UNIVERSITY OF ILORIN
ILORIN, NIGERIA
FACULTY OF PHARMACEUTICAL SCIENCES
DEPARTMENT OF PHARMACEUTICAL & MEDICINAL CHEMISTRY



PRACTICAL PHARMACEUTICAL ORGANIC & INORGANIC CHEMISTRY

200 LEVEL MANUAL

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PRACTICAL

PHARMACEUTICAL

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200 LEVEL MANUAL

STAFF LIST AS AT 13 NOVEMBER, 2019

S/No.	Name	Status
1	Moji T. Bakare-Odunola	Professor
2	A. O. Ogundaini	Visiting Professor
3	Dr. S. T. Abdullahi	Senior Lecturer & Ag. Head
4	N. S. Njinga	Senior Lecturer
5	O. I. Eniayewu	Lecturer II
6	O. D. Bamidele	Lecturer II
7	Fehintola F. Abdulmajeed	Technologist I
8	Khadijat O. Abdulrazaaq	Technologist I
9	Shade O. Aderinola	Technologist I
10	Fausat O. Jenyo	Senior Confidential Secretary
11	B. I. Yusuf	Higher Executive Officer
12	D. S. Muhammed	Senior Laboratory Assistant
13	Shakirat Abdulsalam	Head Laboratory Attendant
14	Hulaimat Soliu	Supervisor Office Assistant

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Prof. Moji T. Bakare-Odunola	Chairperson
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Dr. S. N. Njinga	Member

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Prof. Moji T. Bakare-Odunola	Chairperson
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PART 1

PCH203
INTRODUCTORY PHARMACEUTICAL ORGANIC & INORGANIC CHEMISTRY

SCHEDULE I

1.1 INTRODUCTION TO PRACTICAL

The subject of chemistry cannot be learned from books alone. Many important facts can only be learned in the laboratory. Generally, laboratory experiments are essential for a realistic understanding of science, since they are of great value in furnishing background for the critical judgment needed in reading the work of others, which is one of the most important sources of information for practicing experimental and theoretical sciences.

The main objective of laboratory experiments is to identify the various constituents of a substance and to find the quantities of each constituent in that substance. Identifying the constituents is called qualitative analysis while finding how much of one or more constituents are present in a given amount of substance is called quantitative analysis.

1.1.1 Laboratory Precautions and Directives

1) Remember at all times that the laboratory is a place of serious work.
2) Create habits of careful observation and accurate deductions, tidiness and cleanliness.
3) Try to understand the procedures of the experiment intelligently, making out the special precautions to be observed.
4) Always be certain that a test tube, beaker or a dish that is about to be used is clean and will contain only what you have put into it.
5) Do not spill powders or acids on the desk. Wipe immediately any which accidentally drop. Do not touch chemicals with bare hands unless directed to do so. Never taste anything in chemistry laboratory.
6) Arrange the required apparatus on the bench. Avoid littering your bench with an array of unrelated bottles and remove stoppers by holding the test tube in the left hand and with the aid of the little finger of the same hand remove the stopper from the reagent bottle. Retain the stopper in your finger, add the reagent and at once replace the stopper in the bottle and return it to its correct place.
7) Check the label on a reagent bottle carefully before removing any of its contents. Read the label again to be sure you have the right bottle before adding. Never return unused chemicals to the stock bottles. Remember purity and cleanliness is not a show but a necessity in a chemical laboratory.
8) If you are preserving a solution or precipitate, label it for identification. Do not rely on your memory. Remember that none of us have perfect memories.
9) **Do not**: -
    a) Waste regents: Use minimum quantity that is necessary.

b) All solid wastes e.g pieces of paper, filter paper, broken glass test tube to be discarded into a waste basket. Pour all liquid wastes into the sinks.

c) Dispose burning match stick into the waste box. Negligence may cause fire.

10) Do not keep the water taps open when you are not using it. The Bunsen burner should be put off immediately when you have performed the experiments. Do not keep the gas tap open since the gas is poisonous and also avoid wastage.

11) Report any breakage of apparatus to the teacher at once.

12) Never lose your sense of mind in case of an accident and at once inform the teacher. He will give you the necessary first aid.

13) Observe carefully and write them down immediately in the note – book.

14) Upon completion of the experiment, clean all the apparatus and return them to the laboratory assistant.

15) While attending the practical class, the student should be in possession of:

a) A clean white overall (lab coat)

b) A hand towel

c) A practical notebook (hard cover not graph type)

d) A text book of practical manual

1.1.2 Important Instructions for Use of Reagents

1) Laboratory chemicals are to be used only in the laboratory.
2) Nothing must be taken out from the laboratory.
3) Bottles should never be held by the neck.
4) Anything accidentally taken into the mouth must be spat out and wash with water immediately.
5) Acid or alkali which falls on the skin or clothing must be washed with water immediately.

1.1.3 Presentation of Practical Report

One of the important details of all chemical work is the keeping of complete and legible record of experiments. The qualitative and quantitative analysis provides valuable training in keeping record. The following suggestions should be carefully studied:

1) Use **only bound** notebooks of the type recommended by the instructor
2) Record all data and **never** use loose paper. Loss of data taken on loose papers has cost many students valuable time.
3) Make no erasures. If a value is to be invalidated, draw line through it but in such a way that it is still legible; indicate in the note-book.
4) Head each page with date, experiment number and title of the analysis.

5) Strive for clarity so that any other analyst would be able to interpret the entries made by you. Use tabular form in case of analysis experiments.
6) Complete the exercise assigned in the note – book and take it to your instructor for signature.

1.1.4 Suggestions for Work

In any analysis work, a lot of time is used for carrying out the work. Many students, through inefficient planning of their work, required far more time than necessary and have difficulty in completing the analysis. The following suggestions will be useful to a good analyst: -

1) Study the procedure and notes before beginning an experiment. Know the reason for each operation. Such study should be done outside the laboratory hours. The notes with explanations form an integral part of the procedures.
2) Prepare a written outline of the procedure and work instead of referring back to the book.
3) Do not attempt short cuts. The procedures are based upon approved methods.
4) Get all apparatus and chemicals issued before starting the analysis.
5) Utilize the time spent waiting for cooling, filtration, evaporation and the like by working on other operations of the experiment. Lengthy delays caused by these operations can often be eliminated by proper planning.
6) Keep all containers for each individual sample carefully marked to avoid mixing or inter changing solutions at some stage of the analysis, a great deal of time will be lost by becoming careless.

