মানুষের জ্ঞান ও ভাবকে বইয়ের মধ্যে সঞ্চিত করিবার যে একটা প্রচুর সুবিধা আছে, সে কথা কেহই অস্বীকার করিতে পারে না। কিন্তু সেই সুবিধার দ্বারা মনের স্বাভাবিক শক্তিকে একেবারে আচ্ছন্ন করিয়া ফেলিলে বুদ্ধিকে বাবু করিয়া তোলা হয়।

— রবীন্দ্রনাথ ঠাকুর

ভারতের একটা mission আছে, একটা গৌরবময় ভবিষ্যৎ আছে, সেই ভবিষ্যৎ ভারতের উত্তরাধিকারী আমরাই। নূতন ভারতের মুক্তির ইতিহাস আমরাই রচনা করছি এবং করব। এই বিশ্বাস আছে বলেই আমরা সব দুঃখ কষ্ট সহ্য করতে পারি, অন্ধকারময় বর্তমানকে অগ্রাহ্য করতে পারি, বাস্তবের নিষ্ঠুর সত্যগুলি আদর্শের কঠিন আঘাতে ধূলিসাৎ করতে পারি।

— সুভাষচন্দ্র বসু

Any system of education which ignores Indian conditions, requirements, history and sociology is too unscientific to commend itself to any rational support.

— Subhas Chandra Bose

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CBCS • UG • HCH • CHEMISTRY • CC-CH-06

NETAJI SUBHAS OPEN UNIVERSITY

Choice Based Credit System (CBCS)

SELF LEARNING MATERIAL

HCH

CHEMISTRY

Practical Paper-IV

CC-CH-06

Under Graduate Degree Programme

PREFACE

In a bid to standardise higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, discipline specific, generic elective, ability* and *skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry acquired credits. I am happy to note that the University has been accredited by NAAC with grade 'A'.

UGC (Open and Distance Learning Programmes and Online Learning Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the *six* semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar
Vice-Chancellor

Netaji Subhas Open University

Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject: Honours in Chemistry (HCH)
Course : Practical Paper-IV
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Block –I
(Inorganic Chemistry)

Unit-1 □ Quantitative Analysis

Structure

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1.3 Estimation of available chlorine in bleaching powder using iodometry

1.4 Estimation of available oxygen in pyrolusite using permanganometry

1.5 Estimation of Cu in brass using iodometry

1.6 Estimation of Fe in cement using permanganometry

1.7 Estimation of chloride gravimetrically

1.8 Estimation of Ni (II) using DMG gravimetrically

1.9 Self Assesment Questions

1.10 Suggested Reading

1.1 Objectives

After reading this unit we are able to learn the following issues :

- Estimation of available chlorine in bleaching powder
- Estimation of available oxygen in pyrolusite
- Estimation of Cu in brass
- Estimation of Fe in cement
- Estimation of Ni

1.2 Introduction

In quantitative analysis various methods are adopted. The most useful methods are :

- Volumetric or Titrimetric Analysis.
- Gravimetric Analysis
- Instrumental Analysis

In this unit there are practical applications of lodometry, Permanganometry, Gravimetry, Spectrophotometric method and colorimetric method. Applications of qualitative semi micro analysis of salt mixtures are also shown in this unit.

Iodometry & lodimetry methods : It is known that both the iodometric and iodometric titrations are oxidation-reduction titrations. Iodometry deals with the estimation of iodine liberated in chemical reactions by a standard of a reducing agent whereas iodimetry involves the titration of a reducing agent with a standard solution of iodine which acts as an oxidising agent. In both these analyses, reaction of iodine with thiosulphate is the basis of titration.

The reactions help to estimate the amount of oxidants through the quantitative liberation of iodine. As for examples :

(a) Iodimetry :

(i) Estimation of $S_2O_3^{2-}$: The reactions :

$I_2 + 2e \leftrightarrow 21^-$ Eo = 0.54 V

$S_4O_6^{2-} + 2e \leftrightarrow 2\ S_2O_3^{2-}$ Eo = 0.08 V

$I_2 + 2S_2O_3^{2-}\ 21^- + S_4O_6^{2-}$

(b) Iodimetry :

(i) Estimation of Cr_2O7^{2-} : The reactions :

$Cr_20_7^{2-} + 14H^+ + 6e \leftrightarrow 2Cr_3 + 7H_2O$ Eo = 1.33 V

$I_2 + 2e \leftrightarrow 21-$ Eo = 0.54 V

$Cr_20_7^{2-} + 14H^+ + 61^- \leftrightarrow 2Cr_3 + 3l_2 + 7H_2O$

In this unit by using iodemetry method available chlorine of bleaching powder and Cu in brass are estimated.

Permanganometric Titration : Potassium permanganate is a very powerful and widely used oxidising agent to oxidize many reducing agents in different conditions to estimate the amount of reducing materials. The redox titration with potassium permanganate solution as an oxidant is called permanganometric titration or permanganometry. The powe of $KMnO_4$ as an oxidant depends on the pH of the medium.

Gravimetric Method : Gravimetric analysis based on the principle of precipating

quantitatively an element as its stable and pure salt from solution of a known compound containing the element. This technique of quantitative analysis primarily involves three major steps, viz., (i) preparation of a solution of weighted quantity of the sample. (ii) precipitation of the desire ion from a specific volume of the solution using appropriate chemical reagent and (iii) weighing of the precipitate formed after complete drying.

1.3 Estimation of available chlorine in bleaching powder using iodometry

Principle :

Available chlorine in bleaching powder means the percentage by weight of chlorine that is evolved by the addition of dilute acid to aqueous solution of bleaching powder.

$$Ca(OCl)Cl + 2HCl = CaCl_2 + Cl_2 + H_2O$$

When an aqueous suspension of bleaching powder is treated with excess of KI solution in presence of dilute acid, iodide is oxidized to iodine by the hypochlorite ion OCl^-. The liberated iodine is titrated with standard thiosulphate solution using starch as indicator. From the titrate value of thiosulphate solution, the percentage of the available chlorine may be calculated.

$$OCl^- + Cl^- + 2H^+ = Cl_2 + H_2O$$

$$Cl_2 + 2I^- = I_2 + 2Cl^-$$

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

$$\therefore Cl_2 \equiv I_2 \equiv 2S_2O_3^{2-}$$

$$\therefore 2S_2O_3^{2-} \equiv I \equiv Cl$$

1000 ml of 1(N) thiosuphate solution $\equiv$ 1 g. equivalent of chlorine

$\equiv$ 35.46 g. of chlorine

Chemicals required:

1. ~ (N/20) $K_2Cr_2O_7$ solution
2. ~ (N/20) $Na_2S_2O_3 . 5H_2O$ solution
3. 10% KI solution
4. 1% starch solution
5. 4(N) H_2SO_4
6. Glacial acetic acid

Procedure:

1. *Preparation of 250 ml (N/20) $K_2Cr_2O_7$ solution* :

Table – 1: Preparation of 250 ml ~(N/20) $K_2Cr_2O_7$ solution

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $K_2Cr_2O_7$ solution
W_1	W_2	$W = W_1 - W_2$	0.6129	250	$(W/0.6129) \times (N/20)$

2. *Preparation of* (N/20) $Na_2S_2O_3$ solution

Dissolve 2-3 g. of $Na_2S_2O_3 . 5H_2O$ in 250 ml of distilled water.

3. *Preparation of bleaching powder solution*:

Weigh out accurately 2.5 g. (W_1) of bleaching powder in a small glass mortar, add a little amount of distilled water and triturate to make a paste. After settling, transfer the supernatant liquid into 250 ml volumetric flask. Repeat the procedure till the whole mass of the sample is transferred to the volumetric flask. Make up the volume up to the mark with distilled water, shake well to mix uniformly.

Table – 2 : Preparation of bleaching powder solution

Initial weight (g)	Final weight (g)	Weight taken (g)
W_3	W_2	$W_1 = W_3 - W_2$

4. *Standardisation of sodium thiosulphate solution against standard (N/20) $K_2Cr_2O_7$ solution* :

Pipette out an aliquot of 25 ml of the standard (N/20) $K_2Cr_2O_7$ solution, add 25 ml of 4(N) H_2SO_4 and 10 ml of 10% KI solution. Cover the mouth of the flask with a clock glass, allow to stand in dark for 2-3 minutes. Add 140 ml of distilled water and titrate with the thiosuphate solution till a straw (pale) yellow colour appears. Add 2 ml of 1% starch solution and continue titration with thiosulphate solution till the blue colour of the solution is discharged and a bright green colour appears. Repeat the experiment twice.

5. *Estimation of available chlorine in bleaching powder* :

Take 50 ml of the bleaching powder solution in to a 500 ml conical flask using a

burette. Add 25 ml of distilled water, 20 ml 10% KI solution and 10 ml glacial acetic acid. Cover the mouth of the flask with a clock glass, allow to stand in dark for 2-3 minutes. Titrate the liberated iodine with standard (N/20) $Na_2S_2O_3$ solution till a light yellow colour appears. Add 2 ml of 1% starch solution and continue titration with thiosulphate solution till the blue colour discharged. Repeat the experiment twice.

Experimental Results:

Table – 3 : Standardisation of (N/20) $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution:

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table – 4 : Titration of liberated iodine with standard sodium thiosulphate solution :

No. of obs.	Volm. of Bleaching powder soln. (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	50	0	...	...	
2.	50	...	...	...	V_2
3.	50	...	...	...	

Calculation :

Strength of standard $K_2Cr_2O_7$ solution = (W/0.6129) (N/20).

25 ml $K_2Cr_2O_7 \equiv$ Iodine $\equiv$ V_1 ml thiosulphate solution

$$\text{Srength of thiosulphate solution} = \left(\frac{W \times 25}{0.6129 \times V_1}\right)\left(\frac{N}{20}\right)$$

* $Ca(OCl)Cl \equiv Cl_2 \equiv I_2 \equiv 2S_2O_3^{2-}$

$\therefore S_2O_3^{2-} \equiv I \equiv Cl$

$\therefore$ 1000 ml of (N) thiosulphate $\equiv$ 35.46 g. of Cl.

$\therefore V_2$ ml of $\left(\frac{W \times 25}{0.6129 \times V_1}\right)\left(N/20\right)$ thiosulphate

$$= \frac{35.46}{1000} \times V_2 \times \frac{W \times 25}{0.6129 \times V_1 \times 20} \text{ g of Cl}$$

$$\therefore Cl\% = \frac{35.46 \times 25 \times V_2 \times W \times 100}{1000 \times 0.6129 \times V_1 \times W_1 \times 20}\%$$

$$= \left(\frac{35.46}{8 \times 0.6129}\right) \times \left(\frac{V_2 \times W}{V_1 W_1}\right)\% = \text{Available chlorine (\%)}$$

Result :

The available chlorine (the grams of chlorine liberated from 100 g of the bleaching powder on treatment with dilute acid) = ... g

1.4. Estimation of available oxygen in pyrolusite using permanganatometry

Principle:

Pyrolusite is a mineral consisting essentially of manganese dioxide (MnO_2) and is important as an ore of manganese. It is a black, amorphous appearing mineral, often with a granular, fibrous or columnar structure, sometimes forming reniform crusts. 18.4 % available oxygen means 100% MnO_2 content in pyrolusite. Although the primary use of manganese is in the steel industry, MnO_2 finds its application in glass industry as decolourizer from ancient time. On these occasion, MnO_2 forms Mn^{2+} compounds. So availability of oxygen became the main criterion for the quality of pyrolusite. Hence the measurement of available oxygen was necessary and the method of analysis is easy. Potassium permanganate, $KMnO_4$, is probably the most widely used of all volumetric oxidizing agents. It is a powerful oxidant and readily available at modest cost. The intense color of the permanganate ion, MnO_4^-, is sufficient to detect the end point in most titrations.

Depending upon reaction conditions permanganate ion is reduced to manganese in the 2+, 3+, 4+ or 6+ state. In solutions that are 0.1 M or greater in mineral acid the common reduction product is manganese (II) ion;

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

This is the most widely used of the permanganate reactions. In solutions that are weakly acidic (above pH 4) neutral, or weakly alkaline manganese dioxide is the most common reduction product ;

$$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2(s) + 2H_2O$$

Titration in which manganese dioxide is the product suffer from the disadvantage that the slightly soluble brown oxide obscures the end point; time must be allowed for the solid to settle before an excess of the permanganate can be detected. Some important volumetric analyses based on permanganate involve reduction to manganese ion according to the half reaction given below;

$$MnO_4^- + e^- \leftrightarrow MnO_4^{2-}$$

This stoichiometry tends to predominate in solutions that are greater than 1 M in sodium hydroxide. Alkaline oxidations with permanganate have proved to be most useful in the determination of organic compounds.

Evaluation of pyrolusite is made by its oxygen donation capacity. A weighed amount of pyrolusite is heated with 50 ml of 0.1 (N) oxalic acid and (1:1) H_2SO_4 (25 ml) and 25 ml of water on a water bath. The following reaction takes place.

$$MnO_2 = MnO + O$$

$$MnO + H_2SO_4 = MnSO_4 + H_2O$$

$$H_2C_2O_4 + O = 2CO_2 + H_2O$$

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$$

Or, $$MnO_2 + H_2C_2O_4 + 2H^+ = Mn^{2+} + 2CO_2 + 2H_2O$$

$$\therefore MnO_2 \equiv H_2C_2O_4$$

$$2MnO_4^- + 5\,H_2C_2O_4 + 6H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$\therefore 2MnO_4^- \equiv 5H_2C_2O_4$$

$$\therefore \frac{2MnO_4^-}{5} \equiv H_2C_2O_4$$

$$\therefore (2/5)\ MnO_4^- \equiv H_2C_2O_4 \equiv MnO_2 \equiv O \equiv 16\ g.\ of\ oxygen$$

$$\therefore \frac{MnO_4^-}{5} \equiv 8g\ of\ oxygen\ (more\ accurately\ 7.9997\ g.\ of\ oxygen)$$

The pyrolusite dissolves to a colorless solution, the excess of oxalic acid is back titrated with a standard solution of potassium permanganate. From the amount of oxalic acid reacted with MnO_2, available oxygen and the amount of MnO_2 can be determined.

Chemicals required:

1. Pyrolusite
2. ~ (N/20) Oxalic acid solution
3. ~ (N/20) Potassium permanganate
4. 4 (N) Sulphuric acid

Procedure:

A. Preparation of 250 mL oxalic acid solution :

Table – 1: Preparation of $\left(\frac{N}{20}\right)$ oxalic acid solution

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $H_2C_2O_4$ solution
W_1	W_2	$W = W_1 - W_2$	0.7875	250	$W/0.7875(N/20) = f\left(\frac{N}{20}\right)$

B. Standardisation the $KMnO_4$ solution using standard $\left(\frac{N}{20}\right)$ $H_2C_2O_4$ solution :

Pipette out 25 ml of the standard (N/20) oxalic acid solution in a 250 ml conical flask, add 25 ml 4(N) H_2SO_4, heat the mixture nearly 70^0-80^0C and then titrate with the $KMnO_4$ solution in the hot condition until a faint pink colour appears and persists for ~30 seconds. Repeat the same process twice and record the data.

C. Estimation of available O_2 in Pyrolusite :

Transfer the given quantity (less than ~ 0.1 g) (say w g) of pyrolusite ore into a 250 ml conical flask, add 50 ml 4(N) H_2SO_4 followed by 50 ml (say $25 \times x$ ml) of standard (N/20) oxalic acid solution using a pipette. Cover the flask with short stem-funnel, heat the

flask gently on an asbestos board till all the black particles of pyrolusite dissolve. Back titrate the excess oxalic acid in the hot condition (70^0 – 80^0C) with standard (~ N/20) $KMnO_4$ solution up to the first appearance of faint pink colour that persists for ~ 30 seconds.

Experimental Results :

Table – 2 : Standardisation of $KMnO_4$ solution against standard (N/20) oxalic acid solution

No. of obs.	Volm. of oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ soln. (ml)	Mean volm. of $KMnO_4$ soln. (ml)	Strength of oxalic acid soln.	Strength of $KMnO_4$
		Initial	Final				
1	25	0	...	...	V_1	$f\left(\frac{N}{20}\right)$	$\frac{25\times f}{V_1}\left(\frac{N}{20}\right)$
2	25	...	...	...			
3	25	...	...	...			

Table – 3 : Estimation of available oxygen in Pyrolusite :

Weight taken	Amount of oxalic acid added (mL)	Burette reading		Volume of $KMnO_4$ (ml)	Available % Oxygen
		Initial	Final		
w	25×x	0	V_2	V_2	y

Calculation :

If $(25 \times x$ ml) of f(N/20) oxalic acid $\equiv V_2$ ml of $\frac{25.f}{V_1}\left(\frac{N}{20}\right)KMnO_4 + w$ g. of pyrolusite

Then, w g. of pyrolusite solution $\equiv (V_1 \times x - V_2)$ml of $\frac{25.f}{V_1}\left(\frac{N}{20}\right)KMnO_4$

$$\equiv \frac{(V_1x - V_2)25.f}{V_1 x\, 20}\text{ml of (N)}KMnO_4$$

$$\equiv \frac{8\times(V_1x - V_2)25.f}{1000\times V_1x20}\text{g. of oxygen}$$

(1000 ml (N) $KMnO_4 \equiv$ 8 g. of oxygen)

$$\therefore \text{ Available oxygen (\%)} \equiv \frac{8\times(V_1x - V_2)25.f}{1000\times V_1x\,20\times w}\times 100(\%) = y$$

Result:

The amount of available oxygen present in given sample of pyrolusite is%

1.5. Estimation of Cu in brass using iodometry

Principle :

A weighed quantity of brass is dissolved in (1 : 1) nitric acid by boiling. Copper is the iodometrically estimated by treating the solution containing Cu^{2+} with an excess of KI solution, when sparingly soluble cuprous iodide, (Cu_2I_2), is precipitated with liberation of equivalent of iodine. Copper is estimated by titrating the liberated iodine with a standard solution of sodium thiosulphate.

$$3Cu + 2HNO_3 + 6H^+ = 3Cu^{2+} + 2NO + 4H_2O$$

$$2NO + O_2 = NO_2$$

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

$$2HNO_2 + CO(NH_2)_2 = 2N_2 + CO_2 + 3H_2O$$

$$2Cu^{2+} + 4I^- = Cu_2I_2 + I_2$$

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

$$\therefore 2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-}$$

or, $S_2O_3^{2-} \equiv Cu^{2+} \equiv 1$ equivalent

$\therefore$ 1000 ml of (N) thiosulphate solution $\equiv$ 63.546 g. of Cu

Sodium thiosulphate solution is standardised against a standard $K_2Cr_2O_7$ solution.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- = 2Cr^{3+} + 7H_2O + 3I_2$$

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

Chemicals required :

1. Brass alloy
2. Standard (~N/20) $K_2Cr_2O_7$ solution
3. (~N/20) $Na_2S_2O_3$ solution

4. Solid KI or 10% KI solution
5. 1% starch solution
6. NH_4HF_2
7. Urea (A.R.)

Procedure :

1. Preparation of 250 ml (N/20) $K_2Cr_2O_7$ solution :

Table – 1 :

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $K_2Cr_2O_7$ solution
W_1	W_2	$W=W_1-W_2$	0.6129	250	$(W/0.6129)\times(N/20)$

2. *Preparation of ~ (N/20) $Na_2S_2O_3$ solution* :

Dissolve ~ 12.5 – 13 g. of A.R. $Na_2S_2O_3.5H_2O$ in 500 ml boiled distilled water and dilute to 1 lit. and add 3 drops of $CHCl_3$ to improve its stability and store in amber coloured bottle.

3. *Dissolution of Brass* :

Weigh out accurately about 1 g. of the supplied brass into a 250 ml beaker and add 10 ml of distilled water followed by 10 ml conc. HNO_3 successively down the side of the beaker. Cover the beaker with a clock glass and heat carefully on an asbestos board over a low flame until dissolution is completed. Dilute with 25 ml of distilled water and boil for 5 minutes with 1 g. of urea. Allow it to cool to room temperature. Allow it to cool to room temperature. Transfer the solution quantitatively from the beaker into a 250 ml volumetric flask by washing with distilled water and finally make up the volume up to the mark with distilled water. Mix uniformly (stock solution).

4. *Standardisation of sodium thiosulphate solution against standard ~ (N/20) $K_2Cr_2O_7$ solution* :

Pipette out an aliquot of 25 ml of the standard ~ (N/20) $K_2Cr_2O_7$ solution, add 25 ml of 4(N) H_2SO_4 and 1 g. or 10 ml of 10% KI solution. Cover the mouth of the flask with a clock glass, allow to stand in dark for 2-3 minutes. Add 140 ml of distilled water

and titrate with the thiosuphate solution till a straw (pale) yellow colour appears. Add 2 ml of 1% starch solution and continue titration with thiosulphate solution till the blue colour of the solution is discharged and a bright green colour appears. Repeat the experiment twice.

5. *Estimation of* Cu^{2+} :

Pipette out 25 ml from the above stock solution in a 500 ml conical flask, dilute to 50 ml with distilled water. Neutralise with 1:1 aqueous NH_3 adding dropwise with stirring until a permanent light blue turbidity appears (avoid excess ammonia). Add 2 g. of NH_4HF_2, and shake to obtained a clear solution. Add 10 ml of 10% KI solution and titrate the liberated I_2 immediately with standard ~ (N/20) thiosulphate solution adding the starch indicator near the end point. Continue the addition of thiosulphate solution till the milky white precipitate of Cu_2I_2 is visible at the end point. Repeat the experiment twice.

Experimental Results :

Table – 2 : Standardisation of (N/20) $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1	25	0	...	...	V
2	25	...	...	...	
3	25	...	...	...	

Table – 3 : Estimation of Cu

No. of obs.	Volm. of brass soln. (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1	25	0	...	...	V_1
2	25	...	...	...	
3	25	...	...	...	

Caculation :

1. Strength of $K_2Cr_2O_7$ solution $= \frac{W}{0.6129}(N/20) = S'(N)$

2. Standardisation of thiosulphate solution :

   25 ml S′ (N) $K_2Cr_2O_7$ solution ≡ V ml $S_2O_3^{2-}$ solution

   ∴ Strength of $S_2O_3^{2-}$ solution $= \frac{25 \times W}{V \times 0.6129}(N/20) = S(N)$

3. Estimation of Cu :

   25 ml supplied Cu^{2+} solution ≡ V_1 ml S(N) $S_2O_3^{2-}$ solution

   ≡ $V_1 \times S$ ml (N) $S_2O_3^{2-}$ solution

   We have 1000 ml (N) $S_2O_3^{2-}$ solution ≡ 63.546 g. of Cu

   ∴ V_1 x S ml (N) $S_2O_3^{2-}$ solution ≡ $0.063546 \times V_1 \times S$ g. of Cu

   ∴ 25 ml brass solution ≡ $0.063546 \times V_1 \times S$ g. of Cu

   ∴ 250 ml brass solution ≡ $0.063546 \times V_1 \times S \times 10$ g. of Cu

   ∴ Total amount of Cu in w g. of brass = $0.063546 \times V_1 \times S \times 10$ g. of Cu

   ∴ % of Cu in brass = $0.063546 \times V_1 \times S \times 10 \times 100 / w$ g. of Cu

Conclusion : Amount of Cu present in the given brass sample = ... %

Note :

i) The optimum pH for determination of copper by iodometric method is ~3 to 4.

ii) In this iodometric determination of copper, some amount of iodine may be absorbed by the precipitate of Cu_2I_2 . To release this iodine, small amount of ammonium thiocyanate may be added near the end point (i.e. when the blue colour of starch –iodine adsorption complex fades) and then the titration is completed as quickly as possible to minimize arial oxidation. At the end point the precipitate attains a pale pink shade.

iii) E^0 value of $I_2/2I^-$ couple (0.54 V) is higher than that of the Cu^{2+}/Cu^+ couple (0.15 V). Yet, Cu^{2+} quantitatively oxidises iodide to iodine, since the formal potential of Cu^{2+}/Cu^+ couple is increased sufficiently above the E^0 value of $I_2/2I^-$ couple, as Cu^+ ions disappear from the system due to precipitation of sparingly soluble Cu_2I_2.

1.6 Estimation of Fe in cement using permanganometry

Principle :

Cement contains CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3 etc. along with traces of Na_2O and K_2O. A weighed quantity of finely powdered cement is brought into solution by heating with 1:1 HCl. Then Fe^{3+}, present in the solution, is reduced to Fe^{2+} by $SnCl_2$ method and this is then titrated against the standard $KMnO_4$ solution.

$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$$

$$Sn^{2+} + 2HgCl_2 = Hg_2Cl_2 \downarrow + Sn^{4+} + 2Cl^-$$

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

$$\therefore 1 \text{ mole } MnO_4^- \equiv 5 \text{ moles } Fe^{2+}$$

$$\text{Or, } 1/5 \text{ mole } MnO_4^- \equiv 1 \text{ mole } Fe^{2+} \equiv 1 \text{ equivalent}$$

$$(\text{Since, } MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O)$$

$$\therefore 1000 \text{ ml (N) } KMnO_4 \text{ solution} \equiv 55.847 \text{g. of Fe}$$

Chemicals required :

1. ~ (N/20) $H_2C_2O_4 . 2H_2O$ solution
2. ~ (N/20) $KMnO_4$ solution
3. 4(N) H_2SO_4
4. 15% $SnCl_2$ solution / Al- foil
5. 5% $HgCl_2$ solution
6. Conc. HCl
7. Supplied cement sample

Procedure :

1. *Preparation of 250 ml ~ (N/20) $H_2C_2O_4.2H_2O$ solution* :

   Dissolve accurately weighed ~ 0.7879 g. of oxalic acid in 250 ml volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

2. *Preparation of ~ (N/20) $KMnO_4$ solution* :

   Dissolve ~ 1.6 g. of A.R. $KMnO_4$ in 500 ml distilled water, boil for about 20 to

30 minutes, cool, diluted to 1 lit., then filter through glass wool and store in a amber coloured bottle.

3. *Standardise the ~ (N/20) $KMnO_4$ solution using standard $\left(\frac{N}{20}\right)H_2C_2O_4$ solution* :

Pipette out 25 ml of the standard (N/20) oxalic acid solution in a 250 ml conical flask, add 25 ml 4(N) H_2SO_4, heat the mixture nearly 70^0-80^0C and then titrate with the $KMnO_4$ solution in the hot condition until a faint pink colour appears and persists for ~ 30 seconds. Repeat the same process twice and record the data.

4. *Dissolution of Cement* :

Weigh out accurately about 1 g. of finely powdered cement in a 250 ml beaker. Add 50 ml of (1:1) HCl, partially cover with a clock glass and heat the mixture gently and break up any lumps with a glass rod. When the sample of cement has reacted completely, allow to cool and transfer the mixture quantitatively into a 250 ml volumetric flask by washing with very dilute (N) HCl solution and make up the volume up to 250ml with distilled water. Mix the solution uniformly.

5. *Estimation of Fe* :

Pipette out 50 ml of the above solution in a ml conical flask and add ml of conc. HCl. Heat just to boiling, reduce Fe^{3+} ion with 15% $SnCl_2$ solution adding drop wise until the yellow colour is just discharged and finally add a drop in excess. Cool under tap to room temperature. Add 10 ml 5% $HgCl_2$ solution at a time with vigorous shaking and dilute to 300 ml with water. Add 25 ml Zimmermann – Reinhardt solution. Titrate with the standard (N/20) $KMnO_4$ solution until the solution just turns light pink colour.

***Note*:** The reduction of Fe^{3+} may also be done with Al – foil in 4(N) HCl medium and then the above method is followed.

Experimental Results : Insert paragraph Table – 1 : Weighing of oxalic acid

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $H_2C_2O_4$ solution
W'_1	W'_2	$W' = W'_1 - W'_2$	0.7875	250	W'/0.7875(N/20) $= f\left(\frac{N}{20}\right)$

Table – 2 : Weighing of Portland cement

Initial wt. (g)	Final wt. (g)	Wt. Taken (g)
W_1	W_2	$W = W_1 - W_2$

Table – 3 : Standardisation of $KMnO_4$ solution against standard (N/20) oxalic acid solution

No. of obs.	Volm. of oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ soln. (ml)	Mean volm. of $KMnO_4$ soln. (ml)	Strength of oxalic acid soln.	Strength of $KMnO_4$
		Initial	Final				
1	25	0	...	...	V_1	$f\left(\frac{N}{20}\right)$	$\frac{25 \times f}{V_1}\left(\frac{N}{20}\right)$ =S(N)
2	25	...	...	...			
3	25	...	...	...			

Table – 4 : Estimation of Iron

No. of obs.	Volm. of diluted stock soln. (ml)	Burette reading		Volm. of $KMnO_4$ soln. (ml)	Mean volm. of $KMnO_4$ soln. (ml)	Strength of $KMnO_4$ soln.
		Initial	Final			
1	50	0	...	...	V	S (N)
2	50	...	...	...		
3	50	...	...	...		

Calculation :

Weight of cement taken = W g

Strength of $KMnO_4$ solution = S (N)

50 ml given Fe(III) solution ≡ V ml S (N) $KMnO_4$ solution

≡ V × S ml (N) $KMnO_4$ solution

We have, 1000 ml $KMnO_4$ solution ≡ 55.847 g of Fe

V X S ml (N) $KMnO_4$ solution ≡ 0.055847 × V × S g of Fe/ 50 ml

0.055847 × V × S × 5g of Fe / 250 ml

W g of the given sample cement contain 0.055847 × V × S × 5g of Fe

$\therefore$ Percentage of Fe in the given cement sample $= \frac{0.055847 \times V \times S \times S}{W} \times 100\%$

Result:

The amount of iron present in the given sample of cement

$$= \frac{0.055847 \times V \times S \times S}{W} \times 100\%$$

1.7. Estimation of chloride gravimetrically

Principle :

Chloride is usually estimated as silver chloride, which is precipitated by adding excess of $AgNO_3$ to the solution containing Cl^- ion, acidified with dilute HNO_3 when AgCl is quantitatively precipitated.

$$Ag^+ + Cl^- = AgCl$$

$$143.34 \text{ g AgCl} \equiv 35.46 \text{ of chloride}$$

$$1 \text{ g AgCl} \equiv 35.46 / 143.34 \text{ or, } 0.2474 \text{ g of chloride}$$

The precipitate may be initially colloidal in nature and may be coagulated into filterable from by heating the suspension with vigorous stirring.

Chemical Requirement :

a) 0.1 M $AgNO_3$ solution : 17 g/L.

b) Supplied NaCl solution (0.1M) : 6 g/L.

Procedure :

Pipette out 25 ml of the supplied NaCl solution into a 250 ml beaker providing with a glass rod, dilute to 150 ml with distilled water add 0.5 ml of conc. HNO_3. To the cold solution add 0.1M $AgNO_3$ solution slowly with constant stirring until the precipitation of AgCl is complete. Only slightly excess of the reagent should be used. This can be easily be detected by allowing the precipitate to settle and adding few drops of $AgNO_3$ solution, when no further precipitate should be obtained.

Cover the beaker with clock glass, heat the suspension nearly to boiling for about 2-3 minutes until the precipitate coagulates and the supernatant solution should be clear. Check the completeness of the precipitation by adding a few drops of $AgNO_3$ solution to

the supernatant liquid. Allow to stand for about an hour in a dark place. In the meantime, clean a sinter-glass crucible, Gooch crucible (G-4), make it dry at a temperature of 130^0-150^{0}C and allow to cool in a desiccator for 20 minutes and take the weight of the empty crucible.

Repeat the process of heating and cooling until a constant weight ($\pm$ 0.0002) is attained.

Collect the precipitate in the weighed crucible. Wash the precipitate thoroughly in the crucible with dilute ~ 0.01 N HNO_3 solution until the washings are free from chloride ions, test with $AgNO_3$ solution. Place the crucible with its contents in a air oven at 130^0 – 150^{0}C for about 1 hour. Cool in a desiccator and weigh.

Repeat the process of heating and cooling until a constant weight is attained.

Experimental Results :

Table – 1 : Determination of constant weight of crucible

No. of readings	Weight of empty crucible (g)

Table – 2 : Determination weight of chloride

No. of readings	Weight of crucible + AgCl (g)

Calculation :

Constant weight of empty crucible = W_1 g

Constant weight of crucible + AgCl = W_2 g

$\therefore$ weight of AgCl = $(W_2 - W_1)$ g

$\therefore$ % of chloride in the supplide solution

$= (W_2 - W_1) \times 0.2474 \times 100$ %

Conclusion :

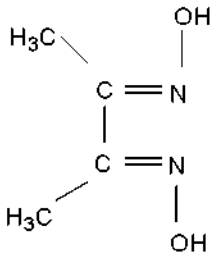
$\therefore$ Amount of chloride present in the supplied solution

$= (W_2 - W_1) \times 0.2474 \times 100$ %

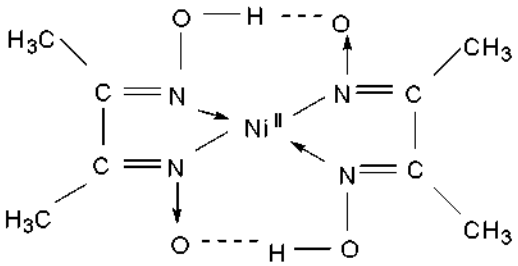
1.8. Estimation of Ni(II) using DMG gravimetrically

Principle :

Nickel is gravimetrically estimated as *bis*-[dimethylglyoximatonickel(II)], $Ni(DMGH)_2$. When a known volume of Ni^{2+} solution is treated with a slightly excess of ethanolic solution of dimethylglyoxime, $DMGH_2$, (1) in ammoniacal medium, $Ni(DMGH)_2$, (2) (solubility product = 3.98×10^{-24}) is quantitatively precipitated as shining red crystals.



$DMGH_2$
(1)



$Ni^{II}(DMGH)_2$
(2)

$$Ni^{2+} + 2DMGH_2 + 2NH_3 = Ni(DMGH)_2 + 2NH_4^+$$

$$\therefore \quad 288.69 \text{ g of } Ni(DMGH)_2 \equiv 58.69 \text{ g of } Ni^{2+}$$

$$\therefore \quad 1 \text{ g of } Ni(DMGH)_2 \equiv 0.2033 \text{ g of } Ni^{2+}$$

The medium must not be acidic, since $Ni(DMGH)_2$ is soluble in acid. The solution should not be strong alkaline, as $Ni(DMGH)_2$ is soluble in strong base. The optimum Ph is ~ 7 – 8. Addition of large excess of $DMGH_2$ is to be avoided, as the reagent itself due to its low solubility in water may precipitate along with $Ni(DMGH)_2$. Proportion of alcohol in the mixture should not be very large as the red precipitate of $Ni(DMGH)_2$ may dissolve in water – alcohol mixture.

Chemicals and Equipments :

i) Dimethyl glyoxime solution : 1% solution in 95% ethanol.

ii) Ammonium nickel sulphate solution, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ (unknown) : ~ 20 g / lit. or $NiSO_4 \cdot 7H_2O$ or, $NiSO_4 \cdot 6H_2O$ in proportional amount in 1(N) H_2SO_4 medium.

iii) G-4 sintered glass crucible.

iv) Desiccator with silica gel drier.

v) Analytical balance with calibrated weight box.

vi) Air oven set at 110^0 – 120^0C.

Procedure :

1. Clean a sintered glass crucible (G-4), and dry it at 110^0 – 120^0C in the air oven for one hour, then cool in a desiccator for about 25 minutes and weight the empty crucible. Repeat the process of heating, cooling and weighing until a constant weight (± 0.0002 g) is attained.
2. Take an aliquot of 10 ml of sample Ni^{2+} solution into a 250 ml beaker. Diluted to 150 ml with double distilled water. Heat to 70^0 – 80^0C on a hot water bath, add 15 ml of 1% dimethyl glyoxime solution (at least 5 ml for every 10 mg of Ni present) and mix thoroughly by stirring with a clean glass rod. Neutralize with (1:1) aqueous ammonia solution by adding dropwise with constant stirring until the smell of ammonia persists and rose-red crystalline precipitate of $Ni(DMGH)_2$ is formed. Cover the beaker with a watch glass and allow to stand on the hot water bath for about 20 minutes. Check the completeness of precipitation by adding a few more drops of the dimethyl glyoxime reagent solution to the supernatant liquid, smelling faintly of ammonia.
3. Filter the precipitate using the previously dried and weighed sintered glass (G-4) crucible. Transfer the quantitatively from the beaker to the crucible using a policeman and washing with hot (70^0 – 80^0C) distilled water. Continue washing till the filtrate is free from chloride or sulphate (test with $AgNO_3$ and $Ba(NO_3)_2$ solutions in HNO_3 medium). Dry the crucible with its contents at 110^0 – 120^0C for one hour in the air - oven. Allow to cool in a desiccator for about 25 minutes and then weigh. Repeat the process of heating, cooling and weighing until a constant weight (± 0.0002 g) is attained.

Calculation :

Weight of empty crucible = W_1 g

Weight of crucible + $Ni(DMGH)_2$ = W_2 g

$\therefore$ Weight of $Ni(DMGH)_2$ = $(W_2 - W_1)$ g

$\because$ 1 g of $Ni(DMGH)_2$ 0.2033 g of Ni^{2+}

$\therefore$ $(W_2 - W_1)$ g of $Ni(DMGH)_2 \equiv 0.2033 \times (W_2 - W_1)$ g of Ni^{2+} in 10 ml solution

$\therefore$ Strength of Ni^{2+} solution $= \dfrac{0.2033 \times (W_2 - W_1) \times 1000}{10}$ g/L

$= 20.33\ (W_2 - W_1)$ g/L

1.9 Self Assesment Questions

1. What are meant by the terms idometry and idometry?
2. What is meant by available chlorine in bleaching powder? How is estimated?
3. What is the commonly used indicator in idimetric titration?
4. How can you prepare 250ml (N/20) $K^2Cr^2O_7$ solution?
5. Define primary and secondary standard solurions? Give examples.
6. What amount of oxalic acid is required to prepare 250 ml (N/20) oxalic acid?
7. Write down the chemical reaction during the estimation of Ni using DMG gravimetrically?
8. What is the role of NH_4HF_2 is estimation of Cu^{2+} using idometry?
9. What is Dq value?
10. How does chloride estimate by gravimetrically?

1.10 Suggested Reading

1. "Text Book on Practical Chemistry"; K. S. Mukherjee,
2. "An Advance Course in Practical Chemistry". A. Ghoshal, B. Mahapatra and A.K. Nad.
3. "Text Book of Quantitative Inorganic Analysis" A.I. Vogel.

Unit-2 □ Quantitative Experiment

Structure

2.1. Objectives

2.2. Introduction

2.3. Paper chromatographic separation of Ni (II) and Co (II)

2.4. Measurement of $10D_q$ by spectrophotometric method

2.5. Preparation of $Mn(acac)_3$ and determination of its λ_{max} colorimetrically

2.6. Self Assessment Questions

2.7. Suggested Reading

2.1. Objectives

After reading this unit we are able to learn the following topics :

- Seperation of Ni (II) and Co(II)
- Measurement of 10 Dq value by spectroscopic method
- Preparation of Mn $(acac)_3$ and determination of λ_{max}

2.2. Introduction

Chromatography : It is one of the most valuable and relatively modern technique. It was first discovered by M. Tswett, a botanist in 199 for the seperation of coloured substances. The basic principle of this technique is the preferential distribution of the components of the mixture in two phases-one is stationary and the other is mobile. The stationery phase may be either said or liquid. When it is solid, the seperation of the constituents occurs through selective adsorption but in the case of liquid stationery phase the seperation is achieved by partition. The mobile phase may be liquid or gas. Different types of chromatography developed namely column chromatography, thin layer chromatography, paper chromatography and gas chromatography.

Paper chromatography is a kind of partition chromatography in which the substances are distributed between two liquids-one is the stationery liquid usually water, held in the

fibres of the paper known as stationery phase and the other is the moving liquid or developing solvent and is normally called as moving phase. The components of the mixture to be seperated migrate at different rates and appear as spots on the paper.

Colorimetric estimation : A sample containing low manganese content can ve conveniently estimated by colorimetric method. The colourmetric determination is based on Lambert-Beer's law, according to which the absorbance (A) of a solution of light absorbing substance is given by

$A = \varepsilon cl$,

Where, I is the path length (usually 1 cm), c is the concentration in molarity and ε is the molar extinction coefficient. If the absorbance (A) of a series of solutions of known concentrations of the substance to be determined is plotted against concentration (c), a straight line passing through origin is obtained. The molar extinction coefficient, ε, may be obtained from the slope of this straight line.

