial concentration of both the reactants we have,

$-\frac{d(a-x)}{dt} = k(a-x)^2$, Where k is the second order rate constant with unit of $mol^{-1}L.s^{-1}$

Or, $\frac{dx}{dt} = k(a-x)^2$

Integrating this equation by imposing boundary condition , at t=0, x=0, we have,

$$\frac{x}{(a-x)} = k \text{ at}$$

The course of the reaction can be monitored by measuring conductance of the reaction mixture with time. In this case the conductance of the reaction mixture decreases with time as the OH^- ions are replaced by CH_3COO^- ions of lower mobility . Therefore from the measured conductance value the relative amounts of the ions present and hence the extent of reaction can be predicted. If C_0, C_t, and $C\infty$ are the values of conductance at time t=0, t=t and t=∞ respectively, then

$a \propto (C\infty - C_0)$

$(a-x) \propto (C\infty - C_t)$

$x \propto (C_t - C_0)$

Substituting in equation (i) we get, $\frac{C_0 - C_t}{C_t - C_\infty} = k \text{ at}$

Plot of $\frac{C_0 - C_t}{C_t - C_\infty}$ vs t should yield a straight line passing through the origin with a slope 'ka'. From the known value of 'a', the rate constant for the saponification reaction, k can be calculated.

Apparatus required:

1) 100ml vol. flask -5

2) 250ml conical flask -1
3) 100ml beaker -1
4) 500ml glass bottle -1
5) Burette -1
6) Pipette 25ml -2
7) Pipette 10ml -1
8) Pipette 1ml -1

Chemicals required:

Oxalic acid, NaOH, Acetic acid, Phenolphthalein, Methyl acetate

Procedure:

1) Prepare 100ml of ~(N/10) oxalic acid solution by exact weighing.
2) Prepare 250ml of ~(N/10) NaOH solution. Standardize this NaOH solution against 10ml standard oxalic acid solution.(Use Phenolphthalein).
3) Dilute the standardized NaOH solution to prepare exact (M/60)NaOH solution of volume 100ml using deionized water.
4) Prepare 100ml of a ~(N/10) acetic acid (HAc) solution. Standardized 10ml of it against the standardized ~(N/10) NaOH solution (Use Phenolphthalein). From the standardized solution prepare 100ml exact (M/60) HAc solution by proper dilution.
5) Take a 100ml volumetric flask with about 50ml of deionized water. Transfer into this exactly 1.0ml of pure methyl acetate, using a 1ml graduated pipette, and make up the volume with deionized water. Estimate the concentration of the solution in molarity using the following data:

Molecular weight of methyl acetate = 74.08

Density of the supplied methyl acetate at room temperature (t^0C)

$=0.932- (t-20)\times 1.25 \times 10^{-4}$ g/ml

Prepare 100ml exact (M/60)methyl acetate solution from this standard methyl acetate solution by proper dilution with deionized water.

6) Prepare 50ml exact (M/120) NaOH solution from exact (M/60) NaOH solution by proper dilution (use a 25ml pipette) with deionized water and note its conductance as C_0.
7) Mix 25ml each of (M/60) NaOH and (M/60) HAc solutions and note its conductance as $C\infty$.
8) Take 25ml (M/60) methyl acetate and add 25ml (M/60) NaOH solution to it. Note the time of half – discharge of the pipette and homogenize the mixture. Measure the conductance (C_t) of the solution at intervals of about 1 minute. Take at least 15 reading.

9) Plot $(C_0-C_t)/(C_t-C\infty)$ versus time to obtain the rate constant of the reaction at room temperature.

Experimental result:

1) Room temperature.
2) Preparation of 100ml 0.1 (N) oxalic acid.
3) Preparation of 250ml approximately 0.1(N) NaOH solution.
4) Standardisation of NaOH solution against standard oxalic acid solution.

Volume of oxalic acid (ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of NaOH solution.

5) Preparation of 100ml exact (M/60) NaOH solution.
6) Preparation of 100ml $\sim \left(\frac{N}{10}\right)$ acetic acid solution.
7) Standardisation of HAc solution against standard NaOH solution.

Volume of HAc (ml)	Burette reading		Volume of NaOH used (ml)	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of HAc solution.

8) Preparation of 100ml exact (M/60) HAc solution.
9) Preparation of 100ml exact (M/60) methyl acetate solution.
10) Measurement of C_0 and $C\infty$

C_0=conductance of (M/120) NaOH solution.
$C\infty$ = conductance of (M/120) sodium acetate solution.

11)Recording of conductance data for saponification reaction.

Conclusion:

Time (t) in minute	Conductance (C_t) (mho)	C_0-C_t(mho)	$C_t-C\infty$ (mho)	$(C_0-C_t)/(C_t-C\infty)$

Plot of $\frac{C_0-C_t}{C_t-C_\infty}$ vs t gives a straight line passing through the origin. From the graph slope = ka.

Or, k=Slope/a, where 'a' is initial concentration of reactants = (M/120).

Experiment 6: Verification of Ostwald's dilution law and determination of Ka of weak acid.

Theory:

Electrolytes obey Ohm's law i.e.,

Current (I) ∝ Voltage (V) applied

The proportionality constant is called conductance (C) [inverse of resistance (R)] of the conductor concerned. The conductance of an electrolyte solution is measured with the help of a conductivity cell. If two parallel electrodes, each of area 'A' are placed 'I' distance apart then the measured conductance (C) of an electrolyte solution will be

C= $\frac{1}{R} = \frac{1}{\rho}\frac{A}{l}$, ρ is the resistivity

= k $\frac{A}{l}$, k is the specific conductance or conductivity of the electrolyte solution.

Or, k = C$\frac{l}{A}$, Where $\frac{l}{A}$ is called cell constant of the conductivity cell

i.e., Specific conductance = Conductance × Cell constant

The specific conductance (k) of an electrolyte solution is its conductance when unit volume of the solution is placed between two parallel electrodes each of unit area and set unit distance apart. In C.G.S. its unit is $ohm^{-1}\ cm^{-1}$.

Cell constant of a conductivity cell is determined by measuring the conductance of an electrolyte solution of known specific conductance at the experimental temperature within the same conductivity cell.

Equivalent conductance (λ) of an electrolyte solution is its conductance associated with a definite volume of the solution containing 1 gm equivalent of the electrolyte placed between two large electrodes set unit distance apart. Therefore,

Equivalent conductance (λ) = Specific conductance (k) × volume of the solution in cm^3 containing 1 gm equivalent of the electrolyte

Unit of 'λ′ in CGS in $ohm^{-1}cm^2g\ equi^{-1}$.

Equivalent conductance of a weak electrolyte will increase with dilution and this is mainly due to increase n degree of dissociation, the variation of ionic mobility with dilution being insignificant due to low concentration of the ions.

Let α be the degree of ionization of a weak acid HA at concentration C equivalent/lit.

Then at equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

$C(1-\alpha)$ $C\alpha$ $C\alpha$

The dissociation constant or ionization constant (K_a) can be represented as

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If equivalent conductance of the weak electrolyte at concentration/ lit and at infinite dilution are λ and λ_0 respectively then,

$$\alpha = \frac{\lambda}{\lambda_0}$$

$$\text{so, } K_a = \frac{C(\lambda/\lambda_0)^2}{1-\frac{\lambda}{\lambda_0}}$$

$$\text{or, } 1-\frac{\lambda}{\lambda_0} = \frac{C\lambda^2}{K_a{\lambda_0}^2} \qquad \text{or, } \frac{1}{\lambda} = \frac{1}{\lambda_0} + \frac{\lambda C}{{\lambda_0}^2 K_a}$$

This is known as Ostwald dilution law. The plot of $\frac{1}{\lambda}$ vs. λC will be a straight line with a positive intercept $\frac{1}{\lambda_0}$ from which λ_0 can be calculated. From the slope $\frac{1}{{\lambda_0}^2 K_a}$, K_a can be calculated using the temperature corrected literature value of λ_0.

Apparatus required:

1) 100ml vol. flask -3
2) 250ml conical flask -1
3) 100ml beaker -2
4) 500ml glass bottle -2
5) Burette -1
6) Pipette 25 ml -2
7) Pipette 10ml -1
8) 250ml vol. flask -2

Chemicals required:

Oxalic acid, Acetic acid, NaOH, KCl, Phenolphthalein

Procedure:

1) Prepare 100ml ~(N/10) oxalic acid solution by accurate weighing.
2) Prepare approximately 250ml of ~(N/10) NaOH solution and standardize the NaOH solution against the prepared standard oxalic acid solution.(use phenolphthalein).
3) Prepare 250ml of ~(N/10) acetic acid solution in conductivity water and standardize the solution against the standard NaOH solution (use phenolphthalein).
4) Prepare 250ml ~ 0.1 (N) [slightly higher than 0.1 (N) KCl solution by accurate weighing and prepare 100ml of an exact 0.1 (N) KCl solution by proper dilution. Prepare 100ml of an exact 0.01 (N) KCl from the exact 0.1 (N) KCl solution. Determine the cell constant of the conductivity cell using the exact 0.1 (N) KCl and the prepared exact 0.01 (N) KCl solution .With the help of the literature value of specific conductances of these solutions at room temperature,

calculate the mean value of cell constant and use it subsequently. Measure the conductance of conductivity water also.

5) Prepare 250ml, exact (N/50) weak acid solution from the standardized solution using conductivity water. With the help of 25ml pipette, take 50ml of this solution in the clean and dry conductivity cell and measure its conductance.
6) Use the same 25ml pipette to take out 25ml of the (N/50) weak acid solution from the conductivity cell. Pipette out 25ml of the conductivity water into the conductivity cell to make the solution exactly (N/100) in situ. Mix the solution well by careful swirling (so that no solution comes out). Measure the conductance and note it as that of exact (N/100) weak acid solution. Separate pipettes for weak acid solutions and conductivity water may be used.
7) Follow the procedure of step (6) to prepare in situ exact (N/200), (N/400), (N/800), and (N/1600) weak acid solutions in steps and note their conductances.
8) Calculate the equivalent conductivities of the diluted solutions of the weak acid using the mean value of cell constant. Apply corrections for specific conductance of conductivity water.
9) From the plot of $1/\lambda$ versus (λC) calculate the λ_0 from the intercept and from the temperature corrected literature value of ion conductances. Calculate K_a and pk_a of the weak acid from the slope using the temperature corrected literature value of λ_0.

Experimental result:

1) Room temperature.
2) Preparation of 100ml 0.1(N) oxalic acid.
3) Preparation of 250ml approximately 0.1(N)NaOH solution.
4) Standardisation of NaOH solution against standard oxalic acid solution:

Volume of oxalic acid (ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of NaOH solution: …….

5) Preparation of 250ml ~(N/10) acetic acid solution:

6) Standardisation of acetic acid solution against standard NaOH solution :

Strength of acetic acid solution:

7) Preparation of 250ml exact (N/50) acetic acid solution.

8) Preparation of 250ml ~0.1 (N) [slightly higher than 0.1 (N) KCl solution.

9) Preparation of 100ml exact 0.1 (N) KCl solution and preparation of exact 0.01 (N) KCl .

Volume of acetic acid solution(ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

10) Determination of cell constant:

Concentration of KCl solution	Conductance (mho)	Specific conductance ($mho.cm^{-1}$)	Cell constant (cm^{-1})	Mean cell constant (cm^{-1})
0.01(N)				
0.1(N)				

11) Determination of equivalent conductance of different acetic acid solutions:

Concentration of acetic acid solution	Observed conductance (mho)	Corrected specific conductance ($mho.cm^{-1}$) {Observed conductance- Conductance of conductivity water) × mean cell constant}	Equivalent conductance (λ) ($mhocm^2eq^{-1}$)	$1/\lambda$ ($mho^{-1}cm^{-2}eq$)	$\Lambda c(mhocm^{-1})$

The plot of $\frac{1}{\lambda}$ vs λC will be a straight line with a positive intercept $\frac{1}{\lambda_0}$ from which λ_0 can be calculated.

From the slope $\frac{1}{{\lambda_0}^2 K_a}$, K_a can be calculated using the temperature corrected literature value of λ_0.

Temperature corrected literature value of $\lambda_0 = \lambda_t^0 (H^+) + \lambda_t^0 (OAc^-)$

λ_t^0 (H^+) = λ_{25}^o [1+1.42× 10^{-2} (t-25)]
λ_t^0 (OAc^-) = λ_{25}^o [1+0.02 (t-25)]

C6P: Inorganic Chemistry Lab

Experiment 1: Estimation of available chlorine in bleaching powder.

Aim

To determine the available chlorine in the given sample of bleaching powder by the iodometric method.

Theory:

Bleaching powder is used as a bleaching agent and also as a disinfectant. The main constituent of bleaching powder is calcium hypochlorite [$Ca(OCl)_2$] which supplies chlorine [Cl_2] with dilute acids. So, the available chlorine is defined as the percentage of chlorine made available by bleaching powder when treated with dilute acids. The available chlorine present in bleaching powder sample is determined iodometricaliy by treating its solution with an excess of potassium iodide solution in the

acidic medium. The liberated iodine (I_2) is treated with sodium thiosulphate ($Na_2S_2O_3$) solution using freshly prepared starch solution as indicator to be added near the end point.

Apparatus:

Digital Balance, Burette, Conical flask, Measuring flask, Funnel, Glass rod, Beakers

Reagents:

Bleaching powder, Standard sodium thiosulphate solution

10% Potassium iodide (KI), dilute acetic acid, freshly prepared starch solution as indicator Bleaching powder is commonly used as a disinfectant. The chlorine present in the bleaching powder gets reduced with time. So, to find the exact quantity of bleaching powder required, the amount of available chlorine in the sample must be found out.

Chlorine will liberate free iodine from potassium iodide solution when its pH is 8 or less. The iodine liberated, which is equivalent to the amount of active chlorine, is titrated with standard sodium thiosulphate solution using starch as indicator.

Apparatus:	**Reagents:**
➢ Mortar and pestle	Concentrated glacial acetic acid
➢ Volumetric flask	Potassium iodide
➢ Burette	Starch indicator

- Erlenmeyer flask.
- Pipette

Procedure

Dissolve 1g bleaching powder in 1 litre of distilled water in a volumetric flask, and stopper the container.

(This can be done by first making a paste of the bleaching powder with mortar and pestle.)

Place 5 mL acetic acid in an Erlenmeyer flask and add about 1g potassium iodide crystals. Pour 25 mL of bleaching powder solution prepared above and mix with a stirring rod.

Titrate with 0.025 N sodium thiosulphate solution until a pale yellow colour is obtained. (Deep yellow changes to pale yellow.)

Add 1mL of starch solution and titrate until the blue colour disappears.

Note down the volume of sodium thiosulphate solution added (V_1).

Take a volume of distilled water corresponding to the sample used.

Add 5 mL acetic acid, 1g potassium iodide and 1 mL starch solution.

If blue colour occurs, titrate with 0.025 N sodium thiosulphate solution until the blue colour disappears.

Record the volume of sodium thiosulphate solution added (A_1).

If no blue colour occurs, titrate with 0.025 N iodine solution until a blue colour appears. Note down the volume of iodine (A_2).

Then, titrate with 0.025 N sodium thiosulphate solution till the blue colour disappears. Record the volume of sodium thiosulphate solution added (A_3). Note down the difference between the volume of iodine solution and sodium thiosulphate as A_4 ($A_4=A_2- A_3$).

Note: Blank titration is necessary to take care of the oxidising or reducing reagents' impurities.

Observation

Bleaching powder solution x Standard sodium thiosulphate solution (0.025 N)

Introduction

In acid solution practically all oxidizing agents will oxidize iodide ion to iodine quantitatively. The iodine formed in the reaction can then be titrated by means of a standard sodium thiosulfate solution. This type of indirect titration is given the general name of **iodometry.**

Iodometric methods of analysis have a wide applicability for the following reasons

1. Potassium iodide, KI, is readily available in high purity.

2. A good indicator, starch, is available to signal the equivalence point in the reaction between iodine and thiosulfate. Starch turns blue-black in the presence of iodine. Therefore, when the blue-black color disappears, the iodine has been completely reduced to the iodide ion.

3. Iodometric reactions are rapid and quantitative.

4. A precise and stable reducing agent, sodium thiosulfate ($Na_2S_2O_3$), is available to react with the iodine.

The amount of iodine liberated in the reaction between iodide ion and an oxidizing agent is a measure of the quantity of oxidizing agent originally present in the solution. The amount of standard sodium thiosulfate solution required to titrate the liberated iodine is then equivalent to the

Trial no.	Volume of bleaching powder solution (mL)	Burette reading		Volume of titrant (mL)
		Initial	Final	

Distilled water × Standard sodium thiosulphate solution (0.025 N)

Trial no.	Volume of distilled water (mL)	Burette reading		Volume of titrant (mL)
		Initial	Final	

Distilled water x Standard iodine solution (0.025N)

amount of oxidizing agent. Iodometric methods can be used for the quantitative determination of strong oxidizing agents such as potassium dichromate, permanganate, hydrogen peroxide, cupric ion and oxygen.

As has been mentioned above, the endpoint in a titration of iodine with thiosulfate is signaled by the color change of the starch indicator. When starch is heated in water, various decomposition products are formed, among which is beta-amylose which forms a deep blue-black complex with iodine. The sensitivity of the indicator is increased by the presence of iodide ion in solution.

Trial no.	Volume of distilled water (mL)	Burette reading		Volume of titrant (mL)
		Initial	Final	

Calculation

$$\text{mg of } Cl_2/\text{mL (B)} = \frac{(V - A_1) \text{ or } (V + A_4) \times N \times 35.46}{\text{mL of bleaching powder solution taken}}$$

1000 mL of bleaching powder solution contains 1000 x B mg of Cl_2
i.e., 1000 mg bleaching powder contains 1000 B mg of Cl_2

$$\text{Therefore, 100 mg of bleaching powder contains} = \frac{1000 \times B}{10}$$

% of chlorine available = ...