1.1.5 Report-Writing Procedure

The main parts of a report are outlined as follows:

1) Date
2) Title of Experiment: This must provide adequate information of both the method and the compound used. Thus, a title such as “Determination of lead” is inadequate. It should be “Determination of lead from lead nitrate by gravimetric analysis.”
3) Introduction and Theory: This is a brief account of the importance of the experiment and its theoretical background. The theory underlying the process, reaction or technique should be described, including equations and mechanisms where relevant.
4) Aim and Objectives.
5) Materials and Apparatus used: A brief account should be given of the apparatus, chemicals, solutions, etc, used, including relevant diagrams or flowcharts illustrating the principles of the experiment.

6) Method: The experimental procedure should be written in the past passive tense, without the use of personal pronouns, e.g. one should not write “I added 5 mL of chloroform,” but rather “5 mL of chloroform was added,” etc.
7) Results: All results, where possible, should be tabulated and adequately labeled with signs and units.
8) Calculations: The calculations should be detailed, showing the stepwise and logical sequence used in arriving at the answer.
9) Discussion and Conclusion: This should contain a brief summary of results obtained and accepted data obtained from reference books where necessary. The reasons given for the observed results should be reported inform of discussion. Draw conclusion from the discussion.
10) Answer to Questions: Questions provided in the manual should be answered.

SCHEDULE II

1.2 IDENTIFICATION, WASHING AND DRYING OF GLASSWARE

1.2.1 Laboratory Glassware

Most glass materials used in chemical laboratories are made from borosilicate glasses which have low coefficient of thermal expansion and are therefore likely to break when suddenly heated or cooled. Pyres is the name for borosilicate glass No. 7740 supplied by the Corning Glass Work whereas Kimax$^{(R)}$ is a similar glass supplied by the kimble Glass Company. Lime soda or flint glasses are less expensive but are likely to get damaged from rapid temperature changes. Actinic glass-ware is particular used for holding light sensitive materials as these glasses are coated with permanently red colour to protect materials that are sensitive to light in 300 – 500 μm range.

1.2.2 Washing of Glassware

It is advisable to clean each piece of glass-ware soon after use since the contaminant is still known and it is easier to remove at this time. Routine and simple cleaning is achieved by brushing with detergent or soap solution.

However, for hard to clean glass-ware, one of the following solutions can be used

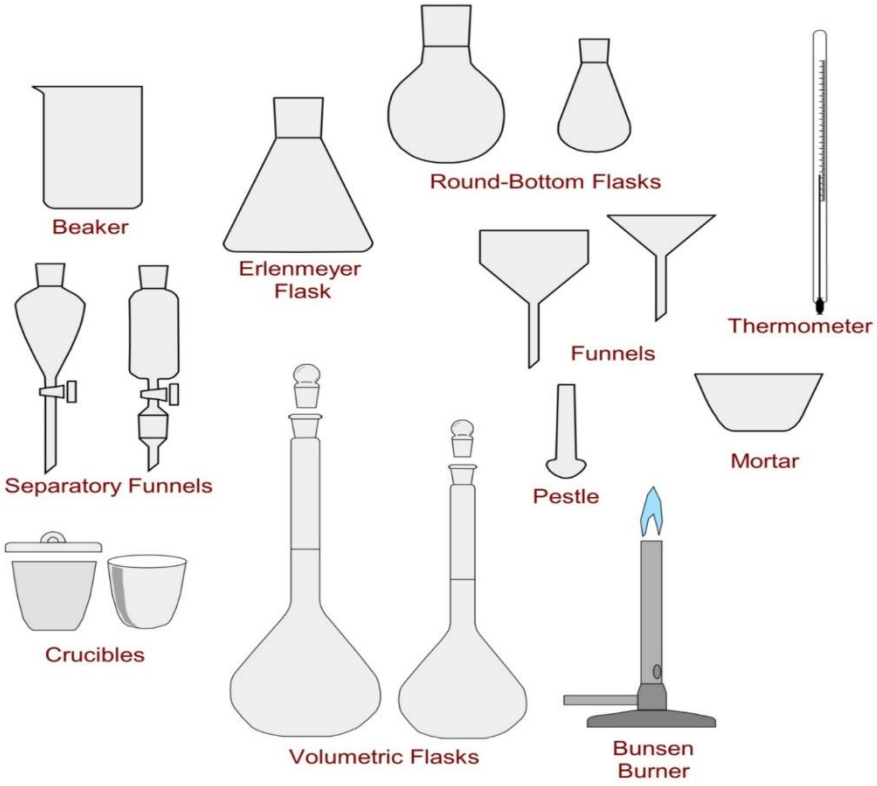
1) Chromic acid: For routine cleaning of burettes, pipettes etc.
2) Alcoholic sodium or potassium hydroxide: This is very powerful cleaning medium but prolong exposure will damage ground glass joint.
3) Novochromix: Non – metallic but stronger inorganic oxidizer than chromic acid.
4) Sulphuric acid or fuming nitric acid is used especially for greasy and dirty glassware. An alternative method for removing grease involves soaking in warm soap solution for about one hour rising with water and soaking in concentrated hydrochloric acid.
5) Trisodium phosphate: - for removing carbon residues.

1.2.3 Drying of Glassware

Ordinarily, glassware is allowed to air dry in the laboratory. However, for rapid drying of the glass-ware, rinsed with acetone (BP of 56.53^{o}C it has high solvent power, is miscible with water and evaporates easily). It is important to note that condensed air is not suitable for drying because it may contain moisture. However, one can drive air through the apparatus at the suction of water pump (or any other vacuum set up).

1.2.4 Experiment

Examine the following laboratory apparatus as shown in the diagram below. Identify as many of these as are available in the laboratory. It is important to know their names and uses.