Such a curve is called a calibration curve. The range of concentration of the substance, where the absorbance vs. concentration curve is linear, is the useful range of concentration for colorimetric determination.

Unknown concentration of the substance in a sample solution may be determined by measuring the absorbance for the light of same wave length and then extrapolating the calibration curve or by simply dividing the experimental absorbance by the extinction coefficient. In colormetric determinations, optical filters are often used for isolating the desired spectral region from the undesired one. Light filters in the wave length region 500-560 nm are generally used in the determination of managanese as MnO^4. Alternatively, a spectrophotometer may be used and measurement may be made at 520 nm.

2.3. Paper Chromatographic Separation of Ni (II) and Co (II)

Theory :

In paper chromatograpy the materials to be separated undergo partition between the aqueous phase held in the inert cellulose matrix and organic solvent used as mobile phase. In paper chromatography the mechanism is mainly partition in nature. Here adsorption may also occur due to presence of – COOH group in cellulose but this effect is minimum in presence of strong acidic medium.

In inorganic separation by paper chromatographic technique the mobility of different

ions depend upon the following factors :

i) If a solute forms a complex with any of the constituents present in the developing solvent , its R_F value will be high due to the solubility of the inorganic solutes increase in organic phase. Thus oxygen containing solvents in presence of little HCl, metal ions may dissolve in organic solvents after forming chlorocomplexes e.g., Co^{2+} ion form chlorocomplex that is more soluble in organic solvent whereas Ni^{2+} cannot form such complex and it is held at the base.

ii) The other factor for the mobility of the metal ions is that which tends to lower the R_F value, i.e., retains the components of the mixture in the stationary aqueous phase of the cellulose. This happens when the metal ions can form strong water soluble complexes with anions present in the developing solvent or which give a precipitate in this medium.

A mixture of metal ions [Co^{2+} and Ni^{2+}] can be separated by paper chromatography where paper itself acts as stationary phase.

On developing paper chromatogram in acetone : ethyl acetate : 6M HCl (9 : 9 : 2) mixed solvent, the sugar will separate and appear as two coloured spots at different distance depending on their respective R_F values. The appearance of blue – purple spot indicates the presence of Ni^{2+} and yellow – orange spot indicates Co^{2+}. The R_F values varies in the order :

$Co^{2+} > Ni^{2+}$ with rubeanic acid as the spraying reagent.

Materials Required :

i) Stationary phase : A paper strip (20 cm x 4 cm) cut from whatman No. 1 paper.

ii) Developing solvent (Mobile phase) : Acetone : ethyl acetate : 6M HCl (9:9:2) v/v.

iii) Developing chamber : A glass jar (25 cm x 5 cm) with a lid.

iv) Spraying reagent : Dissolve 10 mg of rubeanic acid in 10 ml of 95% ethyl alcohol.

v) Standard solutions : Dissolve ~ 4.5 / 5 ml of $CoCl_2 . 6H_2O$ and $NiSO_4 . 6H_2O$ in distilled water to have the solutions containing ~ 1mg / ml of each of Co^{2+} and Ni^{2+}. Label the solutions as **A** for Co^{2+} and **B** for Ni^{2+}.

vi) Unknown sample solution of metal ions. (Mix two solutions and label it as unknown).

vii) Fine capillary tube.

viii) Sprayer.

Procedure :

i) Setting of the solvent jar :

Place 50 ml of the developing solvent into the solvent jar, cover with lid and shake

the jar so that the vessel is saturated with solvent vapour. Allow to stand for 20 minutes.

ii) Application of the sample :

Cut 20 cm × 4 cm piece of a paper strip from Whatman No.1 paper. Draw a light pencil line across the paper strip above 3 cm from the lower end. Put three pencil dots on the line with symmetrical distance. Now place vertically one micro drop of the supplied mixture of the metal ions on middle dot with a fine capillary tube. Label it. Again put two micro drops on the remaining dots of the standard solutions one by one in a similar manner. Label these as **A** and **B**. Allow to dry in the air or by using a hair drier.

iii) Development of the spotted paper chromatogram :

Suspend the paper strip from the glass hook into the solvent to a depth of 5 – 6 mm. When the solvent from ascends about 15 – 20 cm (which requires ~ 2 hours), remove the paper strip. Mark the solvent front ascended with a pencil and dry the paper strip in air or using hair drier.

iv) Identification of metal ions :

Spray the paper strip on both side with the spraying reagent. Two spots are separated and label them as **X** and **Y**. The appearance of blue-purple spot indicates the presence of Ni^{2+} and yellow – orange spot indicates Co^{2+}.

v) Measurement of R_F value :

Measure the distance travelled by the solvent front. Encircle the developed spots with a pencil and measure the distances travelled by the different constituents present in the supplied mixture as well as in the standard sample from base line to the centre of the each spot. Calculate the R_F value of each constituent and compare with the constituents in the standard sample.

Experimental Results :

Table – 1 : Calculation of R_F values of standard samples :

Standard samples (Co^{2+} and Ni^{2+})	**Distance travelled by the solute from the starting line (d_1 cm)**	**Distance travelled by the solvent from the starting line (d_2 cm)**	**$R_F = d_1 / d_2$**
A (Co^{2+})			
B (Ni^{2+})			

Table – 2 : Calculation of R_F values of unknown sample :

Standard samples (Co^{2+} and Ni^{2+})	Distance travelled by the solute from the starting line (d_1 cm)	Distance travelled by the solvent from the starting line (d_2 cm)	$R_F = d_1 / d_2$
A (Co^{2+})			
B (Ni^{2+})			

Note :

a) Care must be taken in handling the paper strip to keep it free from contamination.

b) The centre of the spotted zone is to be taken, to measure the distance travelled by the solute from the starting line.

2.4. Measurement of 10Dq by spectrophotometric method

Theory:

The primary objective of this experiment is to determine the concentration of an unknown $KMnO_4$ solution. The $KMnO_4$ solution used in this experiment has a blue color, so Colorimeter users will be instructed to use the red LED. A higher concentration of the colored solution absorbs more light (and transmits less) than a solution of lower concentration. You will prepare five of known concentration (standard solutions). Each solution is transferred to a small, rectangular cuvette that is placed into the Colorimeter or Spectrometer. The amount of light has penetrated the solution and strikes the photocell is used to compute the absorbance of each solution. When you graph absorbance vs. concentration for the standard solutions, a direct relationship should result. The direct relationship between absorbance and concentration for a solution is known Beer's law. You will determine the concentration of an unknown $KMnO_4$ solution by measuring its absorbance. By locating the absorbance of the unknown on the vertical axis of the graph, the corresponding concentration can be found on the horizontal axis. The concentration of the unknown can a so be found using the slope of the Beer's law curve.

Apparatus & Chemicals required:

1. Colorimeter cuvette (20 × 150 mm)
2. Test tubes

3. Two 10 mL pipettes
4. Graduated cylinders
5. Beakers
6. 0.01M $KMnO_4$ solution
7. Distilled water

Procedure:

1. Obtain small volumes 0.01M $KMnO_4$ solution and distilled water in separate beakers.
2. Label five clean, dry, test tubes 1–5.
3. Use pipets to prepare five standard solutions according to the chart below.
4. Thoroughly mix each solution with a stirring rod.
5. Clean and dry the stirring rod between uses.
6. Prepare a blank by filling a cuvette 3/4th full with distilled water.
7. To correctly use cuvettes, remember: Wipe the outside of each cuvette with a lint-free tissue.
8. Handle cuvettes only by the top edge of the ribbed sides.
9. Dislodge any bubbles by gently tapping the cuvette on a hard surface.
10. Always position the cuvette so the light passes through the clear sides.
11. You are now ready to collect absorbance-concentration data for the five standard solutions.
12. Using the solution in Test Tube 1, rinse the cuvette twice with ~1 mL amounts and then fill it 3/4th full.
13. Wipe the outside with a tissue and place it in the device (Colorimeter or Spectrometer when the absorbance readings stabilize,).
14. Close the lid on the Colorimeter.
15. Discard the cuvette contents as directed.
16. Using the solution in Test Tube 2, rinse and fill the cuvette 3/4th full.

17. Wipe the outside and place the cuvette in the device (close the lid of the Colorimeter).
18. When the absorbance readings stabilize, d. Repeat the procedure for Test Tubes 3 and 4.
19. Trial 5 is the original 0.01M $KMnO_4$ solution.

Test Tube	0.01M $KmnO_4$(mL)	Distilled water (mL)	Concentration (M)
1	2	8	0.002
2	4	6	0.004
3	6	4	0.006
4	8	2	0.008
5	10	0	0.010

20. Determine the absorbance value of the unknown $KMnO_4$ solution. Take about 5 mL of the unknown $KMnO_4$ in another clean, dry, test tube.
21. Record the number of the unknown in your data table.
22. Rinse the cuvette outside of the cuvette, place it into the device. (Close the lid of the Colorimeter.) twice with the unknown solution and fill it about $3/4^{th}$ full.
23. Read the absorbance value displayed in the meter.
24. When the displayed absorbance value stabilizes, record its value as Trial 6 in your data table.
25. Select 'Interpolate' from the 'Analyse' menu.
26. Find the absorbance value that is closest to the absorbance reading you obtained in Step c above.
27. Determine the concentration of your unknown $KMnO_4$ solution and record the concentration in your data table.
28. Dispose of any of the remaining solutions as directed.

Trial	Concentration (mol / L)	Absorbance
1	0.002	
2	0.004	
3	0.006	

Trial	Concentration (mol / L)	Absorbance
4	0.008	
5	0.010	
6	Unknown strength	

2.5. Preparation of $Mn(acac)_3$ and determination of its λ_{max} colorimetrically

Theory:

Manganese is a first row transition metal whose compounds display a tremendous variety of oxidation states ranging from Mn (III), e.g. $Mn(NO)_3CO$, to Mn(VII), e.g. $KMnO_4$. The target complex of this experiment is the acetylacetonatomanganese(III) complex [tris(2,4- pentanediacetonato)manganese(III), often abbreviated as $Mn(acac)_3$] and is often used as a synthetic intermediate for the preparation of analogous Mn(III) compounds. Mn(III) complexes are relatively stable, however, will slowly oxidize water with concurrent evolution of dioxygen. Thus, it comes as no surprise that nature takes advantage of aqueous manganese redox chemistry in the oxygen evolving complex (OEC) of the photosynthetic reaction center to generate dioxygen (the air we breathe today).

$$4Mn^{3+} + 2H_2O \rightarrow 4Mn^{2+} + 4H^+ + O_2$$

In this experiment a solution of manganese (II) chloride ($MnCl_2$) is oxidized with potassium permanganate in the presence of acetylacetone giving the brown $Mn(acac)_3$ solid.

Procedure for preparation of $Mn(acac)_3$:

1. In a 250 mL conical flask prepare a solution of 1.32 g manganese (II) chloride tetrahydrate and 3.59 g of sodium acetate trihydrate in 50 mL water.
2. To this solution add by pipette 5 mL of acetylacetone.
3. Place a small magnetic stirring bar in the solution and place the flask on a magnetic stirrer in the hood.
4. To the stirred mixture add dropwise a solution of 0.28 g of potassium permanganate in 15 mL water (due to the color intensity of the permanganate solution it is difficult to determine if it has completely dissolved, therefore, stir thoroughly and check for undissolved solute).

5. After the addition of the potassium permanganate solution, stir for an additional 5 minutes.
6. Meanwhile, prepare a solution containing 3.59 g of sodium acetate trihydrate in 15 mL of water and add this in approximately 1mL portions to the stirred solution of crude $Mn(acac)_3$.
7. Heat the reaction mixture to near boiling (hot plate) for 10 minutes and subsequently cool to room temperature.
8. Filter the crude dark solid on a small Buchner funnel and wash with three 10mL portions of deionized water.
9. Spread out the crude product on a porcelain dish and dry in an oven at 60°C to 70°C for at least 30 minutes.

Recrystallization:

1. Weigh the dry product and determine the crude percent yield.
2. Under the hood, dissolve the dried $Mn(acac)_3$ in 4.0 mL of toluene contained in a 25mL conical flask.
3. Filter the solution through a Buchner funnel.
4. Transfer the filtrate to a 30-mL beaker and cool in an ice bath (be very careful not to get any water in the toluene solution).
5. Add 15 mL of petroleum ether to the solution to precipitate the product.
6. Collect the recrystallized product in a Buchner funnel and place in a drying oven at 60 C.
7. Weigh the recrystallized product and calculate the percent yield.

Procedure for determination of its λ_{max}:

1. Obtain small volumes of $Mn(acac)_3$ solution and distilled water in separate beakers.
2. Label five clean, dry, test tubes 1–5.
3. Use pipettes to prepare five standard solutions according to the chart below.
4. Thoroughly mix each solution with a stirring rod.
5. Clean and dry the stirring rod between uses.
6. Prepare a blank by filling a cuvette $3/4^{th}$ full with distilled water.

7. To correctly use cuvettes, remember: Wipe the outside of each cuvette with a lint-free tissue.
8. Handle cuvettes only by the top edge of the ribbed sides.
9. Dislodge any bubbles by gently tapping the cuvette on a hard surface.
10. Always position the cuvette so the light passes through the clear sides.
11. You are now ready to collect absorbance-concentration data for the five standard solutions.
12. Using the solution in Test Tube 1, rinse the cuvette twice with ~1 mL amounts and then fill it 3/4th full.
13. Wipe the outside with a tissue and place it in the device (Colorimeter when the absorbance readings stabilize).
14. Close the lid on the Colorimeter.
15. Discard the cuvette contents as directed.
16. Using the solution in Test Tube 2, rinse and fill the cuvette 3/4th full.
17. Wipe the outside and place the cuvette in the device (close the lid of the Colorimeter).
18. When the absorbance readings stabilized.
19. Repeat the procedure for Test Tubes 3 and 4.
20. Trial 5 is the original 0.01M $Mn(acac)_3$solution.

Test Tube	0.01M $Mn(acac)_3$(mL)	Distilled water (mL)	Concentration (M)
1	2	8	0.002
2	4	6	0.004
3	6	4	0.006
4	8	2	0.008
5	10	0	0.010

21. Determine the absorbance value of the unknown $Mn(acac)_3$ solution. a. Obtain about 5 mL of the unknown $Mn(acac)_3$ in another clean, dry, test tube.
22. Record the number of the unknown in your data table.
23. Rinse the cuvette outside of the cuvette, place it into the device. (Close the lid of the Colorimeter.) twice with the unknown solution and fill it about 3/4th full.
24. Read the absorbance value displayed in the meter.

25. When the displayed absorbance value stabilizes, record its value as Trial 6 in your data table.
26. Select 'Interpolate' from the 'Analyse' menu.
27. Find the absorbance value that is closest to the absorbance reading you obtained in Step c above.
28. Determine the concentration of your unknown $Mn(acac)_3$ solution and record the concentration in your data table.
29. Dispose of any of the remaining solutions as directed.

Trial	Concentration (mol /L)	Absorbance
1	0.002	
2	0.004	
3	0.006	
4	0.008	
5	0.010	
6	Unknown strength	

Result:

Yield : .....

Yield percentage : .....; Absorbance : .....

2.6. Self Assessment Questions

1. What is chromatography? Classify chromatography.
2. States Lambert Beer's law?
3. What do you mean by R_F value?
4. How can determine the 10 Dq value?
5. Described the method of preparation of $Mn(acac)_3$?

2.7. Suggested Reading

1. "Text Book on Practical Chemistry"; K.S. Mukherjee.
2. "An Advance Course in Practical Chemistry", A. Ghoshal, B. Mahapatra and A.K. Nad.
3. "Text Book of Quantitative Inorganic Analysis" A.I. Vogel.

Unit-3 □ Qualitative Semimicro Analysis

Structure

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3.6.6. Tests for nitrate and nitrite (spot plate test)

3.6.7. Reactions of the Wet Tests for Acid Radicals

3.7. Wet Test for basic Radicals

3.7.1. Preparation of solution for Group Analysis

3.7.2. General Group Separation

3.8. Treatment of the Aqua Regia Soluble Samples

3.9. Treatment of Insoluble Residue

3.9.1. Dry test for insoluble residue

3.9.2. Wet test for insoluble residue

3.10. Spot Test for Basic Radicals

3.11. Spot Test for Anions

3.12. Analysis of Unknown Inorganic Sample

3.13. Sample Questions

3.14. Suggested Reading

3.1. Objectives

- To give a qualitative idea about colour of the inorganic salts.
- Identifications radicals (acid radical & basic radicals) of the inorganic salts.
- To give a concise idea and practical applications in preliminary examinations for basic & acid radicals in dry way.
- Test for interfering radicals.
- Detailed knowledge on we test of acid and basic redicals.
- To provide the idea and practical applications for specials test of radicals.
- Provide the complete knowledge for analysis of an inorganic salt.

3.2. Introduction

Inorganic Qualitative Analysis has long been considered as the most interesting part of Inorganic Chemistry. But the so-called teacherous role of this part of chemistry has been reduced substantially as plenty of specific, sensitive and reliable reagents are now available by the use of which the hurdles underlying the work have been overcome. For the improvement of performance an analyst should also adopt the systemetic approoach and work with caution, care and cleanliness. A detail discussion on the qualitative semimicro analysis is furnished here to make the students up to date with the analytical process.

Inorganic salts ionise in solution into cations and anions. Cations are called basic radicals and anions are called acid radicals.

The colour of the given substance is one of the important physical characteristics. A list of coloured inorganic compounds is given below :

(a) Black	Ag_2S, Ag_2O, CuO, $CuBr_2$, CuS, HgS, Hg_2O, PbS, Bi_2S_3, Fe_3O_4, FeS, MnO_2, CoO, CoS, NiS, NiI_2, NiO
(b) Red	Pb_3O_4, Cu_2O, HgO, HgS, HgI_2, As_2S_3, Fe_2O_3, CrO_3, $K_3[Fe(CN)_6]$

(c) Green	Cr_2O_4, all Cr(III) compounds (except $Cr(OH)_3$ and $Cr_2(CO_3)_3$ grey), all Fe (II) compounds (except FeS black), all Ni (II) compounds (except NiO, NiS are black), $CuCO_3$, $CuCl_2$, $Cu(OH)_2$, Hg_2I_2
(d) Yellow	AgI, Ag_3AsO_3, Ag_3PO_4, HgO, $Hg_3(AsO_3)_2$, Hg_2I_2, $Hg_2(NO_3)_2$, CdS, As_2S_3, Bi_2O_3, SnS_2, PbI_2, PbO, ferric compounds, all chromates, $K_4[Fe(CN)_6]$.
(e) Brown	Fe_3O_4, Fe_2O_3, $Fe(OH)_3$, CdO, PbO_2, $PbCrO_4$, Ag_3AsO_3, Bi_2O_3, Bi_2S_3, SnS.
(f) Orange red	Dichromates, CdS, Sb_2S_3.
(g) Pink, purple red	Cobalt compounds (except CoO, CoS), chrome alum, manganous salts (except oxides of Mn, MnS, $Mn_3(BO_3)_2$), permanganates.
All alkali or alkaline earth metals are white in colour unless the anion is coloured. Most of the chlorides and oxides are white coloured.	

The colour of the salt solution is also valuable information. A list of coloured ions in solution (aqueous solution) is depicted below :

Compounds	**Colour in aqueous solution**	**Colour in HCl solution**
Dichromate	Orange	Orange
Chromate	Yellow	Orange
Cobalt (II)	Pink	Blue
Permanganates	Purple	-
Copper (II)	Blue	Bluish green
Iron (II)	Light green	Green
Iron (III)	Yellow	Yellowish brown
Manganese (II)	Pale pink	Green
Nickel (II) & Chromium (III)	Green	Green
Aqueous solution of all alkali and alkaline earth metals are colourless unless the anion is coloured.		

Systematic Semimicro Methods of Inorganic Qualitative Analysis:

1. Physical characteristic of the given Inorganic sample:

a) State :

b) Colour :

c) Solubility :

3.3. Preliminary Examination for Basic Radicals in the Dry Way:

3.1.1. Heating in a dry test tube:

<table>
<tr><th>Experiment</th><th>Observation</th><th>Inference</th></tr>
<tr><td>Take little amount of the given sample in a clean and dry test tube. Heat the tube at first gently and then strongly.</td><td>a) Substance changes colour :
<table>
<tr><th>Hot</th><th>Cold</th></tr>
<tr><td>i) Yellow to brown</td><td>Yellow</td></tr>
<tr><td>ii) Yellow</td><td>White</td></tr>
<tr><td>iii) Yellowish brown</td><td>Yellow</td></tr>
<tr><td>iv) Black</td><td>Black</td></tr>
<tr><td>v) Yellow to reddish brown or orange</td><td>Reddish brown or orange</td></tr>
<tr><td>vi) Brown to blackening</td><td>Brown</td></tr>
<tr><td>vii) Green</td><td>Green</td></tr>
</table></td><td>i) Pb-salt
ii) Zn-salt
iii) SnO_2, Bi_2O_3
iv) Cu,Ni,Co& Mn- salts
v) Sb,Cd and Bi-salts
vi) Fe-salts
vii) Cr-salts</td></tr>
</table>

Experiment	Observation	Inference
	b) A gas or vapour is evolved with characteristic smell or/and colour :	
	i) Droplets of water deposited at the cooler part of the test tube	i) Compound with water of crystallisation
	ii) Violet vapour condensing to black crystals	ii) Heavy metal iodide

Experiment	Observation	Inference
	iii) Brown gas iv) Greenish yellow gas with pungent smell, turns starch iodide paper blue v) SO_2 gas with smell of burnt sulphur, turns acidified $K_2Cr_2O_7$ moist paper into green vi) H_2S gas with smell of rotten egg and turns lead acetate paper into black vii) NH_3 gas with characteristic pungent odour turning mercurous nitrate paper black viii) Colourless gas turns clear lime solution milky **c) Colourless melts on heating but solidifies on cooling** **d) Original colour white, remains unchanged on heating** **e) Swells on heating with the deposition of droplets of water at the cooler part of the test tube** **f) A sublimation is formed :** i) White sublimate formed at the cooler part of the test tube ii) White sublimate, changes to yellow when exposed to H_2S iii) White sublimate , changes to orange when exposed to H_2S iv) White sublimate with pungent smell of NH_3, no change of colour with H_2S **g) Coloured sublimate is formed :** i) Black sublimate – turns red on prolonged rubbing with a glass rod ii) Yellow sublimate iii) Orange sublimate iv) Black mirror with garlic smell v) Violet vapours condensed to blue-black sublimate	iii) Nitrite, Nitrate or Bromide of heavy metals iv) Chloride v) Sulphite, thiosulphate vi) Sulphide vii) Ammonium viii) Carbonate, bicarbonate c) Alkaline or alka line earth metallic salts d) Al and all alkali and alkaline earth metal salts e) Borax and alum i) As_2O_3 , Sb_2O_3, NH_4^+, Hg-salts ii) As_2O_3 iii) Sb_2O_3 iv) NH_4^+- salts i) HgS ii) As_2S_3, Sb_2S_3 and sulphur from thiosulphate iii) Sb_2S_3 iv) AsO_3^{3-} v) Iodine set free from its salts

3.3.2. Soda lime test :

When white sublimate is formed in the dry test tube heating test

Experiment	Observation	Inference
Mix 1 part of the sample with 4 parts of soda lime (NaOH + CaO) and 1 part of charcoal powder in a dry test tube, then heat strongly *** In case of NH_3 charcoal powder is not necessary**	i) NH_3 gas evolves with characteristic smell ii) Black mirror	i) NH_4^+ salts ii) As-salts, As_2O_3, AsO_3^{3-}

3.3.3. Heating on a charcoal block in the oxidising flame :

Experiment	Observation	Inference
Place little amount of the given sample in a groove on a charcoal block and heat in the oxidising flame with a blowpipe	i) White residue left on the charcoal. Incandescent when hot (emitting light as a result of being heated).	i) Ca, Sr, Ba, Al, Ag, Sn-salts
	ii) The substance decrepitates on heating (disintegrate audibly when heated).	ii) NaCl, KCl etc.
	iii) The substance catches fire (deflagrated) on heating	iii) Nitrate, Nitrite, Iodates
	iv) The substance melts and is absorbed into porous charcoal	iv) Na, K, alkali salts and few alkaline earth metal salts

3.3.4. Heating on a charcoal block in the reducing flame :

Experiment	Observation	Inference
Place a mixture of 1 part of the given sample and 2 parts of anhydrous Na_2CO_3 in	i) A metallic bead formed ii) Soft malleable bead marks paper	i) Ni) Pb, Bi, Sb, Ag, Sn-salts ii) Pb – salts

Experiment	Observation	Inference
a groove on a charcoal block, moist with 1-2 drops of water and heat in reducing flame with blowpipe.	iii) A cluster of small beads	iii) Sn – salts
	iv) Red scales formed	iv) Cu – salts
	v) Greyish black metallic mass, attracted by magnet	v) Fe, Ni, Co, Mn – salts
	vi) Green residue left on charcoal	vi) Cr – salts
	vii) Incrustation is yellow when hot, white when cold	vii) Zn – salts
	viii) Brown incrustation	viii) Cd - salts

3.3.5. Cobalt nitrate test :

*** Do not perform this test for coloured sample**

Experiment	Observation	Inference
If a white residue is left in charcoal-block oxida-tion, add a drop of cobalt nitrate solution to the white residue and heat strongly with blowpipe in oxidising flame	i) Blue infusible residue	i) Al
	ii) Blue fusible residue	ii) Phosphate, Borate, Arsenate
	iii) Green residue	iii) Zn
	iv) Dirty grey residue	iv) Sn
	v) Pink residue	v) Mg
	vi) Grey residue	vi) Ca, Sr, Ba

3.3.6. Flame test :

Experiment	Observation		Inference
	Without blue glass	**With double blue glass**	
Hold the clean Pt-wire near the base of a non-luminous flame moisten with conc. HCl and a little of the	i) Persistent dazzling golden yellow	i) Ni) Colourless	i) Na
	ii) Bluish violet	ii) Crimson red	ii) K
	iii) Brick red	iii) Light green	iii) Ca
	iv) Persistent crimson	iv) Purple	iv) Sr

Experiment	Observation		Inference
powdered sample at the tip of the wire.	**Without blue glass**	**With double blue glass**	
	v) Persistent apple green	v) Bluish green	v) Ba
	vi) Bluish green	vi) -	vi) Cu
	vii) Blue flame with green edge	vii) -	vii) H_3BO_3, BO_2
	viii) Bluish green	viii) -	viii) Pb, As, Sb, Bi, Sn
	ix) Transient deep red	ix) Crimson red	ix) CaF_2

[Note: i) Pb, As, Sb, Cu and Sn salts corrode Pt- wire. In that case, asbestos fiber can be used in absence of Pt- wire.

ii) $MnCl_2$ gives transient yellowish green flame.**]**

3.3.7. Borax bead test :

*** Borax bead test is performed in case of coloured salts only. ($MnSO_4$ is very light pink).**

Experiment	Observation				Inference
	Oxidising flame		**Reducing flame**		
	Hot	**Cold**	**Hot**	**Cold**	
Prepare a trans parent borax bead in a loop of a clean Pt-wire by heating the Pt- wire with borax. Take a tiny particle by just touching the salt with the hot bead and heat first in the oxidi-sing flame and then in the reducing flame.	i) Green	i) Blue	i) –	i) Opaque red	i) Cu-salt
	ii) Deep blue	ii) Deep blue	ii) Deep blue	ii) Deep blue	ii) Co-salt
	iii) Green	iii) Green	iii) Green	iii) Green	iii) Cr-salt
	iv) Reddish yellow	iv) Yellow	iv) Bottle green	iv) Bottle green	iv) Iron-salt
	v) Violet	v) Violet	v) Colour-less	v) Colour-less	v) Mn-salt
	vi) Reddish brown	vi) Reddish brown	vi) Grey opaque	vi) Grey opaque	vi) Ni-salt

3.3.8. Oxidative fusion test for Mn and Cr :

*** If there is sufficient indication of presence of Cr and/ or Mn then perform this test .**

Experiment	Observation	Inference
Mix 1 part of the sample with 2 parts of anhydrous Na_2CO_3 , 1 bead of NaOH and 1 part of KNO_3. Heat the mixture strongly on a mica foil or on a broken porcelain basin. Dissolve the fused mass in about 10 ml of boiled water and divide in two parts to perform the following tests.		
i) Yellow melt : Acidify one part of the solution with acetic acid then add few drops of Pb – acetate solution.	i) Yellow precipitate	i) Cr-salt
ii) Green melt : Acidify other part of the solution with HNO_3 or dilute acetic acid.	ii) A pink colour develops	ii) Mn-salt

*** If the sample is white in colour do not perform this test.**

3.3.9. Test for Ammonium radical:

Experiment	Observation	Inference
Mix a small quantity of the sample with 2 ml of 20% NaOH solution in a test tube and heat the solution gently.		
i) Place a $Hg_2(NO_3)_2$ moist paper in the issuing gas	i) Paper turns into black	i) NH_4^+ salt

Experiment	Observation	Inference
ii) Add a drop of Nessler's reagent solution in the test tube	ii) Brown precipitate	ii) NH_4^+ salt

3.3.10. Special tests with HCl and HNO_3 extracts :

Experiment	Observation	Inference
1. Heat the sample with conc. HCl and divide the solution into 5 parts.		
i) In one part add 1 ml of amyl alcohol and a little of aqueous solutions of NH_4HF_2 and NH_4SCN	i) Alcohol layer turns blue. Aqueous layer turns pink on dilution with water	i) Co – salt
ii) To the hot extract, add KI solution	ii) Yellow precipitate	ii) Pb – salt
iii) Pour the extract in large excess of water	iii) The water turns milky	iii) Bi, Sb – salts
iv) Dilute one part of the solution and then add few drops of $K_4[Fe(CN)_6]$ solution	iv) Prussian blue colouration or deep blue ppt.	iv) Fe – salt
v) To the rest part add dil. H_2SO_4	v) White precipitate	v) Ba, Sr, Pb – salts
2. Heat the sample with (1:1) HNO_3 and divide the solution into 3 parts.		
i) Add a pinch of $NaBiO_3$ to the one part of the extract	i) Solution turns pink	i) Mn – salt
ii) Alkaline the second part with NH_4OH and then add dimethylglyoxime solution	ii) Rose red precipitate	ii) Ni – salt

Experiment	Observation	Inference
iii) Alkaline the third part with NH_4OH, then acidify with acetic acid. Add $K_4[Fe(CN)_6]$ solution	iii) Chocolate brown precipitate	iii) Cu - salt

3.3.11. Test with NaOH extract :

Experiment	Observation	Inference
Boil a small quantity of the sample with NaOH solution and filter. Divide the filtrate into 3 parts and perform the following experiments.		
i) Heat one part of the extract with excess solid NH_4Cl	i) White gelatinous ppt.	i) Al – salt
ii) Acidify another part acetic acid	ii) Yellow / Orange ppt.	ii) As_2O_3 / Sb_2O_3
iii) Acidify another part with acetic acid and pass H_2S gas	iii) White precipitate	iii) Zn - salt

NOTE : Number of interference will be observed in case of mixed salt.

3.3.12. Reaction of Preliminary Dry Tests for the Basic Radicals

1. Action of heat :

i) Decomposition of the substance :

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

$$4\,BiONO_3 \longrightarrow 2\,Bi_2O_3 + 4\,NO_2 + O_2$$

ii) Elimination of water from water of crystallisation :

$$CuSO_4, 5H_2O\ (Blue) \longrightarrow CuSO_4\ (White) + 5H_2O$$

$Ni(OH)_2\,5H_2O$ (Green) $\longrightarrow$ NiO (Black) + $5H_2O$

iii) A gas is evolved :

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

$$(NH_4)_2CO_3 \longrightarrow 2\,NH_3 + CO_2 + H_2O$$

iv) A sublimate is formed :

As - compound $\longrightarrow$ As_4O_6 (Volatile, garlic odour when hot)

2. Action of heat on the mixture of the sample with soda lime :

a) $2\,NH_4Cl + Na_2CO_3 \longrightarrow (NH_4)_2CO_3 + 2\,NaCl \longrightarrow 2\,NH_3 + H_2O + CO_2$

b) $As_2O_3 + 3C + Na_2CO_3 \longrightarrow 2\,As + 3\,CO$

3. Oxidation on charcoal block :

i) White fumes with garlic odour :

$$2\,As_2S_3 + 9\,O_2 \longrightarrow 2\,As_2O_3 + 6\,SO_2$$

$$As_2O_3 + 3\,C \longrightarrow 2\,As + 3\,CO$$

ii) An incrustation is formed :

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

$$4\,BiONO_3 \longrightarrow 2\,Bi_2O_3 + 4\,NO_2 + O_2$$

4. Reduction on charcoal block :

i) A metallic bead is formed :

$$PbCl_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2\,NaCl$$

$$PbCO_3 \longrightarrow PbO + CO_2$$

$$2\,PbO + C \longrightarrow 2\,Pb + CO_2$$

$$4\,BiONO_3 \longrightarrow 2\,Bi_2O_3 + 2N_2O_4 + O_2$$

$$2\,Bi_2O_3 + 3\,C \longrightarrow 4\,Bi + 3\,CO_2$$

ii) Red scales formed :

$$CuCl_2, 2H_2O + Na_2CO_3 \longrightarrow CuCO_3 + 2NaCl + 2H_2O$$

$$CuCO_3 \longrightarrow CuO + CO_2$$

$$2\,CuO + C \longrightarrow 2\,Cu\ CO_2$$

$$FeSO_4, 7\,H_2O + Na_2CO_3 \longrightarrow FeCO_3 + Na_2SO_4 + 7\,H_2O$$

$$FeCO_3 \longrightarrow FeO + CO_2$$

$$FeO + C \longrightarrow Fe + CO$$

5. Cobalt nitrate test :

Cobalt nitrate $Co(NO_3)_2$ decomposes on heating first

$$Co(NO_3)_2 \longrightarrow 2\,CoO + 4\,NO_2 + O_2$$

This CoO then reacts with metallic oxides

$$CoO + Al_2O_3 \longrightarrow CoAl_2O_4$$

Thenard blue

$$CoO + ZnO \longrightarrow CoZnO_2$$

Rinmann's green

6. Borax bead test :

$$Na_2B_4O_7{\cdot}10H_2O \longrightarrow 2NaBO_2 + B_2O_3 + 10H_2O$$

$$CoCO_3 \longrightarrow CoO + CO_2$$

$$CoO + B_2O_3 \longrightarrow Co(BO_2)_2$$

Blue in both oxidising and reducing flame

i) In Oxidising Flame :

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$$

$$CuO + NaBO_2 \longrightarrow NaCuBO_3$$

$$Fe_2O_3 + 3B_2O_3 \longrightarrow 2Fe(BO_2)_3$$

ii) In reducing Flame :

$$2Cu(BO_2)_2 + C \longrightarrow Cu_2(BO_2)_2 + CO + B_2O_3$$

$$Cu_2(BO_2)_2 + C \longrightarrow 2\,Cu + B_2O_3 + CO$$

$$2Fe(BO_2)_3 + C \longrightarrow 2\,Fe(BO_2)_2 + B_2O_3 + CO$$

7. Oxidative Fusion test for Mn and Cr :

Mn salts are converted to green sodium manganate which on acidification turns to pink permanganate :

$$MnO_2 + KNO_3 + 2\,NaOH \longrightarrow Na_2MnO_4 + KNO_2 + H_2O$$
$$3Na_2MnO_4 + 4\,HNO_3 \longrightarrow 2\,NaMnO_4 + MnO_2 + 2\,NaNO_3 + 2\,H_2O$$

Chromium salts are converted to yellow chromate :

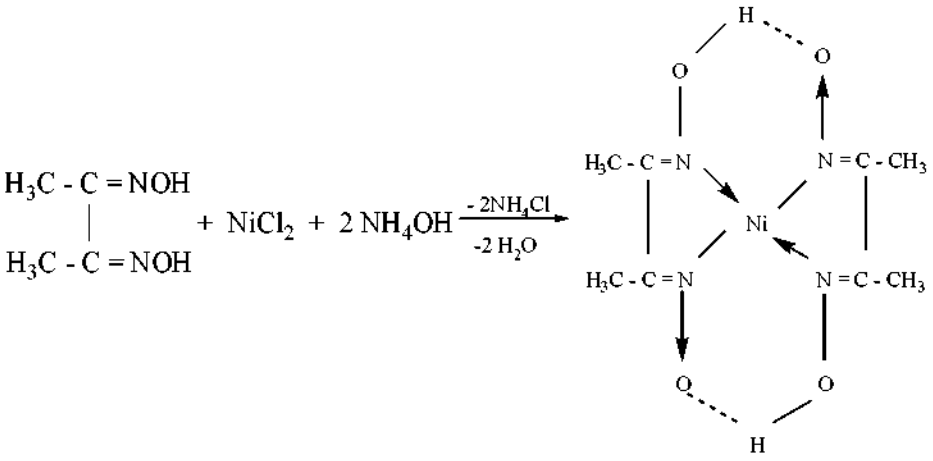
$$Cr_2O_3 + 2\,Na_2CO_3 + 3\,KNO_3 \longrightarrow 2\,Na_2CrO_4 + 2\,CO_2 + 3\,KNO_3$$
$$3\,NaMnO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 + 2\,CH_3COONa$$

8. Special test for Mn, Ni, Fe and Cu :

a) Potassium Ferrocyanide test for Fe :

$$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Prussian blue)}}{KFe[Fe(CN)_6]} + 3\,KCl$$

(b) Dimethyl glyoxime test for Ni :



a) Potassium Ferrocyanide test for Cu(II) :

$$2\,Cu^{2+} + K_4[Fe(CN)_6] = \underset{\text{(Chocolate brown)}}{Cu_2[Fe(CN)_6]} + 4\,K^+$$

b) Sodium Bismuthate test for Mn :

$$2\ MnSO_4 + 5\ NaBiO_3 + 16\ HNO_3 \longrightarrow \underset{(Pink)}{2\ HMnO_4} + 5\ Bi(NO_3)_3 + NaNO_3 + 2\ Na_2SO_4 + 7\ H_2O$$

3.4 Preliminary Tests for Acid Radicals in Dry Way

3.4.1. Treatment with dil. H_2SO_4 :

Experiment	Observation	Inference
Add dil. H_2SO_4 to a little amount of the sample and warm if necessary	i) Effervescence of colourless and odourless gas turning lime solution milky	i) CO_3^{2-}
	ii) A colourless gas is evolved with a smell of rotten egg and turns Pb-acetate paper into black	ii) S^{2-}
	iii) A colourless gas is evolver with a smell of burning sulphur and turns $K_2Cr_2O_7$ moist paper into green	iii) SO_3^{2-}
	iv) Smell of burnt sulphur with deposition of sulphur	iv) $S_2O_3^{2-}$
	v) Evolution of brown fumes	v) NO_2^-

3.4.2. Treatment with conc. H_2SO_4 :

Experiment	Observation	Inference
Place amount of the sample in a dry test tube and add few drops of conc. H_2SO_4 and warm carefully.	i) Evolution of brown fumes	i) NO_3^-, NO_2^-
	ii) Evolution of reddish-brown fumes	ii) Br^-
	iii) Evolution of violet vapour	iii) I^-
	iv) Evolution of a colourless gas with pungent smell–dense white fumes when NH_4OH moist glass rod held at the mouth of the test tube	iv) Cl^-

3.4.3. Chromyl chloride test for Chloride :

Experiment	Observation	Inference
Take little solid sample in a clean dry test tube and mixed thoroughly with equal quantity of $K_2Cr_2O_7$ and few drops of conc. H_2SO_4. Heat the mixture carefully.	i) A orange red gas will evolve, place a NaOH moist filter paper at the mouth of the test tube – it turns to yellow	i) Cl^-
	ii) Pass the vapour into NaOH solution through a bent delivery tube. Acidify the solution with acetic acid and then add lead acetate solution – Yellow ppt.	ii) Cl^-

[* Note : Bromides and Iodides evolved red and violet vapours. Nitrates and Nitrites interfere as NOCl is formed.]