Results
Available chlorine in the given bleaching powder is. ...%

Experiment 2: Iodometric Determination of Cu in Brass

However, if the starch indicator solution is added in the presence of a high concentration of iodine, the disappearance of the blue-black color is very gradual. For use in indirect methods, the indicator is therefore added at a point when virtually all of the iodine has been reduced to iodide ion, causing the disappearance of the color to be more rapid and sudden. The starch indicator solution must be freshly prepared since it will decompose and its sensitivity is decreased. However, a properly prepared solution will keep for a period of a few weeks. A preservative such as a small amount of mercuric ions may be added to inhibit the decomposition.
Solutions of sodium thiosulfate are made up to an approximate concentration by dissolving the sodium salt in water that has previously been boiled. Boiling the water is necessary to destroy

micro-organisms which metabolize the thiosulfate ion. A small amount of Na_2CO_3 is added to the solution in order to bring the pH to about 9. The solution is standardized by taking a known amount of oxidizing agent, treating it with excess iodide ion and then titrating the liberated iodine with the solution to be standardized. Oxidizing agents such as potassium dichromate, bromate, iodate or cupric ion can be employed for this procedure. You will be using potassium iodate, KIO_3, as your primary standard. The reaction between IO_3^- and I^- is given as

$$6H^+ + IO_3^- + 5I^- \text{--- >} 3I_2 + 3H_2O$$

Reactions Involved in Iodometric Processes

Iodometric methods depend on the following equilibrium:

$$I_2 + I^- \text{<===>} I_3^-$$

Since the solubility of I_2 in water is quite low, the formation of the tri-iodide ion, I_3^-, allows us to obtain useful concentrations of I_2 in aqueous solutions. The equilibrium constant for this reaction is approximately 700. For this reason iodometric methods are carried out in the presence of excess iodide ion.

The reaction between iodine and the thiosulfate ion is:

$$I_2 + 2S_2O_3^{2-} \text{<===>} 2I^- + S_4O_6^{2-}$$

This reaction proceeds quantitatively in neutral or slightly acidic solutions. In strongly alkaline or acidic solutions the oxidation of the thiosulfate does not proceed by a single reaction. In the former, the thiosulfate ion is oxidized to sulfate as well as to the tetrathionate. In the latter, the thiosulfuric acid formed undergoes an internal oxidation-reduction reaction to sulfurous acid and sulfur. Both of these reactions lead to errors since the stoichiometry of the reactions differs from that shown above for the thiosulfate as a reducing agent. The control of pH is clearly important. In many cases the liberated iodine is titrated in the mildly acidic solution employed for the reaction of a strong oxidizing agent and iodide ion. In these cases the titration of the liberated iodine must be completed quickly in order to eliminate undue exposure to the atmosphere since an acid medium constitutes an optimum condition for atmospheric oxidation of the excess iodide ion.

The basic reaction in the determination of copper using the iodometric method is represented by the equation:

$$2Cu^{2+} + 4I^- \text{<===>} 2CuI(s) + I_2$$

This is a rapid, quantitative reaction in slightly acidic solutions, if there is a large excess of iodide ion present and if the copper is in the form of a simple ion rather than a complex one. The iodine that is liberated can be titrated in the usual manner with standard thiosulfate solution. The reaction involving cupric ion and iodide takes place quantitatively since the cuprous ion formed as result of the reduction is removed from the solution as a precipitate of cuprous iodide.

Iron interferes since iron(III) ions will oxidize iodide. Since the iron will be found in the +3 oxidation state as a result of the dissolution of the brass sample, a means of preventing this interference is necessary. This can be accomplished by converting the iron(III) to a soluble iron(III) phosphate complex using phosphoric acid. At a pH of 3.0-4.0 the iron phosphate complex is not reduced by iodide ion. If arsenic and antimony are present, they will provide no interference at this pH if they are in their higher oxidation states. Brass formulations also may contain up to 39% Zn,

2.5% Sn and 8.5% Pb. When dissolved in concentrated nitric acid, the zinc and the lead become Pb^{2+} and Zn^{2+} . These do not interfere with the analysis of copper because they are not reduced to the Pb^{+} and Zn^{+} states by the action of iodide ion under the conditions of this experiment. The tin is oxidized to Sn^{4+} by the concentrated nitric acid and after dilution and adjustment of pH this form becomes SnO_2 which is insoluble and may be observed as an inert white precipitate at the bottom of your flask. Under these conditions the tin does not interfere with the analysis.

Sources of Error

The following are the most important sources of error in the iodometric method:
1. Loss of iodine by evaporation from the solution. This can be minimized by having a large excess of iodide in order to keep the iodine tied up as tri-iodide ion. It should also be apparent that the titrations involving iodine must be made in cold solutions in order to minimize loss through evaporation.
2. Atmospheric oxidation of iodide ion in acidic solution. In acid solution, prompt titration of the liberated iodine is necessary in order to prevent oxidation.
3. Starch solutions that are no longer fresh or improperly prepared. The indicator will then not behave properly at the endpoint and a quantitative determination is not possible.

EXPERIMENTAL

Preparation of a 0.10 M Standard $Na_2S_2O_3$ Solution

With a graduated cylinder measure out 1 liter of distilled water. Place it in your 1 liter beaker and boil the water for at least 5 minutes. Weigh out 25 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.1 g of Na_2CO_3. Dissolve the thiosulfate in the hot water and then cool this solution with the aid of an ice bath to room temperature. Then add the carbonate and stir until it is completely dissolved. Transfer the solution to your plastic 1 liter bottle. When not in use store this bottle in the darkness of your equipment cabinet as the decomposition of thiosulfate is catalyzed by light.

Blank Determination

Potassium iodide may contain appreciable amounts of iodate ion which in acid solution will react with iodide and yield iodine. The liberated iodine would react with thiosulfate and thereby cause the apparent molarity of the thiosulfate to be too low. The following procedure allows for the determination of a blank correction which will properly correct for any iodate that might be present. Prepare a solution of exactly 2.00 g of KI dissolved in 50 mL of distilled water and then acidify the solution with 5 mL of 3 M sulfuric acid and then immediately add 5 mL of starch indicator. If a blue-black color appears right after mixing, use the thiosulfate solution in the buret to determine the volume of solution required to cause the color- to disappear. This volume must be subtracted from the standardization and analyses volumes. If the potassium iodide is completely iodate-free no color will of course develop and no blank correction is necessary.

Standardization of the $Na_2S_2O_3$ Solution

Dry approximately 2 g of potassium iodate, KIO_3, at a temperature of 110 ^oC for one hour. Weigh to a precision of ±0.0001g three samples of the potassium iodate having weights near 0.12 g directly into three 250 mL Erlenmeyer flasks. Dissolve the iodate in 75 mL of distilled water. Cover the flasks with parafilm and store them. Rinse and fill your buret with the solution. Add 2.00 g of KI to each of the potassium iodate solutions. If a blank correction is required add exactly 2.00 g of KI to **each**. If no blank determination is required, the exact amount of KI is not crucial but should be close to 2 g. Then add 10 mL of 1 M HCl to one of the solutions. It will turn a dark-brown color. Immediately titrate it with the thiosulfate solution. When the color of the solution becomes very pale yellow add 5 mL of starch indicator. Continue the titration until the blue color of the starch complex just disappears. Follow the same procedure with each of the other two solutions, first adding the HCl then titrating. Correct your titration data for buret error and if necessary apply the blank correction. Calculate the molarity of the $Na_2S_2O_3$ solution. Results should agree to within 0.2% of the average. If you do not achieve that kind of precision, titrate additional samples.

Dissolution of the Brass Sample

The following procedures in this section make use of the hot plates in the fume hoods. The solutions of dissolved brass generally have a low volume and high acid and salt concentrations. "Bumping" or little explosions of steam in the superheated liquid can occur. You don't want your hand to be close to the mouth of the flask should the solution suddenly "bump" because drops of acid (not to mention part of your sample) will fly out of the flask and possibly onto your hand. For that reason you must use your tongs to place the flasks on the hot plate and to remove them. Don't use strips of paper towel or the rubber Hot Hands because your real hand will end up being too close to the mouth of the flask.

The brass sample which you will receive does not have to be dried before use. Accurately weigh out three brass samples, of about 0.3 g each, directly into separate 250 mL Erlenmeyer flasks. In the fume hood add 5 mL of 6 M HNO_3. Warm the solution on a hot plate in the fume hood until dissolution is complete. Add 10 mL of concentrated (not 3 M) H_2SO_4 and continue heating until white SO_3 fumes appear. It is important that you do not mistake ordinary water vapor for SO_3 fumes. It is also important at this point that the flask ***not*** be removed from the hood. SO_3 fumes are dangerous and ought not to be inhaled. Only when the slightly denser white fumes of SO_3 are observed can you be sure that all HNO_3 has been removed. NO_3^- will oxidize I^- and hence will seriously interfere with the procedure. Cool the flask in air for one or two minutes and then in an ice bath, then carefully add 20 mL of distilled H_2O. Boil for one or two minutes then again cool in an ice bath. Continue to keep the flask in the ice bath and using your medicine dropper add

concentrated NH_3(aq) dropwise, and with adequate mixing, until the light-blue color of the solution is completely changed to the dark-blue color of the copper tetraammine complex. As many as 400 drops (20 mL) may be required. The solution must be kept cool in an ice bath since the reaction between the concentrated H_2SO_4 and concentrated NH_3 is highly exothermic. Now add 3 M H_2SO_4 dropwise until the dark-blue color just disappears. You don't have to produce a *complete* disappearance of the dark blue color but you need to approach that point. The subsequent addition of phosphoric acid will lower the pH appropriately to around 3.5. If you add too much 3M H_2SO_4 the pH may turn out to be sufficiently low to cause unwanted side reactions to occur when you reduce the Cu^{2+} with iodide. If you are uncertain about the disappearance of the dark blue color you may put 50 mL of 0.06 M Cu^{2+} in a clean 250 mL flask and add 12 M ammonia dropwise until you have that unmistakable dark blue color. Then add 3M H_2SO_4 dropwise until the blue color *almost* disappears. Then add 2 mL concentrated phosphoric acid and you ought to see the dark color completely disappear. You may copy that procedure to achieve an appropriate pH of around 3.5 for subsequent steps in the analysis. Now, back to your real sample: Once you are confident that you haven't added too much 3M H_2SO_4, but that you have caused the dark color of the copper tetraammine complex almost to disappear, add 2.0 mL of concentrated phosphoric acid, H_3PO_4, to each sample. Verify to yourself that they exhibit the light copper color rather than the dark color and cover the flasks with parafilm and set them aside until you are ready to proceed with the titration.

Titration of the Dissolved Brass Sample

If you have let the dissolved samples stand overnight, be sure to warm the sample on a hot plate (this can be done at your desk) in order to dissolve all larger crystals of copper sulfate that might have formed. Be sure to cool the samples to room temperature, or below, with the aid of an ice bath. The solutions will still contain a fine, white precipitate at this point; however, this will not interfere with the rest of the procedure. From this point on work with only one sample at a time. Add 4.0 g of KI to one of your samples and titrate immediately with the standard thiosulfate solution. The sample contains white CuI precipitate and the color of I_3^- must be observed against that precipitate. The slurry will at first appear brown or dark yellow-brown. Continue adding thiosulfate until the slurry is a light mustard color. At this point add 5 mL of starch indicator and titrate until the mixture in the flask takes on a milky pink or lavender hue. Now add 2 g of KSCN and mix well; the solution will darken somewhat. After the addition of thiocyanate, continue to add more thiosulfate dropwise. You should observe a sudden change to a white or cream color. That is the endpoint of the titration. After you have titrated all three samples calculate the percentage of Cu in each of the brass samples, the average percentage and the average deviation.

The description above applies for brass samples with low concentrations of zinc (<10%). Some of you may have brass samples with higher concentrations of zinc. Such samples will become quite dark after the addition of KI and will lighten only slightly as thiosulfate is added. The "mustard color" will be darker than samples having low percentages of copper. When the starch is added the sample will become dark blue-black again and as you approach the end point with the thiosulfate the slurry will turn a violet color rather than milky pink or lavender hue. With the addition of the

KSCN the solution will darken somewhat as in the case of the other samples, but the final end point will be a bit darker than the white or cream color described above. If you think that you have a sample with high zinc content, observe your progress carefully and take notes which will allow you to achieve repeatability.

Explanation: The reduction of Cu^{2+} to Cu^{+} occurs as the result of the oxidation of I^- to I_2. The I_2 combines with iodide ion to produce the dark brown triodide ion, I_3^-. The excess iodide ion also causes the reduced copper to precipitate as white cuprous iodide, CuI. I_2 and I_3^- in solution tend to adsorb on the surface of CuI thus becoming unavailable for rapid reduction by the thiosulfate. As a result, iodometric titrations involving reduced copper tend to yield lower results unless the adsorbed I_2 can be liberated by adding thiocyanate ion, SCN^-, which competes with the adsorbed iodine molecules on the surface of solid particles of CuI. After the addition of thiocyanate, continue to add more thiosulfate dropwise. You should observe a sudden change to a white or cream color. That is the endpoint of the titration. After you have titrated all three samples calculate the percentage of Cu in each of the brass samples, the average percentage and the average deviation.

REPORT

Your report must include the following information in the two sections below.

1. Unknown number
2. The three weights of KIO_3 used for the standardization of thiosulfate
3. Volume in mL of thiosulfate for each of your standardization titrations
4. Average molarity of the thiosulfate solution
5. Weight of brass used for each sample
6. Volume of thiosulfate solution used for each sample
7. Cu percentage for each sample
8. The average percentage of Cu in your brass sample
9. The average deviation from the mean of the percent Cu for the three samples
10. Pages in your lab notebook containing the pertinent data

Questions on Cu in Brass Analysis

1. Why is it necessary to boil the water used to prepare the thiosulfate solution?
2. Why is Na_2CO_3 added to the thiosulfate solution?
3. Why is the thiosulfate solution stored in the dark?
4. Why is HCl added to the IO_3^- mixture and why must the solution be titrated immediately?
5. Why is the solution containing the dissolved brass sample heated to expel SO_3 fumes?
6. Why is H_3PO_4 added to the brass sample?
7. What is the purpose of the KSCN that is added just before the endpoint in the titration?
8. Why is the solution containing the dissolved brass made basic with concentrated NH_3 and then again acidified with H_2SO_4?
9. What is the formula of the tetrammine copper(II) complex?
10. Why do Zn^{2+} and Pb^{2+} not interfere in this procedure?
11. What sort of complications would arise if the iodinethiosulfate titration were carried out in a highly acidic solution?
12. If the solution were highly basic, how would the iodinethiosulfate reaction be influenced?

13. Why is the starch indicator not added at the beginning of the tritration?

Experiment 3: Estimation of Cu(II)

Aim:

Oxidation-Reduction (Redox) Reactions:

❖ Reaction involving change of oxidation number or transfer of electrons among the reacting substances.

❖ The standard solutions are either oxidising or reducing agents.

❖ The principal oxidising agents are $KMnO4$, $K_2Cr_2O_7$, $Ce(SO_4)_2$, $I2$, KIO_3, and $KBrO_3$.

❖ Frequently used reducing agents are $Fe(II)$ and $Sn(II)$ compounds, $Na_2S_2O_3$, As_2O_3, $Hg_2(NO_3)_2$, VCl_2 or VSO_4, $CrCl_2$ or $CrSO_4$ & $TiCl_3$ or $Ti_2(SO_4)_3$.

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2$$
(Pink) (Colourless)

$$2MnO_4^- + 10Fe^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 10Fe^{3+} + 8H$$
(Pink) (Colourless)

$$Cr_2O_72- + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$
(Orange) (Green)

$$CuSO_4 + 4KI \longrightarrow Cu_2I_2 + K_2SO_4 +$$
(Blue) (White ppt)

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$
(Sod. Thiosulphate) (Sod. Tetrathionate)

❖ The redox titration involving iodine directly or indirectly as an oxidizing agent are called iodine titrations.

Iodimetric Titrations: Titrations with a standard solution of iodine.

Applications of Iodimetric Titrations:

★ Determination of $S2O3^{2-}$

★ Determination of $SO3^{2-}$

★ Determination of $AsO3^{3-}$

★ Determination of $SnCl_2$

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

$$Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$$

$$Na_3AsO_3 + I_2 + H_2O \longrightarrow Na_3AsO_4 + 2HI$$

Iodometric Titrations: Iodine titrations in which some oxidizing agent liberate I_2 from an I^- solution and then liberated I_2 is titrated with a standard solution of reducing agent.

Estimation of $CuSO_4$, $K_2Cr_2O_7$, $KMnO_4$, Fe^{3+}, H_2O_2, Br_2, Cl_2 etc.

$$CuSO_4 + 4KI \longrightarrow Cu_2I_2 + K_2SO_4 + I_2$$

(Blue) (White ppt)

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

(Sod. Thiosulphate) (Sod. Tetrathionate

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$$

Orange Green

$$6KI + 3H_2SO_4 + 3O \longrightarrow 3K_2SO_4 + 3H_2O + 3I_2$$

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

DETECTION OF THE END POINT:

- In this titration a solution of starch is used as indicator.
- Starch reacts with iodine in the presence of iodide to form an intensely blue-colored complex, which is visible at very low concentrations of iodine.
- The color sensitivity decreases with increasing temperature of the solution.
- It cannot be used in a strongly acid medium because hydrolysis of the starch occurs.
- The great merit of starch is that it is inexpensive.