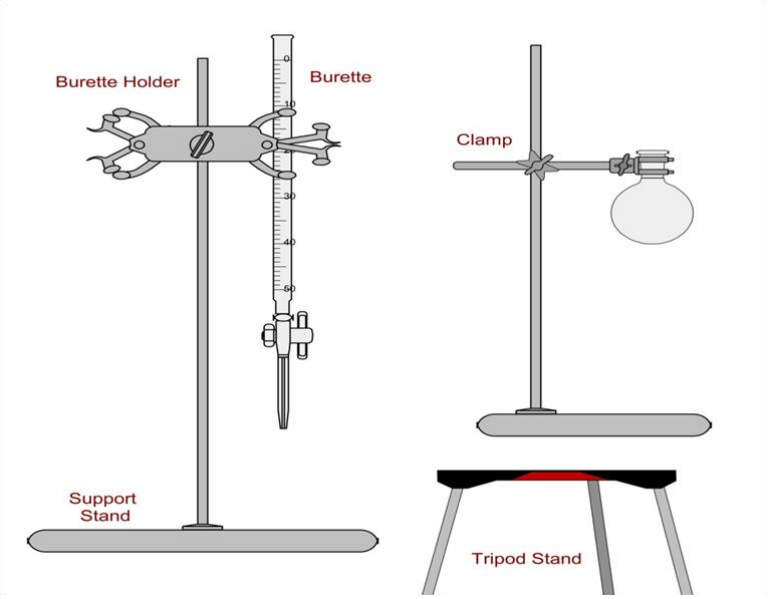


Figure 1.2: Diagram of laboratory apparatuses

SCHEDULE III

1.3 WEIGHING AND CALIBRATION OF VOLUMETRIC APPARATUS

1.3.1 Weighing

1) Introduction: Mass is the fundamental measure of the amount of a substance. It is defined as the amount of matter contained in a substance. Weight is a measure of the effect of gravitational force on that mass. Mass is directly proportional to weight and are sometimes used interchangeably, but the mass of a body remains constant every where, whereas the weight of a body depends on whether it is on the earth or elsewhere. For example when an astronaut stands on the earth surface his mass is pulled toward the centre of the earth with a force of 72 kg, but when he is on the surface of the moon the same man is pulled towards the centre of the moon with a force of only 12 kg i.e. 1/6 of that of the earth.
2) Measurement of Mass: The basic unit of weight in the metric system is the gram and the measurement vary in magnitude (see Table 2.1).

Table 1.3: Prefixes used in the metric system and their values

Prefix	Symbol	Gram equivalence
Peta	P	10^{15}
Tera	T	10^{12}
Giga	G	10^{9}
Mega	M	10^{6}
Kilo	k	10^{3}
Hector	h	10^{2}
Deka	da	10^{1}
-	-	10^{0}
Deci	d	10^{-1}
Centi	c	10^{-2}
Milli	m	10^{-3}
Micro	µ	10^{-6}
Nano	n	10^{-9}
Pico	p	10^{-12}
Femto	f	10^{-15}

1.3.2 Laboratory Balances

This is the laboratory apparatus used in knowing the weight of a substance. The quality of a balance is its precision i.e. its reproducibility. However, the precision obtained on any balance depends not only on the balance but also on the skill of the operator, the environment

and state of the sample. The accuracy which is defined as closeness to the true value required determines the type of balance to use.

1.3.3 Type of Balances

1) Rough Weighing: When expected accuracy is ± milligram and substance to be weighed is a few grams.
    a) A two – pan balance which can take up to 1000 g is popular. The desired weight of the substance is counter-balanced with a standard weight along a calibrated lever.
    b) The Mettler top – loading balances are however more convenient for rough weighing.
2) Analytical Balance: Where the sample required for analysis is minute, an analytical balance is used. Such balance is more sensitive. The use of balance will be demonstrated by instructor in charge.

1.3.4 Errors in Weighing

1) Samples may gain or lose moisture and this is true for finely divided materials. Glass also holds water and therefore changes in daily humidity must be considered as up to 10 µL of water per 100 cm of surface is possible.
2) Weighing paper can also gain or lose moisture. Therefore, never take the weight of an unknown weighing paper for granted.
3) Gases can absorb into or leave samples easily.
4) Liquids may lose mass by sitting open to air due to evaporation, keep liquids covered.
5) Keep samples and their container clean (1 fingerprint = 1 µg) use tongs or forceps for glassware but a strip of paper for weighing bottles.
6) Static charge affects weighing especially when humidity is below 45%. Therefore, do not wipe flasks beakers etc. with a dry cloth before weighing.
7) Temperature gradients cause air turbulence. Do not weigh hot objects because of the large up drafts caused.
8) Do not lean on the weighing bench as this affect the zero setting and weighing data.

1.3.5 Experiment

1) Zero the analytical balance and weigh a piece of weighing paper (filter paper). Remove the paper correctly from the balance hold it on the palm of your hand for 1 minute. Re – weigh the paper and note the difference.
2) Weigh five different tablets. Note the differences. Calculate the mean and standard deviation (SD) of your result. Remember to never place samples directly on the pan – use a weighing bottle, dish, pan watch glass or weighing paper.

QUESTIONS

1) What caused the difference in the weight of the paper?
2) What is the average weight of the five tablets?
3) Are the differences in the weight of the paper and the weight of the tablets glaring?

1.3.6 Calibration of Volumetric Apparatus

1) Introduction: Volumetric apparatus include measuring cylinders, pipettes, burettes etc. the purpose of this experiment is to compare the accuracy and precision of these volumetric apparatus. The technologists will show the correct techniques for using these apparatuses.
2) Procedure:

a) Remove the grease from the burette, pipette and measuring cylinder provided by washing them with cleaning solution. Rinsed with clean water followed by distilled water, and drain.

b) Weigh precisely the five corked flasks provided. The flasks must be clean, dry and cold before weighing. If they are wet, rinse with acetone, dry in the oven and allow cooling before weighing.

c) Rinse the measuring cylinder carefully with distilled water and fill to the 50 mL. mark with distilled water of known temperature. Carefully pour the 50 mL into one of the weighed flasks. Similarly pour 50 mL of distilled water into each of the weighed flask, weigh each flask and calculate the mean weight of water measured. Knowing the density of water at the temperature (consult the lecturer in charge); calculate the mean volume measured and the standard error of the mean.

d) Dry the five flasks by successive rinsing with acetone dry in the oven and cool. Re-weigh the five flasks after drying.

e) Using the procedure given in no 3 above for 25 mL of pipette after carefully rinsing with distilled water. Check the temperature of the distilled water and calculates the mean value and the standard error of the mean as in 3 above.

f) Dry and reweigh the five flasks.

g) Rinse the burette with distilled water and fill it to the above zero mark. Run out water slowly until the bottom of the meniscus is on the zero mark. Run out exactly 25 mL of distilled water into one of the weighed flasks. If by mistake the 25 mL mark is over shot, read the exact value to 0.01 mL and correct the weight of the water to the weight of 25 mL of water by simple proportion. Repeat for the other four flasks. Calculate the mean volume and the standard error of the mean for the burette.

h) Compare the calculated volumes and the standard error with the nominal volumes for the burette, pipette and measuring cylinder and with the values obtained with other students. Comment on any differences observed in terms of relative accuracy and precision of the measuring devices.