3.4.4. Treatment with conc. H_2SO_4 and few pieces of Cu- turnings :

Experiment	Observation	Inference
Warm small quantity of the sample with a few drops of conc. H_2SO_4 and a few pieces of Cu – turnings.	Brown fumes evolved	NO_3^-, NO_2^-

3.4.5. Treatment with conc. H_2SO_4 and MnO_2 :

Experiment	Observation	Inference
Take little amount of the sample in a dry test tube and mixed with a small amount of MnO_2 and 1 ml of conc. H_2SO_4 and then heat gently.	i) Greenish yellow gas of Cl_2 comes out and turned starch iodide paper blue.	i) Cl^-
	ii) Reddish brown gas that turns CS_2 layer yellow when passed in a test tube containing CS_2 and water (*distinction from nitrate or nitrite*).	ii) Br^-
	iii) Violet vapour comes out which turns CS_2 layer violate when passed in a test tube containing CS_2 and water	iii) I^-

3.4.6. Test for SCN^- :

Experiment	Observation	Inference
Dissolve a little amount of the sample in water or dil. Acid and add a drop of $FeCl_3$ solution	Blood red colouration	SCN^-

3.4.7. Iodine- azide test for Sulphur acids (S^{2-} , $S_2O_3^{2-}$ and SCN^-) :

Experiment	Observation	Inference
Take a few drops of iodine – azide reagent in a watch glass and add a pinch of the sample to it.	Fine bubble of N_2 gas evolved with the simultaneous discharge of brown colour of I_2	S^{2-} , $S_2O_3^{2-}$, SCN^-

3.4.8. test for NH_4^+, NO_3^- and NO_2^- :

Experiment	Observation	Inference
1. Place a little amount of the sample in a test tube and add 1 ml of 20% NaOH and boil		
i) Hold a conc. HCl moist glass rod at the mouth of the test tube	i) Dense white fumes	i) NH_4^+
ii) Place $Hg_2(NO_3)_2$ moist paper in the gas	ii) paper turns black	ii) NH_4^+
2. If NH_4^+ is present, first boil a little amount of the with 20% NaOH solution to remove NH_3. Then add Zn – dust at boil gently		
i) Hold a conc. HCl moist glass rod at the mouth of the test tube	i) Dense white fumes	i) NO_3^- , NO_2^-
ii) Place $Hg_2(NO_3)_2$ moist paper in the gas	ii) paper turns black	ii) NO_3^- , NO_2^-

3.4.9. Reactions of Dry Tests of Acid Radicals :

1. Reaction with dil. H_2SO_4 :

i) $MSO_3 + H_2SO_4 = MSO_4 + H_2O + SO_2$

ii) $MS_2O_3 + H_2SO_4 = MSO_4 + S + SO_2 + H_2O$

iii) $MS + H_2SO_4 = MSO_4 + H_2S$

This SO_2 turns acidified dichromate paper green due to formation of Cr(III) - salts :

$$K_2Cr_2O_7 + H_2SO_4 + 3\,SO_2 = Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

but for thiosulphate in addition to these there is ppt. of S.

iv) $M(NO_2)_2 + H_2SO_4 = MSO_4 + 2\,HNO_2$

$3\,HNO_2 = HNO_3 + H_2O + 2\,NO$

$2\,NO + O_2 = 2\,NO_2$

$4\,HNO_3 = 2\,H_2O + 4\,NO_2 + O_2$

2.Heating with conc. H_2SO_4 :

$MX_2 + H_2SO_4 = 2HX + MSO_4$ (X = halide ion)

The halogen acids like HBr and HI on strong heating liberate Br_2 (raddish brown) and I_2 (violate) respectively.

$$2HX + H_2SO_4 = X_2 + SO_2 + 2H_2O$$

3. Chromyl chloride test :

$$2MCl_2 + K_2Cr_2O_7 + 6H_2SO_4 = 2M(HSO_4)_2 + 2KHSO_4 + 3H_2O + 2CrO_2Cl_2$$

$$CrO_2Cl_2 + 4NaOH = Na_2CrO_4 + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + Pb(OAc)_2 = PbCrO_4 + 2NaOAc$$

yellow ppt.

4. Heating with Cu – turnings and conc. H_2SO_4 :

$$MNO_3 + H_2SO_4 = HNO_3 + MHSO_4$$

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(brown)

5. Heating with MnO_2 and conc. H_2SO_4 :

$$2MX + 3H_2SO_4 + MnO_2 = 2MHSO_4 + MnSO_4 + 2H_2O + X_2$$

Cl_2 is yellowish green, Br_2 is reddish brown and I_2 is violet.

6. Heating Nitrate and Nitrite salts with Zn – dust and NaOH :

$MNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O$

$MNO_2 + 3Zn + 5NaOH = NH_3 + 3Na_2ZnO_2 + H_2O$

3.5. Test for Interfering Acid Radicals :

3.5.1. Test for Phosphate and Arsenate :

Experiment	Observation	Inference
1. Dissolve the sample in (1:1) HNO_3 and divide the solution in two parts	1.	1.
i) In one part add about 2 ml of ammonium molybdate solution and warm	i) A canary yellow precipitate	i) PO_4^{3-}, AsO_4^{3-}
ii) In second part add about 2 ml of ammonium molybdate solution – 15% tartaric acid reagent and warm	ii) a) A canary yellow ppt. b) No canary yellow ppt.	ii) a) Phosphate b) Arsenate

3.5.2. Test for Borate and Boric acid :

Experiment	Observation	Inference
1. Take a little amount of the sample in a dry test tube . Add 1-2 ml conc. H_2SO_4 and little amount of methyl alcohol, heat and place the mouth of the test tube near the flame.	1. A green-edged flame	1. Borate, free boric acid
2. Take a little amount of the sample in a dry test tube . Add little amount of methyl alcohol, heat and place the mouth of the test tube near the flame. **[If borate is detected then perform this test]**	2. A green-edged flame	2. Free boric acid

3.5.3. Reactions of the Tests for Interfering Acid Radicals :

1. Test for Phosphate and Arsenate :

$$Na_2HXO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 =$$

$$\underset{\text{(Yellow ppt.)}}{(NH_4)_3[XMo_{12}O_{40}]} + 21NH_4NO_3 + 2NaNO_3 + 12H_2O \quad \textbf{[X=P/As]}$$

Note: The commercial formula ammonium molybdate is $(NH_4)_6Mo_7O_{24}$, but for simplicity in equation the above formula is employed]

2. Test for Borate and Boric acid :

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O = 4\,H_3BO_3 + Na_2SO_4$$

$$H_3BO_3 + 3\,CH_3OH = B(OCH_3)_3 + 3\,H_2O$$

3.6. Wet Test for Acid Radicals :

Preparation of Solution :

1. If the sample is soluble in water, dissolve about 0.5 g of the sample in about 20 ml of distilled water and perform wet tests for acid radicals with this aqueous solution.
2. If the sample is insoluble in water or partly soluble or of dark coloured, mix about 0.5 g of the sample with 2 g of Na_2CO_3 (1:4 ratio) in a 100 ml conical flask, fitted with funnel, boil with about 20 ml of distilled water for about 10-15 minutes. Filter the solution and use the filtrate, "Na_2CO_3 extract", to perform wet tests for acid radicals.

Wet Tests for Acid Radicals with Na_2CO_3 Extract :

3.6.1. Test with Sodium nitroprusside solution :

Experiment	Observation	Inference
1. Add to a small part of the Na_2CO_3 extract a few drops of Sodium nitroprusside solution	1. A purple colouration	1. S^{2-}

3.6.2. Ring test for nitrate :

Experiment	Observation	Inference
1. Take about 1 ml of the Na_2CO_3 extract in a test tube, acidify with dil. H_2SO_4, and boil off CO_2. Add 1-2 ml freshly prepared $FeSO_4$ solution and then add cautiously 2-3 ml conc. H_2SO_4 down the side of the inclined test tube without disturbing the solution	1. a) A brown ring is formed at the junction of the two liquids. b) The whole solution turns brown	1. a) NO_3^- b) NO_2^-

3.6.3. Ring test for nitrite :

Experiment	Observation	Inference
1. Take about 1 ml of the extract in a test tube and acidify with 2(N) acetic acid and add 2-3 ml freshly prepared conc. solution of $FeSO_4$. Slowly transfer the solution by the side of the test tube containing conc. H_2SO_4 without disturbing the solution.	1. A brown ring is found at the junction of the two liquids.	1. NO_2^-

3.6.4. Test for Sulphate :

Experiment	Observation	Inference
1. Take about 1 ml of the Na_2CO_3 extract in a clean test tube, acidify with dil. HCl, boil off CO_2 and then add few drops of $BaCl_2$ solution	1. A heavy white precipitate in soluble in HCl	1. SO_2^{2-}

3.6.5. Test for Cl^-, Br^-, I^- and SCN^- :

Experiment	Observation	Inference
1. Take a few ml of the Na_2CO_3 extract in a test tube , acidify with dil. HNO_3, boil off CO_2 and then add few drops of $AgNO_3$ solution.	1. a) A white precipitate, dissolves readily in dil. NH_4OH solution	1. a) Cl^-, SCN^-
	b) A pale yellow ppt., partly dissolves in dil. NH_4OH but readily in strong NH_3	b) Br^-
	c) A light yellow ppt. does not dissolve even in strong NH_3	c) I^-
2. Take about 1 ml of the Na_2CO_3 extract in a test tube and acidify with dilute HNO_3 until faintly acidic (use litmus paper), then add dilute NH_4OH till smell of NH_3. Boil the solution to drive off excess NH_3 (the solution is neutral). Now add few drops of freshly prepared 1% $FeCl_3$ solution	2. Blood red colouration	2. SCN^-

3.6.6. Tests for Nitrate and Nitrite : (Spot Plate Test)

Experiment	Observation	Inference
1. On a spot plate mix a drop of neutral or acetic acid test solution with a drop of sulphanilic acid reagent and a drop of α-naphthylamine reagent	1. Red colouration	1. Nitrite (NO_2^-)
2. On a spot plate mix a drop of neutral or acetic acid test solution with a drop of sulphanilic acid reagent and a drop of -naphthylamine reagent and a pinch of Zn – dust.	2. Red colouration	2. Nitrate (NO_3^-)

3.6.7. Reactions of the Wet Tests for Acid Radicals :

The salts on boiling with Na_2CO_3 solution are converted into soluble Na- salts.

$$MX_2 + Na_2CO_3 = MCO_3 + 2NaX$$

$$MY + Na_2CO_3 = MCO_3 + Na_2Y \quad [M = \text{Divalent metals}]$$

1. Reaction of Sulphide with Na-nitroprusside :

$$Na_2S + Na_2[Fe(CN)_5NO] = Na_4[Fe(CN)_5NOS] \text{ (Violet)}$$

2. a) Reaction of Thiosulphate with $AgNO_3$:

$$Na_2S_2O_3 + 2AgNO_3 = Ag_2S_2O_3$$

$$Ag_2S_2O_3 + 3Na_2S_2O_3 = 2Na_3\left[Ag(S_2O_3)_2\right]\downarrow \text{(White)}$$

$$g_2S_2O_3 + H_2O = Ag_2S\downarrow + H_2SO_4$$

(Black)

b) Reaction of Halides with $AgNO_3$:

$$NaX + AgNO_3 = AgX\downarrow + NaNO_3 \; ; \; [X = Cl, Br, I, SCN]$$

AgCl , AgSCN - White↓; AgBr - Pale yellow↓; AgI - Yellow ↓

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$$

3. Chromyl chloride test for chloride :

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 = \underset{\text{(Orange red vapour)}}{2CrO_2Cl_2} + 2KHSO_4 + 4NaHSO_4 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH = Na_2CrO_4 + 2NaCl + 2H_2O$$

$$2Na_2CrO_4 + CH_3COOH = Na_2Cr_2O_7 + 2CH_3COONa + H_2O$$

$$Na_2Cr_2O_7 + 2Pb(CH_3COO)_2 + H_2O = 2PbCrO_4\downarrow + 2CH_3COONa + 2CH_3COOH$$

(Yellow)

4. Reaction of Thiocyanate with $FeCl_3$:

$$FeCl_3 + NaSCN = [Fe(SCN)]Cl_2 \text{ (Blood red)} + NaCl$$

$[Fe(SNC)_2]^+$, $[Fe(SCN)_3]$ and $[Fe(SCN)_4]^-$ species are also produced

5. Reaction of Sulphate with $BaCl_2$:

$$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl$$

6. Ring test of Nitrate :

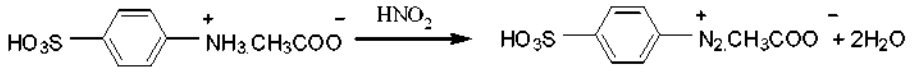
$$2NaNO_3 + 6FeSO_4 + 5H_2SO_4 = 3Fe_2(SO_4)_3 + NO + 2NaHSO_4 + 4H_2O$$

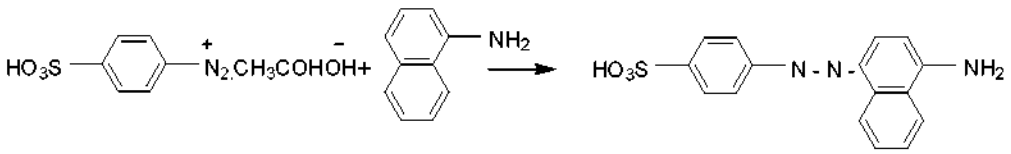
$$[Fe(H_2O)_6]SO_4 + NO = [Fe(H_2O)_5NO]SO_4 + H_2O$$

(Brown ring)

7. Azo – dye test for Nitrite :

$$NaNO_3 + CH_3COOH = HNO_2 + CH_3COONa$$





3.7. Wet Tests for Basic Radicals

3.7.1. Preparation of solution for Group Analysis :

<table>
<tr><td colspan="4">Take about 0.5 g of the sample in a test tube and shake well with about 10 ml of distilled water and filter.</td></tr>
<tr><td rowspan="4">Filtrate :
1 ml of the aqueous extract is evaporated to dryness, if a residue was left, then proceed with the aqueous extract for group analysis.</td><td colspan="3">Residue : It is boiled with about 10 ml dil. HCl and if residue left, then boiled with about 10 ml conc. HCl, filtered and wash the resiue with dil. HCl.</td></tr>
<tr><td rowspan="3">Filtrate :
1 ml of the extract is evaporated to dryness, if residue is left.
Then perform the group analysis with this extract.</td><td colspan="2">Residue : It is boiled with about 10 ml of aqua regia, NO_2 fumes are boiled off, evaporated to dryness and extract with 10 ml dil. HCl. Filter and wash the residue with dil. HCl.</td></tr>
<tr><td>Filtrate : 1 ml of the extract is evaporated to dryness, if residue is left.
Then perform the group analysis with this extract.</td><td>Residue :
Insoluble part.</td></tr>
</table>

3.7.2. General Group Separation :

Test for K^+ and NH_4^+ are to be performed with the aqueous solution of the sample before proceeding for the general group separation.

Table – 1 : Test for K^+ and NH_4^+

Experiment	Observation	Inference
1. Boil 2 ml of the sample solution with dil. NaOH solution to remove NH_3, if any, and divide into two parts	1.	1.
a) Acidify one part of the above solution with acetic acid and add sodium cobaltinitrate solution	a) A yellow precipitate	a) K^+ confirm
b) To the other part of the solution add saturated tartaric acid solution and scratch the inner wall of the test tube with a glass rod.	b) A white crystalline precipitate	b) K^+ confirm
2. a) To the aqueous solution of the sample add NaOH and heat	2. a) Vapour comes with smell of NH_3 and turns red litmus paper to blue.	2. a) NH_4^+ confirm
b) To the aqueous solution of the sample add Nessler's Reagent	b) A brown precipitate	b) NH_4^+ confirm

Table – 2 : General Group Separation of Basic Radicals

<table>
<tr><td colspan="5">To about 5 ml of the aqueous solution of the sample, add few drops of dil. HCl. Or allow to cool the hot HCl solution of the sample and centrifuge</td></tr>
<tr><td rowspan="5">Residue : Gr. – I present White ppt. $PbCl_2$</td><td colspan="4">Centrifugate: [If AsO_4^{3-} is detected, boil the solution with SO_2 – water and then boil off SO_2]. Warm the solution and pass H_2S gas till precipitation is complete and then centrifuge</td></tr>
<tr><td rowspan="4">Residue : Gr. –II (A + B) present CuS, PbS, Bi_2S_3 – All black CdS, As_2S_3, SnS–All yellow Sb_2S_3 – Orange</td><td colspan="3">Centrifugate : Boil off the H_2S and reduce the volume by evaporation, boil the solution with 2-3 drops of conc. HNO_3.
If borate is present evaporate the solution to dryness for 3 to 4 times with conc. HCl.If phosphate is present, remove it completely by $FeCl_3$ – acetate buffer method.
To the centrifugate, add about 1g of solid NH_4Cl and a boil. Now add excess Nh_4OH solution till ammoniacal and centrifuge.</td></tr>
<tr><td>Residue : Gr.-III A present $Fe(OH)_3$ - brown $Cr(OH)_3$ -Dirty green $Al(OH)_3$ - Gelatinous white $MnO_2 6+.xH_2O$ - brown</td><td colspan="2">Centrifugate : Pass H_2S till the precipitation is complete and centrifuge</td></tr>
<tr><td rowspan="2">Residue : Gr.- IIIB present CoS, NiS - All black MnS- Flesh coloured ZnS -White</td><td colspan="2">Centrifugate : Boil off H_2S and reduce the volume to half by evaporation. Add NH_4OH till ammoniacal, then add saturated $(NH_4)_2CO_3$ solution and warm and centrifuge</td></tr>
<tr><td>Residue : Gr. - IV present $BaCO_3$, $SrCO_3$, $CaCO_3$ – All white</td><td>Centrifugate :Add Na_2HPO_4 solution and shake well. White precipitate Mg^{2+} of Gr.– V present</td></tr>
</table>

Table – 3: Treatment of the ppt. of Gr. – I

Group I precipitate is dissolved by heating the precipitate with dil. HNO_3 or distilled water. Divide the solution into three portions and carry out the following tests.

Experiment	Observation	Inference
1. To one portion of the above solution add dilute H_2SO_4.	1. A white precipitate of $PbSO_4$ is obtained	1. Pb^{2+} is confirmed
2. To another portion, add potassium chromate solution	2. A yellow precipitate is obtained	2. Pb^{2+} is confirmed
3. To the 3rd portion, add KI solution To above yellow precipitate, add some H_2O, boil and then cool	3. A yellow precipitate is obtained. Precipitate dissolves and reappears in the form of golden spangles.	3. Pb^{2+} is confirmed

Table – 4 : Separation of Arsenate

If arsenate is present as indicated by the ammonium molybdate test, it should be reduced before proceeding for Gr. – II.

Add sulphurous acid solution or a pinch of $NaHSO_3$ to the filtrate and boil off SO_2. If Ba^{2+}, Sr^{2+} and Pb^{2+} are present, a white precipitate of sulphates of the metals comes down in this case, filter	
Residue : Examine the residue for Ba^{2+}, Sr^{2+} and Pb^{2+}.	**Filtrate :** Pass H_2S and proceed in the usual way from Gr.- II

Table – 5 : Separation of ppt. of Gr. – IIA and IIB

Transfer the precipitate in a 100 ml beaker, add yellow ammonium sulphide solution or 2(N) KOH, warm, filter and wash the ppt. with water	
Residue : Gr.- IIA Residue may contain PbS, Bi_2S_3, CuS, CdS	**Filtrate : Gr. – IIB** Dilute with water. Acidify the filtrate with dilute HCl and filter, reject the filtrate. Yellow or orange ppt. may contain – As_2S_3, Sb_2S_3, SnS

[Analyse the precipitate as per Table]

Table – 6 : Treatment of the precipitate of Gr.- IIA

<table>
<tr><td colspan="3">Transfer the precipitate in a 100 ml beaker and boil with 1:3 HNO_3. Take a little of the solution in a test tube and add few drops of dil. H_2SO_4 – white ppt. – Pb^{2+} present.
If Pb^{2+} is present, add dil. H_2SO_4 and ethyl alcohol to the main bulk and filter.
If Pb^{2+} is absent do not add H_2SO_4 and alcohol.</td></tr>
<tr><td rowspan="2">Residue :
White $PbSO_4$. Dissolve the ppt. in saturated NH_4-acetate solution and add K_2CrO_4 solution – Yellow ppt. – Pb^{2+} present</td><td colspan="2">Filtrate : Boil off alcohol if added earlier and add excess NH_4OH and filter.</td></tr>
<tr><td>Residue : White.Wash the ppt. with water and dissolve in dil. HCl.i) Add 2-3 drops of this solution into a beaker full of water and stir – the water turns milky – Bi^{3+} presentii) To the other part of the solution, add freshly prepared Na-stannite solution – Black ppt. of finely divided metallic bismuth – Bi^{3+} present.</td><td>Filtrate : If filtrate is colourless Cu^{2+} is absent, test directly for Cd^{2+}; pass H_2S – yellow ppt. – Cd^{2+} present. If filtrate is blue; i) Acidify a part of the filtrate with dil. Acetic acid and add $K_4[Fe(CN)_6]$ solution – Reddish brown ppt. – Cu^{2+} presentii) To another part add KCN solution dropwise till the colour of Cu^{2+} is discharged, then pass H_2S for 10 – 20 second (better add H_2S – water) – yellow ppt. – Cd^{2+} present.</td></tr>
</table>

*** Note : To avoid the use of dangerously poisonous KCN for the separation of Cu^{2+} and Cd^{2+} :**

i) Iron fillings may be used in acetic acid medium to reduce Cu^{2+} to Cu

$E^0_{Cu^{2+}/Cu} = 0.35V$, $E^0_{Cd^{2+}/Cu} = -0.40V$ and $E^0_{Fe^{2+}/Fe} = -0.44V$]

ii) Add KI solution to reduce Cu^{2+} into sparingly soluble Cu_2I_2. After filtration, iodine may be removed from the filtrate containing Cd^{2+} by extracting with CCl_4 and pass H_2S through the aqueous solution. Yellow CdS will be precipitated.

Table – 7 : Treatment of the precipitate of Gr.- IIB

Transfer the Gr.-IIB precipitate in a 100 ml beaker and boil with conc. HCl and filter	
Residue : Yellow, may contain As_2S_3.Dissolve the ppt. in aqua regia, evaporate nearly to dryness, dilute with water and divide into two parts : i) Add excess NH_4OH and then add magnesia mixture – A white ppt. – As^{3+} confirm ii) Add ammonium molybdate solution and warm – Canary yellow ppt. – Confirms the presence of As^{3+}.	**Filtrate :** May contain Sb^{3+} and/ or Sn^{2+}.Divide the filtrate into three parts : i) To one part add NH_4OH in excess and then add a little of oxalic acid, boil and pass H_2S – A orange ppt. – Sb^{3+} confirm ii) Other part of the solution partly neutralise with NH_4OH, add few pieces of iron wire and boil for a few minutes (if Sb^{3+} is present will be removed as black ppt.). Filter and add $HgCl_2$ solution to the filtrate – A grey or white ppt. – Confirms Sn^{2+}. iii) Take about 1 drop of the solution in a spot plate and treat with 5-10 mg of Mg powder., add 2 drops of $FeCl_3$ solution, 2-3 drops of tartaric acid solution, 1-2 drops of dimethylglyoxime reagent, and then dilute NH_3 solution until basic. – Red colouration – Sn confirm

Table – 8 : Separation of Phosphate by $FeCl_3$ – Acetate buffer method :

<table>
<tr><td colspan="4">Boil off H_2S from the filtrate of Gr. – II, again boil with few drops of conc. HNO_3 to oxidise Fe^{2+} (if present) to Fe^{3+} (Test for Fe^{3+} with $K_4Fe(CN)_6$]) . Little amount of the solution + $K_4Fe(CN)_6$ – Prussian blue ppt. – Fe^{3+} presentTo the main bulk of the solution, add solid NH_4Cl and NH_4OH in excess, until the smell of NH_3 persists. Dissolve the precipitate formed by adding dilute HCl drop wise. Add NH_4OH dropwise until a faint ppt. just appears. Add equal volume of buffer solution prepared by mixing 4 ml glacial acetic acid and 36 ml of saturated ammonium acetate solution (pH ≈ 4.6), ignore if any ppt. appears. Add freshly prepared $FeCl_3$ solution drop wise with constant stirring until the solution turns to brownish-red (raw tea) colour. Dilute the mixture with water and boil for about 1-2 minutes and filter. Wash the residue with hot water.</td></tr>
<tr><td colspan="2">Residue : [May contain PO_4^{3-}, basic acetate of Fe^{3+}, Al^{3+}, Cr^{3+} and also $Fe_2O_3 \cdot xH_2O$].
Group- IIIA may present.Boil the precipitate with a mixture of 5ml 10% NaOH and 5 ml 3% H_2O_2 for 2-3 minutes and then filter.</td><td colspan="2">Filtrate :
Concentrated the filtrate by evaporation to a small volume. Add solid NH_4Cl and excess NH_4OH solution and filter.</td></tr>
<tr><td>Residue :
($FePO_4$ + $Fe_2O_3 \cdot xH_2O$)
Rejected.</td><td>Filtrate :
May contain $NaAlO_2$ and / or Na_2CrO_4.
Examine for Al^{3+} and Cr^{3+}.</td><td>Residue :
May contain
$Fe(OH)_3$.
Rejected.</td><td>Filtrate :
Check the removal of PO_4^{3-}.
Examine for Groups – IIIB, IV and V.</td></tr>
</table>

Table – 9 : Removal of BO_3^{3-} (Borate) :

Evaporate the filtrate of Group – II nearly to dryness in a porcelain basin. Add about 2 ml of conc. HCl, evaporate to dryness. Repeat the process for 3-4 times with conc. HCl.

Table – 10 : Treatment of ppt. of Gr. – IIIA :

Transfer the precipitate in a test tube, add dil. NaOH solution and 1 g of Na_2O_2 or 3 ml 10 volume H_2O_2 and boil till effervescence ceases and centrifuge.	
Residue : Brown – $Fe(OH)_3$ also $MnO_2.xH_2O$ Dissolve it into dil. HNO_3 and divide in two parts: i) Add $K_4[Fe(CN)_6]$ solution – Deep blue colouration or ppt. – Fe^{3+} ii) Add a pinch of $NaBiO_3$ – solution turns to Pink – Mn^{2+} present	**Centrifugate :** May contain colourless $NaAlO_2$ and / or yellow Na_2CrO_4. Divide it into two parts : i) Add solid NH_4Cl to a part of the solution and boil – A white gelatinous ppt. – Al^{3+} present. ii) Acidify the other part with acetic acid and add lead acetate solution – Yellow ppt. – Cr^{3+} present.

If Fe^{3+} is found in Group – IIIA, then it necessary to find whether iron present in Fe^{2+} or Fe^{3+} state in the original sample.

Prepare original sample solution and perform the following tests :

Table – 11 : Test for Fe^{2+} and Fe^{3+} :

Experiment	Fe^{2+} present	Fe^{3+} present
1. Treat a little part of the solution with $K_4[Fe(CN)_6]$ solution	1. White or pale blue ppt.	1. Prussian blue colour or ppt.
2. Take 1 ml of the sample solution in a test tube and add 1 drop of $K_3[Fe(CN)_6]$ solution.	2. Turnbull's blue.	2. A brown colouration.
3. Take 1 ml of the sample solution in a test tube and add 1 drop of NH_4CNS or KCNS solution.	3. No colour change.	3. A blood red colouration.

Table – 12 : Treatment of the ppt. of Gr. – IIIB :

<table>
<tr><td colspan="3">Transfer the precipitate in a test tube, add 1(N) HCl (i,e. 1:11), warm and centrifuge.</td></tr>
<tr><td rowspan="2">Residue : CoS and NiS
i) Confirm the presence of by borax bead test.
ii) Dissolve the precipitate in aqua regia, evaporate to dryness and extract with dil. HCl and divide into two parts:
a) In one part add NH_4OH till just ammoniacal, add few drops of dimethylglyoxime – Rose red ppt. – Ni^{2+} present
b) In second part add 1 ml NH_4SCN solution, 1 ml amyl alcohol, a pinch of NH_4HF_2 and shake - alcohol layer turns blue - Co^{2+} present.</td><td colspan="2">Centrifugate :
Boil off H_2S, Add excess NaOH solution, warm and centrifuge.</td></tr>
<tr><td>Residue :
Flesh colour due to $MnO_2.xH_2O$.
Dissolve the precipitate in dilute HNO_3 and add a pinch of $NaBiO_3$ - Colour changes to pink - Mn^{2+} present.</td><td>Centrifugate :
May contain Na_2ZnO_2.
Acidify with dil. Acetic acid and pass H_2S - white ppt. – Zn^{2+} present.</td></tr>
</table>

Table – 13 : Treatment of the ppt. of Gr. – IV :

<table>
<tr><td colspan="3">Dissolve the precipitate in hot 2(N) acetic acid in a test tube. Transfer few drops of the hot solution in a test tube and add few drops of K_2CrO_4 solution - Yellow ppt. – Ba^{2+} present.If Ba^{2+} is present, in this case add K_2CrO_4 solution to the main bulk till the solution is coloured slightly yellow, warm the solution and allow the precipitate to settle down and centrifuge.</td></tr>
<tr><td rowspan="2">Residue :
Yellow $BaCrO_4$.
i) Confirm Ba^{2+} by flame test.
ii) dissolve the ppt. in dil. HCl and then treat with dil. H_2SO_4 - A white ppt. - Ba^{2+} present.</td><td colspan="2">Centrifugate :Add a little of Na_2CO_3, white ppt. indicates the presence of $SrCO_3$ and / or $CaCO_3$. Wash the ppt. with hot water and ten dissolve it in dilute acetic acid, add saturated solution of $(NH_4)_2SO_4$, heat to boil and centrifuge.</td></tr>
<tr><td>Residue :
White , $SrSO_4$.
Perform flame test - Crimson flame - Sr^{2+} present.</td><td>Centrifugate :
Add NH_4OH till ammoniacal and add ammonium oxalate solution and warm - White ppt. - Ca^{2+} present.</td></tr>
</table>

3.8. Treatment of the Aqua Regia Soluble Samples

Aqua regia soluble salts are As_2S_3 and SnS_2 :

The residue obtained after treatment with conc. HCl is boiled with about 10 ml of aqua regia, brown coloured NO_2 fumes are boiled off, evaporate to dryness and then extracted with 10 ml of dilute HCl. Filter and wash the residue, if any, with dilute HCl. Perform the analysis with the filtrate following the **tables – 4, 5, 8**.

3.9. Treatment of Insoluble Residue

List of the insoluble substances :

White : Al_2O_3, SnO_2, $PbSO_4$, $SrSO_4$ and $BaSO_4$

Dark red : Fe_2O_3

Green : Cr_2O_3

3.9.1. Dry Test for Insoluble Residue :

Table – 3.9.1 : Dry Test for Insoluble Residue

Experiment	Observation	Inference
1. Heat a little amount of the insoluble residue in a dry test tube.	1. colour changes from pale yellow to orange	1. SnO_2
2. Heat the insoluble residue (white) with ammonium acetate solution in a test tube.	2. Residue dissolves	2. $PbSO_4$
3. Borax bead test (for coloured sample)	3. <table><tr><th>Oxidising flame</th><th>Reducing flame</th></tr><tr><td>i) Green ii) Yellow</td><td>Green Bottle green</td></tr></table>	3. i) Cr_2O_3 ii) Fe_2O_3
4. Flame test	4. i) Apple green colour ii) Persistent crimson colour iii) Lambent blue colour	4. i) Ba^{2+} ii) Sr^{2+} iii) Pb^{2+}

3.9.2. Wet Test for Insoluble Residue

Table – 3.9.2 : Treatment for $PbSO_4$

Boil the insoluble residue with a saturated solution of ammonium acetate and add few drops of acetic acid. Divide the solution in two parts.		
Experiment	**Observation**	**Inference**
i) In one part add K_2CrO_4 solution	i) A yellow precipitate	i) Pb^{2+} confirm
ii) In second part add dil. HNO_3, warm the mixture and then add $Ba(NO_3)_2$ solution	ii) A white precipitate	i) SO_4^{2-} confirm

Table – 3.9.3 : Alkali Fusion for $BaSO_4$, $SrSO_4$, SnO_2 and Al_2O_3

Fuse a mixture of 1 part of the insoluble residue, 4 parts of fusion mixture (or anhydrous Na_2CO_3) and a bead of NaOH in a nickel crucible to a clear melt. Allow to cool, extract the melt with boiling water and filter.	
Residue : May contain carbonate of Ba^{2+} and Sr^{2+} and unreacted solid. Boil with dilute acetic acid and filter. Reject the residue and perform group IV analysis with the filtrate.	**Filtrate :** May contain SO_4^{2-} , AlO_2^- and SnO_3^{2-}. Acidify with conc. HCl.If precipitate appears, boil, evaporate to dryness, bake for about 20 minutes, cool, extract with dilute HCl and filter. Reject the residue.
Fitrate : Divide into four parts and perform the following tests. i) To one part add $BaCl_2$ solution - A white ppt. - SO_4^{2-} confirm ii) Boil another part with solid NH_4Cl - White gelatinous ppt. - Al^{3+} confirm iii) Pass H_2S through the another part - A yellow ppt. - Sn^{4+} confirm (SnO_2) iv) The rest part is made alkaline with NaOH solution, add 2 drops of alizarin – S reagent and then add 2 (N) acetic acid drop wise until the violet colour of the solution just turns to pink, boil in a water bath - A red ppt. - Al^{3+} confirm	

Table – 3.9.4 : Sulphur fusion for SnO_2

Fuse a mixture of 1 part of the residue, 2 parts of anhydrous Na_2CO_3 and 2 parts of sulphur powder in a covered porcelain crucible. Cool and extract with boiling water and filter.		
Experiment	**Observation**	**Inference**
Acidify the solution with dilute HCl	A yellow precipitate	Sn^{4+} (SnO_2) confirm

Table – 3.9.5 : Treatment of Al_2O_3 , Cr_2O_3 and Fe_2O_3 with $KHSO_4$

Mix $KHSO_4$ to the insoluble residue in the portion of 1 : 8 in a nickel crucible. Fuse it to the molten condition. Cool and extract with 2(N) H_2SO_4. Examine the cations according to Gr. – IIIA table.