- It is insoluble in cold water.
- Instability of suspensions in water
- It gives a water-insoluble complex with iodine, the formation of which precludes the addition of the indicator early in the titration (for this reason, in titrations of iodine, the starch solution should not be added until just prior to the end point when the colour begins to fade).
- There is sometimes a 'drift' end point, which is marked when the solutions are dilute.

Preparation and Use of Starch Solution:

- Make a paste of 0.1 g of soluble starch with a little water, and pour the paste, with constant stirring, into 100 mL of boiling water, and boil for 1 minute. Allow the solution to cool and add 2-3 g of potassium iodide. Keep the solution in a stoppered bottle.
- Only freshly prepared starch solution should be used.
- The same volume of starch solution should always be added in a titration.
- In the titration of iodine, starch must not be added until just before the end point is reached.
- Apart from the fact that the fading of the iodine colour is a good indication of the approach at the end point, if the starch solution is added when the iodine concentration is high, some iodine may remain adsorbed even at the end point.

The Starch-Iodine Complex

Numerous analytical procedures are based on redox titrations involving iodine.

❖ Starch is the indicator of choice for these procedures because it forms an intense blue complex with iodine.

❖ Starch is not a redox indicator; it responds specifically to the presence of I_2, not to a change in redox potential.

❖ The active fraction of starch is amylose, a polymer of the sugar -D-glucose. Small molecules can fit into thecenter of the coiled, helical polymer.

❖ In the presence of starch, iodine forms I6 chains inside the amylose helix and the color turns dark blue.
I..I..I..I..I..I

❖ Starch is readily biodegraded, so it should be freshly prepared.

❖ A hydrolysis product of starch is glucose, which is a reducing agent. Therefore, partially hydrolyzed starchsolution can be a source of error in a redox titration.

Preparation of Sodium thiosulphate Solution:

Sodium thiosulphate (Na2S2O3.5H2O) is readily obtainable in a state of high purity, but there is always someuncertainty as to the exact water content because of the efflorescent nature of the salt and for other reasons.

The substance is therefore unsuitable as a primary standard. It is a reducing agent by virtue of the half-cellreaction:

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$$

Recommendations for the Preparation of Sod. Thiosulphate:

❖ Prepare the solution with recently boiled distilled water.

❖ Add 3 drops of chloroform, this improves the keeping qualities of the solution.

❖ Avoid exposure to light, as this tends to hasten the decomposition.

Standardisation of Sod. Thiosulphate Solution:

❖ The standardisation of thiosulphate solutions may be done with potassium iodate, potassium dichromate,copper and iodine as primary standards, or with potassium permanganate or cerium(lV) sulphate as secondary standards.

Estimation of Cu(II) from Copper sulphate solution:

Pipette 10.0 mL of CuSO4 solution into a 250 mL conical flask then add a few drops of dilute sodium carbonate solution until a faint permanent precipitate remains, and this is removed by means of a drop or two of acetic acid. Then 0.25 g KI (or 2 mL of a 10 per cent solution) is added and titrate the liberated iodine with standard solution of sod. thiosulphate until the brown color of iodine fades, then add 0.4 mL of starch solution, and continue the addition of the thiosulphate solution until the blue colour commences to fade. Then add about 0.25 g of potassium thiocyanate or ammonium thiocyanate, preferably as a 10 per cent aqueous solution: the blue colour will instantly become more intense. Complete the titration as quickly as possible. The precipitate possesses a pale pink colour, and a distinct permanent end point is readily obtained.

Experiment

Aim: To estimate the strength in g/L of a given copper sulphate solution being provided with an approx. N/30 sod. thiosulphate (hypo) solution.

Theory:

Step 1: $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

$2Cu^{2+} + 2I^- \longrightarrow 2Cu^+ + I_2$

or $2I^-(aq.) \longrightarrow I_2 + 2e^-$

$2Cu^{2+} + 2e^- \longrightarrow 2Cu^+$

Step 2: $I_2 + I^- \rightleftharpoons I_3^-$

(Water Insoluble) (Water soluble)

Step 3: Starch + I_3^- → Starch-I_3 (Starch-triiodide complex)

(Colourless) (Dark Blue)

Step 4: $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

Note:

Preparation of Standard solution:

W_1 = Weight of bottle + substance = _____ gms

W_2 = Weight of bottle = _____ gms

Weight of substance = (W_1-W_2) = _____ gms.

Normality of the solution = (W_1-W_2) X 10/Equivalent Weight =

= (W_1-W_2) X 10/49=

S.NO	Volume of the standard $K_2Cr_2O_7$ solution (V_1)	Burette Reading		Volume consumed
		final	Intial	
1	20 ml			
2	20 ml			
3	20 ml			

N1 = Normality of K2Cr2O7 solution =

V1 = Volume of K2Cr2O7 solution = 20ml

N_2 = Normality of Hypo =?

V_2 = Volume of Hypo =

$N_1 V_1 = N_2 V_2$

$N_2 = N_1 V_1 / V_2$

N_2 = Normality of Hypo =

S.No	Volume of the Copper solution (V_3)	Burette Reading		Volume of consume (V_4)
		Initial	final	
1	20ml			
2	20ml			
3	20ml			
				V4=

N_3 = Normality of the Copper solution =?
V_3 = Volume of the Copper solution = 20ml
N_4 = Normality of Hypo =?
V_4 = Volume of Hypo =
$N_3 V_3 = N_4 V_4$

Normality of the Copper solution = $N_3 = N_4 V_4 / V_3$

Amount of Copper present in the whole of the given solution (100 ml) = N_3 X 63.54/10

Result: Amount of Copper present in the whole of the given solution (100 ml) = _____ gm.

Why starch is added just before the end point?

The starch is not added at the beginning of the titration when the iodine concentration is high. Instead, it isadded just before the end point when the dilute iodine color becomes pale yellow. There are two reasons for such timing:First reason is that the iodine–starch complex is only slowly dissociated, and a diffuse endpoint would resultif a large amount of the iodine were adsorbed on the starch. The second reason is that most iodometric titrations are performed in strongly acid medium and the starch has a tendency to hydrolyze in acid solution.Starch-iodine complexation is temperature dependent. At 50 ^{0}C, the color is only one-tenth as intense as at 25 ^{0}C. If maximum sensitivity is required, cooling in ice water is recommended. Organic solvents decreasethe affinity of iodine for starch and markedly reduce the utility of the indicator.

Why KSCN or NH_4SCN is added?

When copper(II) is titrated iodometrically, the end point is diffuse unless thiocyanate ion is added. This isdue adsorption of I_2 on the surface of the cuprous iodide precipitate and only slowly reacts with thethiosulfate titrant. The thiocyanate coats the precipitate with CuSCN and displaces the iodine from the surface. The potassium thiocyanate should be added near the end point since it is slowly oxidized by iodineto sulfate. The pH must be buffered to around 3. If it is too high, copper(II) hydrolyzes and cupric hydroxide will precipitate. If it is too low, air oxidation of iodide becomes appreciable because it is catalyzed in the presence of copper.

Experiment 4: Estimation of Vitamin C

Vitamin C or ascorbic acid is essential for human life and is required for a range of physiological functions in human body. It can be found either in fresh fruits and vegetables naturally or in medical forms such as normal tablets, effervescent tablets and liquid vials. It is the most widely taken supplement. Though daily requirements of vitamin C are changeable according to the age, sex and conditions, it is around 75 to 90 mg per day for healthy adults and no more than 2000mg per day is recommended. It is one of the most ubiquitous vitamins ever discovered. Besides plays a paramount role as an antioxidant and free radical scavenger, it has been suggested to be an effective antiviral agent. In addition, ascorbic acid has been widely used in the pharmaceutical, chemical, cosmetic and food industry as antioxidant. Therefore, there is a need to find an accurate, reliable, rapid, and easy-to implement method for measuring the amount of ascorbic acid in a sample. However, there have been difficulties in quantifying ascorbic acid due to its instability in aqueous solution. The instability of ascorbic acid is due to its oxidation to dehydroascorbic acid, which is a reversible reaction, and subsequently to 2,3-diketo-L-gulonic acid. The later reaction is irreversible. Ascorbic acid is a water soluble vitamin with molecular weight of 176.12 g/mol and melting point of 193˚C. World-wide accepted daily requirement of ascorbic acid is about 60–95 mg4. Ascorbic acid is a reducing agent which reverses the oxidation in aqueous solution. Increased amounts of free radicals trigger the condition called oxidative stress which is kept under control by antioxidants. If there are not enough antioxidants some stress related diseases including hypertension, atherosclerosis, chronic inflammatory diseases and diabetes might occur. The following Iodometric titration is performed and the amount of vitamin C was evaluated in given tablet using iodometric titration method. In this method the
reaction between iodine and starch suspension, will indicate the endpoint by producing the blue-black product. The tri-iodide ions are quickly converted into iodide ions when ascorbic acid is present. However, when all of the ascorbic acid is oxidized, the excess iodide will react with starch and will result in blue-black color.

Equipment and apparatus:

- Volumetric flask 250.00 ml (± 0.01 ml)
- Beaker 500.00 ml (± 0.01 ml), 500.00 ml (± 0.01 ml), 100 ml (± 0.01 ml)
- Burette 50.00 ml (± 0.01 ml)
- Graduated cylinder 50.00 ml (± 0.01 ml)
- Erlenmeyer flask 250.00 ml (± 0.01 ml), Erlenmeyer flask 250.00 ml
- Potassium iodide (KI) 15.00g (± 0.001 g)
- Iodine powder 5g
- Balance
- Starch powder 0.25g
- Distilled water
- Heater

- Glass rod
- Vitamin C

EXPERIMENTAL PROCEDURES:

Ascorbic acid is determined by using an oxidation-reduction reaction. The solubility of iodine is increased with iodide and tri-iodide is occurred:

$$I_2\,(aq) + I^- \leftrightarrow I_3^-$$

I_3^- then oxidizes vitamin C to dehydroascorbic acid:

$$C_6H_8O_6 + I_3 + H_2O \longrightarrow C_6H_6O_6 + 3I^- + 2H^+$$

Vitamin C dehydroascorbic acid

The endpoint is production of a blue-black color which occurs as a result of the reaction of iodine with starch suspension. When ascorbic acid is present, I_3^- is converted to iodide and no color change is observed. However, when all ascorbic acid was utilized, expected blue-black color occurs due to the reaction between starch and excess tri-iodide.

This titration procedure is widely accepted and is appropriate for testing the amount of vitamin C in the tablets, liquids and fruits and vegetables.

Preparation of iodine solution:

For preparation of 0.1 M iodine solution, 10g of KI was taken in a 250 ml Volumetric flask and 35 ml of distilled water was added followed by heating the solution; the mixture was cooled to room temperature and 3.15 g of solid Iodine powder was dissolved.

Similarly, to prepare 0.005M of iodine solution 2g of KI was taken in a 500 ml beaker and dissolving in 100 ml of distilled water and 1.3 g of iodine powder was stirred with small quantity of water and qs (quantum satis) to 1 liter.

Preparation of starch solution:

Addition of 0.25 g of starch powder in 50ml warm distilled water, As the starch is insoluble in cold water and needs to be boiled to stay in solution.

Preparation of vitamin C standard solution:

25mg Ascorbic acid was taken in a 100.00 ml beaker and dissolved in 100 ml distilled water.

Preparation of Vitamin C sample solution:

From the strip of Vitamin C random two tablets were weighed and smashed to form powder and average value was calculated.

Weight of two tablets = 1.67g

Average = 1.67/2 = 835 mg

250 mg Ascorbic acid tablet has equivalent weight of = 835 mg

100mg Ascorbic acid tablet has equivalent weight of = 167*2 mg

= 334 mg

334 mg of the powder tablet was taken in a 100.00 ml beaker and dissolved in 100 ml distilled water.

Standardization of the iodine solution with the vitamin C standard solution and sample solution:

The measured volume of 20ml of both standard and sample was taken from each solution and equilibrated with 150 ml distilled water separately into distinct two Erlenmeyer flask 250.00 ml and titrant containing iodine solution was run against analyte containing either sample or standard; 5-6 drops of prepared starch solution were added to the analyte and titration was started.

The burette level for each analyte for distinctive experiment was noted as mentioned below:

For standard solution the volume of iodine solution required for complete reaction = 45 ml

Equally, for Sample solution the volume of iodine solution required = 49 ml

The endpoint was noted when analyte appears blue in color.

CALCULATION

For sample solution

In the beginning of the experiment 20 ml of sample was taken from 100 ml of prepared solution containing 100 mg of Ascorbic acid. As 49 ml of iodine is required for the color change containing 20 ml ascorbic acid solution, the dilution was done 5 times to that of the solution.

Hence, the final volume of the iodine solution = 49× 5

= 245 ml

$$\text{Mole}_{\text{iodine}} = \text{Mass}_{\text{Ascorbic acid}} \times \frac{1\ mole}{176.12g\ of\ ascorbic\ acid} \times \frac{1000ml}{volume\ of\ iodine}$$

$$\text{M}_{\text{iodine}} = 0.1\text{g} \times 1/176.12 \times \frac{1000}{245\ ml}$$

$$= 0.00231\ \text{mol}$$

For standard solution

Mass Ascorbic acid = Mole iodine × Volume of iodine × 176.12

= 0.00231 × 45 × 176.12

= 91.54 mg

Initially, the amount of Ascorbic acid was taken for 100mg and therefore for total amount of ascorbic acid i.e. 250 mg the ratio stands out to be 2.5 (250/100)

RESULT

Therefore, a 250 mg tablet of ascorbic acid from the ACI LIMITED (Nutrivit® C) contain = 2.5 × 91.54 = 228.85 mg

Amount of Ascorbic acid in ACI LIMITED (Nutrivit® C) is 8.46% less than the claimed value.

A relationship among the pharmaceutical companies listed can be illustrated with a bar chart.

The default amount of Ascorbic acid for all the companies in a tablet dosage form is 250mg

Pharmaceutical Company	Brand Name	Amount of Ascorbic acid (mg)	Reduced amount (%)
ACI LIMITED	Nutrivit® C	228.85	8.46
Opsonin	Vasco	248	0.8
ACME	Cecon	232.9	6.84
BEXIMCO	Ascobex	220	12%

Experiment 5: Estimation of Cr and Mn in Steel.

Objectives

After studying and performing this experiment you should be able to:

• Explain the principle underlying simultaneous spectrophotometric determination of species with overlapping spectrum,

• Carry out absorbance measurements for solutions on a spectrophotometer and draw its UV-VIS spectrum,

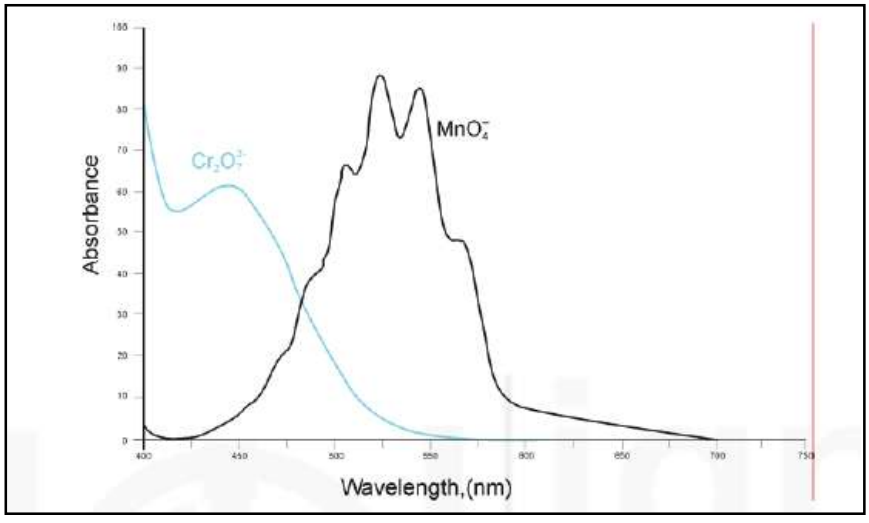
• Determine the wavelength of maximum absorption in the spectrum and compute the corresponding molar absorption coefficient,

• Calculate the concentrations of chromium and manganese in a mixture from the absorption measurements of the mixture at two different wavelengths,

• Apply and adapt the method of simultaneous determination for other similar combination of ions.

Principle:

On dissolution of alloy steel containing chromium and manganese, we get these elements as their ions; Cr3+ and Mn2+ ions respectively. In the determination, these are oxidised respectively to dichromate and permanganate ions using potassium persulphate and potassium periodate, respectively. The orange red coloured dichromate shows maximum absorption (λ_{max}) at 440 nm while for the pink coloured permanganate the λ_{max} is at 545 nm. However, permanganate also absorbs at 440 nm to a smaller extent. Similarly, dichromate ions also have small absorption at 545 nm



Schematic diagrams of the visible spectra of potassium dichromate and potassium permanganate in 1M sulphuric acid, indicating the overlapping of the spectra and the relative values of molar absorption coefficients

In simple words, both the species absorb at the wavelengths of maximum absorptions mentioned above. Thus, the absorption of the solution containing a mixture of dichromate and permanganate ions at these wavelengths would be the sum of the absorbances of the two species. It can be shown that the absorbances of these two ions obey Beer-Lambert's law when measured individually and also in a mixture in presence of 0.5 M sulphuric acid. Under these conditions we can write the following expression assuming a unit path length.

$$A_{440} = \varepsilon_{Cr,440}[Cr_2O_7^{2-}] + \varepsilon_{Mn,440}[MnO_4^-] \quad \ldots (1)$$

$$A_{545} = \varepsilon_{Cr,545}[Cr_2O_7^{2-}] + \varepsilon_{Mn,545}[MnO_4^-] \quad \ldots (2)$$

Here, the meaning of the terms used is self evident. For example, ε Cr, 545 refers to the molar absorption coefficient at 545 nm for chromium as dichromate ion; A_{440} refers to the absorbance of the mixture at 440 nm and $[Cr_2O_7^{2-}]$ represents the concentration of dichromate ions and so on. We need to solve these simultaneous equations to determine both the species without their separation.