SCHEDULE IV

1.4 MELTING POINT DETERMINATION AND PURIFICATION OF SOLID BY RECRYSTALLIZATION

1.4.1 Melting Point Determination

The melting point is a simple and yet one of the most important methods of identifying organic compounds. Most organic compounds melt below 250^{o}C while inorganic substances melt at much higher temperatures. The melting point is the temperature at which a solid and its liquid have equal vapor pressure i.e. the temperature when a solid change to a liquid. Though a pure organic solid will melt sharply, a range in temperature is often recorded due to imperfect heat transfer. A pure compound should generally melt in a range of not more than 2 degrees.

1.4.2 Mixed Melting Point

Even when two organic compounds melt sharply, a mixture of the two compounds will melt at lower temperatures. As a general rule, a mixture of two substances will melt at a temperature lower than either of the two substances alone. For example, both urea and cinnamic acid melt at 133^{o}C. A mixture of the two may start melting at 110^{o}C and continues over 15 to 20^{o}C range. Melting point is therefore not exclusive in identifying a compound but it can often help in establishing the identity or non – identity of two similarly melting compounds.

1.4.3 Procedure

A small quantity of the solid is introduced into a capillary tube which is attached to a thermometer. The thermometer and tube are immersed in a suitable bath liquid (paraffin oil is commonly used) and heated carefully to determine the melting temperature. For an unnamed substance or a substance of doubtful purity, an approximate melting temperature should first be observed followed by a second experiment in which an accurate determination is made. If the result is not within 1^{o}C do a third determination.

1.4.4 Filling in the Melting Point Tube

1) Take about 0.1g (precise weighing is not required) of the dry solid and place it in a clean watch glass or evaporating dish. Powder the solid with a clean spatula or glass rod. Put the powder into a small mound.

2) Push the open end of the capillary tube into the powder and shake it down the tube by gently tapping the closed end on the bench. This procedure may be repeated if the amount of material already introduced is insufficient. Pack the powder uniformly.
3) Wipe off any excess powder from the outside of the tube. The capillary tube is now ready to be attached to the thermometer.

1.4.5 Heating the Liquid Bath

Heat the bath somewhat rapidly and watch the temperature and sample. Note the temperature at which the substance begins to liquefy and also the temperature at which all the solid melted. This is the approximate melting point of the substance.

1.4.6 Determining the Melting Range

Allow the liquid bath to cool to about 20^{o}C below the approximate melting point, while waiting, fill another capillary tube with a fresh sample. When the bath is sufficiently cold, get the sample ready in the bath for heating. Now heat fairly rapidly until the bath temperature is within 15^{o}C, of the approximate melting point. Then heat slowly and at a uniform rate until melting point is complete. Observe the melting range. Repeat the melting point determination once again with a fresh sample and record your result. Melting point of a sample can also be determined by the use of melting point apparatus.

1.4.7 Checking theThermometer

It is good to check the accuracy of the thermometer used by determining the melting point of a pure sample of a substance of known melting point e.g. Benzoic acid is 122^{o}C.

SCHEDULE V

1.5 PURIFICATION OF ORGANIC SOLID SAMPLE BY RECRYSTALLIZATION

When solid organic compounds are isolated or synthesized in the laboratory they are usually contaminated by small amounts of undesired compound. Such impurities can be removed by choosing a solvent that will

1) Dissolve the major component and not the contaminant
2) Dissolve the contaminant and not the major component or
3) Dissolve both but from which the components selectively crystallize on cooling the solvent.

In the re-crystallization of substances, often a combination of the three methods above is encountered. In an ideal situation, a solvent is sought which will dissolve the solid when the solvent is hot and crystallizes on cooling. Therefore, the technique used includes:

1) Dissolving the solid in minimum amount of boiling solvent
2) Filtering any insoluble material by gravitation from the hot solution
3) Allowing the filtrate to cool slowly thereby causing crystallization
4) Separating the crystals from the mother liquor (or supernatant solution) usually by filtration under suction.

1.5.1 Procedure

1) Selection of Solvent: For known compounds, appropriate solvent can be obtained from the literature. For new compounds however, trial and error is always the case. A rule of thumb is that like dissolves like i.e. polar solvents dissolves polar compounds and non – polar solvent dissolve non – polar compounds. The ideal solvent for recrystallization would have the following characteristics:

a) It should have a high temperature coefficient i.e. large amount of the solid should dissolve in a small amount of hot solvent but very little in cold solvent.
b) Impurities should be either moderately soluble in cold solvent or insoluble in hot solvent.
c) The solvent should have a moderate or low boiling point to allow crystals to dry quickly.
d) The solvent should not react chemically with the compound being crystallized.

2) Preparation of the Solution

The solid compound is added to an Erlenmeyer flask (never a beaker unless so specified) preferably containing a boiling stone, and the solvent is added in portions while boiling is maintained (Do not use flame with flammable solvents). Enough solvent is added so that the solid just dissolves while the solvent is still boiling.

In cases where a single solvent cannot be found to recrystallize a solid, co-solvent is also used. The two solvents must be miscible and the solid should be moderately insoluble in one

of the solvents. The solute is dissolved in the solvent in which it is soluble as described above. The hot solution is filtered if necessary. The anti-solvent is then added at the boiling temperature until the solution gives up the cloudiness.