3.10. Spot Tests for Basic Radicals

Test for/Reagent	Experiment	Observation	Inference
Test for Pb^{2+} : **i) Cinchonine Potassium Iodide test :** Reagent :Take 10 ml of distilled water and acidify with dil. HNO_3, and then heat to boiling and dissolve 0.1 g of cinchonine in it. Cool the solution and add 0.2 g of KI in it.	i) Moisten a filter paper with the cinchonine – potassium iodide reagent and then place a drop of faintly acidic test solution containing Bi^{3+}, Pb^{2+}, Cu^{2+} on it. Three zones appear on the filter paper.	i) a) An orange ring is formed b) A deep yellow ring is formed c) A brown ring is formed	i) a) Bi^{3-} confirm b) Pb^{2+} confirm c) Cu^{2+} confirm
ii) Benzidine test : Reagent :Prepare 0.05 per cent solution of benzidine in 10 % acetic acid.	ii) Place a drop of test solution upon drop-reaction paper, and treat successively with 2 drops of 3(N) NaOH solution and 1 drop of saturated bromine water. Add 2 drops of 1:1 ammonia solution; remove the excess ammonia by waving the paper over a small flames. Add 2 drops of the reagent.	ii) A blue colour develops	ii) Pb^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Cu^{2+} : *i)* α **– Benzoin oxime (or Cupron) test:** Reagent: Dissolve 0.5g of α – benzoin oxime in 10 ml 95% alcohol (rectified spirit).	i) Take little amount of the sample in a dry test tube and heat it strongly to remove any ammonium salt which may interfere (perform this if the sample contain NH_4^+ - salt), cool and dissolve the residue in dilute HCl. Place a drop of faintly acidic test solution on a filter paper, add a drop of 10% Rochelle salt solution (to prevent the precipitation other ions) and then add a drop of the reagent. Hold the filter paper over ammonia vapour.	i) Green colouration is obtained.	i) Cu^{2+} confirm
ii) Dithio – oxamide (or Rubeanic acid) test : Reagent :0.5 % solution of Rubeanic acid in 95% ethyl alcohol (It does not keep well and should be prepared as required).	ii) Place a drop of neutral test solution upon a filter paper and exposed it to ammonium vapour and add a drop of the reagent. If test solution contains Cu^{2+}, Ni^{2+}, Co^{2+}; then three zones or circle are formed.[Trace of copper in distilled water give a positive reaction, hence, a blank test must be carried out with the distilled water].	ii) a) At center olive green or black ring b) Green ring surrounded by a yellow-brown ring c) Outer ring is of bluish-violet	ii) a) Cu^{2+} confirm b) Cu^{2+} confirm c) Ni^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Bi^{3+} : **i) Cinchonine Potassium Iodide test :**Reagent :Take 10 ml of distilled water and acidify with dil. HNO_3, and then heat to boiling and dissolve 0.1 g of cinchonine in it. Cool the solution and add 0.2 g of KI in it.	i) Moisten a filter paper with the cinchonine – potassium iodide reagent and then place a drop of faintly acidic test solution containing Bi^{3+}, Pb^{2+}, Cu^{2+} on it. Three zones appear on the filter paper.	i) a) An orange ring is formed (bismuth – cinchonine iodide ppt.) b) A deep yellow ring is formed (PbI_2) c) A brown ring is formed (CuI_2)	i) a) Bi^{3+} confirm b) Pb^{2+} confirm c) Cu^{2+} confirm
ii) With alkaline Stannite solution :Reagent :a) 1 g of $SnCl_2$ mix with 1 ml of conc. HCl and pour into 20 ml of distilled water.b) Prepare 25% NaOH solution.Reagent prepare by mixing equal volumes of (a) and (b).	ii) Place 1 drop of the test solution and 1 drop of freshly prepared stannite solution on a clean spot plate.	ii) Black precipitate is formed (metallic bismuth)	ii) Bi^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Cd^{2+} : i) Diphenyl carbazide test : Reagent : Prepare cold saturated solution of diphenyl	i) Place 1 drop of diphenyl carbazide (saturated with KCNS and KI) on a filter paper, dry by waving, add 1 drop of test solution and exposed on ammonia fumes.	i) A violet ring is formed.	i) Cd^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
carbazide in 90% alcohol, again saturated with KCNS and add a few crystals of KI. [*This test can be performed directly with the HCl solution without separating other ions of Gr. – II].*			
ii) Cadmium sulphide test : [Cd^{2+} in presence of Ni^{2+}, Cu^{2+} , Co^{2+} and Zn^{2+}]	ii) In original acid solution add NH_4OH, warm, centrifuge and carry out the test on the supernatant liquid containing mentioned cations. Place 1 drop of the test solution on a clean spot plate and add 1 drop of KCN solution to discharge the colour of Ni^{2+}, Cu^{2+} , Co^{2+} and then add 1 drop of Na_2S solution.	i) Yellow ppt. is formed.	ii) Cd^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for As^{3+} : **i) $AgNO_3$ solution test :** Reagent : 1% $AgNO_3$ solution.	i) Take 2 drops of the test solution in a semi-micro test tube and add 2 drops of NH_3. Add 2 drops of 6% (20 volume) of H_2O_2. Acidify with dilute acetic acid. Now	i) Red ring is formed.	i) As^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
	place 1 drop of the solution on a filter paper and then add 1 drop of $AgNO_3$ solution.		
ii) Stannous chloride solution test : Reagent : a) 5 (N) NH_4OH b) 6% (20 volume) H_2O_2 c) 10% $MgCl_2$ solution d) 10% $SnCl_2$ in conc. HCl.	ii) take 1 drop of the test solution in a semi- micro crucible or basin is mixed with 2 drops of NH_3 and add 2 drops of H_2O_2 and few drops of $MgCl_2$ solution. Evaporate the mixture to dryness, then ignite strongly and cool. Treat the residue with 1-2 drops of conc. HCl followed by 1 drop of $SnCl_2$ solution.	ii) A brownish black ppt.	ii) As^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Sb^{3+} : **i) Phosphomolybdic acid test :** Reagent : 5% aqueous solution of phosphomolybdic acid ($H_3[PMo_{12}O_{40}]$). [Phosphomolybdic acid is reduced by both Sn^{2+} and Sb^{3+} but ammonium phosphomolybdate is reduced only by Sn^{2+}]	i) The test solution may consist of the filtered solution obtained by treating the Gr.-IIB ppt. with HCl. [*Antimony is present as $SbCl_3$ and the tin as $SnCl_4$, which has no effect upon the reagent*]. Place a drop of the test solution upon a filter paper which has been impregnated with the phosphomolybdic acid reagent and hold the paper in steam.	i) A blue colouration appears	i) Sb^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
ii) Rhodamine – B test : Reagent : 0.01% aqueous solution of the dyestuff.	ii) Place 1 drop of the test solution in conc. HCl on a spot plate .Add a minute crystal of $NaNO_2$ to the solution and stir with a glass rod ($NaNO_2$ oxidised Sb^{3+} to Sb^{5+}), add a drop of the reagent and stir.	ii) The bright red colour of the reagent changes to blue.	ii) Sb^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Sn^{2+} : i) Cacotheline (nitro derivative of brucine, $C_{21}H_{21}N_3O_7$) test : Reagent : 0.25% aqueous solution of cacotheline.	i) The test solution may consist of the filtered solution obtained by treating the Gr.-IIB ppt. with HCl. [*If tin is in the Sn(IV) state, it should be reduced previously with aluminum or magnesium, and the solution filtered*]. Place a drop of the test solution on a spot plate and add a drop of the reagent.	i) A violet (purple) colouration	i) Bi^{3+} confirm
ii) Ammonium phosphomolybdate test : Reagent : Aqueous suspension of ammonium phosphomolybdate.	ii) Place a drop of the acidic test solution on a spot plate and add a drop of aqueous suspension of the reagent.	ii) A change of yellow colour to blue.	ii) Sn^{2+} confirm
iii) Methylene blue test : Reagent : 1% methylene blue in (N) HCl.	iii) Place 1 drop of methylene blue on a clean spot plate and add a drop of the test solution in HCl.	iii) Discharge the blue colour.	iii) Sn^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Fe^{3+} : **i) Ammonium thiocyanate test:** Reagent : 1% aqueous solution of NH_4CNS	i) Place a drop of test solution on a spot plate and add 1 drop of test solution in 2(N) HCI.	i) Blood red colouration	i) Fe^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Fe^{2+} : **i) Potassium ferricyanide test :** Reagent : Aqueous solution of $K_3[Fe(CN)_6]$.	i) Place 1 drop of the test solution and 1 drop of 6(N) HCl on a spot plate. Add 2 drops of $K_3[Fe(CN)_6]$. Solution.	i) A deep blue ppt.	i) Fe^{2+} confirm
ii) **o- Phenanthroline test :** Reagent : 0.1 % aqueous solution.	ii) Place 1 drop of slightly acidic test solution on a spot plate and add 1 drop of the reagent.	ii) Red colouration.	ii) Fe^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Al^{3+} : **i) Alizarin – S or sodium salt Alizarin Sulphonic acid Reagent test :** Reagent : 0.1% aqueous solution of Alizarin-S.	i) Take a little amount of test solution in a test tube and treat with sufficient (N) NaOH solution so that Al^{3+} is converted to AlO_2^-. Place 1 drop of this solution on a spot plate, add a drop of the reagent, then drops of acetic acid	i) A red colouration or precipitate appears.	i) Al^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
	until the violet colour just disappears and 1 drop in excess.		
2. Alizarin test : Reagent : a) 2% alcoholic solution of Alizarin b) 40% $K_4[Fe(CN)_6]$ solution c) Liq. Ammonia Perform a blanc test.	ii) Boil the sample with NaOH solution and centrifuge which may contain AlO_2, ZnO_2, SnO_2 and PbO_2. Impregnate a filter paper with a drop of $K_4[Fe(CN)_6]$ solution, dry and add 1 drop of test solution, then add 1 drop of alcoholic solution of Alizarin on the spot and dry over ammonia.	ii) A red ring forms	ii) Al^{3+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Ni^{2+} : **1. Dimethyl glyoxime test :** Reagent : 1% alcoholic solution of dimethyl glyoxime.	1. Place a drop of test solution and a drop of the reagent on a spot plate, add a drop of NH_4OH solution.	1. A rose red colouration or ppt.	1. Bi^{3+} confirm
2. Rubeanic acid test : Reagent : 0.5% solution in water.	2. One drop of test solution is placed on a filter paper. It is held over ammonia vapours. Then 1 drop of reagent is added. (Cu, Fe and Co interfere).	2. Blue or blue-violet spot	2. Ni^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Co^{2+}: **1. Ammonium thiocyanate test :** Reagent : 10% aqueous solution of NH_4CNS	1. Place 1-2 drops of slightly acidic test solution on a spot plate and add few mg of NH_4HF_2 and 5 drops of NH_4CNS solution in amyl alcohol or acetone.	1. Blue alcoholic or acetone layer	1. Co^{2+} confirm
2. Sodium 1 Nitroso-2 hydroxynaphthalene-3:6 disulphonate (Niroso-R- salt) reagent : Reagent : 1% aqueous solution of Nitroso-R-salt.	2. Place a drop of neutral test solution (buffered with sodium acetate) on a spot plate, and add 2-3 drops of the reagent.	2. A red colouration.	2. Co^{2+} confirm
3. α-Nitroso- β-naphthol reagent : Reagent : 1% solution of α-nitroso –β- naphthol in 50% acetic acid or in ethyl alcohol or in acetone.	3. Place a drop of the slightly acid test solution on a filter paper and add a drop of the reagent.	3. A brown stain will produce.	3. Co^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Mn^{2+} : **1. Sodium bismuthate test :**	1. Place a drop of the test solution on a spot plate, add a drop of conc. HNO_3 and then add a little solid sodium bismuthate ($NaBiO_3$).	1. A purple colour of permanganic acid appears. [If the solution is so dark that the colour cannot be detected, dilute the mixture with water until the colour appears.]	i) Mn^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
2. Formaldoxime reagent : Reagent : 2.5% aqueous solution of formaldoxime.	2. Place 2 ml. of test solution, which has been rendered just alkaline with 4N NaOH, into a semimicro test tube and add 1 drop of the reagent.	2. A red colouration.	i) Mn^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Zn^{2+} : 1. Ammonium mercuri-thiocyanate test : Reagent : i) Dissolve 8 gms of $HgCl_2$ and 9 gms of ammonium thiocyanate in 100 ml of distilled water. ii) 0.1% $CuSO_4$ solution.	1. Place a drop or two of the test solution, which is slightly acidic (preferably with H_2SO_4), on a spot plate, add 1 drop of 0.1% $CuSO_4$ solution and 1 drop of the ammonium mercuric thiocyanate reagent. * The reaction may also be conducted in semimicro test tube ; here 0.3 – 0.5 ml amyl alcohol is added. [*Instead of $CuSO_4$, one drop of 0.02% $Co(NO_3)_2$ solution can be added.*]	1. A violet or blackish- purple precipitate. *The violet precipitate collects at the interface.	i) Zn^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Ca^{2+} : Calcium oxalate test: Reagents: i) 10% Na_2EDTA ii) 10% $Al(NO_3)_3$ iii) 10% potassium oxalate solution iv) Acetate buffer of pH 4 (10 gms CH_3COONa + 20 ml glacial acetic acid + 75 ml water)	Place 1 drop of EDTA and 1 drop of $Al(NO_3)_3$ to 1 drop of the test solution in a semimicro test tube followed by the addition of 4 drops buffer solution and 2 drops of potassium oxalate solution. Warm the mixture on a water bath for about 5 minutes.	White crystalline precipitate (CaC_2O_4)	i) Ca^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for Ba^{2+}/Sr^{2+}: **1. Sodium Rhodizonate test :** Reagent : 0.5% aqueous solution of sodium rhodizonate. [*It does not keep well so that only small quantities should be prepared at a time.*]	1. i) Place a drop of the neutral test solution upon a filter paper and a drop of the reagent. Treat the reddish- brown spot with a drop of 0.5N HCl ***ii) In presence of Ba^{2+}*** : Impregnate a piece of filter paper with saturated $K_2Cr_2O_7$ solution, dry it. Place a drop of the test solution on this paper. After 1 minute add a drop of the reagent (sodium rhodizonate solution).	1. i) A brown or reddish- brown spot appears. a) A bright red stain is formed b) The spot disappears ii) A brownish – red spot or ring forms.	1. i) Ba^{2+} or Sr^{2+} present a) Ba^{2+} confirm b) Sr^{2+} confirm ii) Sr^{2+} confirm
2. Test with 40% aqueous ammonium sulphate solution :	2. In a test tube take 2 drops of test solution, 1 drop of 4N HCl and 2 drops of 40% $(NH_4)_2SO_4$ solution. Place the mixture in a hot water bath for about 5 minutes.	2. A white precipitate.	2. Sr^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Tests for Mg^{2+} : **1. Quinalizarin test:** Reagent : i) 0.02% alcoholic solution of quinalizarin ii) 2N NaOH solution.	1. After the separation of cations up to Gr. IV, take a few drops of the test solution on a spot plate and add 2-3 drops of alcoholic quinalizarin solution and then add few drops of 2N NaOH solution. *(Perform a blank test)*	i) A blue precipitate or colouration	1. Mg^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
2. Titan yellow test: Reagents : i) 0.1% aqueous solution of titan yellow. ii) 0.1N NaOH solution.	2. After the separation of cations up to Gr. IV, take a drops of the test solution on a spot plate, introduce a drop of the reagent and a drop of 0.1N NaOH solution.	2. A red precipitate or colouration	2. Mg^{2+} confirm

Test for/Reagent	Experiment	Observation	Inference
Test for K^+ : Sodium cobalti-nitrite test : Reagents : i) Sodium cobalti nitrite ii) 0.05% $AgNO_3$ solution.	Place a drop of the neutral or slightly acidic test solution on a spot plate. Add a drop of 0.05% $AgNO_3$ solution and a speck of sodium cobalti nitrite and then stir with a glass rod.	A yellow precipitate	K^+ confirm
Test for NH_4^+ : Nessler's Reagent test : Reagent : Nessler's reagent	Place a drop of the test solution on a spot plate. Add 1 drop of conc. NaOH solution and 2 drops of the reagent.	A brown precipitate or colouration	NH_4^+ confirm

3.11. Spot Tests for Anions :

Very few acid radicals show colour reactions with specific reagents, unlike the basic radicals. Spot tests for some acid radicals are given here.

Test for/Reagent	Experiment	Observation	Inference
Test for $S_2O_3^{2-}$: Iodine- azide- test: Reagent : Dissolve 3 gms of sodium azide in 100 ml of 0.1N iodine solution.	Place 2-3 drops of the test solution on a watch glass and add 1-2 drops of the reagent.	A vigorous evolution of bubbles (nitrogen)	$S_2O_3^{2-}$ confirm

Test for/Reagent	Experiment	Observation	Inference
Test for S^{2-} : Sodium nitroprusside test: Reagent : 1% aqueous solution of Sodium nitroprusside.	Mix on a spot plate a drop of the alkaline test solution with a drop of reagent.	A violet colouration.	S^{2-} confirm
Test for NO_2^- : 1. Sulphanilic acid – α- naphthylamine test : Reagent : i) Dissolve 1 gm of sulphanilic acid in 100 ml of 30% acetic acid. ii) Boil 0.3 gm of α-naphthylamine with 70 ml of water, filter or decant the small residue, and mix with 30 ml of glacial acetic acid.	Place a drop of neutral or acetic acid test solution on a spot plate and mix with a drop of sulphanilic acid reagent, followed by a drop of the α-naphthylamine reagent.	A red colouration.	NO_2^- confirm
2. Indole test : Reagent : i) 0.015% ethanolic solution of indole. ii) 15N H_2SO_4	Place a drop of the test solution in a semimicro test tube, add 10 drops of the reagent and 5 drops of 15N H_2SO_4.	A purplish – red colouration.	NO_2^- confirm

Test for/Reagent	Experiment	Observation	Inference
Test for NO_3^- : Sulphanilic acid – α-naphthylamine test :			
i) Sulphanilic acid solution. ii) α-naphthylamine solution. iii) Zn dust	Mix on a spot plate a drop of the neutral or acetic acid test solution with a drop of the sulphanilic acid reagent and a drop of the -naphthylamine reagent, and add a few miligrams of Zn dust.	A red colouration.	NO_3^- confirm
Test for SCN^- : Ferric chloride test:			
Reagent : 1% aqueous solution of $FeCl_3$	Place a drop of the test solution on a spot plate and add 2-3 drops of dil. HCl, and then add 1 drop of reagent.	Blood red colouration.	SCN^- confirm
Test for BO_3^{3-} : **1.** **Turmaric test :**	Take 5 drops of the test solution mixed with 1 ml conc. HCl in a semimicro test tube and boil for about 30 sec. And then cool. Place a drop of this solution on a turmeric paper. Dry the paper and moisten with 2M NaOH solution.	A pink colouration. Pink colour changes to brown-green.	BO_3^{3-} confirm

Test for/Reagent	Experiment	Observation	Inference
2. Glycerol/ Manitol-Bromothymol blue test : Reagent : i) 0.04% ethanolic solution. ii) 50% aqueous solution of glycerol or 10% manitol.	Take 5 drops of the alkaline test solution in a semimicro test tube and add 1 drop of bromothymol blue indicator. Neutralize the solution by drops of dil. HCl. To 1 drop of the solution add a drop of glycerol / manitol solution.	Blue colour changes to green Yellow colouration.	BO_3^{3-} confirm

3.12. ANALYSIS OF UNKNOWN INORGANIC SAMPLE

Sample No. : **Date :**

1. Physical Characteristics :

a) Texture : Amorphous / Crystalline

b) Colour :

c) Solubility :

Cold water	Hot water	Dilute HCl	Conc. HCl	Aqua regia

Perform the analysis in the following order :

a) At first prepare the following solution / extracts in labelled test tubes

i) Water

ii) Conc. HCl

iii) Aqua regia

iv) (1:1) HNO_3

v) 10% NaOH solution

vi) Na_2CO_3 extract

b) Preliminary tests for cations

c) Preliminary tests for anions

d) Test for interfering acid radicals

e) Wet test for acid radicals

f) If the sample contains insoluble part, analyse it first

g) Perform group analysis with different solutions, viz., water soluble part, HCl soluble part, aqua regia soluble part.

2. Preliminary Test for Basi Radicals :

<table>
<tr><th>Experiment</th><th>Observation</th><th>Inference</th></tr>
<tr><td>1. Heating in a dry test tube :
A pinch of the sample is heated in a dry test tube.
2. If white sublimate is formed in the above test:
a) Pass H_2S gas directly over the sublimate
b) Sample + 10% NaOH solution and boil.</td><td>1. a) Change of colour of residue:
<table>
<tr><th>Hot</th><th>Cold</th></tr>
<tr><td>i) Yellow to brown</td><td>Yellow</td></tr>
<tr><td>ii) Yellow</td><td>White</td></tr>
<tr><td>iii) Yellowish brown</td><td>Yellow</td></tr>
<tr><td>iv) Black</td><td>Black</td></tr>
<tr><td>v) Yellow to reddish brown or orange</td><td>Reddish brown or orange</td></tr>
<tr><td>vi) Brown to blackening</td><td>Brown</td></tr>
<tr><td>vii) Green</td><td>Green</td></tr>
</table>
b) Evolution of brown fumes

c) Formation of sublimate :
i) White sublimate formed
ii) Yellow sublimate formed</td><td>i) Pb-salt
ii) Zn-salt
iii) SnO_2,Bi_2O_3
iv) Cu,Ni,Co& Mn- salts
v) Sb,Cd and Bi-salts
vi) Fe-salts
vii) Cr-salts
b) May be NO_2^- or NO_3^- of heavy metals.
c)
i) May be NH_4^+, As^{3+}, Sb^{3+} - salt.
ii) May be As_2S_3 and / or $S_2O_3^{2-}$</td></tr>
</table>

Experiment	Observation	Inference
	iii) No change of colour : The sample is initially white.	iii) May be Al^{3+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}, K^{+} etc.
2. If white sublimate is formed in the above test:	2.	2.
a) Pass H_2S gas directly over the sublimate	a) i) Yellow ppt. ii) Orange ppt.	a) i) May be As-salt ii) May be Sb-salt
b) sample + 10% NaOH solution and boil.	b) A pungent smelling gas evolved which forms dense white fumes with a glass rod moistened with conc. HCl and which turns moist red litmus paper into blue.	b) NH_4^+ present.

ii. Flame test

iii. Borax- bead test

iv. Oxidative Fusion test

v. Test with NaOH extract :

Experiment	Observation	Inference
Sample + 10% NaOH solution, boiled and centrifuged. The centrifugate is used to perform the following tests:		
a) Place 1-2 drops of the extract on a spot plate and acidify with HOAc, add 1 drop very dil. (0.1%) $CuSO_4$ solution, add 2-3 drops of ammonium mercuric thiocyanate reagent and stirred.	a) A violet ppt. or colouration (If $CoSO_4$ is used instead of $CuSO_4$, then blue ppt. or colouration will be formed).	a) Zn^{2+} present.
b) Extract + solid NH_4Cl, shaken.	b) White gelatinous ppt.	b) Al^{3+} may present (*Pb^{2+} may interfere)*

Experiment	Observation	Inference
c) Extract, acidified with dil. HCl.	c) i) Yellow ppt. ii) Orange ppt.	c) i) As_2S_3 and SnS may present ii) Sb_2S_3 may present.
d) Extract, acidify with acetic acid and pass H_2S gas.	d) i) Black ppt. ii) Yellow ppt. iii) Orange ppt. iv) White ppt.	d) i) May be Pb^{2+} ii) May be As and Sn-salts iii) May be Sb- salt iv) May be Zn^{2+}
e) Take about 1 ml of the extract in a test tube, add 0.5 ml Alizarin –S (violet colouration formed), add 2N acetic acid dropwise until the violet colour changes to pink and then heat in a water bath. *[Compare with a blank test]*	e) Red ppt.	e) Al^{3+} present
f) Take 1 ml of the extract in a test tube and acidify with dil. HCl, add 1-2 drops of cacothaline reagent.	f) Violet colouration.	f) Sn^{2+} present.

vi. Fluorescence test

3. Preliminary Tests for Acid Radicals :

Experiment	Observation	Inference
1. Sample + Dil. H_2SO_4 and heated.*(Generally covalent or molecular sulphides like ZnS, As_2S_3, PbS, CdS, ect. cannot evolve H_2S when treated with dil. H_2SO_4.* ***Test no.2 is then necessary.)***	1.a) Evolution of colourless gas having a smell of burnt sulphur, which turned acidified $K_2Cr_2O_7$ moist paper into green. b) A yellow residue is separated along with the observation (a) above. c) Brown fumes evolved.	1.a) SO_3^{2-} present b) $S_2O_3^{2-}$ present c) NO_2^- present.

Experiment	Observation	Inference
	d) Evolution of a colourless gas having a smell of rotten egg, which turns alkaline (NaOH) sodium nitro-prusside soaked paper violet.	d) $S^{=}$ present
2.a) Iodine-azide test :In a watch glass take 2 drops of the reagent then add a pinch of the sample. b) Sample + Zn-dust + Dil. HCl in a test tube and heat.	2.a) An immediate evolution of gas in the form of fine bubbles. b) Same as observation 1. a) & b).	2.a) May be S^{-}, SCN^{-} $S_2O_3^{2-}$ b) May be $S_2O_3^{2-}$ & SO_3^{2-}.
3. Sample + Conc. H_2SO_4 and heated.	3.a) evolution of a pungent smelling gas which formed dense white fumes with NH_4OH moistened in a glass rod & turns moist blue litmus paper red. b) Red vapour evolved. c) Violet vapour evolved. d) Brown vapour evolved.	3.a) May be Cl^- b) May be Br^- c) May be I^- d) May be NO_2^- and NO_3^-

Note : *If the test 2(a) is negative, no need of performing the test 2(b).*

Experiment	Observation	Inference
4. Sample + MnO_2 + Conc. H_2SO_4 and heated.	4.a) Evolution of pungent smelling gas that turned starch-iodine paper blue. b) Red vapour evolved. c) Violet vapour evolved.	4.a) May be Cl^- b) May be Br^- c) May be I^-

Experiment	Observation	Inference
5. Chromyl chloride test : (*If test 4(a) is +ve).*	5.	5.
a) Take a pinch of the sample in a dry test tube and mix with equal quantity of $K_2Cr_2O_7$ and add 1 ml of conc. H_2SO_4 and heat gently. Hold a filter paper moistened with a drop of NaOH soln. Near the mouth of the test tube (do not touch) then add few drops of HOAc followed by a drop of $Pb(OAc)_2$ solution.	a) A yellow stain appears.	a) Cl^- present
b) Take a pinch of the sample in a dry test tube and mix with equal quantity of $K_2Cr_2O_7$ and add 1 ml of conc. H_2SO_4, the mouth of the test tube is closed with a cork fitted bent delivery tube and heat. Pass the gas through NaOH solution. Now place a drop of this yellow solution on a spot plate, acidify with dil. H_2SO_4 and then add a drop of diphenyl carbazide solution.	b) Violet colouration.	b) Cl^- present
6. Sample + Cu- turnings + 1 ml conc. H_2SO_4 and heat.	6. Brown fumes evolved	6. May be NO_2^- and NO_3^-.
7. Azo- dye test :***(If test no. 6 is +ve)*** a) In a spot plate, take 1 drop acetic acid + 1 drop sulphanilic acid + a pinch of the sample,	7. a) A red colouration	7. a) NO_2^- present

Experiment	Observation	Inference
stir with a glass rod and then add 1 drop of α- naphthyl-amine solution. b) Repeat the above test by adding a pinch of Zn- dust. ***(This test is applicable in absence of NO_2^-)***	b) A red coluration	b) NO_3^- present
8. In a spot plate, take 2 drops of 10% $FeCl_3$ solution and add a pinch of the sample.	8. Blood red colouration	8. SCN^- present
9. a) Take 1 ml of the HNO_3 extract in a test tube and then add ammonium molybdate (excess) and warm. b) Take 1 ml of the HNO_3 extract in a test tube and then add ammonium molybdate-tartaric acid reagent, heat.	9. a) Yellow ppt. b) i) Yellow ppt. ii) No yellow ppt. but test 9(a) is positive.	b) NO_3^- present b) i) PO_4^{3-} present ii) AsO_4^{3-} present
10.a) In a dry test tube, take little amount of the sample + 1 ml methyl alcohol + few drops of conc. H_2SO_4 and heat. Ignite the issuing vapours. b) In a dry test tube, take little amount of the sample + few drops of conc. H_2SO_4 and heat. Ignite the issuing vapours.	10. a) The vapour burnt with green edged flame. b) The vapour burnt with green edged flame.	10. a) BO_3^{3-} and free H_3BO_3 present. b) Free H_3BO_3 present.

4. Wet Test for Acid Radicals :

Preparation of solution (sodium carbonate extract)

Take sample (1 part) + anhydrous Na_2CO_3 (4 parts) + 20 to 30 ml of distilled water in a 250 ml conical flask fitted with a funnel and boil for about 15 minutes. The loss due to the evaporation can be make up by occasional adding of water. Filter and the filtrate is "Na_2CO_3 extract".

If the sample is completely soluble in water, the aqueous solution of the should be prepared by dissolving the sample in distilled water. If the sample is partly soluble in water then prepare aqueous extract and perform tests for both cations and anions with this.

5. Some information during analysis of anions with Na_2CO_3 extract :

i) Na_2CO_3 extract of Co^{2+}- salts become blue due to the formation of CoO_2^{2-} species in solution.

ii) If As_2S_3, Sb_2S_3 / SnS and / or SnS_2 is present in the sample, these are present in the Na_2CO_3 extract as thio-salts. During acidification, the precipitate of As_2S_3 and Sb_2S_3 reappear. After filtration the specific wet tests are to be performed with the filtrate.

iii) In case some covalent sulphides e.g., ZnS, CdS, double decomposition with Na_2CO_3 does not occur appreciably and therefore test with sodium nitroprusside may not respond. In this case treat the residue of Na_2CO_3 extract with Zn and dil. HCl and test the evolved gas with $Pb(OAc)_2$ or alkaline sodium nitroprusside moist paper.

iv) If the sample contains As_2O_3, then it reacts with Na_2CO_3 to form Na_3AsO_3 and it will respond to test for AsO_3^{3-}.

$$As_2O_3 + 3Na_2CO_3 = 2Na_3AsO_3 + 3CO_2$$

v) If Al^{3+} or Zn^{2+} be present in the sample, during neutralisation the Na_2CO_3 extract with dil. Acid dropwise a gelatinous precipitate of $Al(OH)_3$ / $Zn(OH)_2$ may appear, which dissolves on complete acidification.

$$Al^{3+} + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 6Na^+ + 3CO_2$$

$$Al(OH)_3 + OH^- = AlO_2^- + 2H_2O$$

6. Wet Test for Basic Radicals (Group Analysis)

i) Preparation of solution for group separation.

ii) Group separation

iii) Treatment of the precipitate obtained in different groups followed by confirmation.

7. Treatment of the Insoluble Residue.

8. Results :

Cations found :

Anions found :

3.13. Self Assessment Questions

1. What is flame test? What are the colours of the following radicals in reducing and oxidizing flame?

   Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}

2. What is the chemistry of borax bead test?
3. What do you mean by interfering acid radicals?
4. How can you seperate nitrate and nitrite redicals?
5. Give the identification test for Phosphate and Arsenate.
6. Mention the group reagents for group seperation of the basic redicals.
7. Write down the chemical reactions for the identification of Cl^{-1}, Br^{-1}, I^{-1} and SCN^{-1}

3.14. Suggested Readings

1. Vogel's Qualitative Inorganic Analysis : Arthur Vogel and G. Svehla
2. An Advance Course in Practical Chemistry, Ghoshal, Mahapatra and Nad.

Block –II
(Organic Chemistry)

Unit-4 □ Chromatographic Separations

Structure

4.1 Objectives

4.2 Introduction

4.3 Basic principles of chromatography

4.4 Column Chromatography (Adsorption Chromatography)

4.5 Experiment-1: TLC separation of a mixture containing 2/3 amino acids (*dl*-Alanine, *l*-Lysine and *l*-Leucine)

4.6 Experiment-2: Column chromatographic separation of mixture of dyes (Fluorescein and Methylene Blue)

4.7 Experiment-3: Paper chromatographic separation of a mixture containing 2/3 sugars (Glucose, Fructose and Sucrose)

4.8 Self Asessment Questions

4.9 Suggested Reading

4.1. Objectives

- To give a brief knowledge on chromatography
- To provide the knowldege on column chromatography
- To give sufficient expertise in TLC seperation of a mixture of amino acids.
- Providing expertise in column chromatographic seperation of a mixture of dyes.
- To make skill for paper chromatographic seperation of a mixture of sugars.

4.2 Introduction

Chromatography is a technique for separation, purification, isolation and identification of organic, inorganic, biochemical compounds.

M. Iswett first used this technique in 1906 for separation of coloured substance

from plants. Chromos means colour and 'graphy' means writing and hence the name chromatography.

The principle of chromatography is based on the differential distribution of the components of a mixture between two phases — one is fixed called the stationary phase and the other is mobile phase that migrates at different rates through the stationary phase. The differential distribution may be either due to difference in partition of the components present in the mixture, between the two phases (partition chromatography) or due to differential adsorption on the stationary phase (adsorption chromatography).

The mixture to be separated is dissolved in a particular mobile phase that may be liquid or gas and then allowed to pass over the stationary phase, which may be an adsorbent plate/column or a paper strip.

Stationary and mobile phases used in common chromatographic methods are listed below:

Type of Chromatography	Stationary phase	Mobile phase
a. Column Chromatography	Solid (Alumina, silica gel)	Liquid (A series of suitable solvents of different polarity and sometimes a mixture of solvents.)
b. Paper Chromatography	Solid *(A paper strip of* suitable size, generally made from Whatman No. 1 paper.)	Liquid (Generally a mixture of solvents.)
c. Thin Layer Chromatography	Solid (A thin layer of alumina, silica gel or cellulose powder)	Liquid (Generally a mixture of solvents.)
d. Gas Chromatography	Solid or nonvolatile liquid	Gas (e.g., N_2, H_2)

Migration parameters:

The positions of the migrated spots on the chromatograms are usually indicated by the term R_F, retardation factor.

R_F means the retardation of the movement of the solid by the stationary phase in presence of developing solvent and is expressed by the ratio:

$$R_F = \frac{\text{Distance travelled by a component from the base line}}{\text{Distance travelled by solvent front from the base line}}$$

4.3 Basic principles of chromatography

The principle of chromatography is based upon the selective separation of the constituents of a mixture (liquid/gas) in the mobile phase during flowing through the stationary phase. The selective separation is dependent upon adsorption (in which the constituents of a mixture in the liquid or gas phase undergo selective adherence to the surface of the stationary phase) and partitioning (in which the constituents of a mixture undergo selective dissolution in the solvent).

Thus chromatography involves differential distribution of the constituents of a mixture between two phases, stationary phase and a moving phase. However, various techniques of chromatography in use differ from one another in the nature of two phases and type of interaction involved and commonly used chromatographic techniques are -

i) Column Chromatography (Adsorption Chromatography)

ii) Thin Layer Chromatography (TLC)

iii) Paper Chromatography

4.4 Column Chromatography (Adsorption Chromatography)

Introduction:

Separation by column chromatography is based upon differential adsorption. This is carried out in the moving phase is a phenomenon whereby a substance gets attracted by electrostatic forces to the surface of adsorbent. The column of adsorbent material is a simple glass tube tapered at the bottom and fitted with a tap. The ratio of, length to diameter = 40:1 is taken as the standard. The tube is about 20-30 cm long and 1.0 - 1.5 cm in diameter. This may hold 50-100g of absorbent that is supported on a plug of cotton or glass wool. The sample, to be chromatographed, is dissolved in a solvent and allows to percolate through the column. During the slow percolation, the solute molecules are adsorbed, released and reabsorbed on the surface of the adsorbent. The molecule with least adsorptivity goes along with the solvent and eluted first, followed by other components. These can be collected in individual flasks. Since a column is used, the technique is also known as column chromatography.

For analytical purposes, column chromatography finds numerous applications. Column chromatography may be used for analytical uses depending on adsorbed components, and solvents.

The nature of adsorbents and type of solvents used hi the column chromatography are:

Adsorbents:

The adsorbents normally used are alumina, silica gel, powdered sugar, activated charcoal or magnesium silicate. The choice of an adsorbent depends on the particular application, although some general considerations apply to all systems. It is to be noted that:

(i) There should not be any chemical reaction between solvent, solute and the adsorbent,

(ii) The size of the adsorbent particles used should be small, as the smaller the size, the greater is the surface area exposed and better is the adsorption efficiency, but too small a size would tend to retard the flow of solvent.

Solvent:

Electrostatic attraction plays an important role in the adsorption phenomena. In adsorption chromatography usually the more polar component is more strongly adsorbed on the stationary phase and will remain in upper part of the column. On the other hand the less polar component is adsorbed weakly, eluted with comparative ease and travels downward causing separation.

The elution capacity of solvents depends on their polarity and is indicated by the eluotropic series: Petroleum ether < cyclohexane < carbon tetrachloride < toluene < benzene < chloroform < diethylether < acetone < n-propyl alcohol < ethanol < methanol for the organic solvents. A mixture of these can also be used to obtain intermediate polarity.

4.5 Experiment-1: TLC separation of a mixture containing 2/3 amino acids (*dl*-Alanine, *l*-Lysine and *l*-Leucine)

Principle:

A mixture of amino acids (*dl*-Alanine, *l*-Lysine and *l*-Leucine) can be separated by thin layer chromatography (TLC) using silica gel as the stationary phase (absorbent).

On developing the TLC plate in n-butyl alcohol-acetic acid-water (8:2:2) mixed

solvent, the amino acids will separate and appear as three purple-coloured spots at different distances depending on their respective R_F values - the upper spot corresponds to *l*-leucine (R_F ~0.65) the middle spot corresponds to *dl*-alanine (R_F ~ 0.36) and the lower spot corresponds to *l*-lysine (R_F ~0.14).

Materials required:

i) Stationary phase: Silica gel - G (or, Alumina).

ii) Chromatographic plate: Glass plate (12cm x 4 cm).

iii) Developing solvent: n-Butyl alcohol: acetic acid: water 8:2:2 (v/v)

iv) Developing chamber: A glass jar (18 cm x 6 cm) with a lid.

v) Solvents: Chloroform, ethanol, n-butyl alcohol, acetic acid.

vi) Spaying reagent: 0.3% Ninhydrin solution in 95% ethanol (or in n- Butyl alcohol containing 3% glacial acetic acid).

vii) Supplied amino acid mixture: Prepare the solution of — 10 mg of each of *dl*-alanine, *l*-lysine and *l*-leucine in 10 mL (1:1) ethanol, Mix any two of the solutions.

viii) Standard samples of amino acids:

a. *dl*-alanine (A),

b. *l*-lysine (B) and

c. *l*-leucine (C), in 10 mg/10 mL(1:1) ethanol.

(ix) Fine capillary tubes

Procedure:

(1) Preparation of the TLC plate (Chromatogram):

Prepare homogeneous slurry of ~20g of silica gel G (200 mesh) in 50 ml of chloroform by shaking in a wide-mouth glass stoppered bottle. Dip a glass plate nearly horizontally, holding the two edges with fingers into the homogeneous slurry. Take out the plate, allow spreading the slurry uniformly over it. Place it horizontally on a rack and dry in air for ~10 minutes. Scrap off the silica gel from the backside of the plate.

(2) Application of the sample:

Place the TLC plate on a piece of paper and draw the outside lines of the glass plate. Now draw a base line at a distance of ~1 cm from the lower edge of the paper and put four pencil dots at equal distance on the base line.

Place the plate on the paper-sketch so that the base line remains just outside the lower edge of the plate. Apply the sample-spot with a fine capillary tube on an imaginary base line at a distance of ~1 cm from the lower edge of the plate corresponding to the pencil-mark. Label it as unknown in the paper-sketch.

Similarly put three other micro drops of the supplied standard solutions on the same imaginary base line at the corresponding positions placed in the paper. Label them as A, B and C in the paper-sketch. Allow the spots to dry in the air till no longer visible.

(3) Development of the spotted plate:

A glass jar with a lid containing 10-15 mL of the developing solvent is allowed to swirl vigorously to saturate the air inside the jar with the solvent vapour. Open the jar and insert the dried plate in vertical position keeping the sample spot downward in such a way that the solvent touches the adsorbent layer well below the spot-level. Replace the lid and allow the solvent to rise about 8-l0cm (time required about half an hour). Take off the plate from the jar and mark the solvent front to the corresponding position in the paper-sketch. Allow it to dry in air oven at 100 - 110°C for about 5 minutes.

(4) Detection of the spot:

Spay the plate with ninhydrin solution and dry again at 100 — 110°C for about 5 minutes when the amino acids will appear as purple-coloured spots at different distances depending on their respective R_F values. Label the two spots separated from the unknown sample as X and Y.

(5) Measurement of R_F value:

Measure the distance traveled by each component from the base line to the separated spots (consider the centre of the spots) in both cases of the unknown and the standard samples and also measure that of solvent-front from the base line.

Calculate the R_F values for different spots and compare those values with the standard samples for the identification of the amino acids present in the mixture.

Experimental Results:

Table - 1: Calculation of R_F values of standard samples

Standard samples of amino acids	Distance traveled by the solute from the starting line (d_1 cm)	Distance traveled by the solvent front from the starting line (d cm)	$R_F = d_1/d$
dl-alanine (A)			

Standard samples of amino acids	Distance traveled by the solute from the starting line (d_1 cm)	Distance traveled by the solvent front from the starting line (d cm)	$R_F = d_1/d$
l-lysine (B)			
l-leucine (C)			

Table - 2: Calculation of R_F values of unknown samples

Constituents present in the unknown mixture	Distance traveled by the solute from the starting line (d_3 cm)	Distance traveled by the solvent front from the starting line (d cm)	$R_F = d_3/d$
X			
Y			

Conclusion:

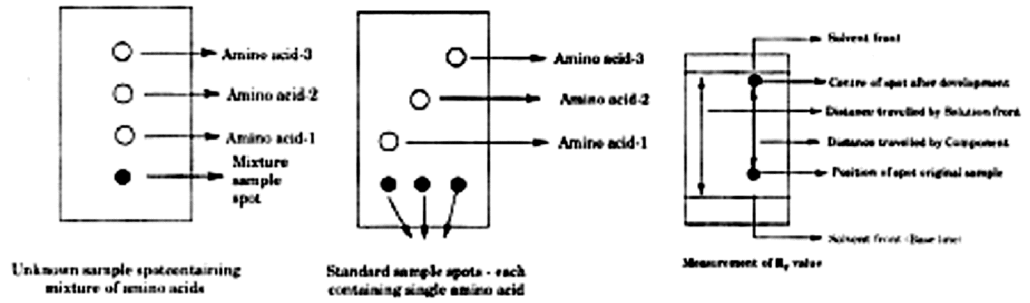
By comparing the R_F values of the constituents in the unknown mixture with those of the standard samples, it is found that the constituent X is..... and Y is .....in the unknown mixture.

Notes:

(i) Care must be taken in handling the plate to avoid placing fingers on the active adsorbent surface to keep it free from contamination.

(ii) It is advised to pre-wash the plate by running developing solvent to remove impurity, if any, present in the layer.

(iii) To measure the distance traveled by the solute from the starting line, the centre of the spotted zone is to be taken.



Unknown sample spot containing mixture of amino acids

Standard sample spots - each containing single amino acid

Measurement of R_f value

Table for R_F Values for Amino Acids in TLC:

Compounds	R_F Values in solvents	
	96% ethanol-water = 7:3	n-Butanol: acetic acid water = 8:2:2
1. *l*-Leucine	0.61	0.65
2. Tryptophan	0.65	0.56
3. Phenylalanine	0.63	0.49
4. Tyrosine	0.65	0.47
5. Methionine	0.59	0.40
6. *dl*-Alanine	0.47	0.36
7. Glycine	0.43	0.22
8. *l*-Lysine	-	0.14

4.6 Experiment-2: Column chromatographic separation of mixture of dyes (Fluorescein and Methylene Blue)

Principle:

A mixture of methylene blue and fluorescein can be separated by column chromatography using alumina as absorbent and ethanol and water as eluents.

Here two coloured bands are separated -lower band of blue band of methylene blue and upper band yellow band of fluorescein. Methylene blue comes out of the column on

eluting with ethanol and fluorescein separated at the top, comes down the column on eluting with water. In case of silica gel (~100 mesh) used as the stationary phase (adsorbent), the sequence of separated coloured bands is just reversed. The lower yellow band of fluorescein comes out first of the column on eluting with ethanol. The upper blue band of methylene blue moves next down the column when the column is eluted with water: acetic acid = 70: 30 (v/v) as the eluent.

Materials required:

i) Stationary phase: Alumina (or, Silica gel - G).

ii) Chromatographic column: Wide glass tube (30 cm x 1.5 cm) or a 50 mL burette.

iii) Solvent: Ethanol

iv) Standard samples of dyes: l0 mg/l0 mL(1:1) ethanol.

(a) Methylene blue,

(b) Fluorescein

v) Unknown Dye mixture: Mix 5 mL of each of methylene blue and fluorescein.

vi) Conical flask (100 mL)

vii) Pipette (5 mL)

Procedure:

(1) Setting of adsorption column:

Clamp vertically the chromatographic column of glass tube. Place a small plug of cotton or glass wool at the bottom of the column using a long piece of glass rod. Pack the column with dried alumina up to ~15-20 cm. Place 1 cm of anhydrous Na_2SO_4 over the top of the column. Keep the stopper open.

(2) Separation of dyes :

Place one 100 ml conical flask under the column. With the help of a pipette add slowly 5mL of the supplied dye mixture on the top of the column and allow the solution to run down the column completely.

Elute with 5 ml of ethanol and allow the eluent to run down the column. When the ethanol level is ~1 cm above the top of the column, add more ethyl alcohol to separate the coloured bands.

Blue band of methylene blue moves down the column while fluorescein remains near the top. Add more of ethanol until the blue band reaches the bottom. Collect this fraction until the lower end becomes colourless.

Replace the 100 ml conical flask by another one and elute the column with water, when the yellow band of fluorescein begins to move down the column. Continue elution with water until the effluent appears colourless. The separated dyes can be obtained in the solid state by evaporating oft' the solvents from the extracts.

Thin Layer Chromatography (TLC)

TLC is a form of chromatography where the stationary phase is a thin uniform layer of the adsorbent on a glass plate or on a solvent-resistant polymer sheet or a thin aluminium sheet. The mobile phase is a solvent of suitable polarity, which rises along the chromatographic plate by capillary action leading to separation of the components of the mixture.