Solving Eq. (1) and (2) we get the following expressions for the concentrations of dichromate and permanganate ions. Thus, the concentrations of the two ions can be obtained from the absorbance measurements at 440 and 545 nm, if we know the molar absorption coefficients for both the ions at these wavelengths.

$$\left[Cr_2O_7^{2-}\right] = \frac{A_{440}(\varepsilon_{MnO_4^-})_{545} - A_{545}(\varepsilon_{MnO_4^-})_{440}}{(\varepsilon_{Cr_2O_7^{2-}})_{440}\ (\varepsilon_{MnO_4^-})_{545} - (\varepsilon_{MnO_4^-})_{440}(\varepsilon_{Cr_2O_7^{2-}})_{545}} \quad \ldots (3)$$

$$\left[MnO_4^-\right] = \frac{A_{545} - (\varepsilon_{Cr_2O_7^{2-}})_{545}\left[Cr_2O_7^{2-}\right]}{(\varepsilon_{MnO_4^-})_{545}} \quad \ldots (4)$$

The values of the molar absorption coefficients are obtained from absorbance measurements of pure solutions of the two substances at the designated wavelengths. Fe^{3+}, Ni^{2+}, Co^{2+} and V^{2+} also absorb in these regions, therefore these should be absent from the analyte solution.

Requirements:

Apparatus		**Chemicals**
Spectrophotometer/ Filter photometer	1	Potassium dichromate
Matched cuvette	2	Potassium permanganate
Volumetric flasks (1 litre)	1	Sulphuric acid
Volumetric flasks (250 cm3)	2	
Graduated pipette (10 cm3)	1	
Beakers (100 cm3)	10	
Weighing bottle	1	
Burettes	2	

Solutions Provided:

i) **1 M sulphuric acid** (**Reference blank):** It is prepared by adding (with constant swirling) 53.3 cm3 of analytical grade concentrated sulphuric acid into a one litre flask containing about 500 cm3 of distilled water, allowing the flask to cool and making up the volume using distilled water.

ii) **Potassium dichromate (0.002 M) in 1M sulphuric acid**: It is prepared by accurately weighing 0.1471 g of analytical grade potassium dichromate and quantitatively transferring to a 250 cm3 volumetric flask and adding sufficient amount of 1 M sulphuric acid to dissolve it. Once the compound dissolves the volume is made upto the mark with 1M sulphuric acid.

iii) **Oxalic acid (0.005 M)**: It is prepared by accurately weighing 0.063 g of oxalic acid and quantitatively transferring to a 100 cm3 volumetric flask and adding sufficient amount of water to dissolve it. Once dissolved the volume is made upto the mark with distilled water.

iv) **Potassium permanganate (0.002 M**) **in 1 M sulphuric acid:** It is prepared as follows.

- Weigh about 1.8 g A.R. potassium permanganate and dissolve in 50 cm3 of distilled water taken in a 100 cm3 beaker.
- Heat the solution to boiling and gently continue for about fifteen minutes.
- Cool the solution and filter through a plug of glass wool in the funnel.
- Take 10 cm3 of the filtrate in a 100 cm3 beaker and dilute to 100 cm3 with 1M sulphuric acid.
- Standardise the solution by titrating with a standard solution of oxalic acid in acidic medium.
- Calculate the volume of the solution required to prepare 250 cm3 of 0.002 M solution.
- Take the requited volume of the standardised solution of potassium permanganate in a 250 cm3 volumetric flask. Make up the volume with 1M sulphuric acid.

v) **Sample solution**: prepared by suitably mixing the 0.002 M solutions of potassium dichromate and potassium permanganate to make 10 cm3 of the mixture and adding 10 cm3 of 1M sulphuric acid to it.

Procedure:

The procedure for the experiment can be divided into three components. These are given below.

a) Determination of molar absorption coefficients of dichromate and permanganate ions

b) Establishing the additivity of absorbance values of dichromate and permanganate ions

c) Determination of the concentrations of dichromate and permanganate ions in the mixture.

Follow the instructions given below in the sequential order to accomplish these tasks.

a) **Determination of molar absorption coefficients for dichromate and permanganate ions**

1. Pipette out 20 and 40 cm3 respectively of the 0.002 M stock solution of potassium dichromate into two 100 cm3 standard flasks and make up the volume with 1M sulphuric acid. This would give 0.0004 M and 0.0008 M solutions respectively of potassium dichromate. Mark the flasks accordingly.

2. Pipette out 20 and 40 cm3 respectively of the 0.002 M stock solution of potassium permanganate into two 100 cm3 standard flasks and make up the volume with 1M sulphuric acid. This would give 0.0004 M and 0.0008 M solutions respectively of potassium permanganate. Mark the flasks accordingly.

3. Measure the absorbance values at 440 nm and 545 nm for the stock solutions (0.002 M) of potassium dichromate and potassium permanganate and the dilutions prepared in step 1 and 2. Make measurements in cuvettes of 1 cm path length and use 1M sulphuric acid as the reference. Record the values in Observation Table 1.

4. Calculate the molar absorption coefficients for potassium dichromate and potassium permanganate at 440 nm and 545 nm as per the expressions given under column 4 and 6 and record appropriately in the Observation Table 1.

b) **Establishing the additivity of absorbance values of dichromate and permanganate ions at 440 and 545 nm**

1. Take two clean burettes and fill them with 0.0008 M potassium dichromate and 0.0004 M potassium permanganate respectively.

2. Take 7 beakers of 100 cm3 capacity labelled from 1 to 7 and transfer the solutions of 0.0008 M potassium dichromate, 0.0004 M potassium permanganate and 1M sulphuric acid as per the details given in column 2, 3 and 4 of the Observation Table 2.

3. Measure the absorbance values of the resulting solutions using 1M sulphuric acid as the reference and record your observations in the column 5 and 7 of Observation Table 2. You must use cuvettes having a path length of 1 cm.

4. Calculate the absorbance values for the mixtures of potassium dichromate and potassium permanganate at 440 nm and 545 nm by using Eq. (1) and Eq. (2) respectively and record them in the column 6 and 8 of Observation Table 2.

5. Compare the observed and calculated absorbance values for the validation of additivity. Record your observations in the space provided after Observation Table 2.

c) **Determination of the concentrations of dichromate and permanganate ions in the mixture.**

1. Measure the absorbance values of the given sample solution taken in a cuvette of path length equal to 1 cm. Use 1M sulphuric acid as the reference and record your observations in the column 1 and 2 of Observation Table 3.

2. Calculate the concentration of potassium dichromate and potassium permanganate in the mixture by using Eq.(3) and Eq. (4) respectively and record your results in the column 3 and 4 of Observation Table 3.

Observations and Calculations:

A. Determination of molar absorption coefficients for dichromate and permanganate ions

Observation Table-1: Determination of molar absorption coefficients for $K_2Cr_2O_7$ and KMnO4 at 440 and 545 nm

A: Potassium dichromate					
Column					
1	**2**	**3**	**4**	**5**	**6**
S. No.	**Concentration of $K_2Cr_2O_7$** $c_{K_2Cr_2O_7}$	**Absorbance at 440 nm** $= A_{440nm}$	$\varepsilon_{440\ mm}$ # $= \frac{A_{440nm}}{c_{K_2Cr_2O_7}}$	**Absorbance at 545 nm** $= A_{545nm}$	$\varepsilon_{545\ mm}$ # $= \frac{A_{545nm}}{c_{K_2Cr_2O_7}}$
1	0.002				
2	0.0004				
3	0.0008				
			Average =		**Average =**
B: Potassium permanganate					
S. No.	**Concentration of $KMNO_4$** c_{KMnO_4}	**Absorbance at 440 nm** $= A_{440nm}$	$\varepsilon_{440\ mm}$ # $= \frac{A_{440nm}}{c_{KMnO_4}}$	**Absorbance at 545 nm** $= A_{545nm}$	$\varepsilon_{545\ mm}$ # $= \frac{A_{545nm}}{c_{KMnO_4}}$
1	0.002				
2	0.0004				
3	0.0008				
			Average =		**Average =**

The expression is valid only if the absorbance measure is made in a cuvette of path length=1cm.

The molar absorption coefficients for the $[Cr_2O_7^{2-}]$ and $[MnO_4^-]$ ions are found to be:

$\varepsilon_{440\,nm}[Cr_2O_7^{2-}] =$

$\varepsilon_{545\,nm}[Cr_2O_7^{2-}] =$

$\varepsilon_{440\,nm}[MnO_4^-] =$

$\varepsilon_{545\,nm}[MnO_4^-] =$

B. Establishing the additivity of absorbance values of dichromate and permanganate ions at 440 and 545 nm

Observation Table 2: The observed and calculated absorbance values for the mixtures of potassium dichromate and potassium permanganate.

Column							
1	2	3	4	5	6	7	8
S. No.	Volume of 0.0008 M $K_2Cr_2O_7$ (cm^3)	Volume of 0.0004 M $KMnO_4$ (cm^3)	Volume of 1 M H_2SO_4 (cm^3)	Absorbance at 440 nm $= A_{440nm}$		Absorbance at 545 nm $= A_{545nm}$	
				Obsd.	Calc.*	Obsd.	Calc.**
1.	50	0	1				
2.	40	10	1				
3.	30	20	1				
4.	25	25	1				
5.	20	30	1				
6.	10	40	1				
7.	0	0	1				

* The absorbance value is calculated as per Eq. (3.1.)

** The absorbance value is calculated as per Eq. (3.2.)

Write your conclusions about the additivity of the absorbance values here.

……...

……...

……...

……...

……...
……...

C. Determination of the concentrations of dichromate and permanganate ions in the mixture.
Observation Table 3: Determination of the concentrations of dichromate and permanganate ions in the mixture

Absorbance at 440 nm $= A_{440nm}$	**Absorbance at 545 nm** $= A_{545nm}$	$C_{K_2Cr_2O_7} = \frac{A_{440}(\varepsilon_{MnO_4^-})_{545} - A_{545}(\varepsilon_{MnO_4^-})_{440}}{(\varepsilon_{Cr_2O_7^{2-}})_{440}\ (\varepsilon_{MnO_4^-})_{545} - (\varepsilon_{MnO_4^-})_{440}(\varepsilon_{Cr_2O_7^{2-}})_{545}}$	$C_{KMnO_4} = \frac{A_{545} - (\varepsilon_{Cr_2O_7^{2-}})_{545}\left[Cr_2O_7^{2-}\right]}{(\varepsilon_{MnO_4^-})_{545}}$

$C_{K_2Cr_2O_7} =$

$C_{KMnO_4} =$

RESULT

i) The concentrations of potassium dichromate in the given mixture is found to be
=.....M

ii) The concentrations of potassium permanganate in the given mixture is found to be
= .....M

PRECAUTIONS

· All the reagents used must be of AR grade.

· All the glassware used must be quite clean.

· The measurements should preferably be made in cuvettes of 1 cm path length. (In the absence of these the expressions given for calculation of molar absorption coefficients and concentrations would need to be modified.)

Experiment 6: Estimation of (i) arsenite and (ii) antimony in tartar-emetic iodimetrically

Objectives:

1. The student will titrate using iodine as a titrant.
2. The student will use a buffer to control the reaction of the titration.
3. The student will use both acid and base to get the desired pH.
4. The standard and unknown are treated in the same manner.
5. Starch will be used as an indicator.

Procedure:

Preparation of Iodine Solution: Dissolve approximately 25 g of potassium iodide in about 50 mL of water. Add to this 6.5 g of iodine crystals. When the iodine has dissolved completely, dilute the solution to about500 mL. Do in a 600 mL beaker, not a volumetric flask!

Preparation of Starch Solution: Dissolve 1 gram of soluble starch in about 5 mL of cold d.i. Slowly add the starchsuspension to 95 mL of rapidly boiling water. Boil until the solution clears. Cool to roomtemperature. NOTE: Starch solutions often do not keep. Make it the day you will need it (ifyou also will need it the following period try to keep it--if it has a mold growth then it mustbe discarded).

Standardization of the Iodine Solution: Weigh out into 250 mL Erlenmeyer flasks FOUR samples of pure As2O3 of about 0.20 geach. Add 10 mL of 4% NaOH solution. Swirl until all As2O3 has dissolved. (You maywarm it to hasten solution, if necessary) Dilute to 50 mL. Cool to room temperature andadd 1:5 HCl until the solution turns pink with methyl red and cool again. Add SOLIDsodium bicarbonate in small portions until you are sure that no more will dissolve; thenadd about 3 g in EXCESS. If the bicarbonate is dissolved before a titration is completed,add more bicarbonate. Add 3 mL of starch solution and titrate with the iodine solutionimmediately. Continue the titration to the first permanent blue color. Calculate thenormality of the iodine solution.

Titration of Unknown Arsenic: Dry the unknown for 1 hour at 105 ^{o}C. Do not OVERHEAT. Cool it in a desiccator. Weighout into 250 mL Erlenmeyer flasks four samples of 0.4 to 0.5 g each. Add 10 mL of 4%NaOH solution. It may be necessary to warm it in order to hasten solution. Dilute to 50 mL.Cool to room temperature and add 1:5 HCl until solution turns pink with methyl red. Coolagain. Add bicarbonate in small portions until you are sure no more will dissolve; then addabout 3 g in excess. If the bicarbonate is dissolved before a titration is completed, add morebicarbonate. Add 3 mL of starch indicator and titrate IMMEDIATELY with the standardiodine solution. Calculate the percentage of As2O3 in the unknown.

PRECAUTIONS:

1. Arsenic is a very poisonous element. Fatal dose is the amount that you can balance on thehead of a pin. Wash carefully before eating.
2. It is important that there be an excess of sodium bicarbonate throughout a titration.
3. Solutions of trivalent arsenic may be oxidized appreciable by air if allowed to stand. Thetitration should be completed as soon as possible after the sample is dissolved in alkali.

NOTES: Use 250 mL Erlenmeyer flasks for the titrations. *Do not use aliquots.*

The initial sample of arsenic oxide should be dried for one hour at 100o C.

CALCULATION: Calculate the percent of arsenic oxide (As2O3) present in the sampleafter calculating the molarity of the titrant from the known arsenic titrations. Include aspread sheet and computer print-out for the calculation.

SAFETY AND DISPOSAL INFORMATION**:** Dispose of all solutions in the "As WASTE" container. Do not mix the wastes from the I2 and $KMnO_4$ Determinations. CAUTION: Remember to treat all chemicals with respect. Arsenic is BAD!

Experiment 7: Estimation of Fe in cement.

Aim: Estimation of Fe in cement colorimetrically. The method is based on the reaction of iron with ammonium thiocyanate forming a complex having a maximum absorption at 450 nm. Iron is estimated, the results are found to be reproducible and the method is economical and less time consuming. The method is successfully applied to cement sample and results is found to be accurate and precise as the more sophisticated colorimeter is commonly used for ferrous determination.

Composition of Cement

There are seven major ingredients of cement.The general percentage of these ingredients in cement is given below in Table 1:

Iron oxide: Chemical formula is Fe_2O_3.

- Iron oxide imparts color to cement.
- It acts as a flux.
- At a very high temperature, it imparts into the chemical reaction with calcium and aluminum to form tricalcium alumino-ferrite.
- Tricalcium alumino-ferrite imparts hardness and strength to cement

Colorometric measurements were made using a colorimeter and samples were analysed at 450 nm .The basis of spectrophotometric methods is the simple relationship between the absorption of radiation by the solution and the concentration of species in the solution. When monochromatic light passes through a transparent medium (coloured solution) the rate of decrease in intensity with the concentration and thickness of the medium is directly proportional to the intensity of the light .In order to determine a species or analyte in the solution spectrophotometrically, it is usually converted into a colored complex. Ammonium thiocyanate yields a blood red colour with ferrous iron and the colour produced is stable in nitric acid medium. The sample of cement was analysed with certain colouring reagent and optical density of the coloured compound is measured at 450 nm since the maximum absorption

was at 450nm , hence all measurements were made at 450 nm. Its optical density is measured in a colorimeter and the concentration of ferrous iron is found from the standard calibration curve.

Methodology:

Dissolve the given ferrous ammonium sulphate (0.7022 gms) in 100 ml of water and add 5 ml of 1 : 5 H_2SO_4 followed by dil. $KMnO_4$ solution through burette until light-pink colour appears. Dilute the solution to 1 L such that 1 ml of solution contains. 0.1 mg of Fe^{+2}. From the above solution, take 1,2,3,4,5 ml separately into 100 ml standard volumetric flasks. Add 1 ml of nitric acid and 5 ml of 40% ammonium thiocyanate solution to all the above samples to get blood red colour and make up the solutions to the mark by adding distilled water. Before recording the optical densities values for the above prepared solutions filter selection is done to know the maximum absorption in table 2.1. Now measure the optical densities of all the solutions using colorimeter table 2.2 and plot a graph by taking amount of ferrous iron on x-axis and optical density on the y-axis. The curve obtained is called standard calibration curve in figure 2.1

Ingredient	Percentage in cement
Lime	60-65
Silica	17-25
Alumina	3-8
Magnesia	1-3
Iron oxide	0.5-6
Calcium Sulfate	0.1-0.5
Sulfur Trioxide	1-3

Dissolution of sample

Weight out 0.1 gm of the cement sample into a beaker. Add 5 ml of water and stir with a stirrer. Add few drops of concen HCl through the walls of the beaker and stir again. Heat the mixture until the moisture is evaporated. Then add 20 ml of distilled water and dissolve the content and make up the solution with distilled water to 100 ml. Shake well for uniform concentration.