3) Filtering the Hot Solution: This step may be omitted if there are no insoluble impurities. However, should a clear solution be coloured then decolorizing charcoal (e.g Norit) is employed. The charcoal is added to the hot solution and filtered to obtain a clear colourless solution. Too much charcoal should be avoided as it may itself absorb some of the desired compound. Should the charcoal filtered through a filter aid (e.g. Celite – finely divided silica) may be used. While performing hot filtration, it is important to avoid crystallization during the process. It is therefore necessary to use short stem funnels and filter paper (the filter paper should not extend above the rim of the funnel). These measures allow for rapid filtration. Before filtering, the receiving vessel, filter paper and funnel should be warmed by running some boiling solvent through them. The hot solution is added to the filter and the funnel covered with a watch glass to reduce evaporation. Finally, the filter paper is rinsed with a little hot solvent (remember too much solvent will prevent maximum crystallization from occurring).

   N.B: Only filtration with gravity and not with suction is allowed.

4) Cooling the Filtrate: Crystal form on cooling: The slower the cooling the bigger the crystals whereas rapid cooling and agitation result in finer crystals. In general, neither very large nor very small crystals are advisable since it increase the amount of impurities remaining with the crystals. Crystallization could occur slowly even after it has started, enough time should be allowed for this.

   Should crystal fail to form well after the solution reached to room temperatures the flak can be cooled in an ice bath Crystallization also can be induced by adding a small crystal to the solution (a process called seeding) or by scratching the walls of the flask preferably just above the surface of the solution. The crystals are filtered as described below and some of the solvent is incorporated from the filterable to allow a second crop of crystals to form.

5) Collecting the Crystals: Suction filtration is usually employed to separate the crystals from the mother liquor. The technologist in charge will demonstrate a typical suction filtration set up. The filter paper which is smaller size than the usual filter space on the Buchner funnel is wetted with the solvent used. The suction is put on and the content in the vessel is poured through the filter paper with continuous swirling. A glass rod may be used to dislodge any crystal adhering to the flask. A small portion of the mother liquor is poured into the flask swirling to recover any remaining crystals. The crystals are then

sucked dry and washed thrice with small portions of chilled solvent. Crystals may be dried in air or in the oven.

QUESTIONS

1) What criteria would you utilize to select a suitable solvent for recrystallization?
2) In purifying by recrystallization from a solvent, is it advisable to cool the solution slowly or rapidly, explain?

SCHEDULE VI

1.6 PREPARATION OF BARIUM CHLORIDE ($BaCl_2.2H_2O$) AND ESTIMATION OF WATER OF CRYSTALLIZATION

1.6.1 Introduction

The work of an analyst is to discover and determine the qualitative and quantitative composition of the substances and mixtures of substances, whether solid, liquid, or gaseous, which come within the scope of human interest and inquiry.

The student will gain confidence that he may be able eventually to analyze substances of unknown composition, if he first prepares and analyze some well-known substances which can be easily obtained in a state of purity. Consequently, this section of the manual contains instructions for the preparation and partial quantitative analysis of some representative salts.

Barium Chloride is easily prepared by decomposing barium carbonate with dilute Hydrochloric acid.

$$BaCO_3 + 2HCl \rightarrow BaCl_2 + H_2O + CO_2.$$

The salt is much more soluble in hot water than in cold water, and crystallizes readily on cooling its hot concentrated solution. Since other chlorides with which it might be contaminated are more soluble in water than barium chloride, this salt will be obtained pure with single crystallization, and when dried in the air will be found to contain its proper amount of combined water since it is neither deliquescent nor efflorescent. Moreover, when the hydrated salt is heated gently in a crucible till it ceases to lose weight all the combined water is expelled, leaving the pure anhydrous salt.

1.6.2 Experiment 1: Preparation of Barium Chloride

Weigh 10 g of precipitated Barium carbonate on a balance and transfer into a small conical flask, together with a little water. Place a funnel in the neck of the flask, and carefully pour dilute hydrochloric acid upon the salt, a little at a time, so as to keep under control the effervescence due to escape of carbon dioxide gas. Enough acid should be used to dissolve all the salt, but excess should be avoided. Boil the flask to expel dissolved CO_2 and filter into a beaker. Evaporate the clear solution till a little of it, on a glass rod crystallizes. Cool the solution by staring well or by placing the beaker in ice bath in order to obtain the salt in fine crystals form. Filter and drain the salt using a Buchner funnel. Remove the crystal, dry on a piece of porous plate or filter paper, then weigh and store in a desiccator.

QUESTIONS

1. What is the shape and colour of the crystal obtained?
2. Calculate the percentage yield.

1.6.3 Experiment 2: Estimation of Water of Crystallization in Barium chloride

Procedure: Weigh an empty crucible, transfer some of your barium chloride into it and weigh again, support the crucible over a flame by means of a triangle. Turn the flame low in such a way that it does not touch the bottom of the crucible. As the salt loses its water it becomes whiter and more opaque. Finally increase the flame to raise the crucible to a dull red heat. Let the crucible cool sufficiently, transfer it to the desiccator and close the lid. After about fifteen minutes, weigh the crucible. Repeat the heating and the weighing until the difference between the two successive weighing do not exceed 0.5 mg.

The following is the form in which the results of the above experiment should be entered:

Weight of crucible	=	g
Weight of crucible + hydrated salt	=	g
Weight of hydrated salt taken	=	g
Weight of crucible + salt after heating	=	g
Loss of weight	=	water expelled

QUESTIONS

1) Calculate the percentage of water in the hydrated salt.

$$\% \text{ of water} = \frac{\text{loss of weight}}{\text{weight of hydrated salt}} \times 100$$

2) Why was the heating of the salt in the crucible done gradually?

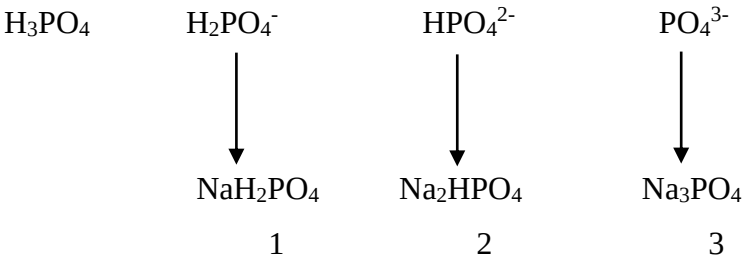
3) Why was the heating and weighing repeated?