The various adsorbents used in this method are:

(i) Silica gel G (G stands for gypsum): It is used for separation of neutral and acidic compounds

(ii) Silica gel g-F which is a mixture of silica gel g and some UV fluorescent agent like ZnS (2%) or Rhodamine 6G (0.003%)

(iii) Alumina: It is more reactive than silica gel and used for separation of neutral and basic compounds like alkaloids

(iv) Cellulose (with $CaSO_4$ binder): This supplements paper chromatography and is faster

(v) Kieselgurh (with $CaSO_4$ binder)

For qualitative purposes, an aqueous slurry (30% w/v) of the adsorbent of about 200-mesh size with l0-15% $CaSO_4$ as binder is evenly spread over the plate either manually or with the help of an applicator. The thickness of the layer is generally maintained in the range 0.2- 0.3 mm. The plate is then allowed to stand for 15 -20 minutes in the horizontal position and is dried either overnight in air or in an air- oven at 80- 90°C for about 30 minutes.

4.7 Experiment-3: Paper chromatographic separation of a mixture containing 2/3 sugars (Glucose, Fructose and Sucrose)

Principle:

Chromatography on paper (cellulose) is basically a solvent extraction type of process.

The materials to be separated undergo partition between the aqueous phase held in the inert cellulose matrix and organic solvent used as the mobile phase.

A mixture of sugars (glucose, fructose and sucrose) can be separated by paper chromatography where paper itself acts as the stationary phase.

On developing the paper chromatogram in 1-butanol-acetic acid-water (4:1:5) mixed solvent, the sugars will separate and appear as three yellow-coloured spots at different distances depending on their respective R_F values - the upper spot corresponds to fructose (R_F ~0.25) the middle spot corresponds to glucose (R_F ~0.17) and the lower spot corresponds to sucrose (R_F ~0.08).

Materials Required:

i) Stationary phase: A paper strip (20 cm x 4 cm) cut from Whatman No.1 paper.

ii) Mobile phase (Developing solvent): 1-butanol: acetic acid: water = 4:1:5 (v/v)

iii) Developing chamber: A glass jar (25 cm x 5 cm) with a lid.

iv) Spaying reagent: (a) Aniline oxalate: Dissolve 0.093 g of aniline (~10 drops) in 50 mL of 95% ethanol and mix with 50 mL of 0.2M aqueous oxalic acid, or (b) Anisaldehyde reagent: Freshly prepare a mixture of 9 mL 95% ethanol, 0.5 mL cone. H_2SO_4 and 0.5 mL anisaldehyde.

v) Standard sugar solutions: Prepare the solution of ~120 mg/mL of each of glucose, fructose and sucrose in water and label as (A). Glucose, (B). Fructose, (C). Sucrose.

vi) Unknown sample of sugars: Mix any two of the above solutions and label it as unknown.

vii) Fine capillary tubes.

viii) Sprayer

Procedure:

(1) Application of the sample:

Draw a base line at a distance of ~ 2 cm above from the lower edge of the paper strip and put four pencil dots at equal distance on the base line.

Apply the sample-spot vertically with a fine capillary tube on one of the four pencil-dots in the paper strip. Label it as unknown.

Similarly put three other micro drops of the supplied standard solutions on the other three dots. Label them as A, B and C in the paper-strip. Allow the spots to dry in the air till no longer visible.

(2) Development of the spotted paper chromatogram:

A glass jar with a lid containing 10-15 mL of the developing solvent is allowed to swirl vigorously to saturate the air inside the jar with the solvent vapour. Open the jar and insert the dried paper strip in vertical position keeping the sample spot downward in such a way that the solvent touches the adsorbent layer well below the spot-level. Replace the lid and allow the solvent to rise about 8-10 cm (time required about half an hour). Take off the paper strip from the jar and mark the solvent front ascended. Allow it to dry in air oven at 100 — 110°C for about 5 minutes.

(3) Detection of the spot:

Spay on the both sides of the paper strip with the aniline oxalate spraying reagent followed by drying at 90°-100°C in an air oven for 5-10 minutes when the sugars appear as yellow spots at different distances depending on their respective R_F values. Label the two spots separated from the unknown sample as X and Y.

Calculate the R_F values for different spots and compare the R values with the standard sample of equal concentration.

Alternatively, spray with a freshly prepared mixture of 9 mL 95% ethanol, 0.5 mL conc, H_2SO_4 and 0.5 mL anisaldehyde followed by drying at 90-100°C in an air oven for 5-10 minutes; characteristic colour developed are: sucrose-violet (R_F = 0.08), glucose-light blue (R_F = 0.17) and fructose - violet (R_F = 0.25).

Experimental Results:

Table-1: Calculation of R_F values of standard samples

Standard samples of amino acids	Distance traveled by the solute from the starting line (d_1 cm)	Distance traveled by the solvent front from the starting line (d cm)	$R_F = d_1/d$
A (glucose)			
B (fructose)			
C (sucrose)			

Table-2: Calculation of R_F values of unknown samples

Constituents present in the unknown mixture	Distance traveled by the solute from the starting line (d_s cm)	Distance traveled by the solvent front from the starting line (d cm)	$R_F = d_s/d$
X			
Y			

4.8 Self Assesment Questions

1. Define Column chromatography, paper chromatography, and thin layer chromatography.
2. What is retardation factor (R_f)?
3. What do you mean by stationery and mobile phase?
4. What do you mean by elution capacity of solvent?
5. How can you prepare a TLC plate?
6. What are the adsorbents used in the TLC method?
7. How can you seperate glucose, fructose and sucrose?
8. What are the spraying reagents?

4.9 Suggested Reading

1. "Text Boon on Practical Chemistry"; K.S. Mukherjee.
2. "An Advance Course in Practical Chemistry". A. Ghoshal, B. Mahapatra and A.K. Nad.
3. "Text Book of Quantitative Ignoric Analysis" A.I. Vogel.
4. R.K. Bansal. "Laboratory Manual of Organic Chemistry" Second Edition. Wiley Eastern Limited, New Delhi (1990).
5. H.T. Clarke. "A Handbook of Organic Analysis" Fifth Edition, Arnold Publishers, London.

Unit-5 □ Spectroscopic Analysis of Organic Compounds

Structure

5.1 Objectives

5.2 Introduction

5.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

5.3.1 Nuclear Resonance

5.3.2 Chemical shift

5.3.3 Spin-Spin coupling and splitting of signals

5.3.4 n + 1 rule for splitting pattern and intensities of lines

5.3.5 Assignment and Example of ^{1}HNMR values

5.4 Infrared Spectroscopy (IR)

5.4.1 Molecular Vibrations

5.4.2 Factors affecting vibrational frequencies

5.4.3 Assignment and Example of IR values

5.5 Few example of typical spectral data

5.5.1 Spectral data for 4-Nitroaniline

5.5.2 Spectral data for 2-Bromo-4'-methylacetophenone

5.5.3 Spectral data for Vanillin

5.5.4 Spectral data for 2-Methoxyacetophenone

5.5.5 Spectral data for 4-Aminobenzoic acid

5.5.6 Spectral data for 1-pentyn-3-ol

5.5.7 Spectral data for 2'-Hydroxyacetophenone

5.5.8 Spectral data for 1,3-Dinitrobenzene

5.5.9 Spectral data for Benzylacetate

5.5.10 Spectral data for 3-hydroxy-4-nitrobenzaldehyde

5.5.11 Spectral data for 3-Ethoxy-4-hydroxybenzaldehyde

5.5.12 Spectral data for 4-Nitrobenzaldehyde

5.5.13 Spectral data for Methyl 4-aminobenzoate

5.5.14 Spectral data for 2-Methoxybenzaldehyde

5.5.15 Spectral data for 4-Hydroxybenzaldehyde

5.5.16 Spectral data for Ethyl-3-aminobenzoate

5.5.17 Spectral data for 2,3-Dimethylbenzonitrile

5.5.18 Spectral data for 4-Aminobenzoic acid

5.5.19 Spectral data for Methyl 3-hydroxybenzoate

5.6 Self Assessment Queations

5.7 Suggested Reading

5.1. Objectives

- Detail of nuclear we are able to know the following issues :
- Definition of chemical shift.
- Spin-Spin coupling and splitting of signals.
- Detail of infrared spectroscopy
- Typical spectral data of many organic molecules

5.2 Introduction

There are several spectroscopic techniques which can be ustd to identify organic molecules : Infrared (IR), mass spectroscopy (MS) UV/visible spectroscopy (UV/Vis) and nuclear magnetic resonance (NMR).

IR and NMR spectroscopy are based on observing the frequencies of eletromagnetic radiation absorbed and emitted by molecules. Ms is based on measuring the mass of the molecule and any fragments of the molecule which may be produced in the Ms instrument. Nuclear Magnetic Resonance (NMR) Spectroscopy is one of the most useful analytical techniques for determining the structure of an organic compound. There are two main types of NMR, ^{1}H-NMR (Proton NMR) and ^{13}C-NMR (Carbon NMR), NMR is based on the fact that the nuclei have a quantized property called spin.

Absorbing infrared rediation makes covalent bonds vibrate. Different types or bond absorb different wavelengths of infrared :

Instead of wavelength, infrared spectroscopists record the wave number : the number of waves that fit into 1 cm. (This is easily converted to the energy of the wave).

For some reason the spectra are recorded backwards (from 4000 to 500 cm^{-1} is typical), often with a different scale below 1000 cm^{-1} (to see the fingerprint region more clearly) and upside down (% radiation transmitted is recorded instead of the absorbance of radiation).

The wave numbers of the absorbed IR radiation are characteristic of many bonds, so IR spectroscopy can determine which functional groups are contained in the sample. For example, the carbonyl (C=O) bond will absorb at 1650-1760 cm^{-1}.

5.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclei of certain isotopes possess a mechanical spin, or angular momentum. Since nuclei possess electrical properties, mechanical spin generates a magnetic field whose axis coincides with the axis of spin. Thus the nucleus is equivalent to a minute bar magnet of magnetic moment μ.

The magnitude of the magnetic moment of the nucleus, which is also quantized by the spin quantum number, is characterized of that nucleus.

The total angular momentum of a spinning nucleus is symbolized as *I*, which may have values of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, – – – – – depending on the particular nucleus. The numerical value of spin number *I* is related to the mass number and the atomic number as follows:

Mass number	Atomic number	Spin number (*I*)
odd	even or odd	0, $\frac{1}{2}$, 1, $\frac{3}{2}$, – – –
even	even	0
even	odd	1,2,3

Nuclear spin may be related to the nucleon composition of a nucleus in the following manner: Odd mass nuclei (i.e. those having an odd number of nucleons) have fractional spins. Examples are *I*=1/2 (^{1}H, ^{13}C, ^{19}F), *I*=3/2 (^{11}B) and *I*=5/2 (^{17}O). Even mass nuclei

composed of odd numbers of protons and neutrons have integral spins. Examples are I = 1 (^{2}H, ^{14}N).

Even mass nuclei composed of even numbers of protons and neutrons have zero spin (I = 0). Examples are ^{12}C, and ^{16}O.

Fortunately for organic chemists, ^{1}H and ^{13}C nuclei are common in organic compounds and the ability to probe these nuclei NMR is invaluable for structure determination of the organic molecules. Since the proton magnetic resonance (PMR or $^{1}HNMR$) is the most common type, the behaviour of ^{1}H nuclei in magnetic field will serve as a model for other nuclei which have spin quantum numbers I=1/2 and thus behave similarly.

If a magnetic nucleus is placed in a uniform magnetic field, it is found that the magnetic dipole assumes a discrete set of orientations. The magnetic nucleus may assume any one of ($2I$ + 1) orientations with respect to the direction of the applied magnetic field, H_o. Thus a proton with I=1/2, will be able to assume only two orientations that corresponding to energy levels ± μH_0 in an applied magnetic field of field strength H_o.

5.3.1 Nuclear Resonance:

A tiny nuclear magnet like proton is restricted to two possible orientations when placed in a static magnetic field arid these can be considered to be a low energy or parallel orientation in which the magnet is aligned with the applied field and a high energy or anti parallel orientation in which it is aligned against the applied field (i.e. N pole nearest the N pole of the static applied field). The transition between the two states can be induced by electromagnetic radiation of frequency ν. The energy (ΔE) necessary for this process of flipping from one orientation to the other is given by the following expression.

$$\Delta E = h\nu = \frac{\mu\beta_N H_0}{I} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

H_o = Strength of the applied external field

μ = magnetic moment of the particular nucleus

β_N = nuclear magneton constant

h = Planck's constant (6.626 x 10^{-34} J.s)

I = spin number

ν = frequency of electromagnetic radiation

The equation (1) can also be written as (2).

$$\Delta E = \frac{\gamma H_0}{2\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where γ is known as ***gyromagnetic ratio***.

Gyromagnetic ratio is related to magnetic moment 'μ' of the spinning bar magnet (proton) by the following expression.

$$\gamma = \frac{2\pi\mu}{hI} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where, I = spin number of the spinning magnet and h = Planck's constant. The value of 'γ' for proton is '26750'

Hydrogen nucleus has a magnetic spin number I=1/2, therefore it can assume $\left[2\times\frac{1}{2}+1\right]=2$ spin states, when placed in a strong magnetic field. One spin state has the orientation aligned with the direction of the applied external field and the other opposed to it Former has the lower energy relative to the other. The difference in energy (ΔE) between the two states is given by the following expression:

It is dependent on the cross product of the applied field H_0 and the magnetic moment ν.

Since ν is the same for the for all hydrogen nuclei, the energy difference between the two allowed orientations is proportional to the applied field H_0.

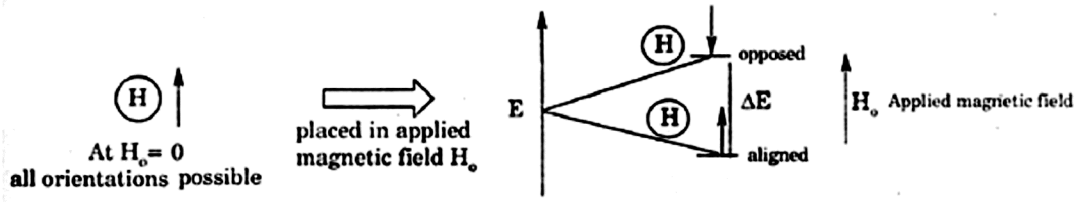


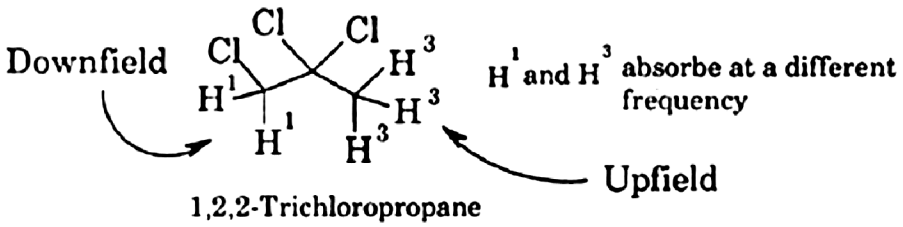
Fig. 1

If the magnetic field H_0 is kept fixed and constant, the energy gap between the two spin states of the hydrogen nuclei will remain constant, Irradiation of the system at the appropriate

Frequency (ΔE =hν) will cause the energy to be absorbed and the nucleus will flip from the low energy state (aligned) to the higher energy state (opposed). It is this absorption of energy which is used to probe the structural features of the molecule.

Since the magnetic moment of a nucleus (μ) is an atomic property, for magnetic field H_0, all hydrogens should absorb energy at the same frequency. However, examination of

a molecule such as 1, 2, 2-trichloropropane reveals that the two different types of hydrogen absorb at two different frequencies.



1,2,2-Trichloropropane

Since the applied field H_0 is constant, and all hydrogen nuclei have the same magnetic moment μ, and since H^1 and H^3 absorb at two different frequencies, the magnetic field that is actually experienced (H_{eff}) by each set of nuclei must be different. Stated differently, even though a constant magnetic field H_0 is applied to the sample, each type of hydrogen experiences a unique magnetic field H_{eff} (where $H_{eff} \neq H_0$) and consequently absorbs energy at a different frequency, ν_1 and ν_3 . Thus, different types of protons are distinguished by the different frequencies at which they absorb energy.

Why should the proton nuclei in different compounds behave differently in the PMR experiment? Shielding and Deshielding of Protons:

It is the electron density around the nucleus which **shields** the nucleus from the applied field. It follows, the greater the electron density around a proton, the larger will be the induced field H_{ind}, and the **more shielded** the proton will be. It will appear more **up-field** and will have a smaller chemical shift (δ values). Conversely, the lower the electron density around a proton, the **less shielded** it will be, the more **downfield** it will be, and numerically the larger will be its δ value.

5.3.2 Chemical shift :

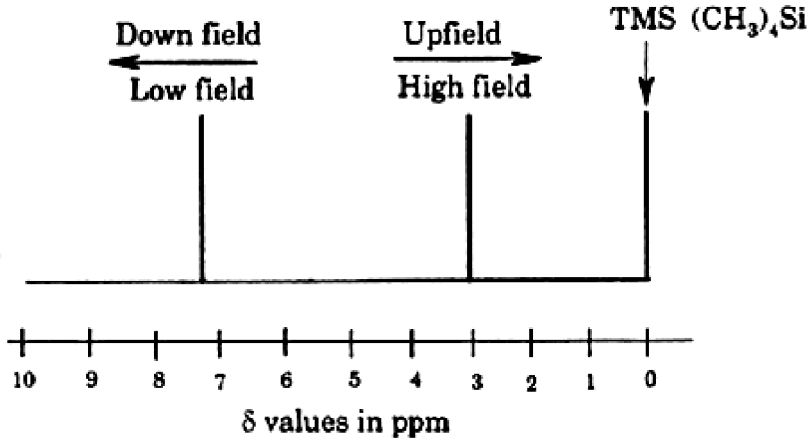
The range of frequencies over which protons of organic molecules absorb depends on the applied field. **The actual range of frequency of absorption depends on the magnetic field of the instrument**. This is exactly as expected, since the energy gap between the spin states and hence the frequency of absorption are both dependent on the applied field H_0. To compare absorption values from different instruments, a dimensionless scale must be devised that is independent of the magnetic field of the instrument. This is accomplished by using the absorption of tetramethylsilane (TMS) as a spectral anchor. The frequency of absorption of a given set of protons is measured relative to the frequency of

absorption of TMS. This absorption frequency difference ($\Delta\nu$) in hertz (cps) is symbolized as δ, the chemical shift of the protons in ppm, where,

$$\delta = \frac{\Delta\nu\ (\text{Hz}) \times 10^6 \text{ppm}}{\text{operating frequency of the spectrometer (Hz)}} \quad \ldots\ldots\ldots\ldots (5)$$

From the equation (5), it is evident that the chemical shift is dimensionless and independent of the spectrometer. Since normal absorption range $\Delta\nu$ are about 0- 600Hz for an operating frequency of 60 $x10^6$ Hz (60MHz), or 0-1000Hz at 100 $x10^6$ Hz (100MHz), chemical shifts range from 0-10 ppm for most protons. In practice a small amount TMS is added to the NMR sample, the TMS signal is set at 0 ppm , and the protons of the sample are then measured in ppm relative to TMS.

The choice of TMS as a standard is due to the fact that all protons of organic molecules absorb at frequency lower than TMS. It is practice to present NMR spectra with low frequency on the left and high frequency on the right. Thus TMS signal defines δ =0 ppm on the right side of the spectrum and other proton signals are found to the left, or **down field**, from TMS, from 0-l0ppm. The left side of the spectrum is low field and the right side is described as **up field/ high field**.



This secondary field **shields** the nucleus from the applied field, so H_0 must be increased in order to achieve resonance (absorption of radio frequency energy), shielded

from the applied field by its electron field. Thus H_0 must be increased to compensate for the induced shielding field.

Aromatic protons in the plane of the ring, are usually found to exhibit PMR signals in the range of 6.8-7.5 δ due to (π-electron circulation called 'ring current effect'. Thus they are in deshielding region.

5.3.3 Spin-Spin coupling and splitting of signals:

Consider the NMR of 1,1-dichloro-2,2-dibromoethane (Fig.2.) Based on the different electronegativities of chlorine and bromine, the protons in the molecule are environmentally on equivalent and should thus give signals at different chemical shifts. The dichloromethyl proton would appear down field (higher ä -value) relative to the dibromomethyl proton. The actual NMR spectrum indeed shows two different signals, one for H_a and one for H_b, but each absorption consists of two lines and is termed a doublet. The signal for each proton is thus split" into two resonances. This splitting is due to the fact that spin state of each proton is perturbed by the spin state of the neighboring proton.

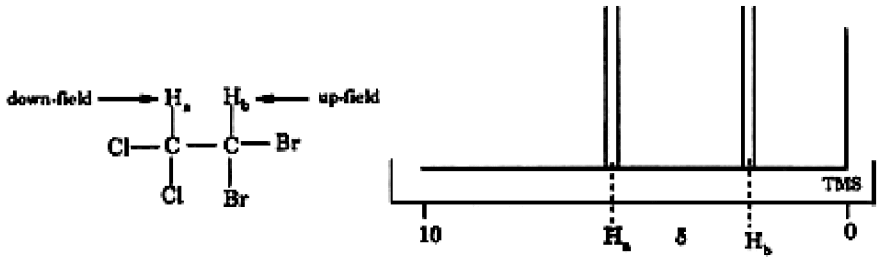
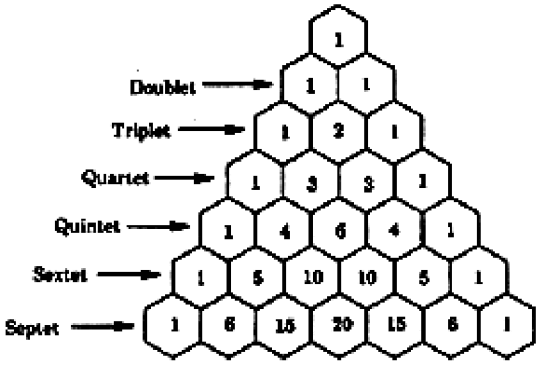


Fig.2

5.3.4 n + 1 rule for splitting pattern and intensities of lines:

The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the '**n+1 rule'**, where n is the number of neighboring spin-coupled nuclei. If there are 2 neighboring, spin-coupled, nuclei the observed signal is a triplet (2+1=3); if there are three spin-coupled neighbors the signal is a quartet (3+1=4). In all cases the central line(s) of the splitting pattern are stronger than those on the periphery. The n+1 rule for predicting the multiplicity of given proton signal holds when the coupling constants with all the nearest neighbours are the same. The intensity ratio of these lines is given by the numbers in Pascal's triangle. Thus a doublet has 1:1 or equal

intensities, a triplet has an intensity ratio of 1:2:1, a quartet 1:3:3:1 etc. Pascal's triangle is given below.



Pascal's Triangle

In fact, the relative intensities of the individual lines of a multiplet correspond to the numerical coefficient of the lines in the binomial expression: $(1+x)^n$, where n= number of neighbouring protons to the concerned proton whose signal is being investigated.

When n=1, the result of the above equation is 1+x. Therefore, the spectrum will be doublet with the intensity 1:1. If n=2, then the expression is $(1+x)^2$ and on expansion, the result is $(1+2x+x^2)$. The spectrum would, therefore, be a triplet and the ratio of the intensities of the lines would be 1: 2: 1, i.e., the ratio of the coefficients.

If n= 3, then $(1+x)^3 = 1 + 3x^2 + 3x + x^3$. Thus the signal would be a quartet and the ratio of the intensities of lines would be 1: 3: 3:1.

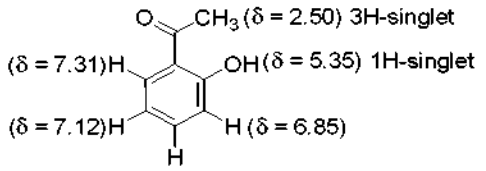
Since the present book is on the practical syllabus, detail discussions on NMR spectroscopy are beyond the scope of this book. Interested students consult the references given at the end of the chapter.

5.3.5 Assignment and Example of ^{1}HNMR values:

Each student in the laboratory should give an assignment to distinguish various peaks and label the peak in the ^{1}H NMR spectra of the known organic compounds explaining the relative δ-values and splitting pattern. The students must record ^{1}H NMR spectral analysis of at least 15 (fifteen) compounds. This assignment will enable the student to characterize unknown organic compounds. Example of labelling some molecules from actual ^{1}HNMR data are given below. Only the δ values with some comments are given.

Actual nature of the curves of some compounds have been shown at the end of this topic.

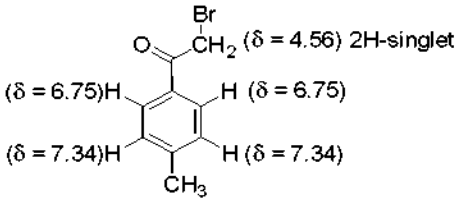
1.



Ranges of aromatic protons have been shown. They appear as multiplet within a range of 6.85-7.47 δ

NMR signals of o-Hydroxyacetophenone

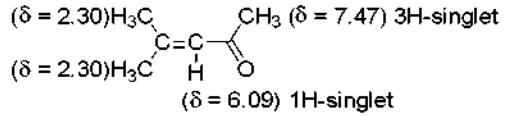
2.



Ortho aromatic protons at (6.75 δ) will appear as 2H doublet and so also protons at(7..4 δ)

NMR signals of p-Methyl-α-bromoacetophenone

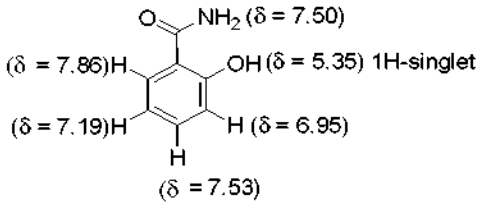
3.



Two CH_3 group at (2.30 δ) will appear as 6H singlet. The only plefinic H will appear as 1H singlet at (6.09 δ)

NMR signals of Mesityl oxide

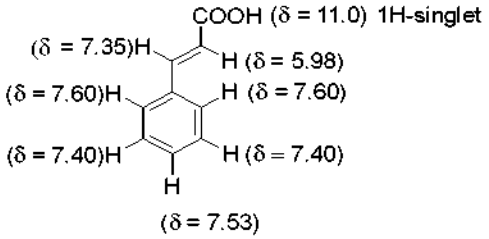
4.



Aromatic -OH proton appears as 1H-siglet at (5.35 δ). All other aromatic protons appear as multiplate signals in the range between 6.96-7.86 δ

NMR signals of Salicylamide

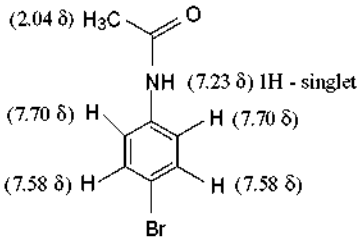
5



COOH proton appears at a very down-field of (11.0 δ). Benzylic hydrogen of the double bond gives signal at (7.35 δ). The proton on the α-carbon of the acid gives signal at (5.98 δ) as a doublet. All other aromatic protons appear as multiplet in the range of 7.33-7.60 δ.

NMR signals of p-Methyl-α-bromoacetophenone

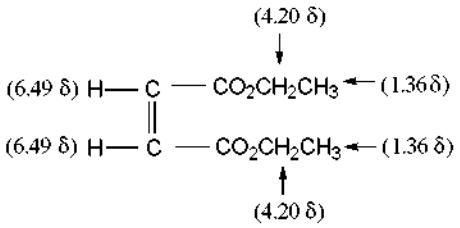
6.



NMR signals of p-Bromoacetanilide

CH_3 protons appear as singlet at (2.04 δ).
NH proton also appear as singlet at (7.23 δ).
Ar-H ortho to Br atom gives doublet at (7.58 δ) and Ar-H ortho to NH give singlet at (7.70 δ). They appear as doublet.

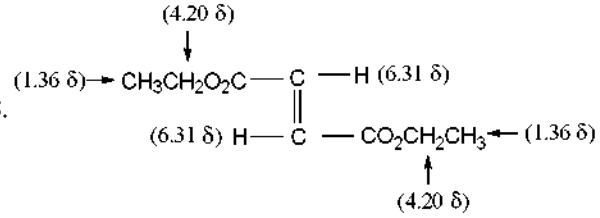
7.



NMR signals of Diethyl malonate

CH_2 protons appear as 4H quartet at (4.20 δ).
CH_3 protons appear as 6H triplet at (1.36 δ).
Two olefinic protons appear as singlet at (6.49 δ).

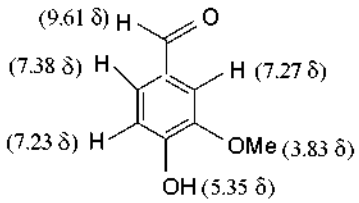
8.



NMR signals of Diethyl furanate

CH_2 protons appear as 4H quartet at (4.20 δ).
CH_3 protons appear as 6H triplet at (1.36 δ).
Two olefinic protons appear as singlet at (6.49 δ).

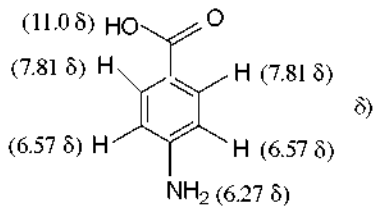
9.



NMR signals of Vanillin

Aldehyde proton gives a down-feild signal at (9.61 δ). CH_3 protons of methoxyl group gives signal at (3.83 δ) as 3H singlet.
OH proton gives a 1H singlet at (5.35 δ). Three Ar-H give a combination of signals around (7.23 δ).

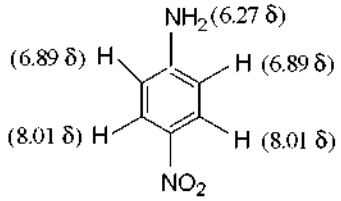
10.



NMR signals of p-Aminobenzoic acid

Acidic proton gives a signal at (11.0 δ).
NH_2 protons appear at (6.27 δ) as a singlet.
Two aromaticprotons ortho to NH_2 group give at (6.57 δ) in the form of doublet.
Two aromatic protons ortho to COOH group gives signal at (7.81 δ) as doublet.

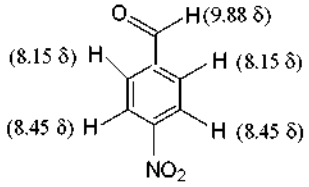
11.



NMR signals of p- Nitroaniline

Two NH_2 protons appear at (6.27 δ) as singlet.
Two Ar-H ortho to NH_2 group give doublet signal at (6.89 δ).
Two Ar-H ortho to NO_2 group give signal as singlet at (8.01 δ).

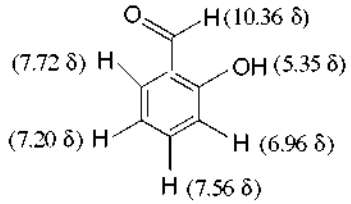
12.



NMR signals of p- Nitrobenzaldehyde

Aldehyde proton appears at (9.88 δ) as singlet.
Two Ar-H ortho to aldehydic group give signal at (8.15 δ) as doublet.
Two Ar-H ortho to NO_2 group come at (8.45 δ) as doublet.

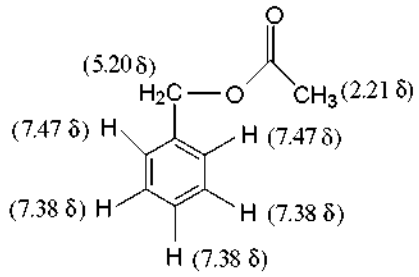
13.



NMR signals of o- Hydroxybenzaldehyde

Aldehyde proton appears at (10.36 δ) as singlet.
Proton of OH group appears at (5.35 δ) as singlet.
Four Ar-H give combination of signals around (6.96 - 7.72 δ).

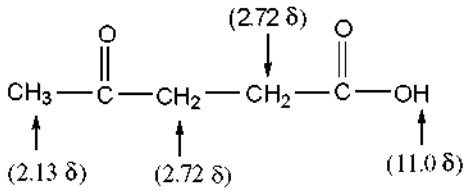
14.



Acetate CH_3 group appears at (2.21 δ) 3H singlet. Two benzylic protons give a signal at (5.20 δ). Five aromatic protons give a multiplet around (7.40 δ)

NMR signals of Benzyl acetate

15.



Due to similar electronic enviroments both the CH_2 groups appear at (2.27 δ) 4H singlet. CH_3 group gives a 3H singlet at (2.13 δ). Acidic hydrogen is highly deshielded and gives a singlet at (11.0 δ)

NMR signals of 4-Oxopentanoic acid

5.4 Infrared Spectroscopy (IR)

The light our eyes see is but a small part of a broad spectrum of electromagnetic radiation. On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the low energy side is the infrared. The portion of the infrared region most useful for analysis of organic compounds is not immediately adjacent to the visible spectrum, but is that having a wavelength range from 2,500 to 16,000 nm, with a corresponding frequency range from 1.9×10^{13} to 1.2×10^{14} Hz.

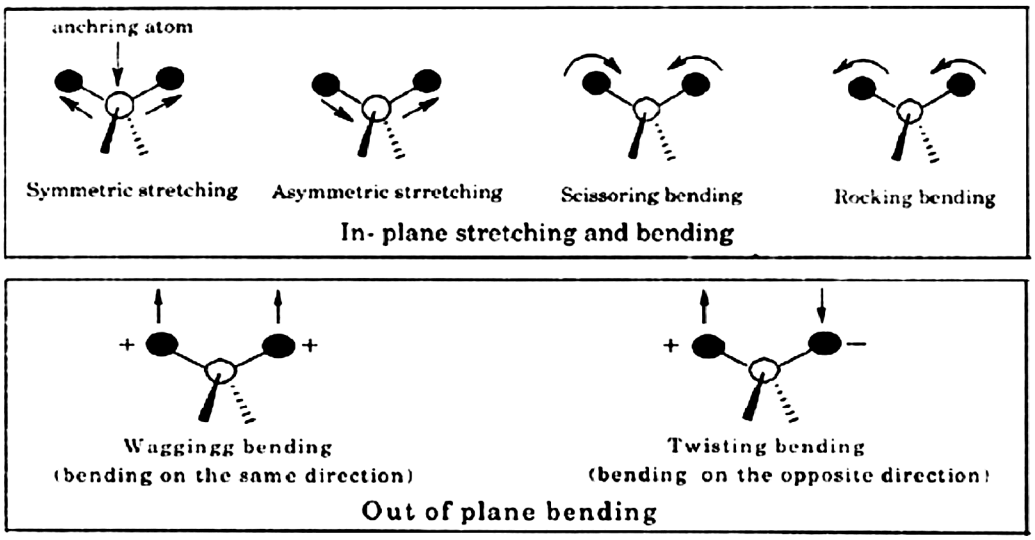
Light energies associated with this part of the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of **covalently bonded atoms and groups**. The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent.

5.4.1 Molecular Vibrations:

Two kinds of fundamental vibrations for covalent molecules are a) **Stretching (and compressing)** and b) **Bending**. Stretching is **in-plane** vibrations in which the bond distance between two atoms increase or decreases, but the atoms remain in the same bond axis. Bending is **out of plane** vibrations in which the position of the atoms changes relative to the original bond axis. The various stretching and bending vibrations of a bond occur at certain quantized frequencies, i.e., definite amount of energy is required for the execution

of the process. Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting.

Some of the various stretching and bending vibrations that can exist within a molecule are shown schematically in the following Fig.-1, taking A_2X type molecule as example. In this case X is the anchoring atom 'O' and '●' are 'A' atoms. The two A-X bonds stretches or bends. Anchoring atom is not displaced from its position during stretching and bending processes.



It should be noted that infrared spectrum of a molecule occurs due to the transitions between two different vibrational energy levels. The vibrational energy levels of various bonds of each molecule are quantized and are naturally fixed. The quantized nature of vibrational energy of a chemical bond is given by the expression;

$$E_{vib} = \left(V + \frac{1}{2}\right)h\nu \quad \text{.....(1)}$$

where V is the number of the vibrational level and can have the values 0,1,2,3..... etc., h = planck's constant, ν = vibrational frequency. Vibrational stretching frequency of a bond between two atoms, if considered as two masses of m_1 and m_2 are joined by a spring, can be calculated in cm by the application of Hooke's law, which is a simple law of mechanics. IR peaks are normally expressed in terms of ν (wave number). The necessary equation, according to the Hooke's law, is given below.

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\frac{m_1 m_2}{m_1 + m_2}}} \quad \text{.....(2)}$$

$\bar{\nu}$ is the wave number in cm^{-1} where c = velocity of light electromagnetic radiation), k= force constant and is directly proportional to bond strength, and $(\frac{m_1 m_2}{m_1 + m_2})$ is called reduced mass. From the equation (2), it is evident that frequency $\bar{\nu}$ is directly proportional to the force constant 'k' and inversely proportional to the reduced mass $\left(\frac{m_2 m_2}{m_2 + m_2}\right)$, often symbolized as μ. When energy is absorbed, the frequency of vibration (shown as waves) is not changed but the amplitude of the wave is changed.

5.2.2 Factors affecting vibrational frequencies:

Several factors like (i) resonance effect (ii) inductive effect (iii) intra and inter molecular hydrogen bondings (iv) steric factor (v) conformations and (vi) reduced mass can influence vibrational frequencies of same types of bonds, when present in different molecules.

One fundamental fact to be remembered is that, any effect which decreases the bond strength of a bond would cause the value of absorption frequency to decrease and vice versa.

It is to be noted that IR spectroscopy is mostly used to find out the nature of the functional groups during the determination of structures of organic molecules. Most of the functional groups comprising different types of bonds have specific absorption regions. These bands are recorded in spectrophotometer and analyzed using spectra of certain standard molecules. Extensive standard data are available today for comparison of spectra. Vibrational frequency values of a few very important bonds are recorded below as examples. IR values are expressed as $\bar{\nu}_{max}(cm^{-1})$.

Unlike UV spectrum, IR band carries no values for absorption intensity. Spectrum shows strong peaks and weak peaks. Mother important fact is that in an IR curve, frequency (wave number in cm^{-1}) and also wavelength in micron, i (or in $\mathring{A}$) are plotted in X-axis and %Transmittance (inverse of Absorbance) is plotted in Y-axis.

It is to be noted that stretching of a bond requires more energy than that of bending. Therefore, stretching frequency- values are always higher than that of bending frequency values. In structure determination maneuver, stretching frequency of a bond is more important than bending frequency. Following table gives the stretching frequency values of

a few important functional groups.

Functional group	**Frequency** (cm^{-1})
Alcohol O — H (free)	3640 — 3610
Alcohol O — H (H-bonded)	3500 — 3200 (variable)
Amine N — H	3500 — 3300 (1° d), 2° (s)
Terminal Alkyne C — H	3315 - 3270
Olefinic and Aromatic C — H	3080 — 3020
Aliphatic C — H	2990 — 2850
Aldehyde C—H	2900—2.700
Nitrile —C ≡ N	2300 — 2200
Terminal —C ≡ C	2260 — 2210
Internal —C ≡ C—	2140 — 2100 (weak)
Ester C=O	1750—1740
Aldehyde C=O	1740 — 1720
Ketone C=O	1700— 1720
Amide C=O	1715—1650
A β-Unsaturated ketone	1680 — 1660
Alkene C=C	1675 — 1640
Aliphatic C — O	1280 — 1000 (strong)

For more data, see the references given at the end of this Chapter.