Development of Colour

Pipette out 10 ml of above solution, into 100 ml std. flask add 1 ml of con HNO_3 and then add 5 ml of 40% NH_4SCN with a Burette. Make up the solution upto the mark with distilled water. Now take the sample solution into colorimeter tube and measure the O.D. (optical density) using the photo colorimeter. From the O.D. we can measure the concentration of Fe^{2+} from the calibration curve. The calibration curve is as follows in figure 1.

Table 1. Filter selection:

Filter Number	Absorbance
45	0.52
47	0.41
51	0.34
52	0.29
54	0.21
57	0.12

67	0.01

Table 2. Absorbance of solutions with various concen of Ferrous(Fe^{+2})

S.No	Concentration of Fe+2 in mg	Absorbance
1	0.2	0.18
2	0.4	0.39
3	0.6	0.58
4	0.8	0.81
5	1	0.98

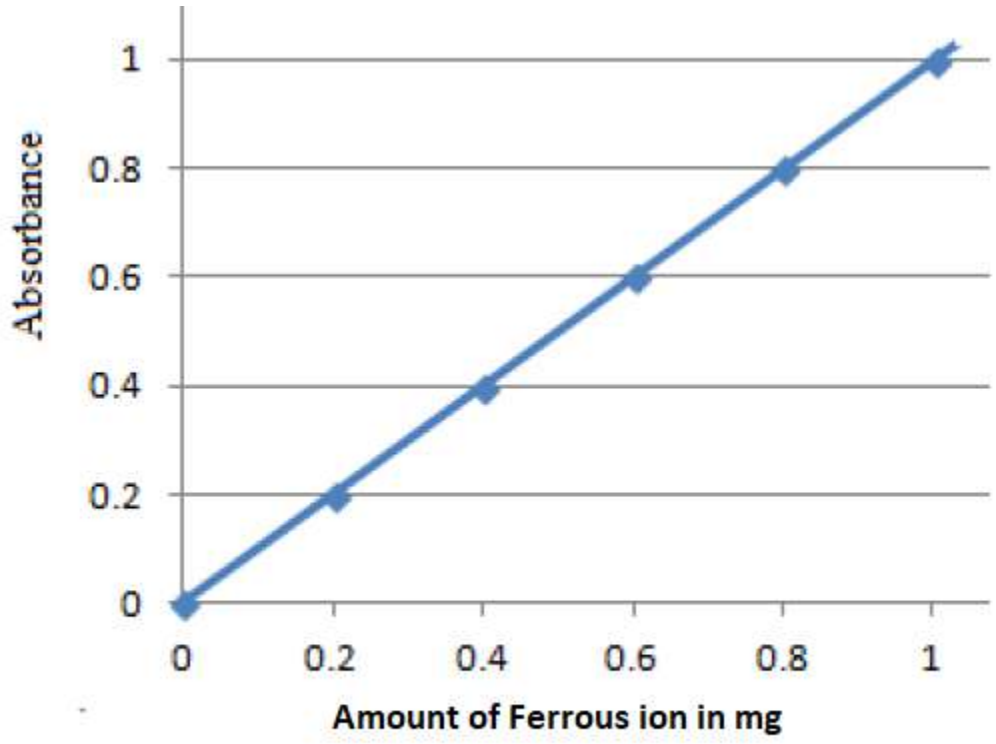


Figure 1 CALIBRATION CURVE

Calculation: From the calebration curve we determined the concentration of iron in cement.

C7P: Organic Chemistry Lab

Background

Organic chemists often must identify unknown compounds. In some cases, such as a reaction, you may have a good idea of what the compound in question is. However, in other cases, such as when you isolate a compound from a natural source, you may have no idea what the compound might be. In this experiment you will determine the identity of an unknown compound. First, you will need to purify your compound, then you will need to identify its functional group (it will contain only one), and finally you will need to make a derivative of the compound. You will confirm your results with boiling or melting point, IR, and NMR.

Impurities in your compound will make it extremely difficult to identify. Thus, before you do anything else, you will need to make sure your unknown compound is pure. Consider each of the following purification techniques you have learned over the course of the year.

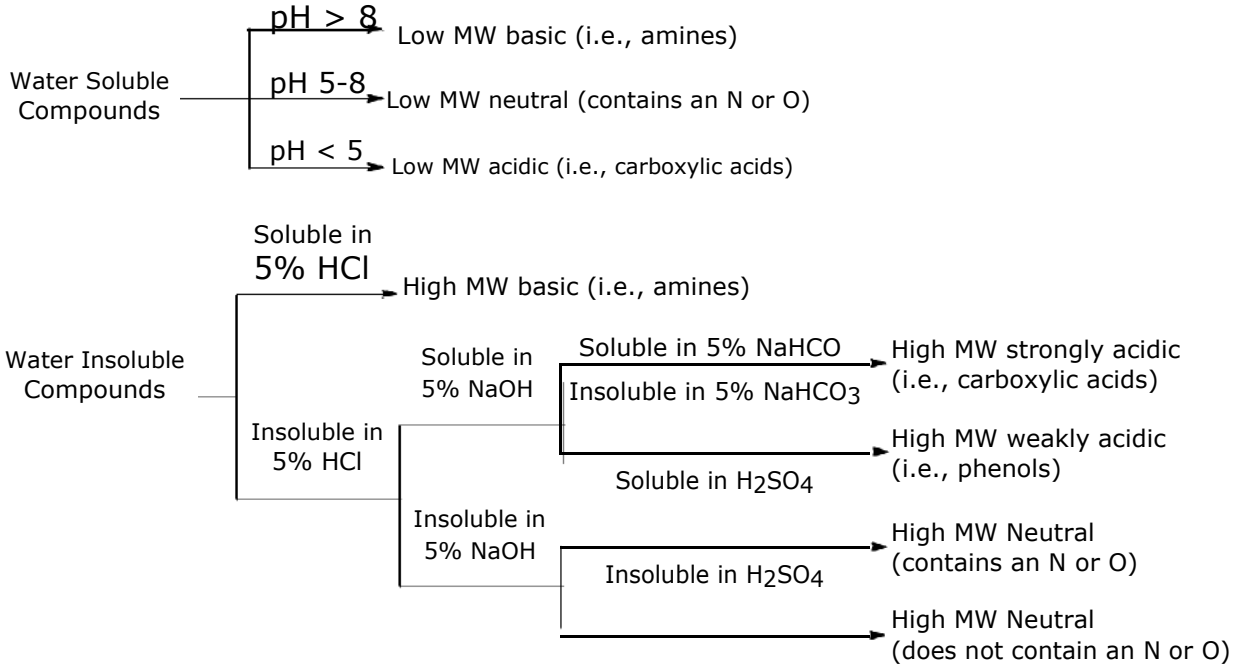
1. *Recrystallization:* Works well for solid compounds. You will need to find an appropriate recrystallization solvent. Consider a variety of solvents and mixed solvent systems.
2. *Distillation:* Works well for liquids that have a boiling point of <250 ◦C. (Note: Fractional distillation may be required if you suspect impurities close to the boiling point of your unknown.)

3. *Column Chromatography:* Works well for UV active compounds. You will need to use TLC to identify a solvent system that will separate your unknown from any impurities.

After you have purified your unknown, verify that it is pure enough to proceed by measuring the boiling or melting point. Note that while you will not know what the melting point or boiling point of your unknown should be, the narrowness is an excellent indicator of whether or not your product is pure. Also pay attention to the appearance of your unknown and see if it has changed (hopefully for the better) during the course of the purification process.

Once your unknown is pure, you will need to identify its functional group. Your unknown will have one major functional group (alcohol, ketone, aldehyde, amide, amine, carboxylic acid, or ester). Additionally, your unknown compound may or may not contain an aromatic ring. To determine the functional group, it is recomanded that you start with solubility tests, and then conduct functional group classification tests. IR spectroscopy may also be useful at this point. Solubility can sometimes provide a surprisingly useful amount of information. First, you will test your unknown's solubility in water. Compounds with 4 carbons

or less will easily dissolve in water, whereas compounds with 8 carbons or more will be insoluble. Compounds containing 5----7 carbons may or may not dissolve (often they will display "partial" solubility). If your compound dissolves in water, you will also want to check the pH of the solution. Amines will typically be basic, and carboxylic acids will typically be acidic. Most other compounds will be neutral. Compounds that are insoluble in water should then be subjected to a solubility test in 5% HCl. Typically, only amines will be soluble in HCl because they form water-soluble hydrochloride salts when they react with HCl. Compounds that are not soluble in HCl, should be subjected to testing in basic solutions (5% NaOH and 5% $NaHCO_3$). Both strong and weak acids (Carboxylic acids and phenols) will be deprotonated by NaOH to form water-soluble alkoxides. Only strong acids like carboxylic acids will react with $NaHCO_3$. Compounds that are not soluble in base should then be reacted with a very strong acid, sulfuric acid (note that in the case of sulfuric acid, "solubility" is also indicated by any type of reaction such as heat, gas generation, or a color change). Compounds that cannot become protonated by sulfuric acid at all (i.e., alkanes, alkyl halides, and aromatic carbons) will still remain insoluble. These solubility tests are summarized in the flow charts below.



The results from the solubility tests can significantly help in determining which classification tests should then be performed, or at least narrow down the list. By no means do you need to conduct all classification tests. In fact, you should do your best to select only tests that will provide you with additional information about your unknown and/or confirm results. Also, make sure that your glassware is clean and dry so you do not get any false positive or false negative results. Keep in mind that a negative result for a classification test provides useful information, so be sure to keep track of negative results as well as positive results. Also, for each classification test that you perform, be sure to run a blank, and one or more controls. These will help you to determine if a reaction actually occurred. A blank includes everything but the unknown, and a control includes a compound for which the outcome is known in place of the unknown. Controls can be positive (a compound you know will react) or negative (a compound that you know will not react). The classification tests are summarized in the table below.

Functional group	Test	Test no	Notes
Elemental analysis	Lassaigne test	C-1	Test for nitrogen, sulphur, halogens
Amine	Basicity test Bleaching powder test Dye test	C-2 C-3 C-4	Test for aromatic amine
Nitro	Reduction test Muliken and barker test	C-5 C-6	Test for aromatic nitro group
Amido	Nitrous acid test Hydrolysis test	C-7 C-8	Test for amido group
Phenolic –OH	Ferric chloride test Back dye test	C-9 C-10	Test for phenolic-OH
Carboxylic acid	Bicarbonate test Esterification test	C-11 C-12	Test for carboxylic acid
Aldehyde	Benedict test Tollens test	C-13 C-14	Test for aldehyde
Ketone	2,4-Dinitrophenoyl Hydrazine test	C -15	Test for ketone

At this point, you should be able to use your boiling or melting point data combined with the results of your functional group data to develop a hypothesis as to what your unknown might be or at least narrow down the list to only a few candidates. Note tha due to the accuracy (or lack thereof) of our thermometers, your boiling or melting points may be up to 15◦C lower than the literature values.

Once your functional group has been determined, you will prepare a derivative of your unknown. To prepare a derivative, you will select a suitable reaction that converts your unknown into a different functional group for which the boiling or melting point is known. This is particularly useful because compounds that have similar boiling or melting points will oftenhave derivatives that differ significantly in terms of boiling or melting point. You should then be able to identify your unknown using this information.

Finally, you can confirm the identity of your product using IR and NMR. Note that these measurements can be taken at any time during the course of the lab after you purified your product. In fact, it is recommended that you conduct them sooner rather than later as they may provide valuable information as to the identity of your unknown (e.g., IR may reveal your functional group).

Lab Notebook Preparation A

Before coming to lab on the first day of this experiment, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. Outline of your plan for determining the identity of your unknown
4. Hazards of and appropriate precautions for the safe handling of unknown organic compounds
5. References

Lab Notebook Preparation B

Before coming to lab on the day you plan to prepare a derivative, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. List of possible unknowns
4. The chemical reaction(s) you are attempting (with skeletal structures…R groups are okay if you do not know the identity of your unknown yet)
5. For each reaction you are attempting, include a table with information about your starting materials. Include molecular weight, molar equivalents, and mmoles to be used. For solids include grams. For liquids, include grams, density, and volume. For solutions, include the concentration and volume. (Note: You will not be able to completely fill in the table if you do not know the identity of your unknown yet. If that is the case, list whatever data you can.)
6. Any relevant physical properties (i.e., melting points or boilingpoints of possible unknowns and their derivatives)
7. Hazards of and appropriate precautions for the specific reaction(s) you are conducting
8. References

Safety Notes

- Assume that all unknowns are flammable and harmful by inhalation, ingestion, and skin absorption. Do not inhale their vapors and avoid contact with eyes, skin and clothing.

Directions

1. Purify your unknown using distillation, recrystallization, or column chromatography. It is recommended that purify the entire unknown provided so that you have enough pure material for all of the tests.
2. Measure the boiling or melting point of your unknown to confirm its purity.
3. Confirm with your instructor that the boiling or melting point you obtained for your unknown is within 15 ◦C of the reported literature value before proceeding.
4. Test the solubility of your unknown in water. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or smallvial.
    b. Add 1 mL of water and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, test the pH of the solution and then skip to step 9.
5. Test the solubility of your unknown in 5% HCl. (If your unknown is a solid, crush it intoa fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of 5% HCl and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, skip to step 9.
6. Test the solubility of your unknown in 5% NaOH. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of 5% NaOH and shake vigorously for approximately 30 seconds. If the unknown appears to be insoluble, skip to step8.
7. Test the solubility of your unknown in 5% $NaHCO_3$. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of 5% $NaHCO_3$ and shake vigorously for approximately 30 seconds.
    c. Note whether your unknown is soluble or insoluble and then skip to step 9.

8. Test the solubility of your unknown in concentrated H_2SO_4. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of concentrated H_2SO_4 and shake vigorously for approximately 30 seconds.
    c. Note whether your unknown is soluble or insoluble. (Any indication of a reaction such as heat, gas generation, or a color change also indicates solubility.)
9. Conduct classification tests as needed. See directions for specific tests below.
10. Confirm the identity of your functional group with your instructor before proceeding.
11. Prepare one or more derivatives of your unknown. See directions for specific derivatives below.
12. Measure the melting point of any derivatives.
13. Confirm with your instructor that the melting point you obtained for your derivative is within 15 °C of the reported literature value.

Classification Tests

C-1 Elemental Analysis

This reaction tests for the presence of nitrogens, sulphur and halogens.

Safety Notes: Sodium can cause serious burns and the sodium-lead alloy may react violently with some substances. Wear gloves, avoid contact, and keep the sodium-lead alloy away from other chemicals.

Recommended Controls: butylamine, acetamide, bromobenzene

Procedure:

1. In the fume hood or under a snorkel, place 0.25 g of 10% sodium-lead alloy in a small, dry test tube held vertically by a clamp.

2. Melt the alloy with a Bunsen burner flame and continue heating until the sodium vapor rises about 1 cm up the tube.

3. Using a Pasteur pipet, add 2 drops of the unknown (or 10 mg of a solid) directly onto the molten alloy so that it does not touch the sides of the tube.

4. Heat gently to start the reaction, remove the flame until the reaction subsides, then heat the tube strongly for a minute or two, keeping the bottom a dull red color.
5. Let the tube cool to room temperature.

6. Dropwise add 1.5 mL of water and heat gently for a minute or so until the excess sodium has decomposed and gas evolution ceases.

7. Filter the solution through a Pasteur pipet with a small plug of cotton, wash the cotton with 1 mL of water, and combine the wash water with the filtrate. (Use a rubber bulb to expel any liquid that adheres to the cotton.) The filtrate should be colorless or just slightly yellow. If it is darker, repeat the fusion with stronger heating or more of the alloy.

To test for nitrogen:

1. Put 5 drops of the sodium fusion solution into a small test tube.

2. While stirring, add enough solid sodium bicarbonate, to saturate it (a little excess solid should be present).

3. Add 1 drop of this solution to a test tube containing 10 drops of PNB reagent (*p*-nitrobenzaldehyde in dimethyl sulfoxide) and note any color change.

To test for halogens:

1. Acidify 10 drops of the sodium fusion solution with dilute nitric acid.

2. Boil it gently under the hood for a few minutes.

3. Add a drop or two of 0.3 M aqueous silver nitrate, and note the color and volume of any precipitate that forms. (If a voluminous precipitate forms, let the precipitate settle and then remove the solvent using a pipet.)

4. Add 2 mL of 3 M aqueous ammonia to the solid, shake vigorously, and note your observations.

5. To test further for bromine and iodine, acidify 1 mL of the original sodium fusion solution with 1 M sulfuric acid, boil for a few minutes, and add 0.5 mL of dichloromethane and a then a drop of freshly prepared chlorine water. Shake and look for a color in the dichloromethane layer.

To test for sulphur:

1. Put 1ml of sodium-extract into a test tube.
2. Add 1 ml dil.NaOH solution followed by 2-3 drops of sodium nitroprusside.

Interpretation*:* In the PNB test, a purple color indicates the presence of nitrogen (green indicates sulfur). In the halogen tests, formation of a voluminous precipitate on addition of silver nitrate indicates that a halogen is present, and the color of the precipitate (a silver halide) may suggest which halogen: white for chlorine, pale yellow for bromine, and yellow for iodine. If only a faint turbidity is produced, it may be caused by traces of impurities or by incomplete sodium fusion. If the precipitate is silver chloride, it will dissolve in aqueous ammonia; silver bromide is only slightly soluble and silver iodide is insoluble. In the chlorine water test, a red-brown color is produced by elemental bromine and a violet color by elemental iodine. In the sulphur test, a violet or purple color indicates the presence of sulphur.