SCHEDULE VII

1.7 PREPARATION OF DISODIUM PHOSPHATE ($Na_2HPO_4.12H_2O$)

1.7.1 Introduction

Among the three phosphates of sodium, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 the first is acid, the third is strongly alkaline and the second faintly alkaline to litmus. The second is the easiest salt to prepare, and is formed by adding the require quantity of NaOH or Na_2CO_3 to an aqueous solution of phosphoric acid. Because phosphoric acid is polybasic, it ionizes as follows:



1.7.2 Preparation

Measure 1.25 mL of concentrated phosphoric acid, and dilute it to 12.5 mL with water. Warm the solution and add anhydrous sodium carbonate (2.5 g) little by little until effervescence ceases. Heat the solution to boiling, and filter if necessary. Receive the hot filtrate in a flask, and quickly cool it so as to separate the sodium phosphate in small crystals. Filter off the crystals and dry in the air in the usual way.

QUESTIONS

1) What is the percentage yield?
2) Outline the procedure you will use to estimate the water of crystallization.
3) Calculate the percentage of the water of crystallization.

SCHEDULE VIII

1.8 PREPARATION OF DOUBLE SALTS

1.8.1 Introduction

When two simple salts crystallize together in definite molecular proportions a so-called Double Salt is formed. Unlike complex salts which yield complex ions in solution, a double salt decomposes in solution to the ions of the component's salts.

1.8.2 Experiment 1: Preparation of $CuSO_4.(NH_4)SO_4.6H_2O$ from Ammonium and Cupric Sulphate.

Place 2 g of cupric sulphate pentahydrate ($CuSO_4.5H_2O$) and ammonium sulphate [$(NH_4)_2SO_4$] in a 100 mL beaker. Add 40 mL of boiling distilled water. Stir until dissolved completely. Cool slowly in ice bath until crystals separate. Collect the product on a Buchner funnel with suction. Dry on a filter paper in air.

i. Record actual yield in grams, and calculate % yield based on theory.
ii. Describe the product formed and compare this with the starting salts.

1.8.3 Experiment 2: Preparation of $CuCl_2.2KCl.2H_2O$ from Cupric and Potassium Chloride

Dissolve 2 g of cupric chloride hydrate and 0.30 mole potassium chloride in 40 mL boiling water using a 100 mL beaker. Cool slowly in ice bath and collect product as in Experiment 1 above.

The crystals should be dried over wet calcium nitrate to ensure retained water of hydration.

i. Record actual yield in grams and calculate % yield based on theory.
ii. Compare the crystal form of your product with those of the original salts used.
iii. Dry the crystals over wet calcium nitrate to ensure its retained water of hydration.
Compare the product formed with the original salts used.

1.8.4 Experiment 3: Preparation of Tetramine Cupric Sulphate (Tetramine Copper II) Sulphate Monohydrate [$Cu(NH_3)_4SO_4.H_2O$].

Place 2 g of powdered Cupric sulphate pentahydrate in a 100 mL flask, add 20 mL of concentrated ammonium hydroxide solution and 12 mL of water, then 20 mL of ethanol. Allow to stand undisturbed for about an hour, then cool in ice. Collect product on a Buchner funnel with suction and wash with equal volume of concentrated ammonia and ethanol, then with ether. Dry in the desiccator over calcium oxides.

1) Record actual yield and calculate % yield based on theory.
2) Compare this salt in appearance with the double salt, $CuSO_4.(NH_4)_2SO_4$ of Experiment 1 above.
3) Dissolve a little sample of each in water and compare the two solutions.

SCHEDULE IX

1.9 DETERMINATION OF ALKALINITY ($CaCO_3$) IN WATER

1.9.1 Introduction

Alkalinity is a measure of the presence of bicarbonate, carbonate or hydroxide constituents. Concentration less than 100 ppm are desirable for domestic water supplies, the recommended range for drinking water is 30 to 400 ppm. A minimum level of alkalinity is desirable because it is considered a "buffer" that prevents large variation in pH.

Alkalinity is not detrimental to humans, moderately alkaline water (less than 350 mg/L) in combination with hardness, form a layer of calcium or magnesium carbonate that tends to inhibit corrosion of metal piping. Many public water utilities employ this practice to reduce pipe corrosion and to increase the shelf -life of the water distribution system.

High alkalinity (above 500 mg/L) is usually associated with high pH values, hardness and high dissolved solids and has adverse effects on plumbing system especially on hot water system (water heaters, boilers etc) where excessive scale reduces the transfer of heat to the water, thereby resulting in greater power consumption and increase costs.

Water with low alkalinity (less than 75 mg/L) especially some surface waters, and rainfalls, is subject to change in pH due to dissolved gases that may be corrosive to metallic fittings.

1.9.2 Procedure for the Determination of Alkalinity ($CaCO_3$) in Water

1) ***Phenolphthalein Alkalinity (PA):*** Add two drops of Phenolphthalein to 100 cm^3 of the water sample in a conical flask. Some solutions do not change colour indicating a zero (PA) while some turned red, indicating the presence of (PA); whose magnitude will be determined by titrating the contents of the flask with 0.1 M HCl to a colourless end point. The (PA) is computed using the relation;

$$PA(mmol/l) = \frac{Ca\ Va}{Vs}$$

Ca = Concentration of the acid

Va = Volume of acid used to reach to Phenolphthalein end point

Vs = Volume of sample (cm^3).

2) ***Total Alkalinity (TA):*** To the sample solution from (PA) titration above, add 3 drops of methyl orange and titrate to pinkish end point using standard acid. (TA) is then computed using the relation; -

$$TA\ (mmol/l) = \frac{CaVa}{Vs}$$

Ca = Concentration of acid (mmol/l)

Va = Total volume of acid used to titrate to pinkish end point

V = Volume of sample (cm^3).

QUESTIONS

Determine total alkalinity (TA) of the following sample of water provided and suggest which of them would be ideal for use by the public water supplies and why?

SCHEDULE X

1.10 TEST FOR HARDNESS OF WATER

1.10.1 Introduction

Hard water is water-containing calcium and magnesium in significant amounts. It often requires softening to improve their suitability for washing and heating purposes. Potable supplied water with up to about 75 mg/L hardness ($CaCO_3$) is usually considered as soft, but some surface waters and many ground waters can have hardness levels of several hundred mg/l. Hardness greater than 300 mg/L normally considered undesirable. The need for softening of domestic supplies depends on reasons of convenience and economy rather than of health, since even at very high concentration of up to 1000 mg/L hardness is quite harmless, indeed there is statistical evidence to suggest that artificially softened waters may increase the incidence of some forms of the heart disease.