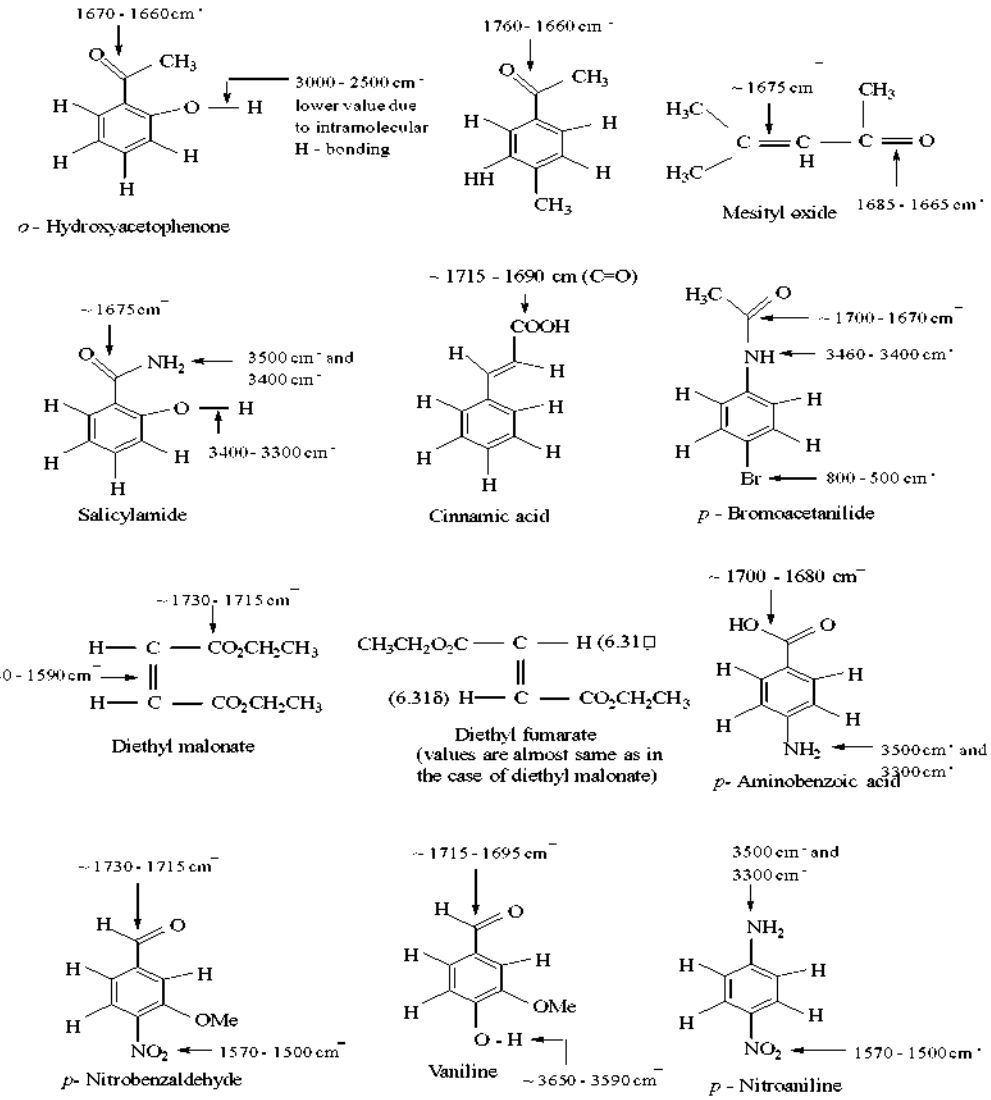
Several general facts on IR frequencies are summarized as follows:

1. Multiple bonds are stronger than single bonds, and thus have larger force constants and at higher frequencies than single bonds.
2. More polar bonds are generally stronger than less polar bonds and consequently absorb at higher frequencies.
3. Conjugation always lowers the absorption frequency of each conjugated group because the contributions of resonance forms with lower bond orders.
4. Hydrogen bonding causes the absorption frequency of acidic protons to vary widely, depending on the solution environment. In general, the greater the H-bonding, the lower is the absorption frequency. For example, normal alcohol OH groups in dilute, nonbasic solvents come at 3610-3650 cm^{-1} (called the free OH stretch). As the concentration is increased, and H bonding increases, the OH absorption becomes broad and moves to lower frequencies.

5.4.3 Assignment and Example of IR values:

Each student in the laboratory should give an assignment to distinguish various peaks peaks in the IR spectrum of the known organic compounds explaining the relative frequencies of the absorptions. The students must record IR spectral analysis of at least 15 (fifteen) compounds. This assignment will enable the student to characterize unknown organic compounds.

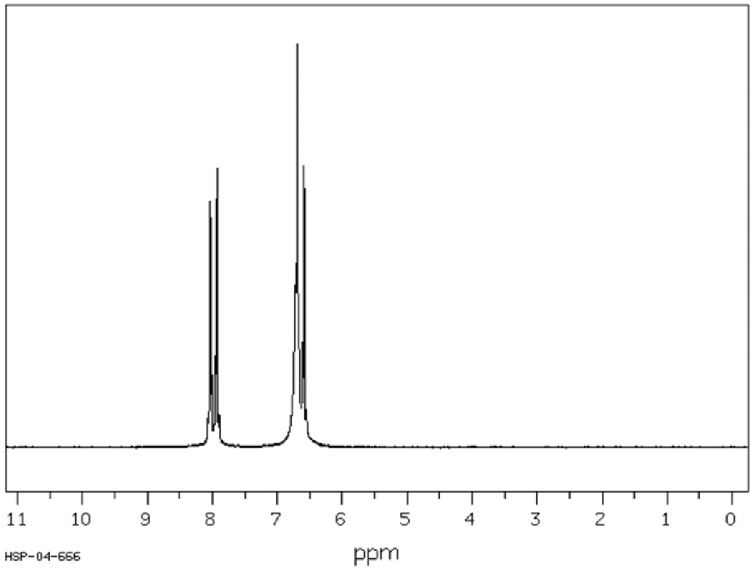
A few examples of IR spectra of compounds are given below. In all these case, the stretching frequencies of strong peaks characteristics for each compound is given. The values may be slight more or less depending on the nature of the solvents used and the concentration of the solutions. These factors cannot be discussed here.

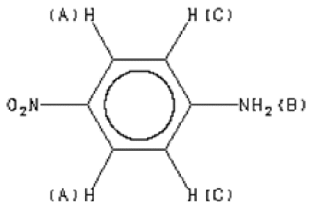


5.5 Few example of typical spectral data:

Here we will see actual nature of spectral data (NMR & IR spectra) of some compounds within the syllabus, full data of which have to analysis (at least 15 compounds) by the students during the practical practice. All the data picture has been collected from the Spectral Database for Organic Compounds SDBS (SDBS Web): https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, August 2019)

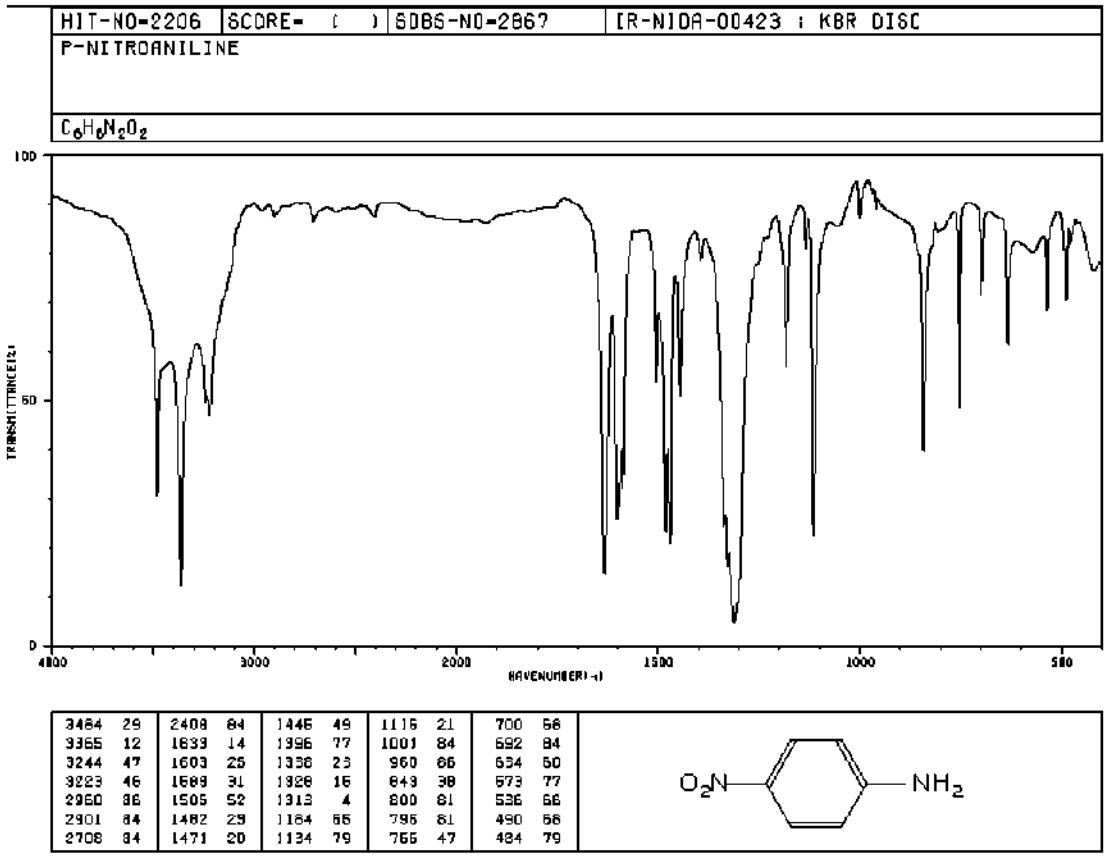
5.5.1 Spectral data for 4-Nitroaniline : A typical NMR spectrum for Nitroaniline is shown below





Assign.	Shift (ppm)
A	7.972
B	6.71
C	6.64

A typical IR spectrum for Nitroaniline is shown below



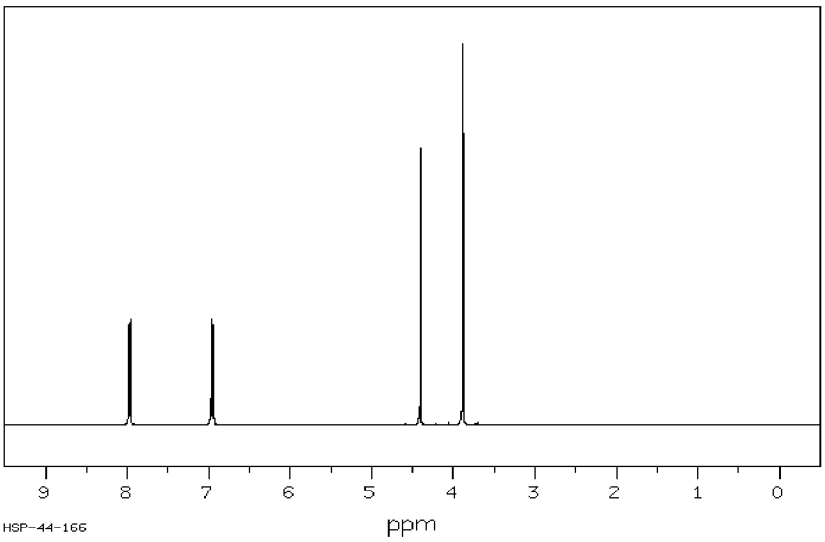
3484	29	2408	84	1446	49	1116	21	700	56
3365	12	1633	14	1396	77	1001	84	692	84
3244	47	1603	25	1336	23	960	66	634	60
3223	46	1569	31	1328	16	849	38	573	77
2960	86	1505	52	1313	4	800	81	536	66
2901	84	1482	29	1164	66	795	81	490	66
2708	84	1471	20	1134	79	755	47	484	79

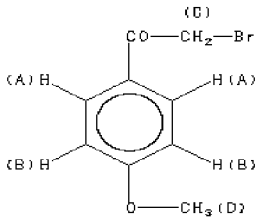
5.5.2 Spectral data for 2-Bromo-4'-methylacetophenone:

Typical NMR spectrum for 2-Bromo-4'-methy lacetophenone is shown below

399.65 MHz

0.042 g : 0.5 ml $CDCl_3$

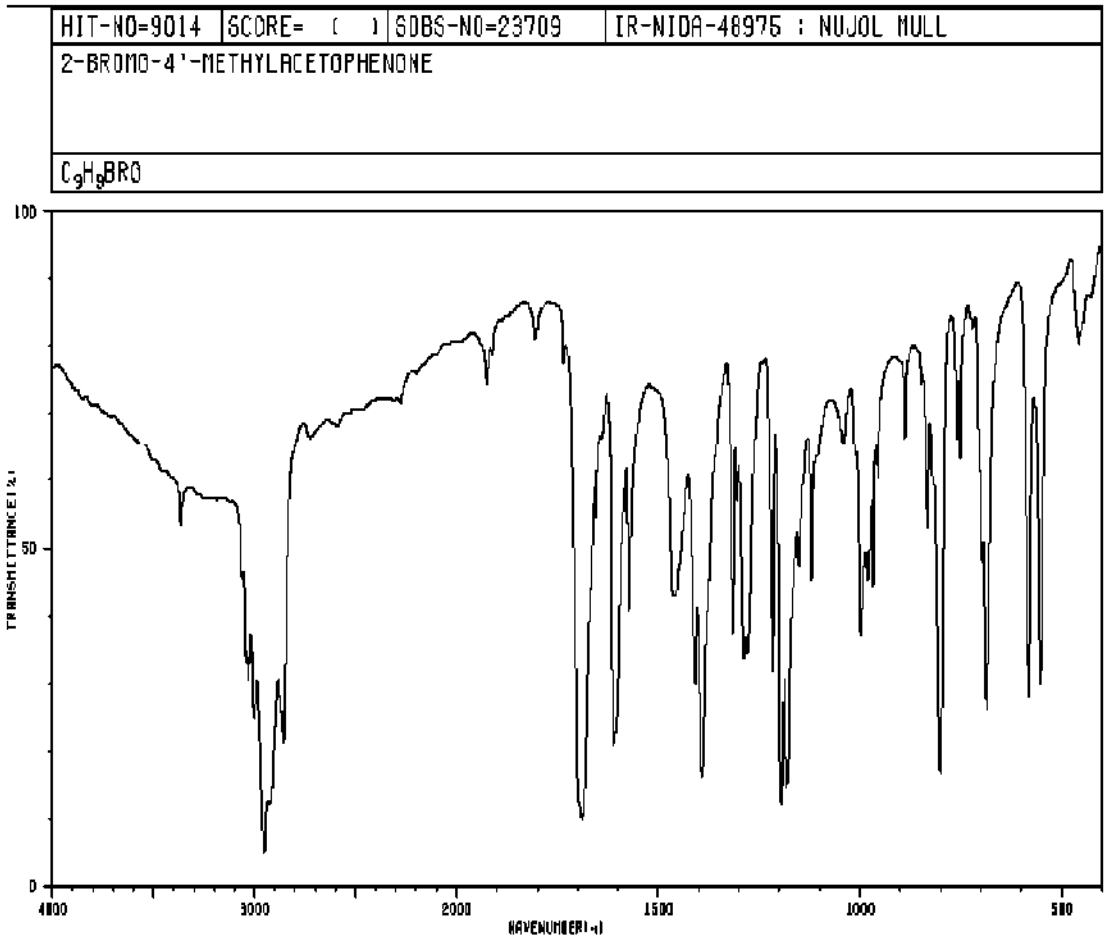




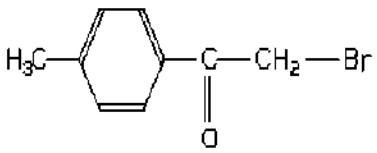
标记氢	化学位移(ppm)
A	7.966
B	6.957
C	4.402
D	3.880

Hz	ppm	Int.
3190.92	7.985	51
3188.11	7.978	269
3186.04	7.973	89
3181.15	7.960	95
3179.20	7.955	277
3176.27	7.948	28
2787.35	6.975	53
2784.42	6.968	277
2782.47	6.963	90
2777.59	6.951	90
2775.51	6.945	262
2772.58	6.938	25
1759.40	4.403	726
1550.90	3.881	1000

Typical IR spectrum for 2-Bromo-4'-methylacetophenone is shown below



3368	50	1688	9	1316	36	1162	45	836	50
3032	29	1655	52	1306	55	1121	43	801	16
3002	23	1611	20	1266	32	1108	60	752	50
2963	4	1573	38	1201	33	998	36	699	46
2927	11	1460	41	1217	30	981	43	687	25
2869	25	1409	28	1196	11	969	42	564	26
2856	20	1393	16	1184	13	966	58	552	28



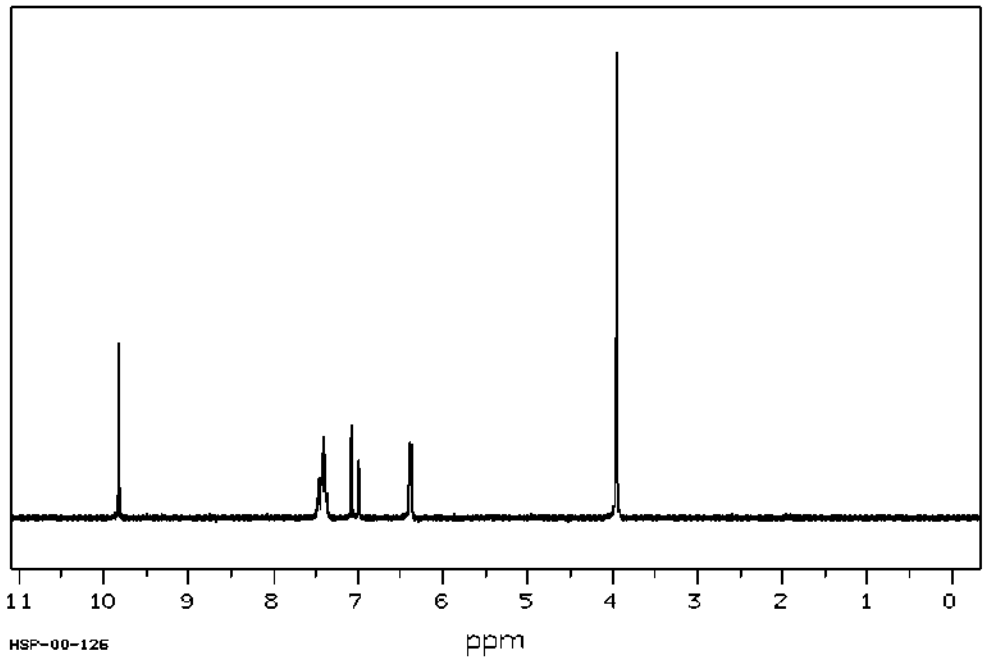
5.5.3 Spectral data for Vanillin:

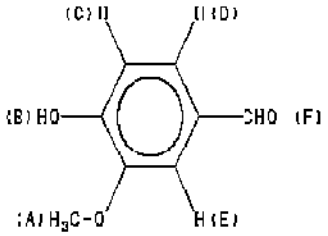
Typical NMR spectrum for Vanillin is shown below:

SDBS-^{1}H NMR SDBS No. 726HSP-00-126 89.56 MHz

$C_8 H_8 O_3$ 0.037 g : 0.5 ml $CDCl_3$

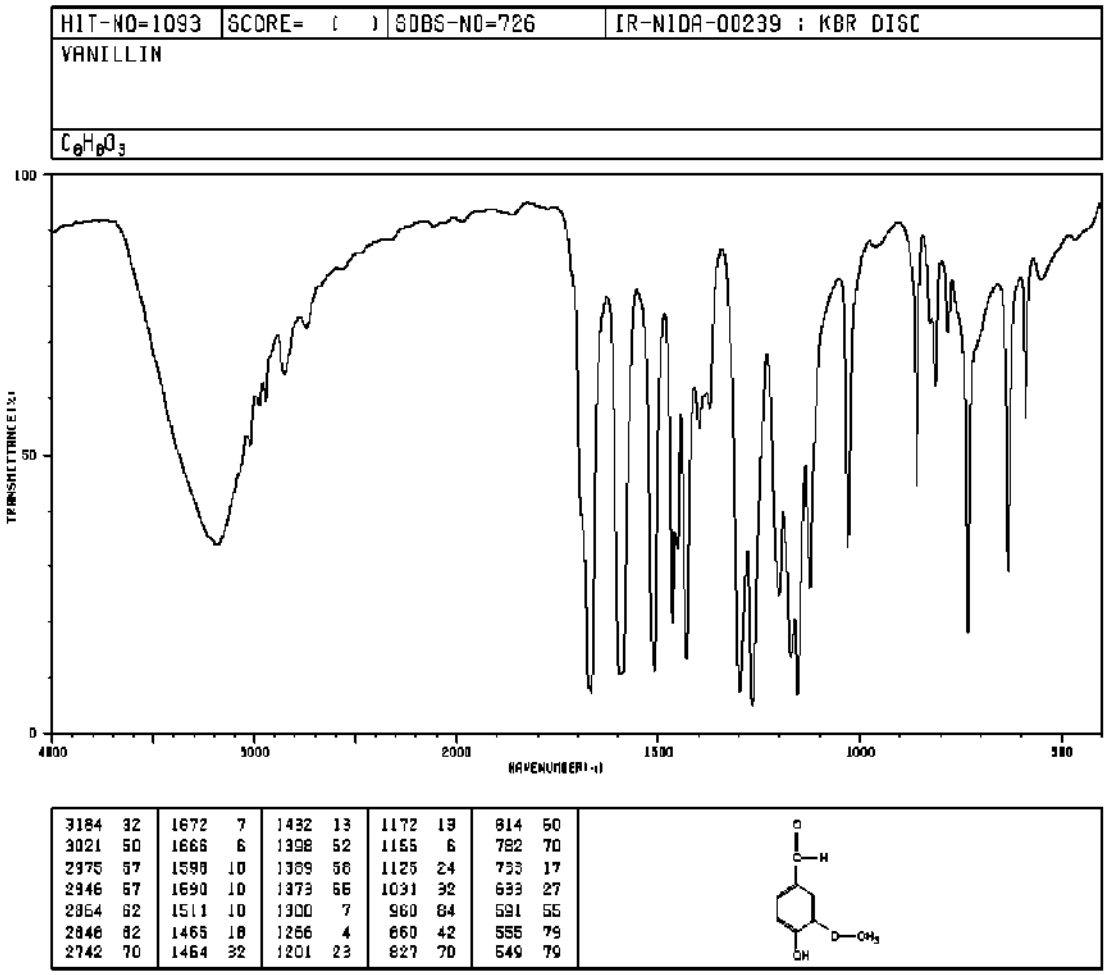
vanillin





Assign.	Shift (ppm)
A	3.959
B	6.39
C	7.047
D	7.42
E	7.42
F	9.823

Typical IR spectrum for Vanillin is shown below:



3184	32	1672	7	1432	13	1172	19	814	50
3021	50	1666	6	1398	52	1155	6	782	70
2975	57	1598	10	1369	56	1125	24	733	17
2946	57	1590	10	1373	56	1031	32	633	27
2864	62	1511	10	1300	7	960	84	591	55
2846	62	1465	18	1266	4	860	42	555	79
2742	70	1464	32	1201	23	827	70	549	79

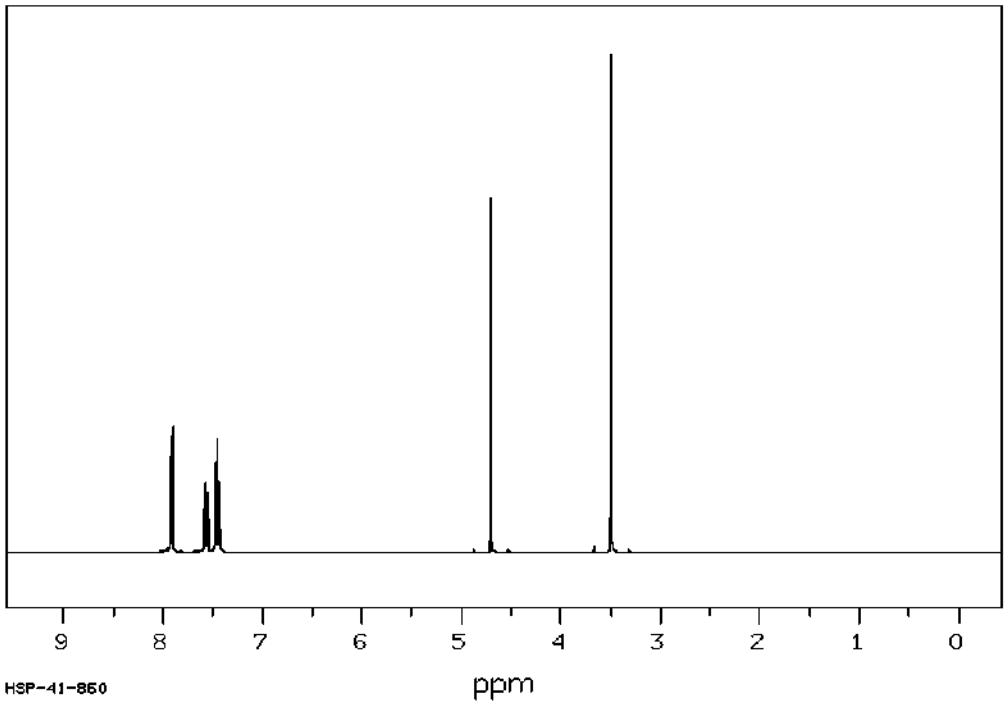
5.5.4 Spectral data for 2-Methoxyacetophenone :

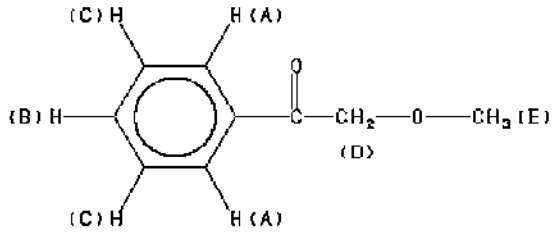
Typical NMR spectrum for 2-Methoxyacetophenone is shown below:

SDBS-^{1}H NMRSDBS No. 13382HSP-41-860 399.65 MHz

$C_9 H_{10} O_2$ 0.05 ml : 0.5 ml $CDCl_3$

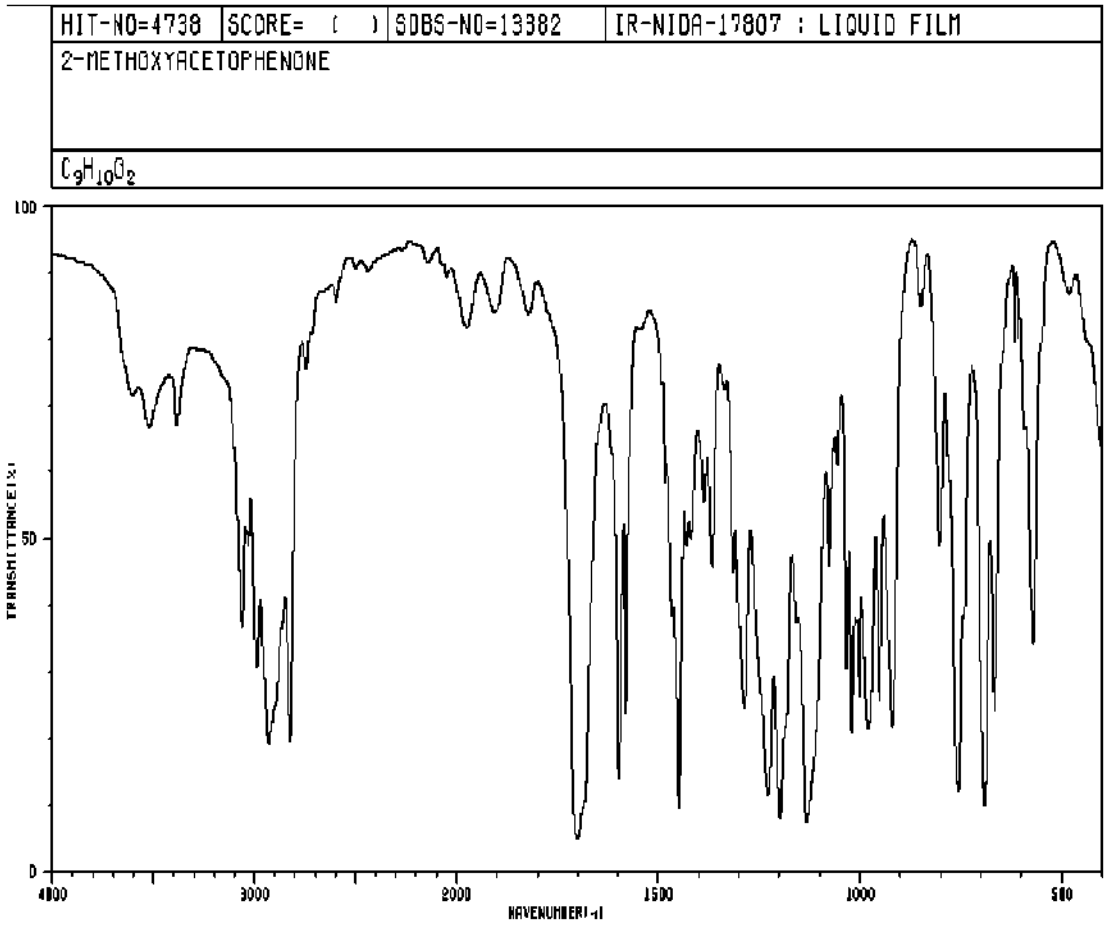
2-methoxyacetophenone



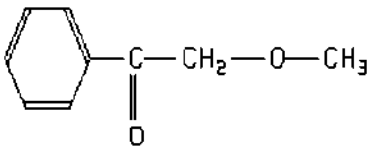


Assign.	Shift(ppm)
A	7.912
B	7.565
C	7.449
D	4.702
E	3.493

Typical IR spectrum for 2-Methoxyacetophenone is shown below:



3062	36	1698	19	1367	44	1077	49	920	21
3030	47	1581	23	1315	43	1033	29	803	47
2990	29	1467	36	1266	23	1021	20	757	11
2931	18	1460	9	1228	10	1011	36	691	9
2898	23	1432	47	1199	7	1002	25	667	23
2825	16	1418	47	1186	20	979	20	577	41
1701	4	1387	59	1131	7	953	24	570	33



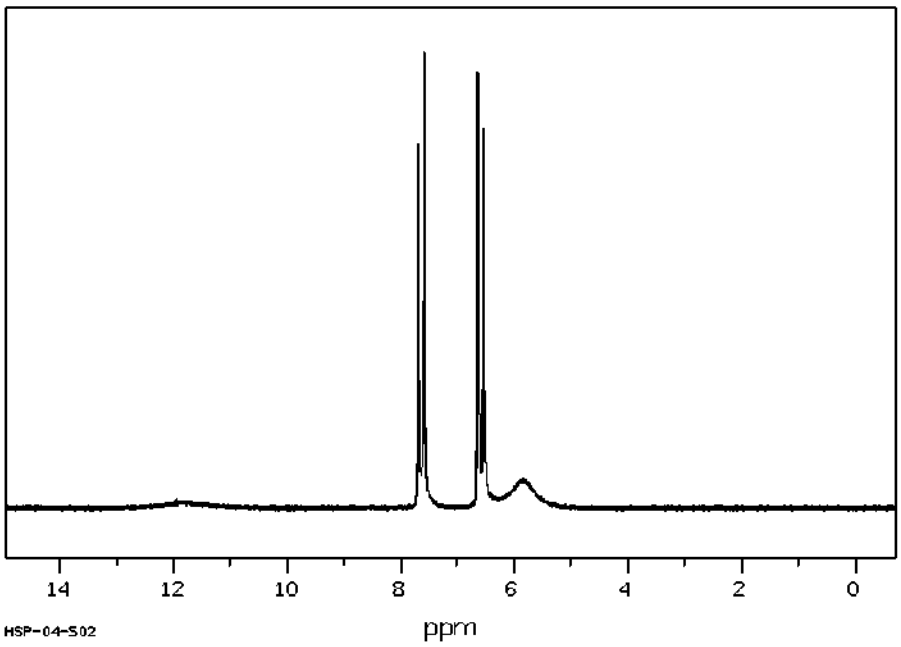
5.5.5 Spectral data for 4-Aminobenzoic acid:

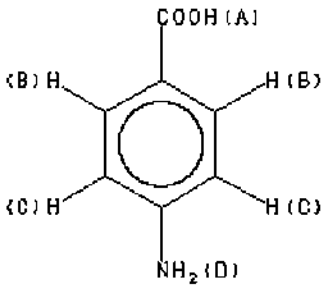
Typical NMR spectrum for 4-Aminobenzoic acid is shown below:

SDBS-^{1}H NMRSDBS No. 1152HSP-04-502 89.56 MHz

$C_7 H_7 N O_2$ 0.039 g : 0.5 ml DMSO-d_6

p-aminobenzoic acid

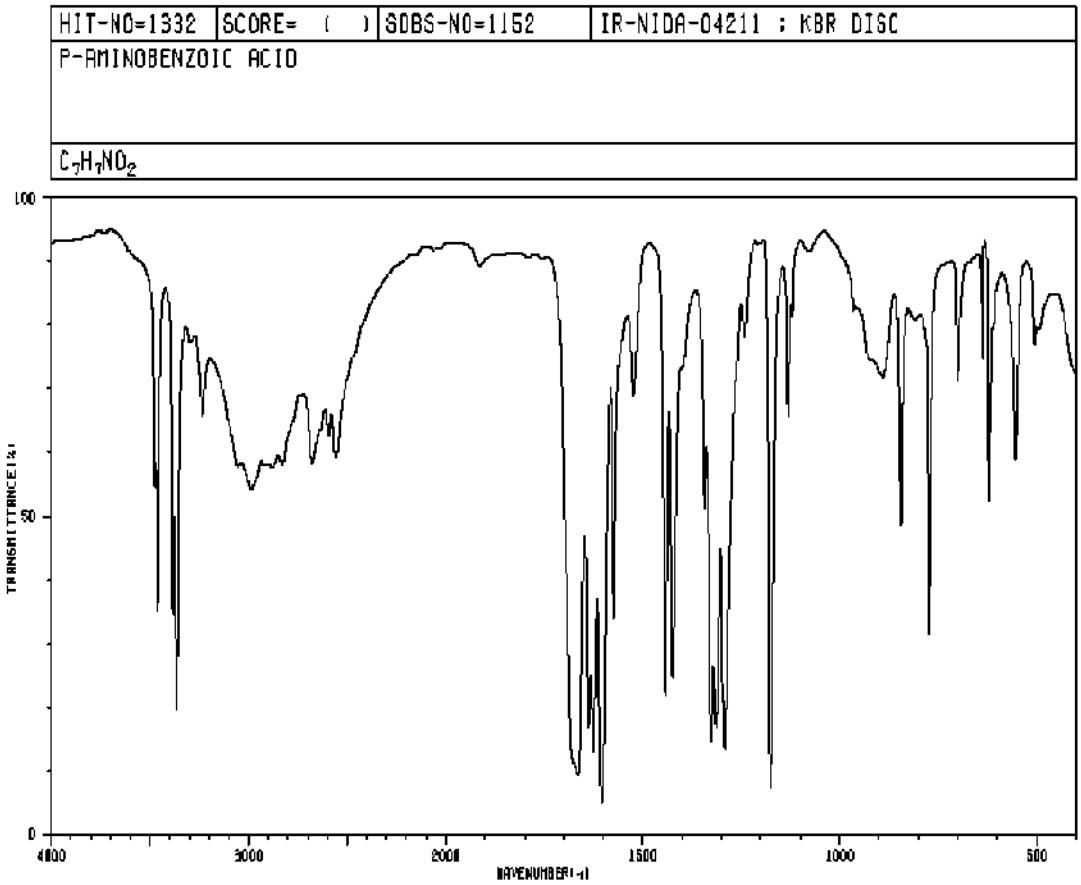




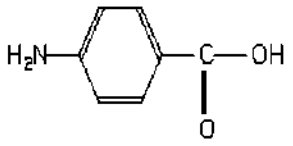
Assign.	Shift(ppm)
A	12.
B	7.648
C	6.577
D	5.9

J(B,C)=8.8HZ

Typical IR spectrum for 4-Aminobenzoic acid is shown below:



3476	62	2829	66	1604	4	1314	16	843	47
3461	34	2679	57	1575	33	1298	20	773	30
3383	33	2598	60	1524	86	1291	15	700	58
3366	18	2567	67	1449	21	1242	74	699	72
3293	74	1665	9	1424	23	1177	7	622	50
3234	84	1638	16	1343	49	1130	64	554	57
2986	62	1626	12	1328	14	891	70	506	74



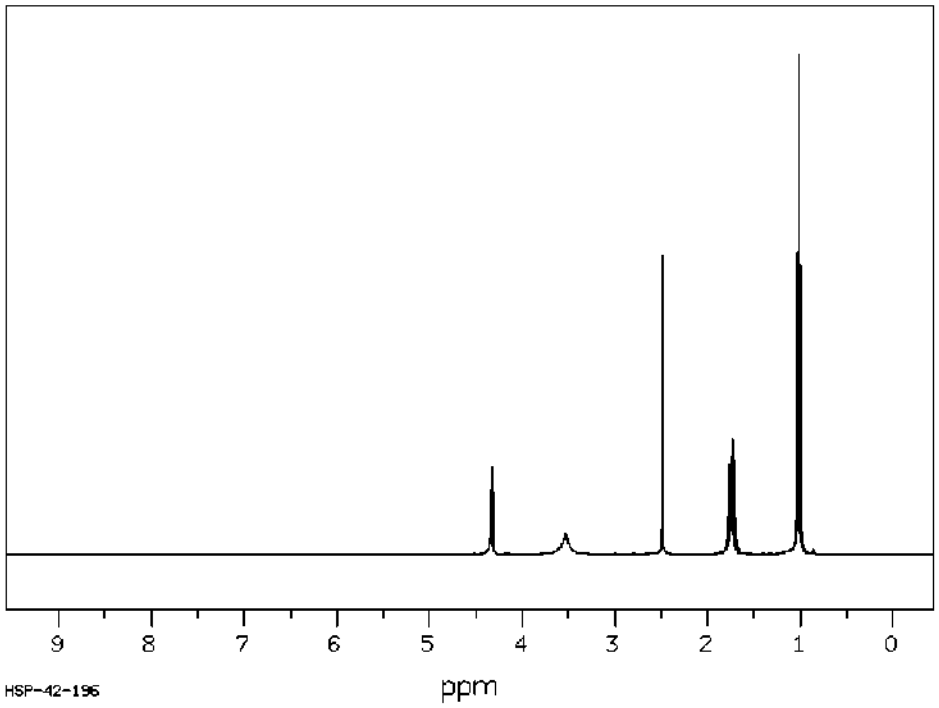
5.3.6 Spectral data for 1-pentyn-3-ol:

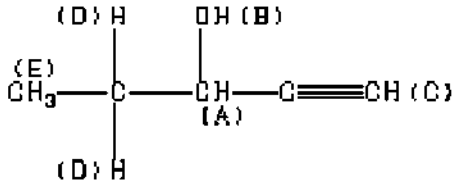
Typical NMR spectrum for 1-pentyn-3-ol is shown below:

SDBS-^{1}H NMRSDBS No. 259HSP-42-196 399.65 MHz

C_5H_8O 0.05 ml : 0.5 ml $CDCl_3$

1-pentyn-3-ol



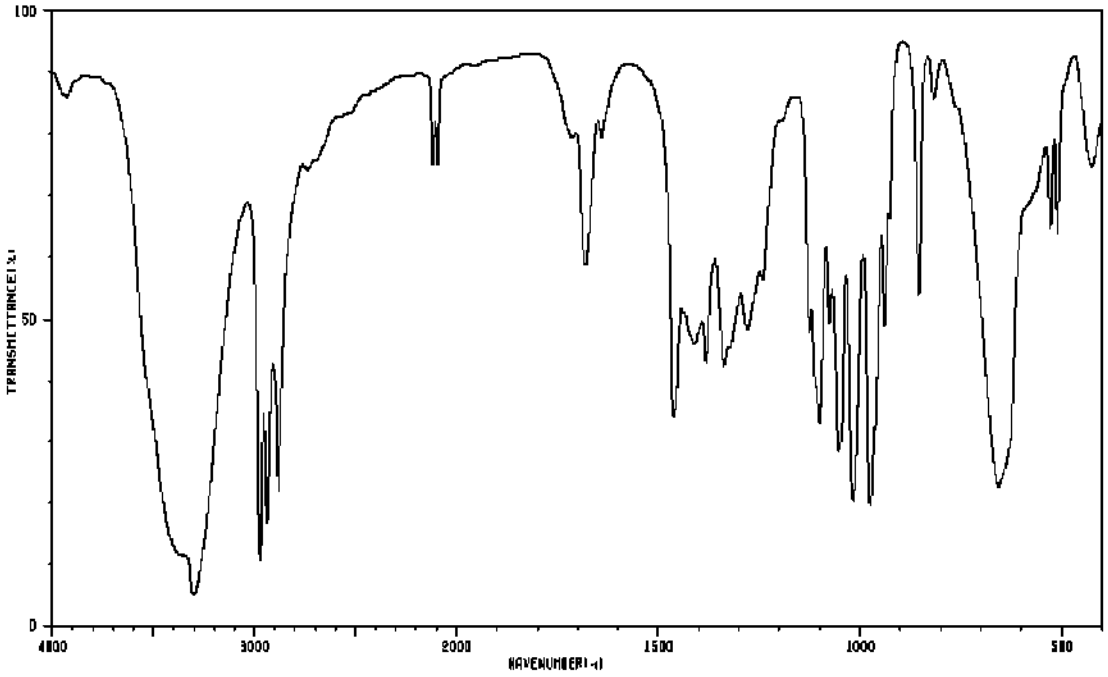


Assign.	Shift (ppm)
A	4.330
B	3.53
C	2.483
D	1.78 to 1.70
E	1.014

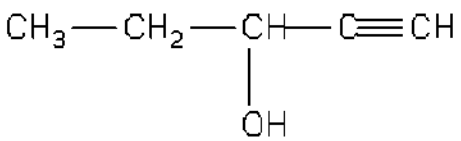
J(A,C)=2.0HZ

Typical IR spectrum for 1-pentyn-3-ol is shown below:

HIT-NO=912	SCORE= ( )	SDBS-NO=259	IR-NIDA-27065 : LIQUID FILM
1-PENTYN-3-OL			
C_5H_8O			



3928	84	1680	67	1280	46	975	18	611	52
3300	4	1641	77	1242	55	962	31	426	72
2971	10	1462	35	1125	46	939	47		
2939	16	1410	44	1101	32	865	62		
2881	21	1362	41	1076	47	818	81		
2116	72	1338	41	1053	27	658	21		
2094	72	1327	48	1017	20	629	62		

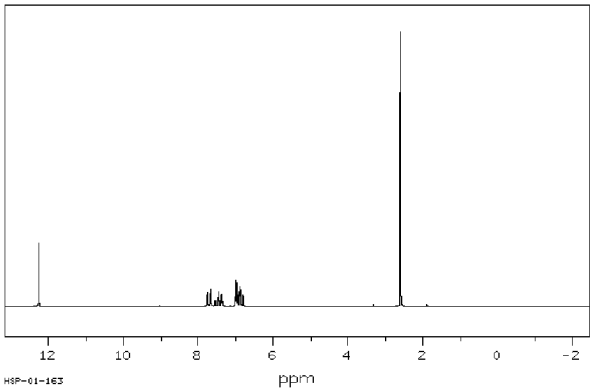


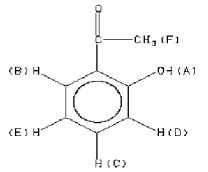
5.5.7 Spectral data for 2'-Hydroxyacetophenone :

Typical NMR spectrum for 2'-Hydroxyacetophenone is shown below :

89.56 MHz

0.04 ml : 0.5 ml $CDCl_3$

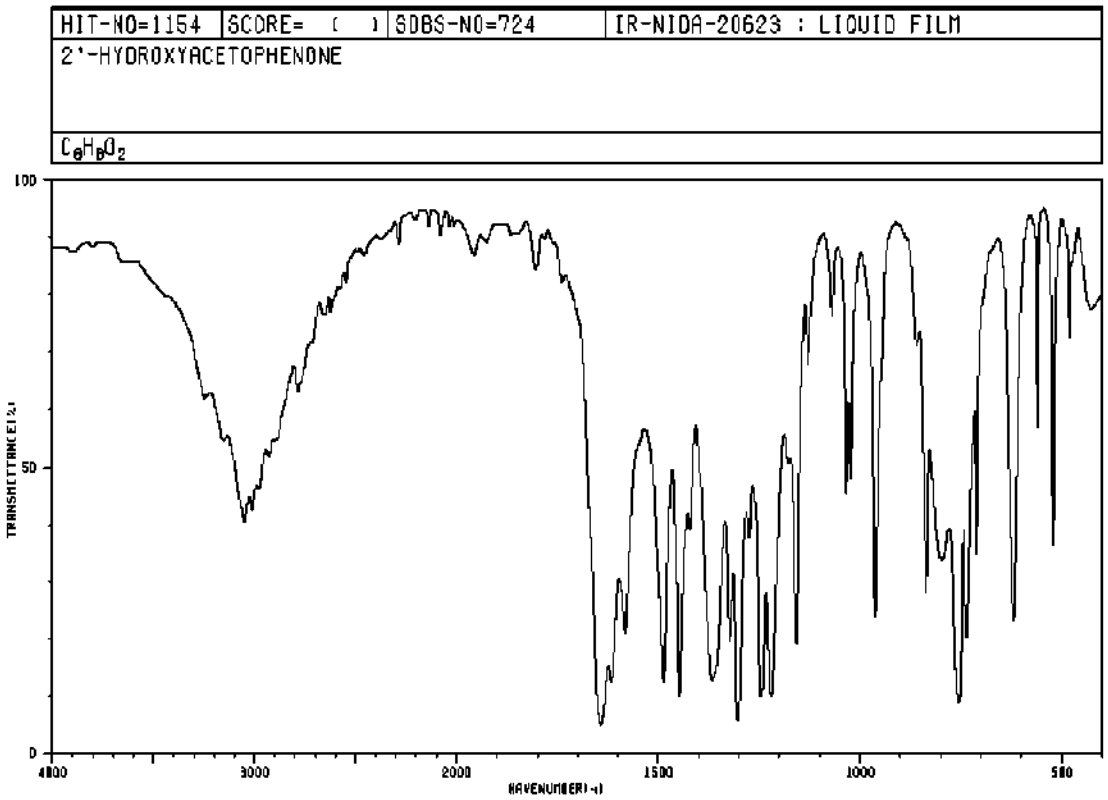




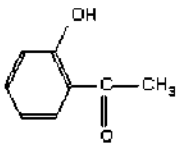
标记氢	化学位移(ppm)
A	12.25
B	7.71
C	7.44
D	6.96
E	6.89
F	2.609

Hz	ppm	Int.
1097.25	12.252	224
1096.83	12.247	230
696.24	7.775	35
695.73	7.769	39
694.10	7.751	50
688.38	7.687	41
687.87	7.681	46
686.24	7.663	62
669.41	7.475	30
667.87	7.458	53
666.67	7.444	34
666.25	7.440	34
661.29	7.384	40
660.86	7.379	44
659.16	7.360	40
627.97	7.012	36
627.45	7.006	60
626.77	6.999	94
626.17	6.992	81
624.04	6.968	85
622.75	6.954	40
619.42	6.917	39
618.99	6.912	51
618.23	6.903	58
617.71	6.898	57
617.11	6.891	67
616.26	6.881	71
615.83	6.877	59
614.98	6.867	51
609.17	6.802	41
607.89	6.788	37
233.62	2.609	1000

Typical IR spectrum for 2'-Hydroxyacetophenone is shown below:



3061	36	1617	12	1303	6	1069	74	766	6
3011	41	1582	20	1275	36	1034	43	737	19
2786	80	1488	12	1245	9	1023	45	712	33
2773	82	1448	9	1221	9	963	22	621	22
2650	74	1421	37	1173	49	860	68	582	55
2823	74	1368	12	1156	16	837	25	522	35
1643	4	1323	18	1129	66	797	32	482	70



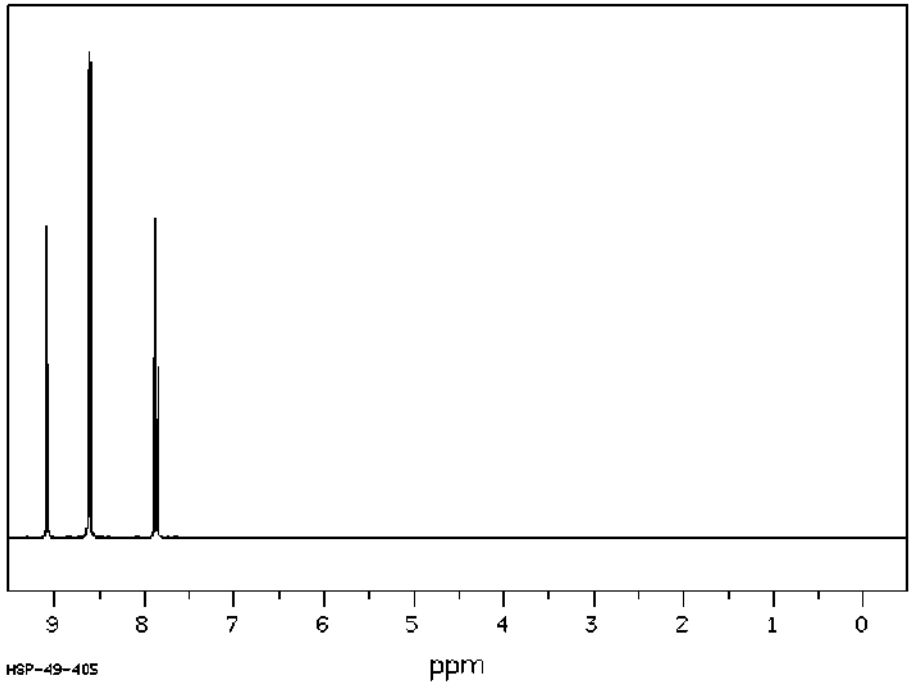
5.5.8 Spectral data for 1,3-Dinitrobenzene :

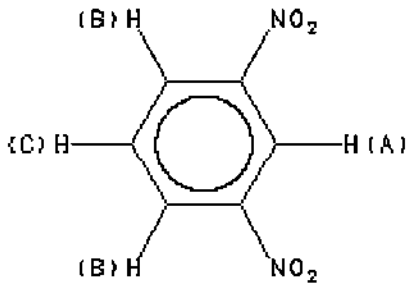
Typical NMR spectrum for 1,3-Dinitrobenzene is shown below :

SDBS-^{1}H NMRSDBS No. 1117HSP-49-405 399.65 MHz

$C_6H_4N_2O_4$ 0.036 g : 0.5 ml $CDCl_3$

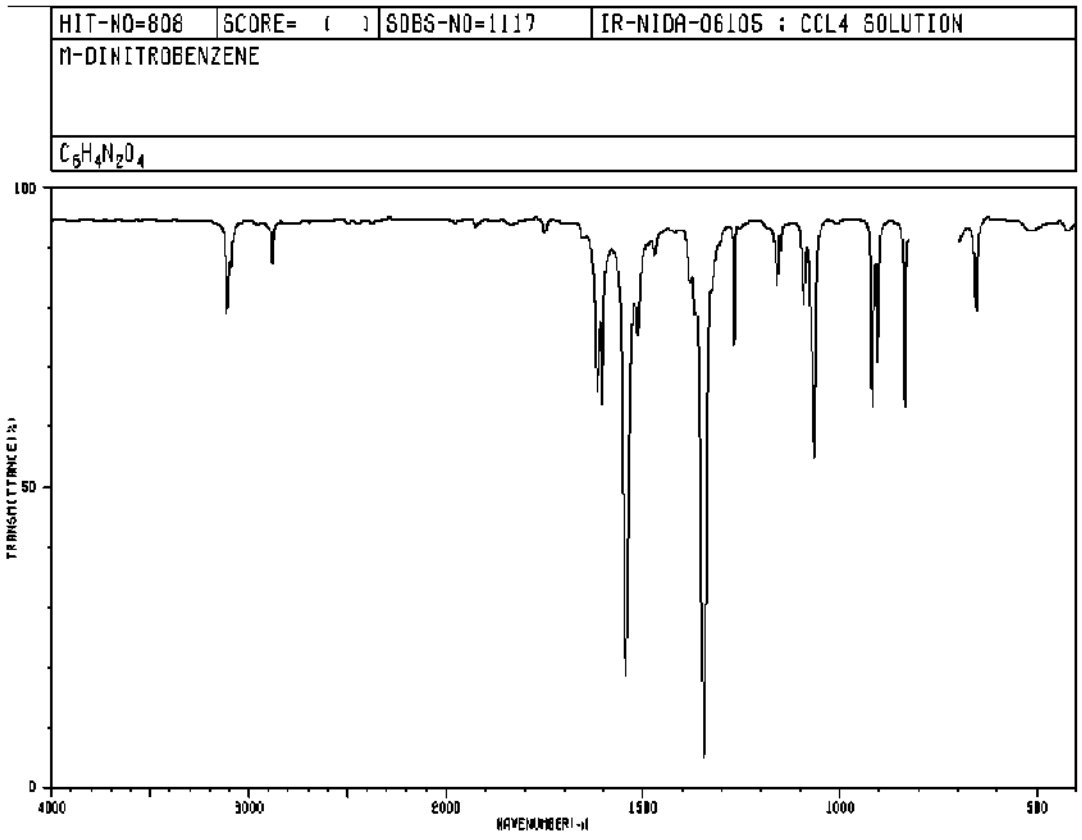
m-dinitrobenzene



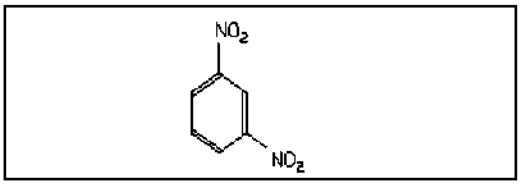


Assign.	Shift(ppm)
A	9.083
B	8.615
C	7.871

Typical NMR spectrum for 1,3-Dinitrobenzene is shown below:



3112	77	1471	86	918	60
3090	84	1346	4	905	68
2863	84	1269	70	835	60
1616	64	1160	81	662	77
1605	60	1151	86		
1544	17	1092	77		
1514	72	1066	69		



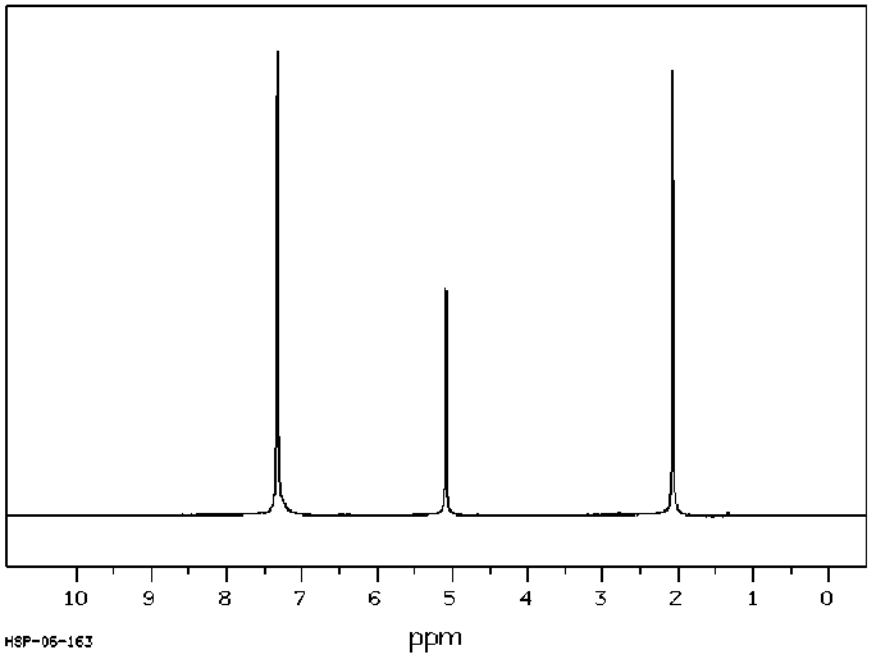
5.5.9 Spectral data for Benzylacetate :

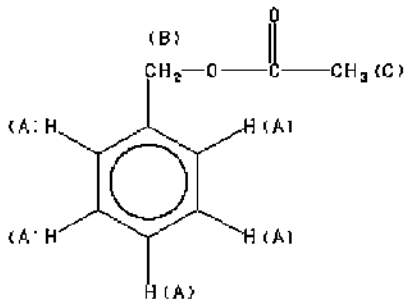
Typical NMR spectrum for Benzylacetate is shown below:

SDBS-^{1}H NMRSDBS No. 810HSP-06-163 89.56 MHz

$C_9H_{10}O_2$ 0.05 ml : 0.5 ml $CDCl_3$

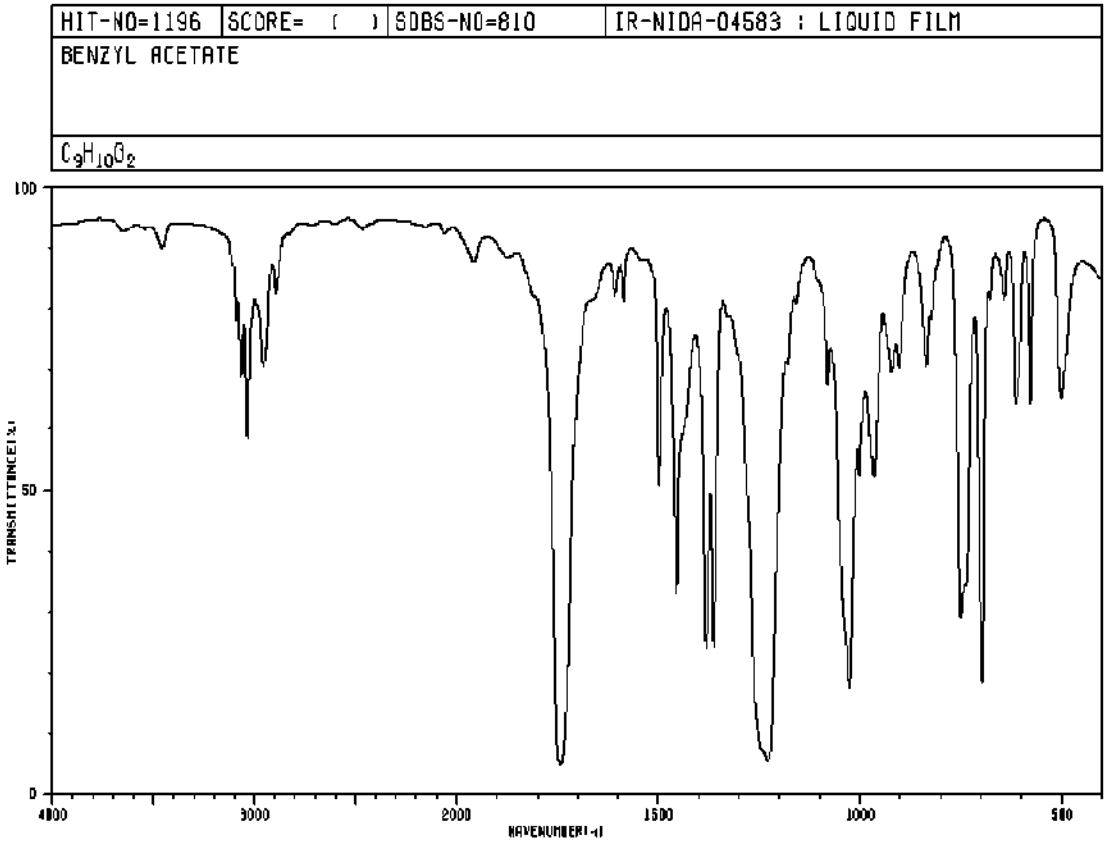
benzyl acetate



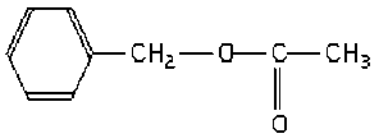


Assign.	Shift (ppm)
A	7.33
B	5.085
C	2.064

Typical IR spectrum for Benzylacetate is shown below:



3091	74	1608	79	1081	64	824	74	578	62
3067	66	1587	79	1027	16	751	27	502	62
3035	57	1498	49	1003	50	739	39	487	72
2966	68	1466	31	966	50	698	17		
2895	79	1381	23	922	66	679	79		
1956	84	1363	29	903	86	644	79		
1743	4	1229	6	837	68	614	62		



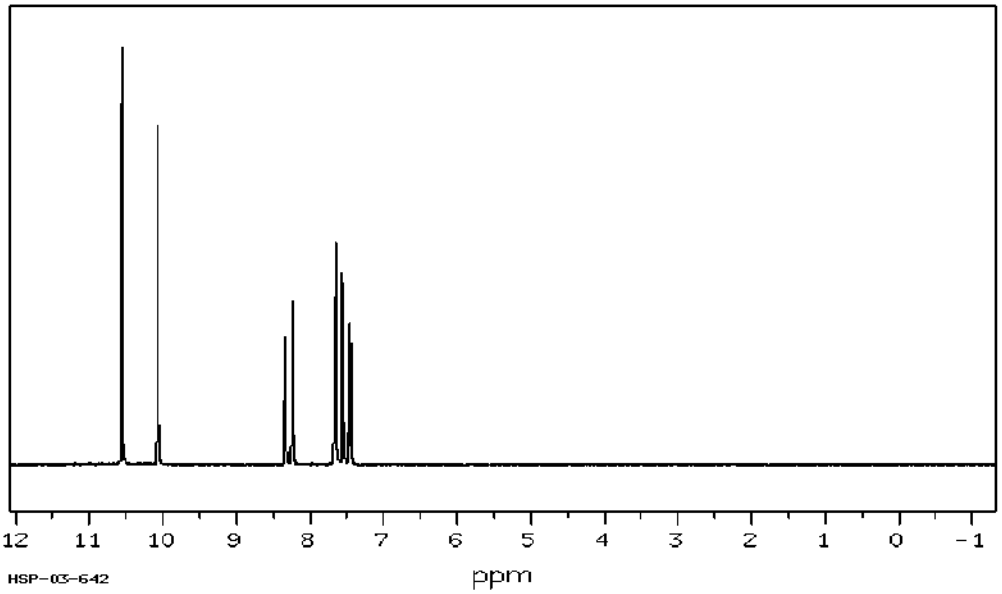
5.5.10 Spectral data for 3-hydroxy-4-nitrobenzaldehyde :

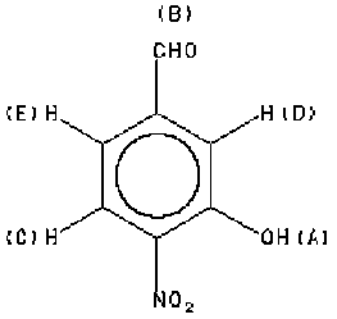
Typical NMR spectrum for 3-hydroxy-4-nitrobenzaldehyde is shown below:

SDBS-^{1}H NMRSDBS No. 13315HSP-03-642 89.56 MHz

$C_7 H_5 N O_4$ 0.041 g : 0.5 ml $CDCl_3$

3-hydroxy-4-nitrobenzaldehyde





Assign.	Shift(ppm)
A	10.56
B	10.068
C	8.281
D	7.660
E	7.514

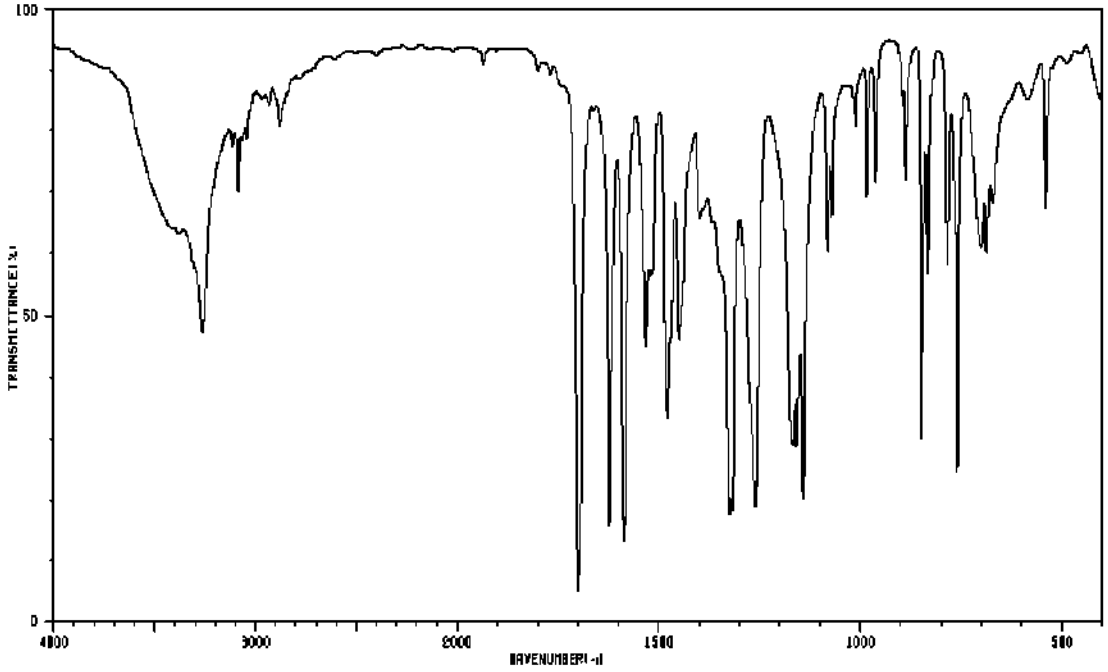
J(B,C)=0.6HZ, J(C,D)=0.4HZ, J(C,E)=8.6HZ, J(D,E)=1.8HZ

Typical IR spectrum for 3-hydroxy-4-nitrobenzaldehyde is shown below:

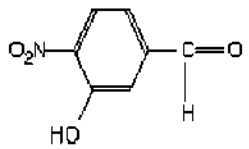
HIT-NO=6883	SCORE= ( )	SDBS-NO=13315	IR-NIDA-17062 ; KBR DISC

3-HYDROXY-4-NITROBENZALDEHYDE

$C_7H_5NO_4$



3262	46	1686	12	1391	64	1081	58	833	65
3112	74	1533	43	1325	17	1072	64	784	57
3087	86	1520	55	1319	17	1013	77	760	23
3043	77	1480	32	1261	18	984	66	701	60
2879	77	1472	43	1169	27	962	66	688	52
1699	4	1450	44	1159	27	866	70	671	66
1622	15	1399	64	1142	19	848	28	641	64



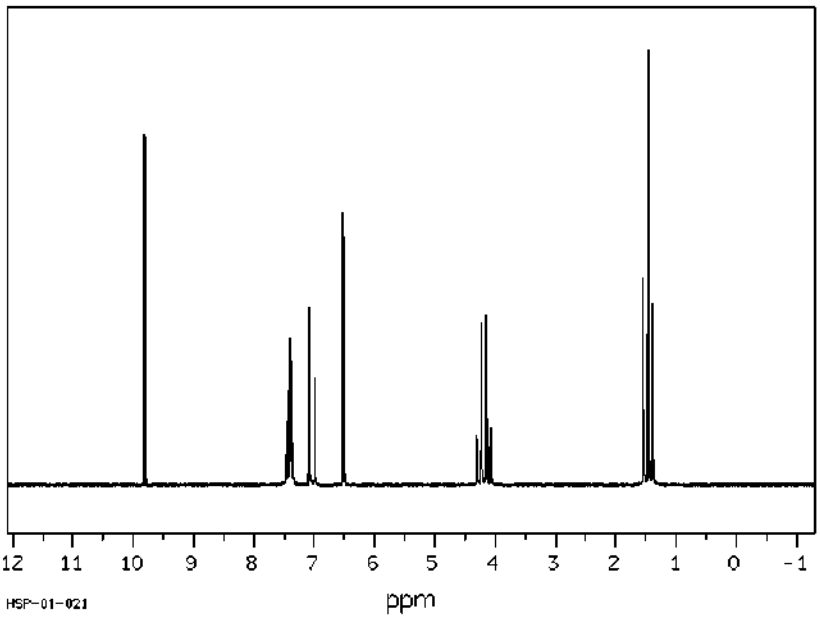
5.5.11 Spectral data for 3-Ethoxy-4-hydroxybenzaldehyde :

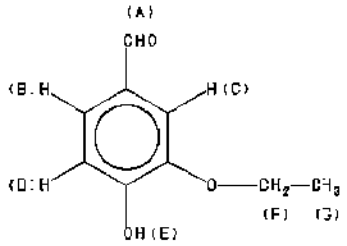
Typical NMR spectrum for 3-Ethoxy-4-hydroxybenzaldehyde is shown below:

SDBS-^{1}H NMRSDBS No. 6355HSP-01-021 89.56 MHz

$C_9H_{10}O_3$ 0.048 g : 0.5 ml $CDCl_3$

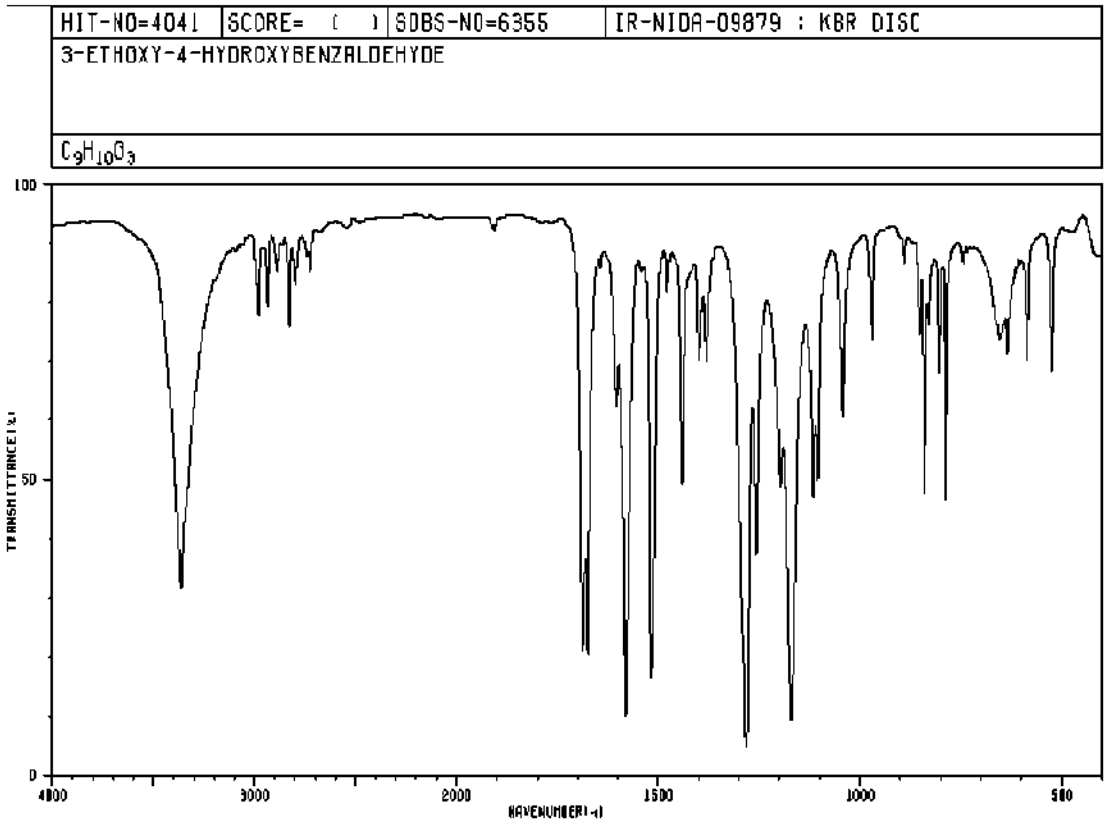
3-ethoxy-4-hydroxybenzaldehyde



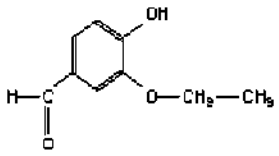


Assign.	Shift (ppm)
A	9.811
B	7.40
C	7.40
D	7.045
E	6.52
F	4.183
G	1.466

Typical IR spectrum for 3-Ethoxy-4-hydroxybenzaldehyde is shown below:



3364	30	1675	20	1381	66	1043	68	786	44
2980	74	1604	60	1282	4	971	70	655	70
2934	77	1581	9	1256	36	852	72	646	72
2888	81	1516	16	1198	46	840	46	636	68
2830	72	1479	79	1170	9	831	74	613	81
2796	79	1440	47	1117	44	803	66	567	66
1687	20	1399	68	1106	47	796	81	526	66



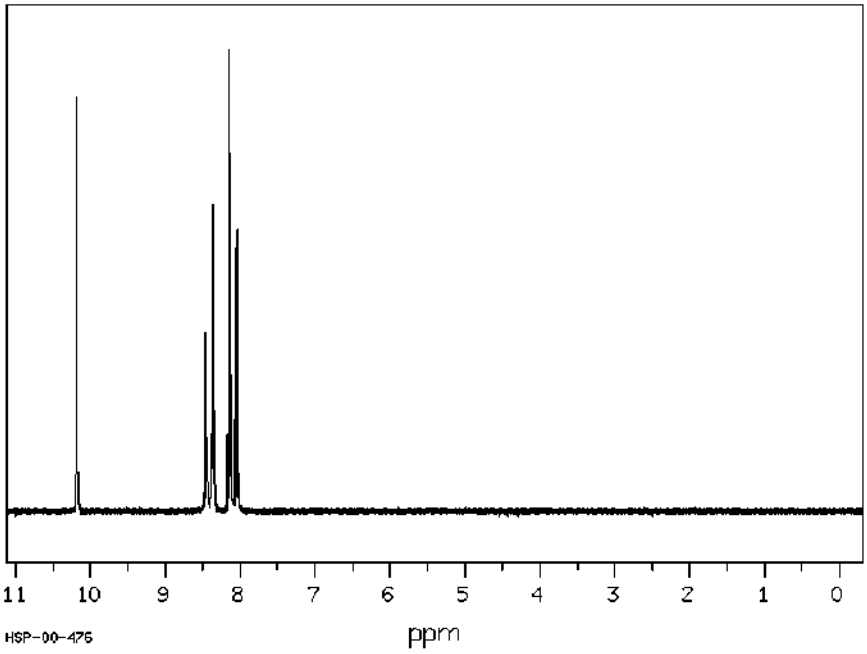
5.5.12 Spectral data for 4-Nitrobenzaldehyde :

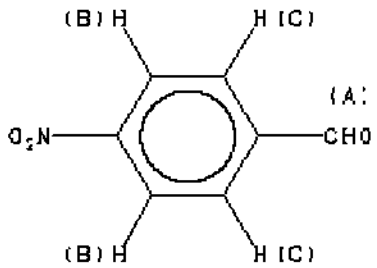
Typical NMR spectrum for 4-Nitrobenzaldehyde is shown below:

SDBS-^{1}H NMRSDBS No. 2868HSP-00-476 89.56 MHz

$C_7 H_5 N O_3$ 0.044 g : 0.5 ml $CDCl_3$

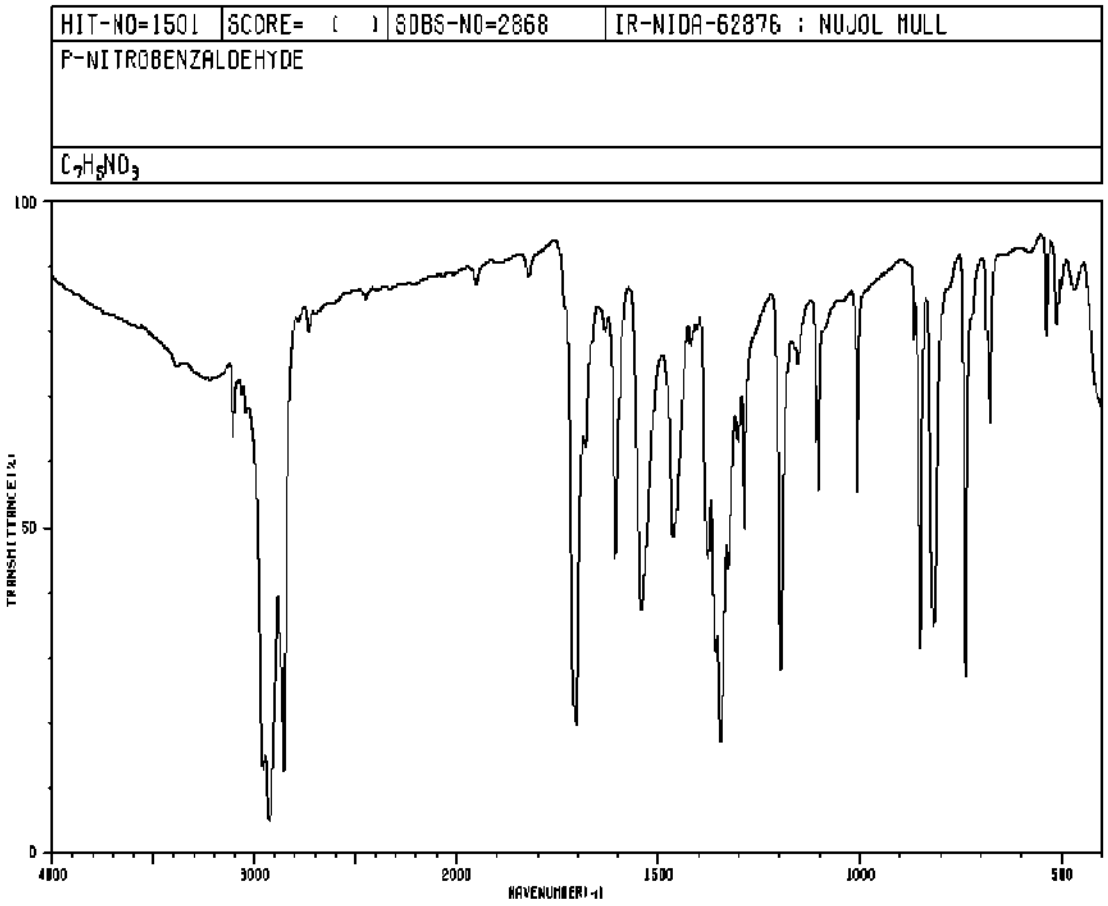
p-nitrobenzaldehyde



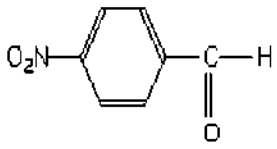


Assign.	Shift (ppm)
A	10.181
B	8.399
C	8.106

Typical IR spectrum for 4-Nitrobenzaldehyde is shown below:



3107	82	1681	60	1378	43	1164	72	846	56
3066	68	1632	77	1360	29	1110	60	818	33
2956	12	1608	48	1346	16	1104	59	740	26
2926	4	1598	64	1327	42	1091	77	687	77
2854	12	1544	35	1302	60	1008	53	679	64
2732	77	1464	46	1287	47	867	77	539	77
1706	18	1420	74	1197	26	862	30	613	79



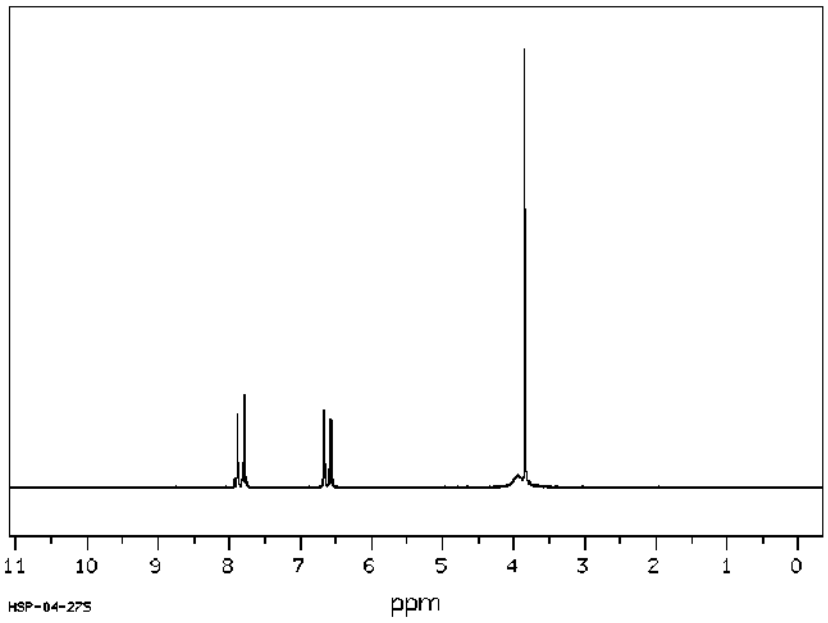
5.5.13 Spectral data for Methyl 4-aminobenzoate :

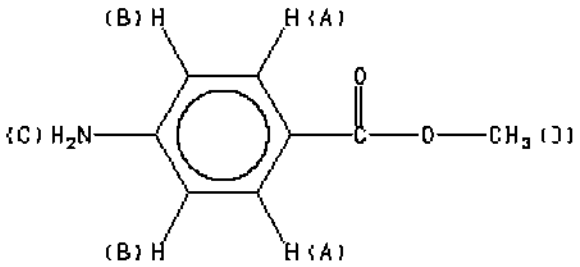
Typical NMR spectrum for Methyl 4-aminobenzoate is shown below :