C-2 Basicity Test

This test is useful if you have already determined that you have an amine. It is used to distinguish alkyl amines from aromatic amines.

Recommended Controls: p-toluidine, dibutylamine

Procedure for water-soluble compounds:

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of water.

2. Measure the pH of the solution using pH paper.

Procedure for water-insoluble compounds:

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of a pH 5.5 acetate-acetic acid buffer.

2. Mix thoroughly.

Interpretation: Water-soluble alkyl amines give pH values above 11, whereas water-soluble aromatic amines have pH values below 10. Water-insoluble alkyl amines should dissolve in the buffer, but water-insoluble aromatic amines will not dissolve.

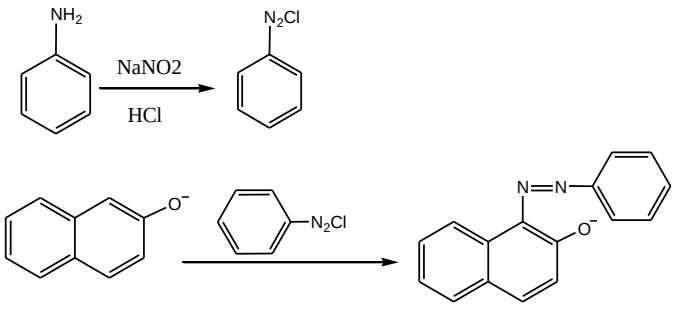
C-3 Bleaching powder test

Procedure:

1. Dissolve 0.05 g of your unknown in 5 mL of water.
2. Add 3-4 drops of bleaching powder solution.
3. Shake vigorously.

Interpretation: Transient purple color which soon turns brown or light purple color.

C-4 Dye test:

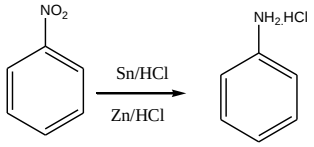


Procedure:

1. 0.1 g of organic sample is dissolved in 5ml of dil.HCl.
2. The mixture is cooled at 0º-5ºC in an ice-bath.
3. Then add 1ml of ice cold solution of dil. $NaNO_2$.
4. The mixture is added to ice-cold alkaline solution of β-Napthol.

Interpretation: Red or orange red dye (brown or raddish purple or violet dye indicates the presence of two amino groups; soluble dye indicates the presence of SO3H or Ar-OH along with Ar-NH_2 group).

C-5 Reduction test



1. A mixture of 0.1 g of organic sample, few pieces of granulated tin or zinc and 3ml of Conc. HCl is warmed gently with occasional shaking till the reaction is complete.
2. The mixture is cooled.
3. Filtered, if required, diluted and diazo-coupling reaction is performed.

Interpretation: Brilliant red or scarlet dye obtained.

C-6 Muliken and Barker Test

Procedure:

1. 0.1 g of organic sample is dissolved in 5 ml of 50% alcohol.
2. A little solid NH_4Cl or 10% $CaCl_2$ solution and a pinch of Zn-dust is added to it.
3. The mixture is boiled for a few minutes.
4. Then the mixture is cooled and allowed to stand for 5 minutes and then filtered.
5. With the filtrate following three tests are performed:

a) A portion of the solution is added to Tollen's reagent and then warmed in a water bath.

b) Two drops of benzoyl chloride and 2 drops of conc. HCl are added to another portion of the filtrate followed by 12 drops of $FeCl_3$ solution.

c) The last portion of the filtrate is warmed with a little Fehling's solution.

Interpretation: From the part (a), a silver mirror or black or grey precipitation is obtained. From part (b), a wine-red color of ferric hydroxamate is present, from last part (c), a red precipitation is obtained.

C-7 Nitrous Acid Test

Procedure:

1. A little of the aqueous solution of organic sample is treated with with a few drops of HNO_2 (NaNO2 and HCl).

Interpretation: Effervescence due to evolution of N_2 gas.

C-8 Hydrolysis Test

Procedure:
0.2 g of organic sample is heated with 2ml of 50% NaOH solution.

Interpretation: Characteristics smell of NH_3 which turns mercurous nitrate paper black or copper sulphate paper deep blue.

C-9 Ferric Chloride

This reaction tests for the presence of phenols.

Recommended Control: phenol

Procedure:

1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of water. If(you know based on the results of your solubility tests that the unknown is insoluble in water, use 0.5 mL of water and 0.5 mL of methanol instead of 1 mL of water.)
2. Add two drops of 2.5% ferric chloride solution.

Interpretation: Formation of an intense red, green, blue, or purple color suggests a phenol or an easily enolizable compound (such as an aldehyde or ketone). Some phenols do not react under these conditions.

C-10 Back Dye Test

This reaction tests for the presence of phenols.

Procedure:

1. A few drops of aniline dissolved in dil. HCl.
2. Few drops of cold dil. $NaNO_2$ solution is added.
3. Then the clear solution is added to the cold solution of organic sample in NaOH.

Interpretation: A brilliant red dye is obtained. Phenolic OH group present and confirmed.

C-11 Bicarbonate Test

This reaction tests for the presence of carboxylic acid.

Procedure:

1. A small amount of organic sample is sprinkled over aqueous solution of sodium bicarbonate.

Interpretation: Effervescence due to the evolution of CO_2.

C-12 Esterification Test

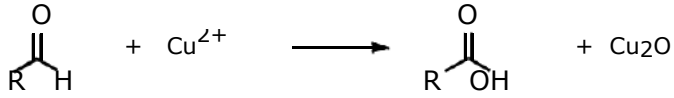
This reaction tests for the presence of carboxylic acid.

1. 0.5 g of organic sample is taken in a dry test tube.
2. To this, add 1 ml of dehydrated ethanol.
3. Then 2-3 drops of conc. H_2SO_4 is added and heated for 5 minutes in a water bath.
4. The mixture is then poured into a beaker containing large volume of Na_2CO_3 solution.

Interpretation: Characteristics sweet fruity smell of ester.

C-13 Benedict's Test

This reaction tests for the presence of aldehydes. Note that most ketones and aromatic aldehydes will not react.



Recommended Controls: butanal

Procedure:

1. Add 2 drops of the unknown (80 mg if it is a solid) to 2 mL of water.
2. Add 2 mL of Benedict's reagent.
3. Heat the mixture to a boil.
4. Observe if a precipitate forms, and note its color.

Interpretation: Benedict's reagent contains copper(II) sulfate,sodium citrate, and sodium carbonate. Aldehydes will react with the Cu_{2+} from the copper(II) sulfate to form copper(I) oxide which appears as a yellow or orange precipitate (it may look a little green in the blue reaction solution). Note that most ketones and aromatic aldehydes will not react.

C-14 Tollen's Test

This reaction tests for the presence of aldehydes.

Recommended Controls: benzaldehyde

Procedure:

1. Measure 2 mL of 0.3 M aqueous silver nitrate into a test tube and add 1 drop of 3 M sodium hydroxide.
2. Add 2 M aqueous ammonia drop by drop, with shaking, until the precipitate of silver oxide just dissolves (avoid an excess of ammonia).
3. Add 1 drop of the unknown (40 mg of a solid) to this solution, shake the mixture, and let it stand for 10 minutes. (If a silver mirror is observed at this point, this is considered a positive result.)
4. Heat the mixture in a 35 °C water bath for 5 minutes.
5. Immediately after the test has been completed, dissolve any solid residue in 1M nitric acid and then dispose of the solution in the designated waste container.
6. *Interpretation:* Formation of a silver mirror on the inside of the test tube is a positive test for an aldehyde. (Note that if the tube is not sufficiently clean, a black precipitate or a suspension of metallic silver may form instead.)

C-15 2,4-Dinitrophenylhydrazine

This reaction tests for the presence of aldehydes and ketones.

Safety Notes: 2,4-Dinitrophenylhydrazine (DNPH) is harmful if absorbed through the skin. Wear gloves and avoid contact.

Recommended Controls: cyclohexanone, benzaldehyde

Procedure:

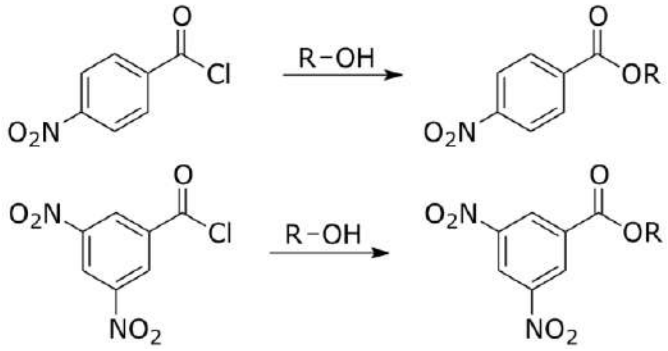
1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of 95% ethanol (use more ethanol if necessary to completely dissolve the unknown).
2. Add this solution to 2 mL of the DNPH reagent.
3. Shake and let the mixture stand for 15 minutes or until a precipitate forms. (If a precipitate is observed at this point, this is considered a positive result.)
4. Scratch the inside of the test tube and observe if a precipitate forms, and note its color.

Interpretation: Formation of a crystalline yellow or orange-red precipitate indicates an aldehyde or ketone. The color of the precipitate may give a clue to the structure of the carbonyl compound (unconjugated aliphatic aldehydes and ketones usually yield a yellow precipitate, while aromatic and α,β-unsaturated aldehydes and ketones yield a orange-red precipitate).

Derivatives of Alcohols

D-1* p-*Nitrobenzoates and 3,5-Dinitrobenzoates

For these derivatives, it is extremely important to ensure that your glassware and your alcohol are dry (i.e., free of water). Water can easily react with the acid chlorides to form carboxylic acids to form the respective carboxylic acids rather than the desired esters. (Note: The *p*----nitrobenzoic acid has a melting point of 237 °C. and the 3,5----dinitrobenzoic acid has a melting point of 205----207 °C.) If necessary, dry your glassware in an oven before proceeding.



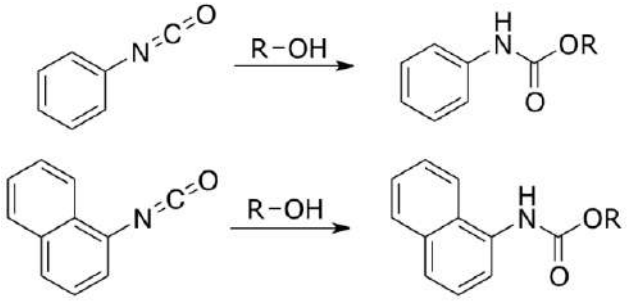
Procedure:

1. Dry your unknown alcohol with magnesium sulfate or sodium sulfate.
2. Filter to remove the drying agent.
3. If you are making the *p*-nitrobenzoate derivative, add 0.20 g of *p*-nitrobenzoyl chloride to a small round bottom flask. If you are making the 3,5-dinitrobenzoate derivative, add 0.20 g of 3,5-dinitrobenzoyl chloride to a small round bottom flask.
4. In the fume hood or under a snorkel, dropwise add 0.10 g of your unknown alcohol to the acid chloride while stirring.
5. Heat the mixture in a 60-70 °C water bath. If your alcohol has boiling point of < 160 °C, heat the mixture for 5 minutes. If your alcohol has boiling point of > 160 °C, heat the mixture for 15 minutes.
6. Stir in 4 mL of 0.2 M sodium carbonate.
7. Heat the mixture to 50-60 °C for 30 seconds.
8. Cool to room temperature and then in an ice bath.
9. Collect the precipitate by small-scale vacuum filtration. Wash with cold water.

10. Recrystallize the precipitate from ethanol or an ethanol-water mixture.

D-2 Phenylurethanes and 1-Naphthylurethanes

For these derivatives, it is extremely important to ensure that your glassware and your alcohol are dry (i.e., free of water). Water can easily react with the isocyanates to form the respective ureas rather than the desired carbamates. (Note: The dipheylurea has a melting point of 241 °C, and the di-1-naphthylurea has a melting point of 297 °C.) If necessary, dry your glassware in an oven before proceeding.



Safety Notes: Isocyanates are irritants and lachrymators. Avoid contact with these reagents and use in a fume hood or under a snorkel.

Procedure:

1. Dry your unknown alcohol with magnesium sulfate or sodium sulfate.

2. Filter to remove the drying agent.

3. If you are making the phenylurethane derivative, add 5 drops of phenyl isocyanate to a small round bottom flask. If you are making the 1-naphthylurethane derivative, add 5 drops of 1-naphthyl isocyanate to small round bottom flask.

4. In the fume hood or under a snorkel, dropwise add 5 drops of the dry alcohol to the isocyanate. If no reaction is apparent, heat the mixture in a 60-70 °C water bath for 15 minutes.

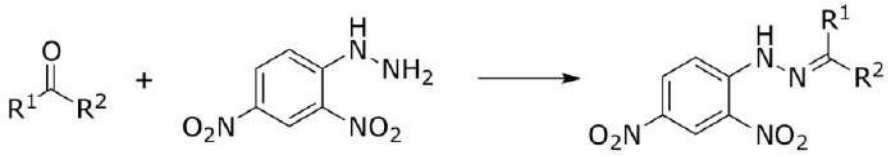
5. Cool to room temperature and then in an ice bath.

6. Collect the precipitate by small-scale vacuum filtration.

7. Recrystallize the precipitate from petroleum ether or heptane. (If necessary, perform a hot gravity filtration.)

Derivatives of Aldehydes and Ketones

D-3 2,4-Dinitrophenylhydrazones

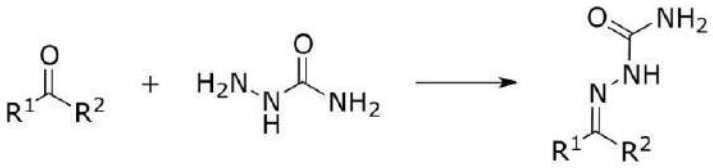


Safety Notes: 2,4-Dinitrophenylhydrazine is toxic and sulfuric acid is corrosive. Avoid contact with these reagents and use in a fume hood or under a snorkel.

Procedure:

1. In a small round bottom flask, dissolve 0.10 g of the unknown aldehyde or ketone in 1 mL of ethanol. (If your unknown is not completely dissolved, add ethanol drop bydrop until it goes into solution).
2. In the fume hood or under a snorkel, dropwise add 3 mL of the 2,4-dinitrophenylhydrazine-sulfuric acid reagent.
3. Allow the solution to stand at room temperature until crystallization is complete. If no crystals form, heat the mixture in a 60-70 °C water bath for 15 minutes, and then it cool again. If there is still no precipitate, add cold water drop by drop to the solution until precipitate is observed.
4. Collect the precipitate by small-scale vacuum filtration. Wash once with 5 mL of cold 5% $NaHCO_3$ and once with cold water.
5. Recrystallize the precipitate from ethanol or an ethanol-water mixture. (Note: If more than 6 mL of ethanol is needed for recrystallization, add ethyl acetate drop by drop to the hot solution until everything is dissolved.)

D-4 Semicarbazones



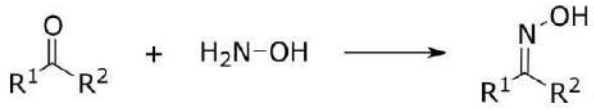
Safety Notes: Semicarbazide hydrochloride is a suspected carcinogen. Avoid contact with the reagent.

Procedure:

1. Mix together 0.20 g of semicarbazide hydrochloride, 0.30 g of sodium acetate, and 2 mL of water in a small round bottom flask.
2. If your unknown aldehyde or ketone is water soluble, add 0.20 g of it directly to the flask and stir to dissolve. If your unknown aldehyde or ketone is not water soluble, add a minimum amount of ethanol to the mixture until your unknown goes into solution.

3. Stir the mixture for two minutes.
4. Cool the mixture in an ice bath. If no crystals form, heat the mixture in a 60-70 °C water bath for 5 minutes, and then it cool again.
5. Collect the precipitate by small-scale vacuum filtration. Wash with cold water.
6. Recrystallize the precipitate from ethanol or an ethanol-water mixture.

D-5 Oximes



Safety Notes: Hydroxylamine hydrochloride is toxic and mutagenic. Avoid contact with the reagent.

Procedure:

1. Mix together 0.125 g of hydroxylaminehydrochloride, 0.30 g of sodium acetate, and 2 mL of water to a small round bottom flask.
2. If your unknown aldehyde or ketone is water soluble, add 0.20 g of it directly to the flask and stir to dissolve. If your unknown aldehyde or ketone is not water soluble, add a minimum amount of ethanol to the mixture until your unknown goes into solution.
3. Stir the mixture for two minutes.
4. Cool the mixture in an ice bath. If no crystals form, heat the mixture in a 60-70 °C water bath for 15 minutes, and then it cool again. If there is still no precipitate, add cold water drop by drop to the solution until precipitate is observed.
5. Collect the precipitate by small-scale vacuum filtration. Wash with cold water.
6. Recrystallize the precipitate from ethanol or an ethanol-water mixture.

Reporting Your Results

Write your report according to the guidelines described in “Topic 4: Writing an Organic Chemistry Lab Report”. Work by yourself on this report.

References & Additional Resources

1. Lehman, J. W. *Operational Organic Chemistry: A Problem----Solving Approach to the Laboratory Course*, 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 1999; pp 529----572.