Hardness of water is normally expressed in term of calcium carbonate whereas chemical analyses for individual ions are usually given in term of that ion. It is thus necessary to convert the analytical results to the common denominator

$$X\ (mg/L\ CaCO_3) = \frac{X\ (mg/l) \times \text{Equivalent weight } CaCO_3}{\text{Equivalent weight X}}$$

Where X is any ion or radical

Thus, for a typical water analysis, conversion to concentration in terms of $CaCO_3$ may be carried out as follows,

40 mg/L Ca^{2+} x 50/20.04	=	99.0 mg/L as $CaCO_3$
24 mg/L Mg^{2+} x 50/12.16	=	98.5 mg/L as $CaCO_3$
9.2 mg/L Na^{+} x 50/23	=	20.0 mg/L as $CaCO_3$
183 mg/L HCO_3^{-} x 50/61	=	150.0 mg/L as $CaCO_3$
57.5 mg/L SO_4^{2-} x 50/48	=	58.0 mg/L as $CaCO_3$
7.0 mg/L Cl^{-} x 50/35.5	=	9.5 mg/L as $CaCO_3$

Note that the cations and anions both sum to 217.5 mg/L

1.10.2 Determination of Calcium Ion in Water

To 10 mL of the test sample (water) to be analysed, add 80 mL of distilled water followed by the addition of 2 mL of 2 M NaOH. Shake the mixture well and then add 0.2 g of Eriochrome black indicator with constant shaking. The resultant solution is then titrated with 0.0l M EDTA until the colour of the mixture changes from purple to blue to make end point of the titration.

Calculation.

1 mL of 0.0l M EDTA = 0.4008 mg Ca^{2+}

Since the hardness of water is normally expressed in terms of $CaCO_3$,

X mg/L of Ca^{2+} ($CaCO_3$) = $\frac{\text{X mg/L x Equivalent weight of } CaCO_3}{\text{Equivalent weight of } Ca^{2+}}$

QUESTIONS

1) Using water from different sources (i.e. well, tap and packaged water), calculate their individual Ca^{2+} ion content and total hardness.
2) Suggest possible ways of removing hardness from water

SCHEDULE XI

1.11 DETERMINATION OF TOTAL SOLIDS

1.11.1 Introduction

The total dissolved solids test measures the total amount of dissolved minerals in water. The solids can be iron, chlorides, sulfates, calcium or other minerals found on the earth's surface. The dissolved minerals can produce an unpleasant taste or appearance and can contribute to scale deposits on pipe walls.

1.11.2 Procedure for Determining Total Solids in Water

Take 50 cm^3 of the water sample in a clean pre – weighed pyrex beaker of 100 mL capacity. Evaporate the content to dryness at 110^oC in an oven. Heat further until a constant weight is obtained, the total solid is then computed using the expression;

$$\text{Total solids (mg/L)} = \frac{(A-B)\ X100}{\text{Sample volume (mL)}}$$

A = weight of beaker + sample.

B = weight of an empty beaker

The following levels of total dissolved solids are expressed in mg/l: -

<500	satisfactory
500 – 1000	less than desirable
1000 –1500	undesirable
>1500	unsatisfactory

QUESTIONS

Calculate the total dissolved solids of the samples of water provided and comment on your results.

SCHEDULE XII

1.12 DETERMINATION OF CHLORIDE IN WATER

1.12.1 Introduction

Chlorides in ground water can be naturally occurring in deep aquifers or caused by pollution from seawater, brine or industrial or domestic wastes. Chloride concentration about 250 mg/L can produce a distinct taste in drinking water. Where chloride content is known to be low, a noticeable increase in chloride concentration may indicate pollution from sewage sources.

The following level of chlorides are expressed in mg/L:

0 – 250	Acceptable.
250- 500	Less than desirable
500 – 1000	Undesirable
Over 1000	Unsatisfactory.

1.12.2 Procedure for Chloride Determination in Water

To 100 mL of the water sample placed in 250 mL volumetric flask, add 1 mL of K_2CrO_4 solution as indicator. Then titrate the solution with standard $AgNO_3$ solution (0.0141M) from the burette until a permanent brick red colour is observed. The chloride (Cl^-) content is then calculated using the following expression;

$$\text{Chloride content (mg/L)} = \frac{A \times N \times 35450}{\text{X mL of sample used (i.e. 100 mL)}}$$

A = the volume of $AgNO_3$ used.

N = Normality (molarity) of $AgNO_3$ (0.0141 M)

QUESTION

Determine the chloride content of the samples of water provided and comment on your results.

PART 2

PCH202 PHARMACEUTICAL INORGANIC QUALITATIVE ANALYSIS

INTRODUCTION

The objective of qualitative inorganic analysis is the detection of the elements or radicals contained in an inorganic salt or a mixture of salts. A salt is made up of two parts – basic radical and acid radical. A salt in a solution of water undergoes ionization to produce hydrated ions.

e.g. $NaCl \rightarrow Na^+ + Cl^-$

The basic radical forms positive ion and acid radical constitutes the negative ion. The process of qualitative analysis takes place in aqueous solution; thus, the reaction is consequently ionic in nature. Test solution must be examined for both basicity and acidity since the properties of each salt are those of the basic and acid radicals.

In summary, qualitative analysis involves the detection of basic and acidic radicals present in a given sample of unknown salt(s) by a systematic procedure which consists of the following steps:

1) Preliminary test
2) Wet tests for basic radicals
3) Wet tests for acid radicals

SCHEDULE I

2.1 PRELIMINARY TESTS

2.1.1 Physical Appearance: Spread out a small portion of the sample on a piece of white paper and note the colour of the mixture.

OBSERVATIONS	INFERENCE
Bluish or bluish green	Copper salt
Greenish or greenish blue	Nickel salts
Light green	Ferrous or nickel salt
Dark green	Chromium salt
Brown or yellowish brown	Ferric or manganese salt
Yellow	Iron oxalate, chromate
Reddish	Ferric oxide
Pink violet	Cobalt salt
Light pink	Manganese salt
White powder	Absence of Cu, Ni, Fe, Cr, Co, Mn salts.