SDBS-^{1}H NMRSDBS No. 6174HSP-04-275 89.56 MHz

$C_8 H_9 N O_2$ 0.044 g : 0.5 ml $CDCl_3$

methyl p-aminobenzoate



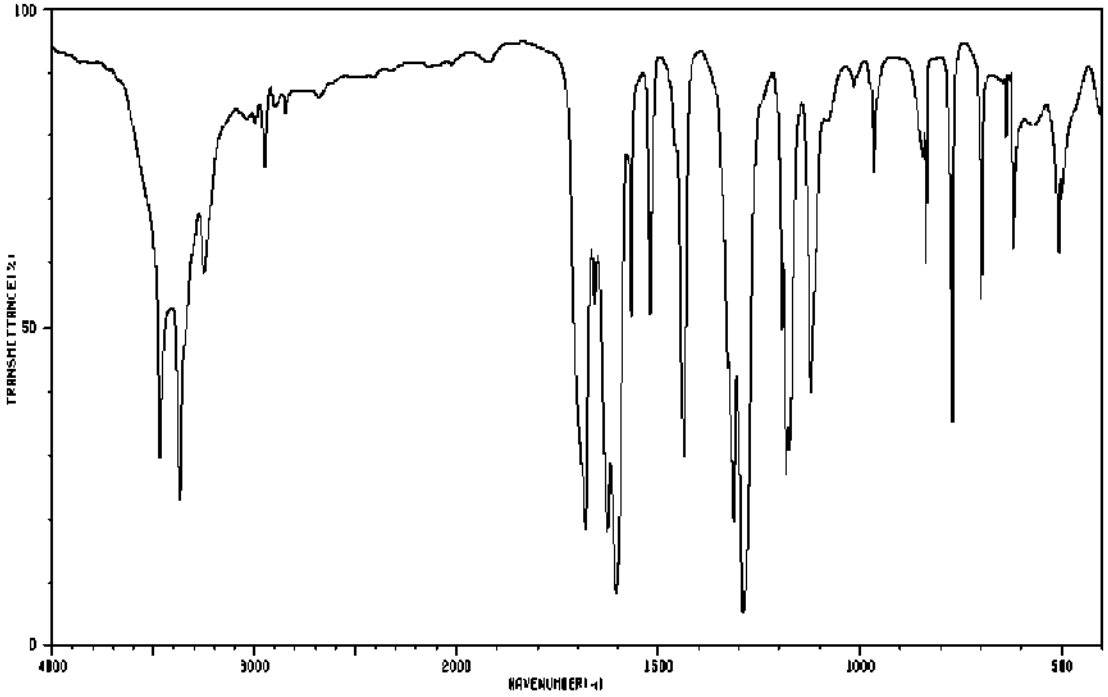


Assign.	Shift(ppm)
A	7.835
B	6.621
C	3.94
D	3.842

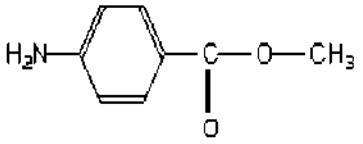
J(A,B) = 8.8HZ

Typical IR spectrum for Methyl 4-aminobenzoate is shown below :

HIT-NO=3940	SCORE= ( )	SDBS-NO=6174	IR-NIDA-10035 ; KBR DISC
METHYL P-AMINOBENZOATE			
$C_8H_9NO_2$			



3468	26	2847	81	1626	62	1175	29	700	52
3371	21	2662	84	1519	50	1123	38	639	77
3251	57	1681	17	1435	26	966	70	621	60
3036	79	1668	62	1314	16	862	77	613	72
2995	79	1627	17	1290	4	842	74	608	77
2951	72	1605	7	1193	47	837	58	572	79
2896	81	1568	49	1184	26	771	34	508	58



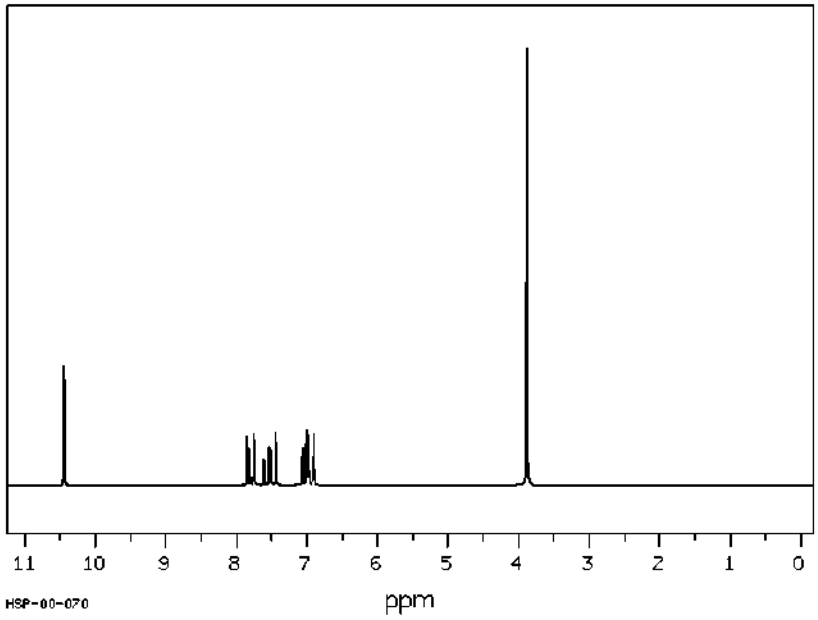
5.5.14 Spectral data for 2-Methoxybenzaldehyde :

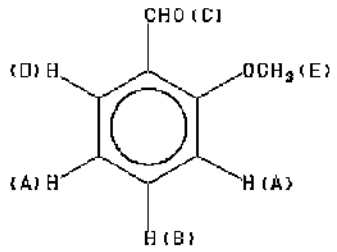
Typical NMR spectrum for 2-Methoxybenzaldehyde is shown below:

SDBS-^{1}H NMRSDBS No. 1680HSP-00-070 89.56 MHz

$C_8 H_8 O_2$ 10.0 mol% in $CDCl_3$

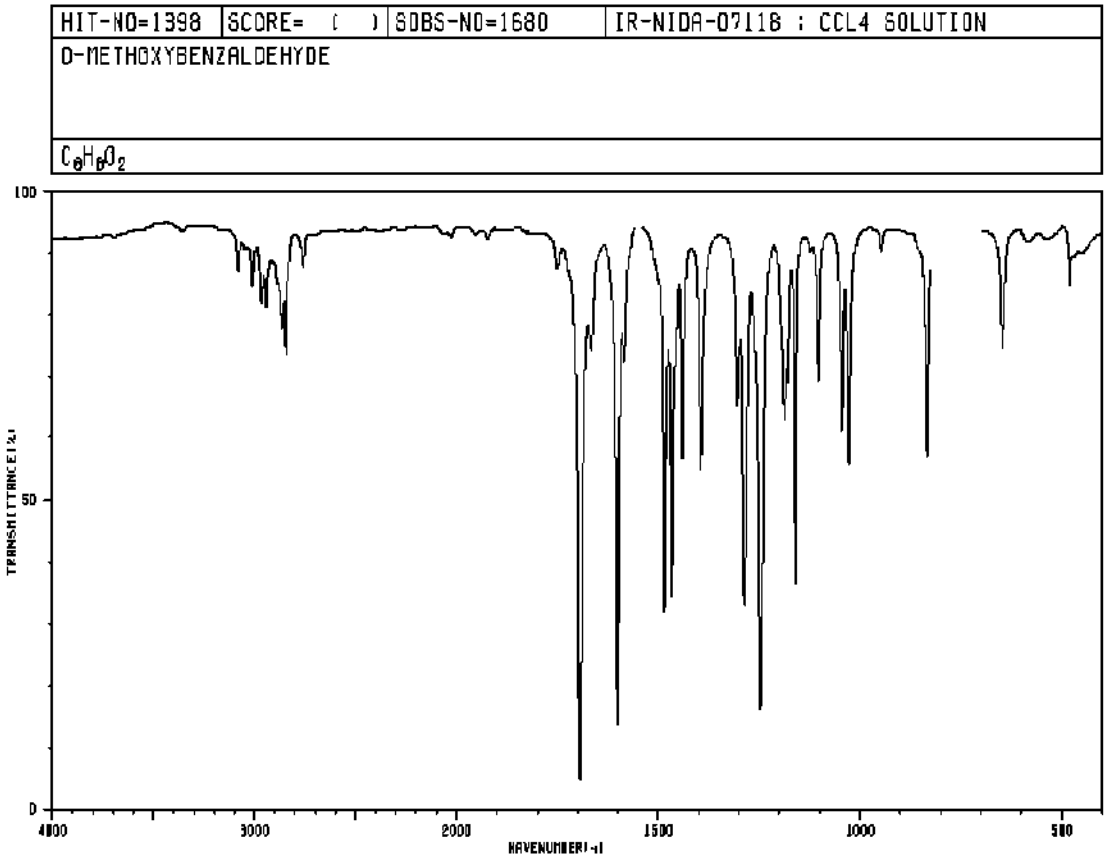
o-methoxybenzaldehyde



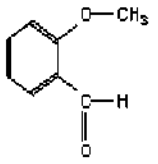


Assign.	Shift (ppm)
A	6.88 to 7.09
B	7.51
C	10.445
D	7.79
E	3.884

Typical IR spectrum for 2-Methoxybenzaldehyde is shown below :



3081	84	1760	84	1646	96	1287	92	1029	53
3011	81	1694	4	1541	95	1246	15	835	55
2965	79	1667	72	1486	31	1187	60	648	72
2945	79	1602	19	1468	33	1181	66	481	81
2863	74	1586	70	1440	55	1162	35
2844	70	1558	95	1395	53	1104	68
2759	84	1661	96	1304	62	1046	69



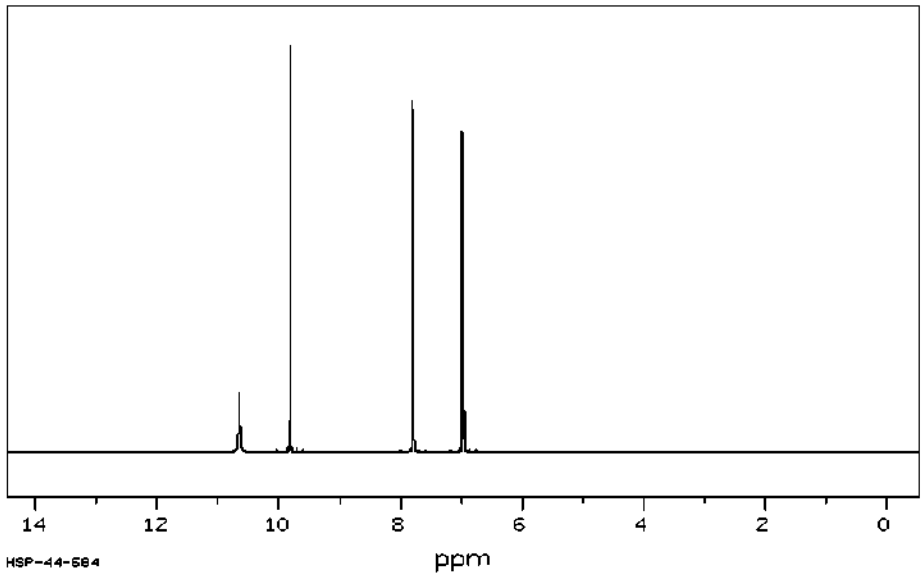
5.5.15 Spectral data for 4-Hydroxybenzaldehyde :

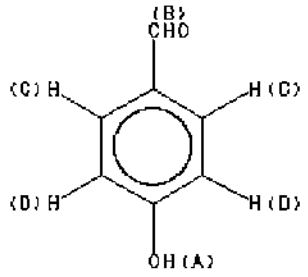
Typical NMR spectrum for 4-Hydroxybenzaldehyde is shown below:

SDBS-^{1}H NMRSDBS No. 3444HSP-44-684 399.65 MHz

$C_7H_6O_2$ 0.037 g : 0.5 ml DMSO-d_6

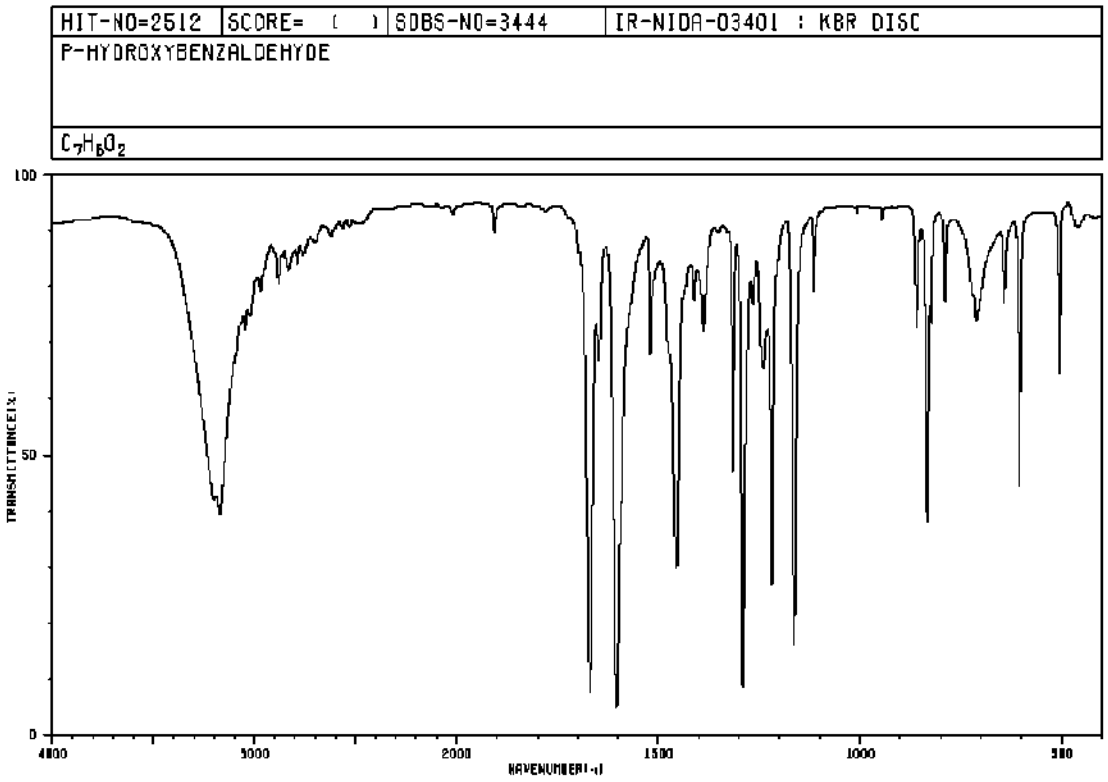
p-hydroxybenzaldehyde



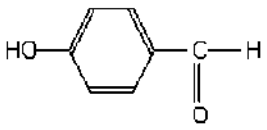


Assign.	Shift(ppm)
A	10.6
B	9.815
C	7.789
D	6.965

Typical IR spectrum for 4-Hydroxybenzaldehyde is shown below:



3199	41	2760	81	1466	28	1220	25	712	70
3171	37	2622	86	1413	74	1164	15	644	74
3044	70	1905	86	1389	70	1115	77	606	42
2968	77	1668	7	1316	44	868	70	607	62
2880	77	1649	64	1291	8	835	36		
2851	79	1604	4	1265	74	623	70		
2789	81	1519	66	1241	62	789	74		



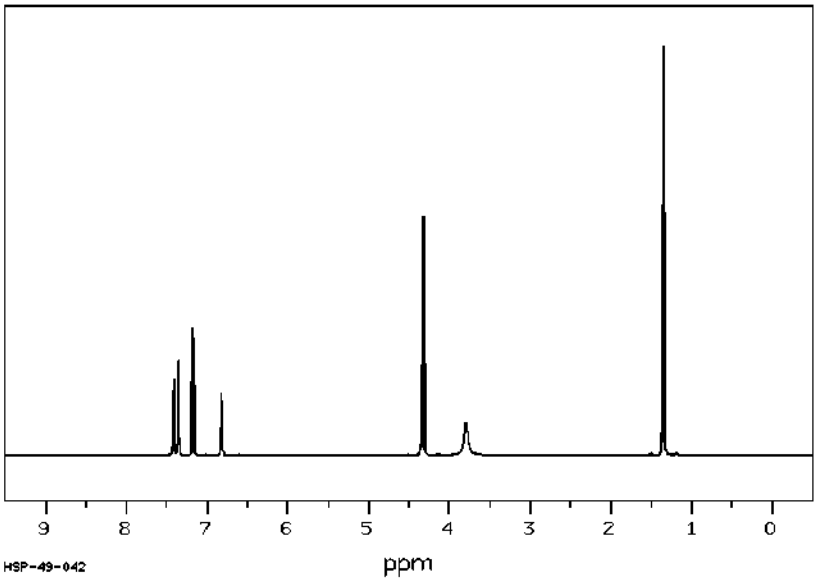
5.5.16 Spectral data for Ethyl-3-aminobenzoate :

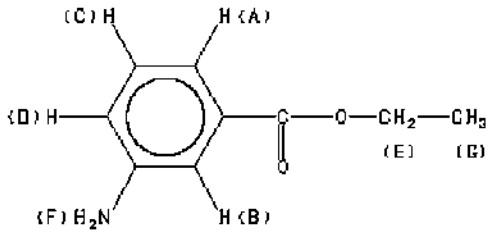
Typical NMR spectrum for Ethyl-3-aminobenzoate is shown below:

SDBS-^{1}H NMRSDBS No. 15377HSP-49-042 399.65 MHz

$C_9 H_{11} N O_2$ 0.05 ml : 0.5 ml $CDCl_3$

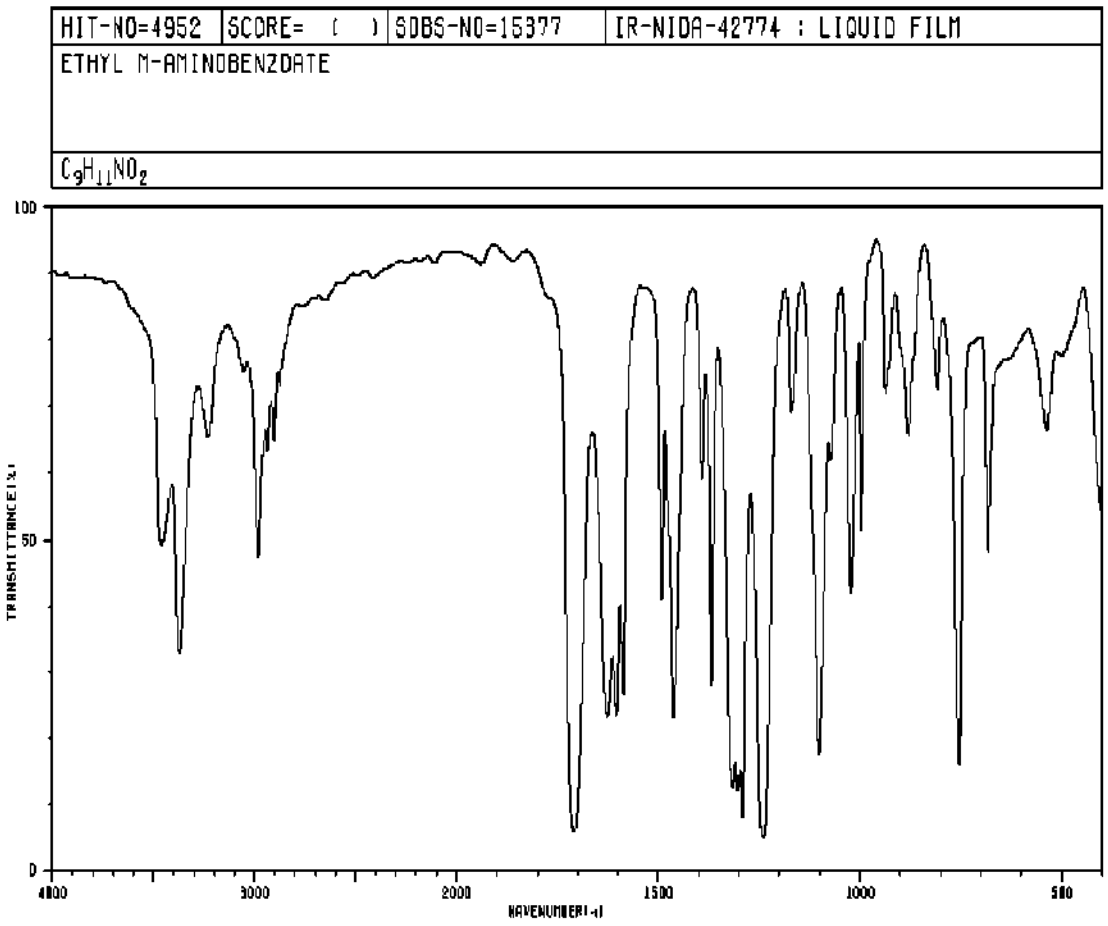
ethyl m-aminobenzoate



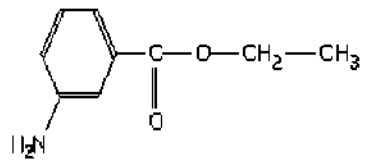


Assign.	Shift(ppm)
A	7.413
B	7.352
C	7.174
D	6.817
E	4.325
F	3.79
G	1.346

Typical IR spectrum for Ethyl-3-aminobenzoate is shown below :



3461	47	2873	70	1392	57	1102	15	766	16
3374	31	1708	5	1368	26	1072	60	683	46
3226	62	1628	22	1317	12	1023	41	546	56
3069	72	1604	22	1303	11	996	49	537	54
2982	46	1568	25	1292	7	937	70		
2936	60	1493	39	1240	4	880	64		
2906	62	1462	21	1171	66	809	70		



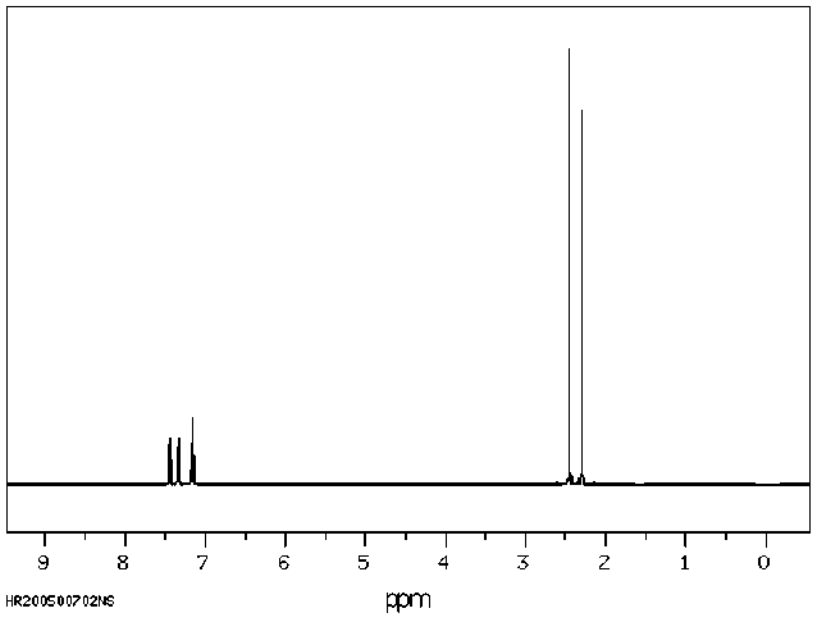
5.5.17 Spectral data for 2,3-Dimethylbenzonitrile :

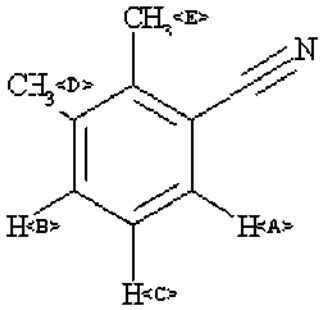
Typical NMR spectrum for 2,3-Dimethylbenzonitrile is shown below:

SDBS-^{1}H NMR 399.65 MHz

C_9H_9N 0.017 g : 0.5 ml $CDCl_3$

2,3-dimethylbenzonitrile





Assign.	Shift(ppm)
A	7.443
B	7.343
C	7.167
D	2.469
E	2.314

Typical IR spectrum for 2,3-Dimethylbenzonitrile is shown below:

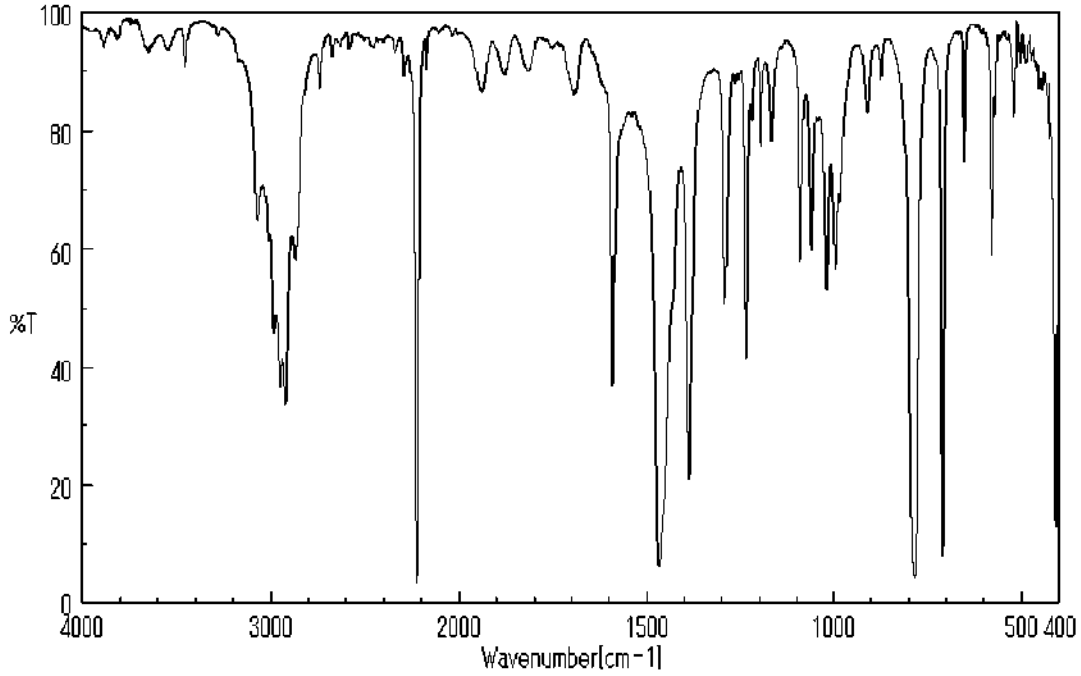
SDBS-IR

2,3-dimethylbenzonitrile

Molecular Formula: C_9H_9N **SDBS No.:** 51231

Spectral Code: IR2005-85047TK

CAS Registry No: 5724-56-1 **IR:** Liquid film



Wave number (cm^{-1}) and Transmittance (T%)

3072 65	1592 37	1196 78	996 57	579 59
3011 61	1467 6	1167 78	910 83	52082
2922 34	1388 21	1091 58	784 4	
2868 58	1293 51	1060 60	710 8	
2222 4	1235 42	1020 53	652 75	

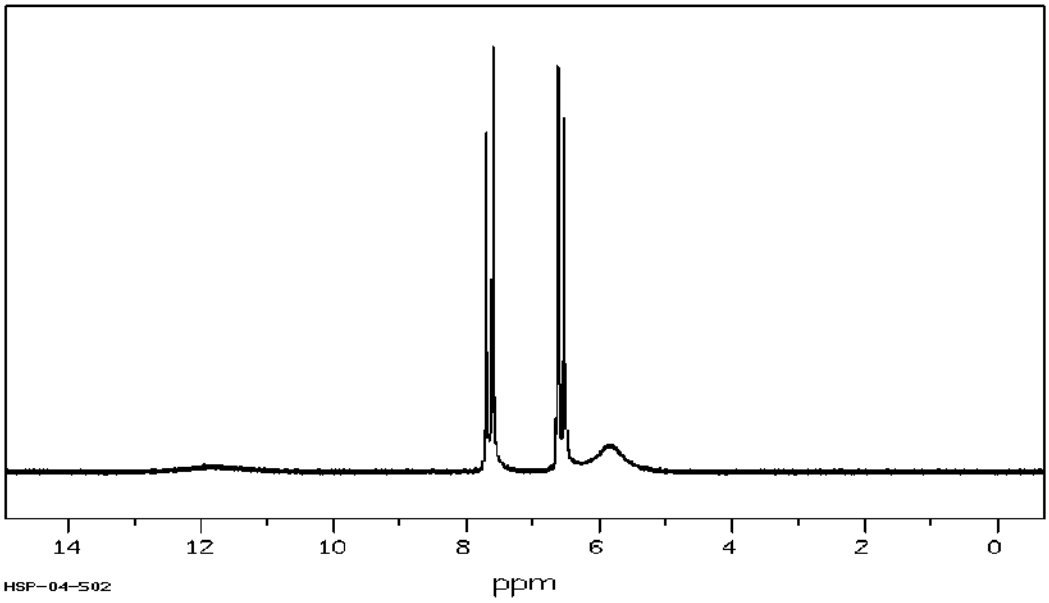
5.5.18 Spectral data for 4-Aminobenzoic acid :

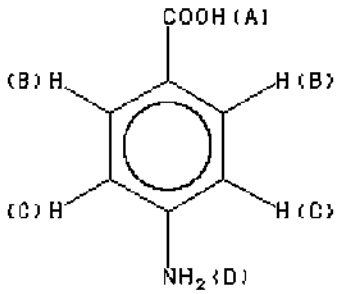
Typical NMR spectrum for 4-Aminobenzoic acid is shown below:

SDBS-^{1}H NMRSDBS No. 1152HSP-04-502 89.56 MHz

$C_7H_7NO_2$ 0.039 g : 0.5 ml DMSO-d_6

p-aminobenzoic acid

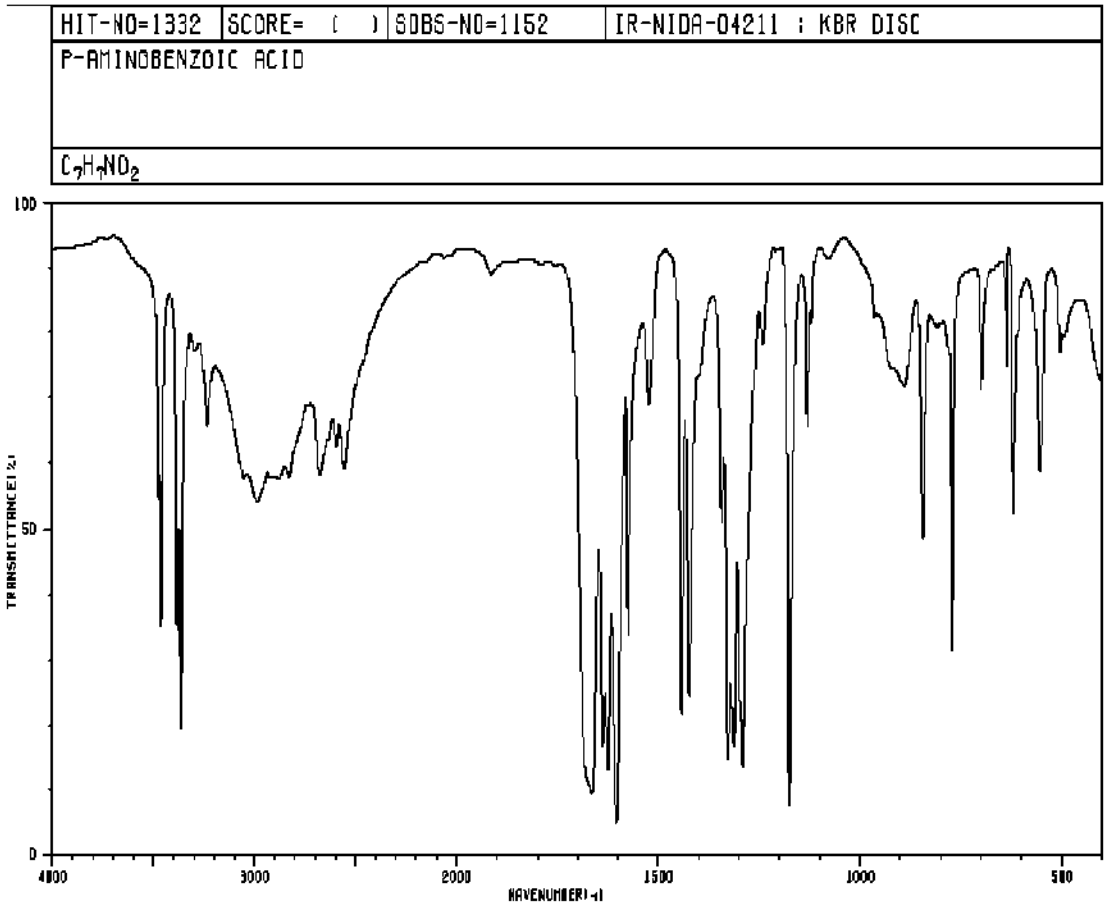




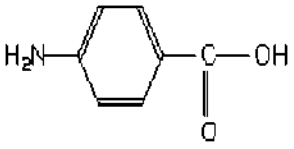
Assign.	Shift(ppm)
A	12.
B	7.648
C	6.577
D	5.9

J(B,C)=8.8HZ

Typical IR spectrum for 4-Aminobenzoic acid is shown below:



3476	52	2829	66	1604	4	1314	16	843	47
3461	34	2679	57	1575	33	1298	20	773	30
3383	33	2598	60	1524	86	1291	15	700	56
3366	16	2667	67	1443	21	1242	74	638	72
3293	74	1665	9	1424	23	1177	7	622	50
3234	64	1638	16	1343	49	1130	64	554	57
2986	52	1626	12	1328	14	891	70	506	74



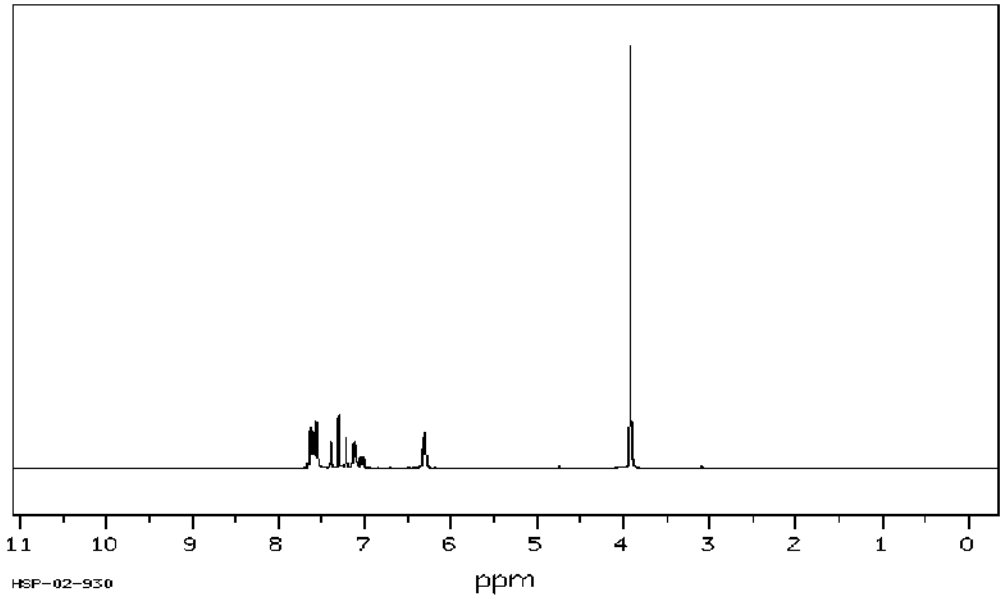
5.5.19 Spectral data for Methyl 3-hydroxybenzoate :

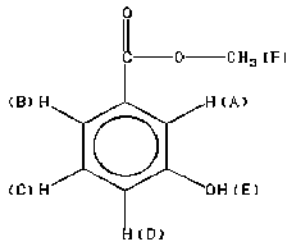
Typical NMR spectrum for Methyl 3-hydroxybenzoate is shown below:

SDBS-^{1}H NMRSDBS No. 1492HSP-02-930 89.56 MHz

$C_8 H_8 O_3$ 0.041 g : 0.5 ml $CDCl_3$

methyl m-hydroxybenzoate

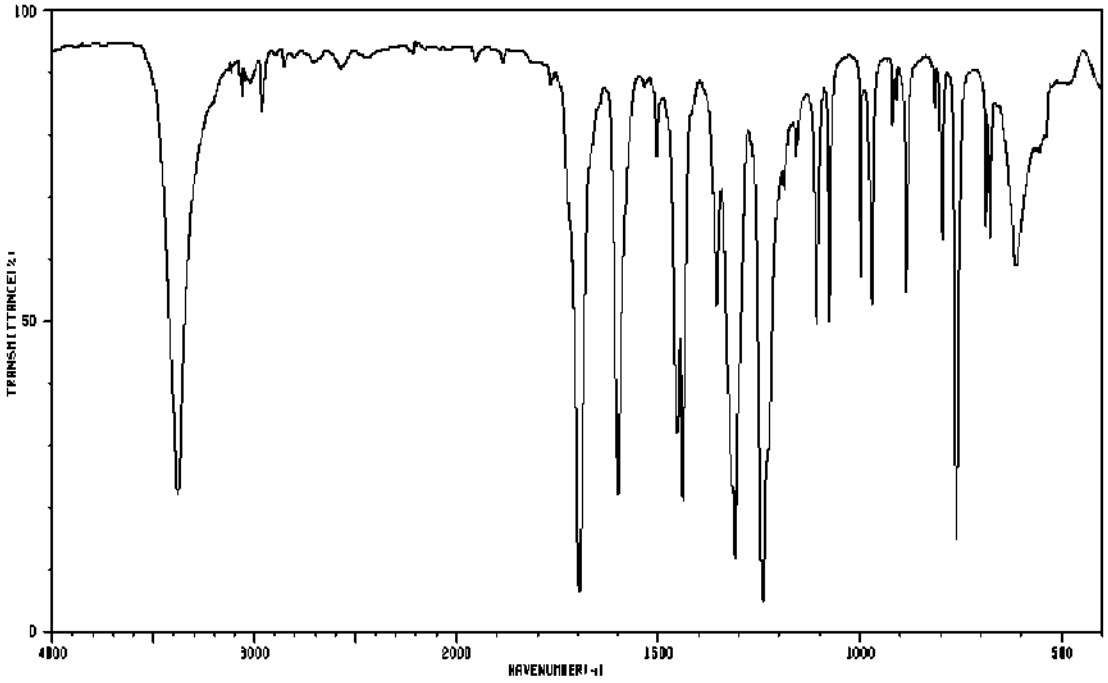




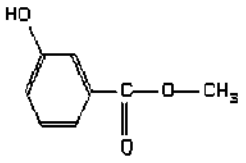
Assign.	Shift(ppm)
A	7.61
B	7.60
C	7.300
D	7.089
E	6.31
F	3.91

Typical IR spectrum for Methyl 3-hydroxybenzoate is shown below:

HIT-NO=1502	SCORE= ( )	SDBS-NO=1492	IR-NIDA-61091 ; KBR DISC
METHYL M-HYDROXYBENZOATE			
$C_8H_8O_3$			



3356	32	1766	64	1357	50	1076	47	797	50
3280	21	1695	6	1317	21	998	55	791	84
3064	84	1600	21	1310	11	972	50	762	14
3046	86	1534	84	1242	4	919	79	688	62
3030	86	1504	74	1188	68	911	81	679	62
3016	84	1455	51	1160	74	885	52	614	57
2962	81	1439	20	1108	47	816	81		



5.6 Self Assessment Questions

1. Define following terms : Nuclear resonance, Chemical shift, spin-spin coupling.
2. What is (n+1) rule for splitting pattern and intensities of lines?
3. What is infrared Spectroscopy? How it is related with molecular vibrations?
4. What are the factors affecting in vibrational frequencies?
5. Analyse the typical spectral data of the following

   4-nitroaniline, Vanilllin, 4-aminobenzoic acid, 1-pentyn 3-01, 1,3-dinitrobenzene, Benzylacetate, 4-nitrobenzaldehyde.

5.7 Suggested Readings

1. Introduction to Spectroscopy, Donald L. Pavia, Gary M. Lampman, George S. Kriz, and James R. Vyvyan, Fifth edition, 2013.
2. Spectroscopy of Organic compounds, P.S. Kalsi, Wiley Eastern Limited, 1995.
3. Elementary Organic Spectroscopy, T.R. Sharma, S Chand and company Pvt Ltd, 2008.
4. Organic spectroscopy, L.D.S Yadav, Kluwer Academic Publishers, 2004.

NOTE