Table 1. Possible Alcohol Unknowns

Alcohol	BP (°C)	3,5-Dinitro benzoate MP (°C)	4-Nitro benzoate MP (°C)	1-Naphthyl urethane MP (°C)	Phenyl urethane MP (°C)
methanol	65	108	96	124	47
ethanol	78	93	57	79	52
2-propanol	83	123	110	106	88
2-methyl-2-propanol	83	142	-	-	136
2-propen-1-ol	97	49	28	108	70
1-propanol	97	74	35	105	57
2-butanol	99	76	26	97	65
2-methyl-2-butanol	101	116	85	72	42
2-methyl-1-propanol	108	87	69	104	86
3-pentanol	116	101	17	95	48
1-butanol	118	64	36	71	61
2-pentanol	119	62	24	74	-
3-methyl-3-pentanol	123	94 (62)	69	104	43
3-methyl-1-butanol	132	61	21	68	57
4-methyl-2-pentanol	132	65	26	88	143
1-pentanol	137	46	11	68	46
cyclopentanol	141	115	62	118	132
2-ethyl-1-butanol	148	51	-	60	-
1-hexanol	157	58	5	59	42
cyclohexanol	161	113	50	129	82
furfuryl alcohol	172	80	76	130	45
1-heptanol	177	47	10	62	60
2-octanol	174	32	28	63	114
1-octanol	195	61	12	67	74
1-phenylethanol	202	95	43	106	92
benzyl alcohol	204	113	85	134	77
2-phenylethanol	219	108	62	119	78
1-decanol	231	57	30	73	60
3-phenyl-1-propanol	236	45	47	-	92
1-dodecanol	259	60	45 (42)	80	74

*A dash indicates that no information is reported in the literature

**Melting points in parenthesis represent conflicting literature values

Table 2. Possible Aldehyde Unknowns

Alcohol	BP (°C)	MP (°C)	2,4-Dinitro phenylhydrazone MP (°C)	Semicarbazone MP (°C)	Oxime MP (°C)
ethanal	21		168 (157)	162	47
propanal	48		148 (155)	154	40
propenal	52		165	171	-
2-methylpropanal	64		187 (183)	125 (119)	-
butanal	75		123	106	-
3-methylbutanal	92		123	107	48
pentanal	103		106 (98)	-	52
2-butenal	104		190	199	119
2-ethylbutanal	117		95 (30)	99	-
hexanal	130		104	106	51
heptanal	153		106	109	57
2-furaldehyde	162		212 (230)	202	91
2-ethylhexanal	163		114 (120)	254d	-
octanal	171		106	101	60
benzaldehyde	178		239	222	35
phenylethanal	195	33	121 (110)	153 (156)	99
4-methylbenzaldehyde	204		234	234 (215)	80
3,7-dimethyl-6-octenal	207		77	84 (91)	-
2-chlorobenzaldehyde	209		213 (209)	229 (146)	76 (101)
4-methoxybenzaldehyde	248		253d	210	133
2-methoxybenzaldehyde		38	254	215	92
4-chlorobenzaldehyde		48	265	230	110 (146)
3-nitrobenzaldehyde		58	290	246	120
4-nitrobenzaldehyde		106	320	221 (211)	133 (182)

*A dash indicates that no information is reported in the literature
**Melting points in parenthesis represent conflicting literature values

***If the substance changes color and smokes, this is considered decomposition (d = decomposes)

Table 3. Possible Ketone Unknowns

Ketone	BP (°C)	MP (°C)	2,4-Dinitro phenylhydrazone MP (°C)	Semicarbazone MP (°C)	Oxime MP (°C)
acetone	56		126	187	59
2-butanone	80		118	146	-
3-methyl-2-butanone	94		124	113	-
2-pentanone	101		143	112 (106)	58
3-pentanone	102		156	138	69
3,3-dimethyl-2-butanone	106		125	157	75 (79)
4-methyl-2-pentanone	117		95 (81)	132	58
2,4-dimethyl-3-pentanone	124		95 (88)	160	34
2-hexanone	128		110	125	49
4-methyl-3-penten-2-one	130		205	164 (133)	48
cyclopentanone	131		146	210 (203)	56
4-heptanone	144		75	132	-
2-heptanone	151		89	123	-
cyclohexanone	156		162	166	91
2,6-dimethyl-4-heptanone	168		92	122	210
2-octanone	173		58	124	-
cycloheptanone	181		148	163	23
acetophenone	202		238	198 (203)	60
2-methylacetophenone	214		159	205	61
propiophenone	218	21	191	182 (174)	54
3-methylacetophenone	220		207	203	57
4-methylacetophenone	226	28	258	205	88
2-undecanone	228		63	122	44
4-phenyl-2-butanone	235		127	142	87
3-methoxyacetophenone	240		-	196	-
2-methoxyacetophenone	245		-	183	83 (96)
4-methoxyacetophenone		38	228	198	87
4-phenyl-3-buten-2-one		42	227 (223)	187	117
benzophenone		48	238	167	144
2-acetonaphthone		54	262d	235	145
3-nitroacetophenone		80	228	257	132
9-fluorenone		83	283	234	195

*A dash indicates that no information is reported in the literature

**Melting points in parenthesis represent conflicting literature values

***If the substance changes color and smokes, this is considered decomposition (d = decomposes)

GE-3: Lab

Identification of a pure organic compound

Liquid Compounds

1. Methyl Alcohol

CH_3-OH

Physical characteristics and preliminary test :

1. State	**: Liquid**
2. Colour	**: Colorless**
3. Odour	**: Pungent but faint alcoholic**
4. Miscibility	**: Miscible With water**
5. Litmus	**: Neutral**
6. Action of heat	**: Volatilises**
7. Ignition test	**: Blue non-sooty flame**

Special Tests

Experiment	Observation
1. Oxidation test : A Cu-spiral is made repeatedly red hot and introduced into 2 ml of O.S. kept in a test tube dipped in a beaker containing cold Water. The solution is then divided into four pan ts.	1.
(a) Schiffis test : One part is added to Schiff s.	(a) Pink color which deepens slowly.
(b) Tollen's test: Another part is added to Tollen's reagent and heated in a water-bath.	(b) Bright mirror of silver on the side of the test tube.
(c) Resorcinol test: A mixture of 0.5 ml of oxidised liquid and a drop of 0.5% aq. Solution of resorcinol is added carefully	(c) A reddish -violet ring appears at the junction of two liquid layers. A white ppt.

down the side of the test tube held in an inclined position containing 2ml of conc. H_2SO_4.	changing to reddish-violet appear in the aq. Layer above the ring after a little while.
2. Denige's reagent: To about 5ml of aq. Solution of o.s. in a porcelain basin placed on ice-water, 2-3 ml of 2.5% soln. of $KMnO_4$ soln. is added followed by few drops of conc. H_2SO_4 when a brown color developes. The brown color is destroyed by addition of saturated soln. of oxalic acid. A freshly prepared soln.of schiffs reagent is added dropwise to it with stirring.	2. A violet color develops deepening on standing.
3. Oil of wintergreen test: 0.5 ml of o.s. and 3 drops of conc. H2SO4 are added to 0.5 g of salicylic acid and heated for one minute and finally the reaction mixture is poured into 50 ml of water taken in a beaker.	3. Characteristics smell of methyl salicylate.
4**. Iodoform test** in NaOH is performed (vide test 3a for ethanol)	4. The test is negative i.e., no yellowish ppt. of iodoform (*distinction from ethyl alcohol and acetone*)

2. Ethanol

CH_3CH_2OH

Physical characteristics and preliminary test :

1. State : Liquid
2. Colour : Colorless
3. Odour : Pungent but faint alcoholic
4. Miscibility : Miscible with water
5. Litmus : Neutral
6. Action of heat : Volatilises
7. Ignition test : Blue non-sooty flame

Special Tests

Experiment	Observation

1. Oxidation test : A Cu-spiral is made repeatedly red hot and introduced into 2 ml of O.S. kept in a test tube dipped in a beaker containing cold Water. The solution is then divided into four parts.	1.
(a) Schiff's test : One part is added to Schiff s.	(a) Pink color which deepens slowly.
(b) Tollen's test: Another part is added to Tollen's reagent and heated in a water-bath.	(b) A silver mirror is disposited on the walls of the test tube.
(c) To another part equal volume of very dilute solution of sodium nitroprusside solution is added followed by a few drops of NaOH solution.	(c) Wine-red color develops.
(d) To another part a very dilute solution of sodium nitroprusside solution is added followed by a few drops of piperidine.	(d) A deep red color develops.
2. Ethyl acetate formation: About 0.2 ml of O.S. and an equal volume of glacial acetic acid and a little conc. H_2SO_4 (or 0.2 g of fused sodium acetate) are taken in a test tube and warmed in a water-bath for about 5 min. the mixture is then poured into water taken in a beaker to which a little Na_2CO_3 has been added.	2. Pleasant fruity smell.
3. Iodoform test: (a) To 2 ml of aq. soln. of o.s. an equal volume of a conc. solution of iodine in potassium iodide is added and then dil. NaOH solution is added dropwise with stirring until violet color of iodine disappears. Then the mixture is warmed and cooled under tap with shaking.	3. (a) Yellow ppt. of iodoform and its characteristic smell. (*distinction from methanol*)
(b) The iodoform test is repeated by adding NH_4OH instead of NaOH.	(b) No ppt. of iodoform. (*distinction from acetone*)

3. Chloroform

$CHCl_3$

Physical characteristics and preliminary test :

1. State : Liquid
2. Colour : Colorless
3. Odour : Sweet

4. Miscibility : **Immiscible with water and much heavier than water**

5. Litmus : **Neutral**

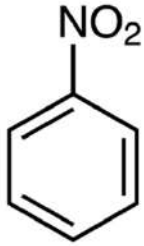
6. Action of heat : **Volatilises**

7. Ignition test : **Yellow sooty flame**

Special Tests

Experiment	Observation
1. Hydrolysis test: O.S. is treated with aq. KOH or NaOH solution and boiled. The mixture is acidified with conc. HNO_3 and then $AgNO_3$ is added.	1. Curdy white ppt. soluble in NH_4OH but reappears on addition of conc. HNO_3.
2. Fehlings test: O.S and Fehlings solution (I + II equal vol.) is warmed with constant shaking.	2. A yellowish red ppt.
3. Resorcinol test: A little powdered resorcinol and few drops of O.S. is taken in a basin, about 1 ml of conc. solution of NaOH is added to it, then the mixture is warmed gently.	3. A brilliant reddish colouration is developed in aq. layer.
4. Carbylamine test: Few drops of O.S. aniline and alc. KOH are warmed in a diy test tube and the ensuing gas is smelt by placing the thumb at the mouth of the test tube and then holding tfie thumb near the nostrils.	4. Intolerable obnoxious smell of carbylamine. (*Not recommended to perform)*

4. Nitrobenzene



Physical characteristics and preliminary test :

1. State : **Liquid**

2. Colour : **Pale yellow**

3. Odour : **Characteristic smell of bitter almonds**

4. Miscibility : **Immiscible with water**

5. Litmus : **Neutral**

6. Action of heat : **Volatilises without leaving any residue**

7. Ignition test : **Yellow sooty flame**

Special Tests

Experiment	Observation
1. Caustic soda test : About 0.2 ml of O.S. is heated with conc. solution of caustic soda.	1. The color darkens.
2. Reduction and diazocoupling test: 0.5 ml is reduced by tin or zinc and dil. HCl for 5 minutes. The decanted solution is cooled and very dilute cold solution of $NaNO_2$ is added to it. The diazotised soln. is added to cold alkaline soln. of. β-naphthol.	2. Brilliant scarlet-red dye.
3. Muliken-Barker test: An aq. ethanolic solution of few drops of given sample is boiled with a pinch of zinc dust and little solid NH_4Cl. The mixture is cooled and filtered into Tollen's reagent.	3. Grey or black ppt..

5. Acetone

CH_3COCH_3

Physical characteristics and preliminary test :

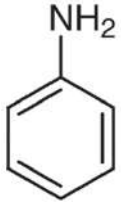
1. State : **Liquid**
2. Colour : **Colorless**
3. Odour : **Pleasant ethereal odour**
4. Miscibility : **Miscible with water**
5. Litmus : **Neutral**
6. Action of heat : **Completely Volatilises without leaving any residue**
7. Ignition test : **Blue non-sooty flame**

Special Tests

Experiment	Observation
1. Brady's test : A small amount of O.S. is added to 2-4-dinitrophenylhydrazine solution	1. Yellow ppt. on mixing.
2. Denige's test: An equal volume of Denige's reagent is added to an aqueous solution of O.S and the test tube is then kept in a boiling water bath for few minutes.	2. Heavy white ppt. of double compound of acetone and basic mercuric sulphate.
	3. A ruby red (reddish-purple) color develops

3. Legal's test: A few drops of a very dil. solution of sodium nitroprusside is added to 2-3 ml of aqueous solution of O.S. followed by a few drops of dil. NaOH solution.	which disappears on warming but reappears on cooling.
4. Iodoform test: (a) iodoform test is performed with I2 in KI solution and NaOH solution. (b) the iodoform test is repeated by adding NH_4OH solution instead of NaOH solution.	4. (a) Yellow ppt. of CHI_3 having characteristics sweeet smell. (b) Yellow ppt. of CHI_3 having characteristics sweet smell. (*Distinction from ethanol*)

6. Aniline



Physical characteristics and preliminary test :

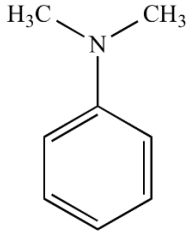
1. State	**: Liquid**
2. Colour	**: Colorless when freshly distilled but turns brown on exposure to light and air**
3. Odour	**: Characteristic aromatic smell**
4. Miscibility	**: Immiscible with water but soluble in dil. HCI**
5. Litmus	**: Neutral**
6. Action of heat	**: Completely volatilises without leaving any residue**
7. Ignition test	**: Yellow sooty flame**

Special Tests

Experiment	Observation
1. Bleaching powder test: A few drops of bleaching powder solution is added to a dilute solution of O S. in HCl.	1. Purple-violet colouration.
2. Potassium dichromate test: A drop of O.S. is added to 5 to 6 drops of conc. H_2SO_4 taken in a spot plate and the mixture is stirred well with glass rod. Then a drop of $K_2Cr_2O_7$ solution is added to it.	2. Intense blue colour develops.
3. Diazocoupling test: 5-6 drops of O.S are dissolved in dil. HCl in a test tube and cooled in ice-water. Then 3-4 drops of very dilute ice cold solution of sodium nitrite are added to it. Then the solution is added dropwise to 2 mL of	3. Brilliant scarlet-red dye.

ice-cold alkaline solution of β-naphthol; finally solution should remain mild alkaline	

7. *N*,*N*-Dimethylaniline



Physical characteristics and preliminary test :

1. State : Liquid
2. Colour : Colorless when freshly distilled but turns brown on exposure to light and air
3. Odour : Characteristic bad smell
4. Miscibility : Immiscible with water but soluble in dil.HCI
5. Litmus : Neutral
6. Action of heat : Completely volatilises without leaving any residue
7. Ignition test : Yellow sooty flame

Special Tests

Experiment	Observation
1. Bleaching powder test: A few drops of bleaching powder solution is added to a dilute solution of O S. in HCl.	1. Purple-violet colouration.
2. Potassium dichromate test: A drop of O.S. is added to 5 to 6 drops of conc. H_2SO_4 taken in a spot plate and the mixture is stirred well with glass rod. Then a drop of $K_2Cr_2O_7$ solution is added to it.	2. Intense blue colour develops.
3. Nitrous acid test: 5-6 drops of O.S are dissolved in dil. HCl in a test tube and cooled in ice-water. Then 3-4 drops of very dilute ice cold solution of sodium nitrite are added to it.	3. A colour appears at this stage. (No red dye after addition to alkaline 2-naphthol solution) (*distinction from aniline*)
4. **Malachite green test**: See test of benzaldehyde below. Use benzaldehyde and this sample.	4. An intense green colouration

8. Benzaldehyde

C_6H_5CHO

Physical characteristics and preliminary test :

1. State	**: Liquid**
2. Colour	**: Colorless**
3. Odour	**: Characteristic smell of bitter almonds**
4. Miscibility	**: Immiscible with water**
5. Litmus	**: Neutral**
6. Action of heat	**: Volatilises**
7. Ignition test	**: Yellow sooty flame**

Special Tests

Experiment	Observation
1. 2,4-D.N.P test: A few drops of 2,4-D.N.P solution is added to 1 mL alcoholic solution given sample.	1. Reddish yellow ppt. forms immediately simply on mixing.
2. Tollen's test: An alcoholic solution of the given sample is added to 2 mL of Tollen's reagent, warmed gently.	2. Black ppt.
3. Malachite green test: 0.5 ml of O.S is heated with 1 ml of dimethyl aniline and a small bit of anhydrous $ZnCl_2$ in a dry test tube for one minute. The leucobase produced is oxidised with lead dioxide in a solution of acetic acid and excess conc. HCl is added.	3. A intense green coloration.

Solid compounds

1. Oxalic acid

$[(COOH)_2]$

Physical characteristics and preliminary test :

1. State	**: Solid**
2. Colour	**: Colorless**
3. Texture	**: Crystaline**
3. Odour	**: Odourless**
4. Solubility	**: Soluble in cold water**
5. Litmus	**: Blue litmus turns red**

6. Action of heat : Volatilises completely without charring when heated slowly and

a sublimation is formed but decomposed with evolution of gases when heated strongly

7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is heated with conc. H_2SO_4 and the evolved gas is passed into lime water.	1. Lime water turns milky.
2. Soda-lime test: A small amount of O.S. is heated in a hard glass test tube with sodalime.	2. The gas burns at the mouth of the test tube.
3. Calcium chloride test: Calcium chloride solution is added to neutral solution of O.S. The ppt is divided into two parts	3. A white ppt. forms immediately.
(i) Dil. acetic acid is added to one portion.	(i) The ppt does not dissolve. (*Distinction from tartaric and succinic acids*)
(ii) Dil. HCl or dil. HNO_3 is added to another portion.	(ii) The ppt. dissolves
4. Silver nitrate test : $AgNO_3$ solution is added to neutral solution of O.S. The ppt. is divided into three parts :	4. A white crystalline ppt.
(il Dil. NaOH is added to one portion. (ii) Dil. HNO_3 is added to another portion.	(i) The ppt. dissolves (ii) The ppt. dissolves
(iii) The third portion is warmed, dried and heated strongly in a dry test tube	(iii) Metallic silver is formed
5. Denige's test (C.T.): Denige's reagent is added to neutral solution or aqueous solution of O.S.	5. White ppt. in the cold which does not dissolve
6. Potassium permanganate test: A little of dil. H_2SO_4 is added to a solution of O.S or neutral soln. of O.S. The solution is warmed and dil. $KMnO_4$ solution is added drop by drop with shaking.	6. The pink colour of permanganate disappears.

2. Succinic acid

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Blue litmus turns red

6. Action of heat : Melts and then boils giving off extremely irritating vapours. A sublimate is forme d at the cooler part of the test tube

7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: Few crystals of O.S. is warmed conc. H_2SO_4 and then heated strongly.	1. O.S dissolves without charring. Slight chairring occurs on strong heating and the solution turn brown with evolution of SO_2.
2. Calcium chloride test: An equal volume of Calcium chloride solution is added to neutral solution of O.S. The mixture is shaken vigorously inner side of the test tube is scratched with glass rod and finally boiled.	2. A white ppt. soluble in acetic acld. (*Distiction from oxalic macid*)
3. Silver nitrate test : $AgNO_3$ solution is added to neutral solution of O.S.	3. Buff-colored ppt. soluble in dil. HCl.
4. Denige's test (C.T.): Denige's reagent is added to neutral solution or aqueous solution of O.S. and then a drop of 2% $KMnO_4$ solution is added.	4. No ppt. in the cold but the color of permanganate presists.
5. Fluorescein test: A small quantity of the sample ix mixed with resorcinol and 2 / 3 drops of c. sulfuric acid and heated. Then poured into large volume of water.	5. A beautiful reddish green fluorescence, intesifies to a beautiful green fluorescence on addition of alkali..

3. Resorcinol

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : feebly acidic
6. Action of heat : Melts and volatiles
7. Ignition test : Yellow sooty flame

Experiment	Observation
1. H_2SO_4 test: Few crystals of O.S. is warmed with conc. H_2SO_4.	1. O.S dissolve without charring.
2. Ferric chloride test: A few drops of $FeCl_3$ solution is added to aqueous solution of O.S.	2. Bluish-violet color.
3. Bromine writer test: Bromine writer is added to aq. solution of O.S. and shaken.	3. White ppt.
4. Tollen's test: Aqueous solution of O.S is added to Tollen's reagent and warmed.	4. Black ppt of silver mirror.
	5. An intense reddish-green fluorescein, intesifies to a beautiful green

5. Fluorescein test: A small quantity of O.S. is mixed with succinic acid / phathalic acid and 2 drops conc. Sulfuric acid and heated. Then poured into a large volume of water. **6.** O.S. is mixed with 3 - 4 drops $CHCl_3$ and gently heated on a basin with NaOH solution.	fluorescence on addition of alkali. 6. A brilliant reddish colouration is developed in aq. layer.

4. Urea

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Neutral
6. Action of heat : Melts and gives off characteristic smell of NH_3
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. Nitrous acid test: Dil. HCl and dil. $NaNO_2$ solution is added to aq. Solution of O.s in a test tube and shaken.	1. Effervescence with evolution of gas.
2. Nitric acid test: 2 mL of conc. HNO_3 is added to aqueous concentrated solution of O.S.	2. A white crystalline ppt.
3. Oxalic acid test: A concentrated solution of oxalic acid is added to conc. solution of O.S.	3. A white crystalline ppt.
4. Biuret test: About 0 5 g of O.S. is heated gently# to melt. The heating is continued till the molten mass solidifies at once when test tube is taken out of flame. If there is no solidification the process is repeated. The residue is cooled and dissolved in I ml of NaOH solution by warming and shaking. The solution is cooled again and a drop or two of a very dilute copper sulphate solution is added to it.	4. A pink or violet colour develops. [#strong and rapid heaing leads to formation of cyanuric acid and then the test will fail]

5. Benzoic acid

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : White
3. Texture : Plate-shaped or needle shaped Crystal
3. Odour : Odourless
4. Solubility : Insoluble in cold water but Soluble in hot water
5. Litmus : Blue litmus turns red
6. Action of heat : Melts and sublimates
7. Ignition test : Yellow sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. Dissolves without charring.
2. Soda-lime test: A small amount of O.S. is heated in a hard glass test tube with sodalime.	2. Characteristics smell of benzene.
3. Denige's test: Denige's reagent is added to neutral solution of O.S.	3. White ppt. dissolves on boiling but appears on cooling.
4. Ferric chloride test: (a) A drop or two of freshly prepared solution of $Fecl_3$ is added to neutral solution of O.S. (b) Dilute HCl is added to it.	4. (a) a buff-colored ppt. (Distinction from salicylic acid) (b) buff-colored ppt dissolves with appearance of white ppt.
5. Esterification test: About 0.1 g of O.S and 2 mL of dehydrated alcohol are taken in a clean test tube and shaken well. Then a few drops of conc. H_2SO_4 is added and the test tube is waremd in a hot water bath. The test tube is cooled and content of the test tube is poured into 50 mL of dilute sodium cxarbonate solution taken in a beaker.	5. Characteristics fruity smell of ester.

6. Salicylic acid

Physical characteristics and preliminary tests:

1. State	**: Solid**
2. Colour	**: White**
3. Texture	**: needle shaped Crystal**
3. Odour	**: Odourless**
4. Solubility	**: Sparingly soluble in cold water but readily Soluble in hot water**
5. Litmus	**: Blue litmus turns red**
6. Action of heat	**: Melts and sublimes**
7. Ignition test	**: Yellow sooty flame**

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. The solid dissolved, charring occurs after some time, solution darkens and gas evolve.
2. Soda-lime test: A small amount of O.S. is heated in a hard glass test tube with sodalime.	2. Characteristics smell of phenol.
3. Denige's test: Denige's reagent is added to neutral solution of O.S.	3. White ppt. dissolves on boiling but appears on cooling.
4. Ferric chloride test: A drop or two of freshly prepared solution of $Fecl_3$ is added to neutral solution of O.S.	4. An intense violet color
(a) Dilute HCl is added to it.	(*Distinction from benzoic acid*)
(b) acetic acid is added to another part.	(a) The color discharges
5. Oil of wintergreen test: About 0.1 g of O.S and 1 mL of methanol and few drops of conc. H_2SO_4 are warmed in aclean dry test tube.	(b) The color persists 5. A characteristics pungent fragnant odor which intensifies on pouring the mixture to dil. Sodium carbonate solution.

7. Tartaric acid

Physical characteristics and preliminary test :

1. State	**: Solid**
2. Colour	**: Colorless**
3. Texture	**: Crystalline**
3. Odour	**: Odourless**
4. Solubility	**: Soluble in cold water**
5. Litmus	**: Blue litmus turns red**
6. Action of heat	**: Chars and gives off smell of burnt sugar**
7. Ignition test	**: Blue non-sooty flame**

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. charrs immediately.
2. Calcium chloride test: Excess of calcium chloride solution is added to neutral solution of O.S. shaken and inside of the test tube is scratched with a glass rod.	2. A white crystalline ppt. soluble in hot dilute acetic acid.
4. Silver nitrate test : (a) $AgNO_3$ solution is added to neutral solution of O.S. (b) Addition of AgNO3 solution is continued till the precipitation is complete. Then dil.	4. (a) A white crystalline ppt. (b) shining silver mirror forms at the inner of the test tube.

NH4OH is added dropwise with constant shaking till the ppt. almost and not completely dissolved as revealed by slight turbidity.	(*Distinction from oxalic, citric, succinic acids)*
5. Denige's test (C.T.): Denige's reagent is added to neutral solution or aqueous solution of O.S.	5. Permanganate color discharges immediately without turbidity.

8. Glucose

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystalline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Neutral
6. Action of heat : Charrs and gives off smell of burnt sugar
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. No charring in cold but darkens on heating immediately.
2. Sodium hydroxide test: 2 ml of 3% solution of NaOH is added to conc. solution of O.S. and the mixture is heated. The mixture is then acidified with dil. HNO_3.	2. The solution turns first yellow and then raddish brown.
3. Tollen's test: 5 ml of aqueous solution of O.S. is added to equal volume of Tollen's reagent taken in a clean test tube and then the test tube is placed in a beaker of boiling water bath for a few minutes.	3. Black or grey precipitate or shining silver mirror.
4. Fehling's test: The sample is added to a mixture of Fehling A and Felling B and heated for 1 minute.	4. Brick red precipitate.
5. Lead acetate test: Lead acetate solution is added to solution of o.s and the mixture is boiled for few seconds. Then dil. NH_4OH solution is added dropwise till just sufficient to produce a permanat white ppt. then the mixture is boiled again.	5. The white ppt. turns salmon-pink in color.

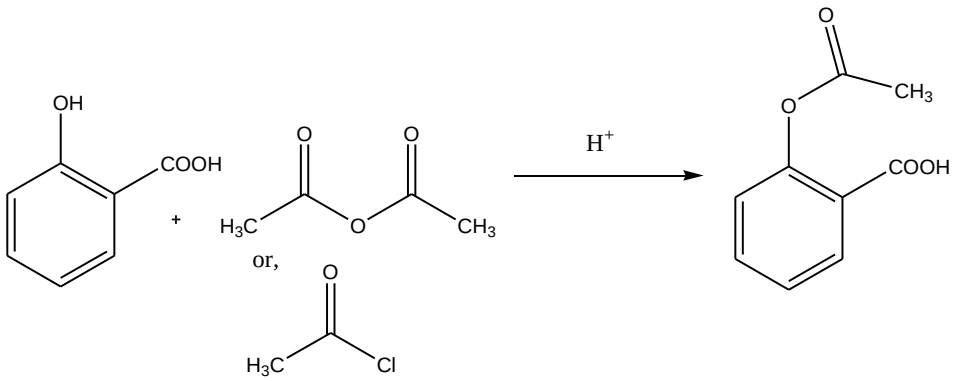
SEC1P: Pharmaceutical Chemistry

1. Preparation of Aspirin and its analysis

Principle:

Acetylsalicylic acid or aspirin is acetyl derivative of salicylic acid. It is prepared by acetylation reaction of salicylic acid using acetyl chloride or acetic anhydride under acidic condition.

Reaction:



Chemicals required:

Salicylic acid : 5 gm
Acetyl Chloride : 9 ml
Conc. H_2SO_4: 5 ml
Ice cold water: 100 ml
Ethanol: 10 mL
$FeCl_3$ solution

Procedure:

1. 5 gm of salicylic acid was taken in a 200 ml of conical flask and to this add 9 ml of acetyl chloride was added and they were mixed properly with the help of a glass rod.
2. To this, a few drops of conc. H_2SO_4 was added and mixing was done with the help of a glass rod.
3. After that 50 mL of ice cold water was added to the reaction mixture, scratch the sides of flask with glass rod and filter the solution.
4. The residue was dried in hot oven and, weighed. and recrystallized from ethanol.
5. 10 mg of crude aspirin was taken in a test tube and dissolve it in about 1 ml of alcohol. 1 drop of 1% $FeCl_3$ solution was added to it. Absence of blue or green colour indicate the absence of unreacted salicylic acid.
6. Recrystalization was done by taking half of the crude sample and dissolve it in minimum quantity of ethanol and to this few drops warm water was added until a turbidity persist. The solution was then cooled, filtered and the filtrate was kept for crystallization.
7. The crystals were collected by filtration, washed and dried. Then weight was measured.
8. Melting point of the crystalized sample was checked.

Result:

Weight of crude product:
Weight of the crystalized product:

..... g of acetylsalicylic acid was obtained from 5 g of salicylic acid.
Theoretical yield = 6.52 g
% Yield = (Yield obtained × 100)/Theoretical Yeild
. The melting point of aspirin was found to be = ...°C.

2. Preparation of magnesium bisilicate (Antacid):

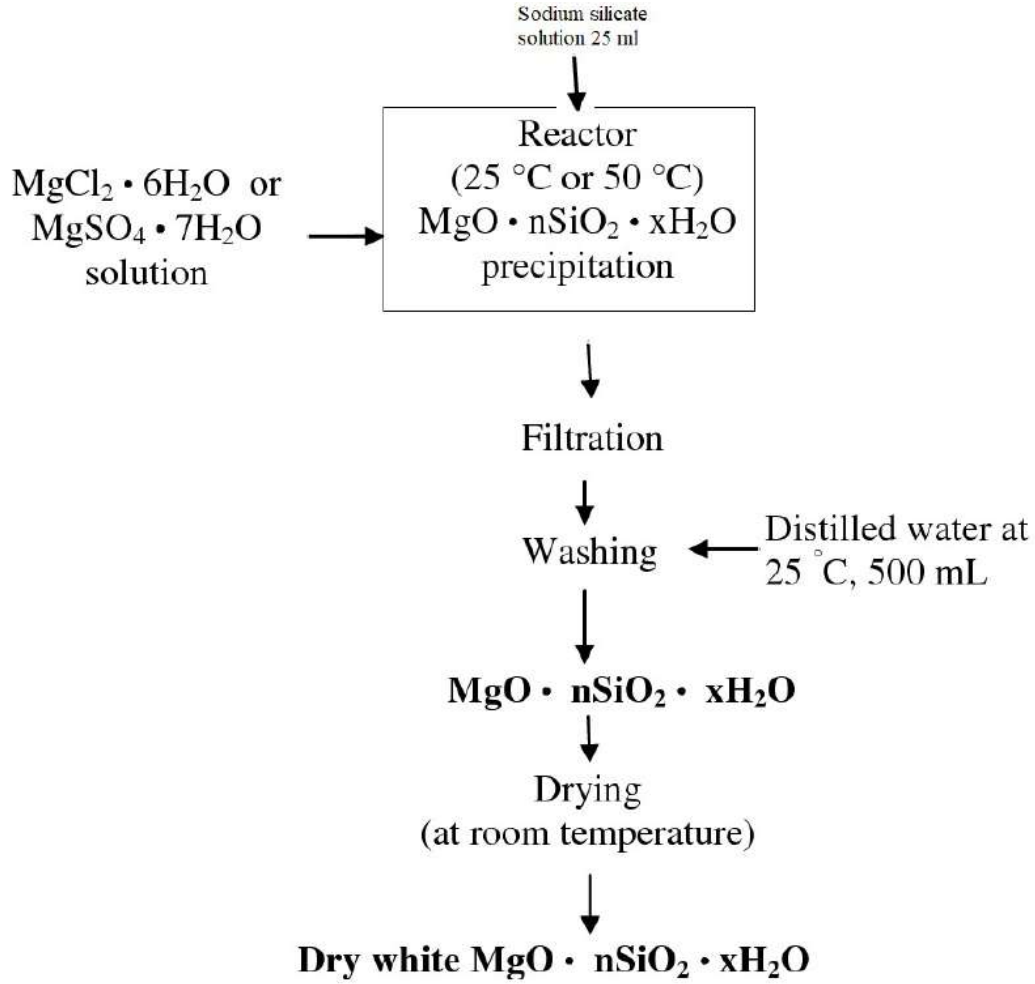
Magnesium silicate is manufactured by the precipitation reaction between sodium silicate and a water-soluble magnesium salt such as magnesium chloride, magnesium nitrate or magnesium sulfate. Magnesium silicate powders were prepared by a hydrothermal method. Na_2SiO_3 with the volume of 0.9 mL was dissolved in water, while 1.48 g of $Mg(NO_3)_2.6H_2O$ was dissolved in the mixture of propylene glycol–400 and ethanol with the volume ratio of 3 to 1. After the two solutions were mixed, a white precipitate was formed. The aqueous suspension of the precipitate is filtered and the collected solid washed, dried. After the magnesium silicate has been filtered and dried, the prepared cake discharged from the dryer may then be used in tablets, granulations and the like or the magnesium silicate may be added directly as a constituent of a liquid antacid preparation. The composition of the precipitate depends on the ratio of the components in the reaction medium, the addition of the correcting substances, and the way in which they are precipitated. The molecular formula is typically written as $MgO: XSiO_2$, where X denotes the average mole ratio of SiO_2 to MgO. The product is hydrated and the formula is sometimes written $MgO: XSiO_2 \bullet H_2O$ to show the water of hydration. Although magnesium silicate is of variable composition, the molar ratio of MgO to SiO_2 is approximately 2:5.

The reaction involved in the described process may be typically illustrated by the following equation:

$$Na_2O: x\ SiO_2 + MgSO_4 \rightarrow MgO.SiO_2 + Na_2SO_4 + y\ SiO_2$$

Sodium Silicate	Magnesium Sulfate	Magnesium Silicate	Sodium Sulfate	Silica

Wherein x and y depend upon the type silica fed into the processing system.


Sodium silicate solution 25 ml
Reactor
(25 °C or 50 °C)
MgO • nSiO2 • xH2O
precipitation
MgCl2 • 6H2O or
MgSO4 • 7H2O
solution
Filtration
Washing
Distilled water at
25 °C, 500 mL
MgO • nSiO2 • xH2O
Drying
(at room temperature)
Dry white MgO • nSiO2 • xH2O