2.1.2 Dry Heating Test

Heat a small quantity of the sample in a dry test tube at first gently and then strongly. Note any condensation of water, cracking sound, swelling, sublimation, gas evolved and colour changes that takes place.

OBSERVATIONS		INFERENCE
a)	The mixture melts	Hydrated salts nitrates of alkali metals
b)	Crackling sound is produced	$Pb(NO_3)_2$, NaCl, Kl, KBr;
c)	Water condenses in upper part of test tube	Hydrate salts
d)	Swelling	Borax, alum or phosphates
e)	Gases are evolved:	
	O_2 gas - rekindles a glowing splinter.	Due to nitrates
	CO_2 gas - turns lime water milky	Due to bicarbonates, carbonates and oxalates
	CO gas - burns with a pale blue flame	Due to oxalate
	NH_2 gas- Ammoniacal smell turns most red litinus blue, turns Nessler's reagent reddish brown	Due to ammonium salt
	Acetic acid vapour- vinegar-like smell	Due to acetate

Acetone vapour- sweet smell, burn with yellow flame	Due to acetate
SO_2 gas - pungent and suffocating, turn moist litmus blue paper red	Due to sulphide, sulphate and thiosulphate
H_2S gas - rotten egg smell turns moist lead acetate paper black	Due to hydrate sulphide and thiosulphide
HCl gas - fumes in air, pungent and irritating, turns moist litmus paper red	Due to hydrated chloride
NO_2 gas - reddish brown vapours, turns $FeSO_4$ solution brown or black.	Due to nitrates and nitrite
Br_2 vapours – yellowish brown vapours - turns starch paper yellow, dissolve in CS_2 to form an orange colour	Due to bromide
I_2 vapours - violet vapours forms brownish sublimate in cooler parts, turns starch paper blue, dissolve in CS_2 to form a violet solution.	Due to iodides
f) Sublimation – a sublimates is formed on the cooler part, which may be	
i) White	Ammonium salts, Hg_2Cl_2 or $HgCl_2$
ii) Grey form globules when robbed	Due to Hg salts
iii) Yellow – due to sulphur	Thiosulphate
iv) Black and shines with garlic smell.	Arsenic salts
g) Colour of residue	
i) Colour changes due to loss of water of crystallization	
from blue to white	Hydrated copper sulphate
from green to yellow	Nickel salt
from reddish pink to blue	$CoCl_2$ salt
from pale brown to black	$FeCl_3$ salt
from violet to green	Chrome alum
ii) Colour of residue change when hot or cold:	
white cold, yellow hot, pale	Zn or Sn salt
yellow cold, brown hot.	Pb or Bi salt

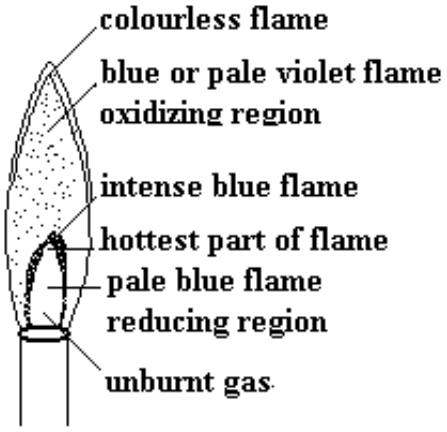
From violet to green	Chrome alum
iii) Colour of residue remains:	
reddish brown	Fe salt
brown	Cd salt
black	Cu, Ni, Co, Mn, salts and charring
white	Absence of Cu, Fe, Ni, Co_2, Cr, Mn salts

2.1.3 Flame Test

Procedure: Make a loop of the platinum wire at the end using pencil point and clean the wire by alternately dipping in concentrated hydrochloric acid taken in a watch glass and heating it in the oxidizing flame of Bunsen burner till it imparts no colour to the flame. Clean the watch glass and take 1-2 mL of pure concentrated hydrochloric acid and add a pinch of the sample given and make a paste with the tip of the platinum wire. Introduce the loop of the wire with the paste into the oxidizing flame of the Bunsen burner and note the colour imparted to the flame with the naked eye first and again examine the flame using a blue glass.

OBSERVATIONS		**INFERENCE**
NAKED EYE	BLUE GLASS	
Persistent golden yellow	Not visible	Sodium
Violet	Pinkish	Potassium
Crimson	Crimson	Strontium
Red	Light yellow	Calcium
Green	Green	Barium
Bluish green	-	Copper
Greenish flashes	-	Zinc, Manganese
Characteristic colour	-	Absence of Na, K, Ba, Sr, Ca, Cu salts

3.1.4.0 Bunsen burner flame



2.1.4 Borax Bead Test (for Coloured Salts)

Procedure: Make a loop of platinum wire using pencil point. Heat the loop in the Bunsen flame. Dip the hot loop into borax powder and heat again. The borax swells up and melts to give colourless transparent glass which fills the loop completely. Continue to heat the loop in the flame till it becomes clear. Touch the hot bead on the platinum wire with small portion of the sample given and heat the bead again in the oxidizing flame of the Bunsen burner till a transparent bead is produced. Note the colour of the bead when hot and also when it cools down. Heat the bead again in the reducing flame and note the colour of the bead. The bead is removed from the loop by tapping with glass rod when it is red hot.

Colour of bead in oxidizing flame		Colour of bead in reducing flame	Inference
When bead is hot	When bead is cold		
Deep blue	Deep blue	Deep blue	Cobalt present
Green	Blue	Reddish or colourless	Copper present
Brown	Brown	Grey or black	Nickel present
Deep green	Deep green	Deep green	Chromium present
Brownish	Yellowish	Light green	Iron present
Pinkish	Pinkish	Colourless	Manganese present

2.1.5 Dilute Sulphuric Acid Test

To a pinch of mixture in a test tube add 2-3 mL of dilute sulphuric acid. Note whether the reaction takes place in cold. If not, slightly warm (do not boil) and identify the gases liberated by colour, smell and chemical tests using litmus paper, lead accetate paper, dichromate paper, lime water or ferrous sulphate solution.

OBSERVATION	INFERENCE
1) Colourless gas with no smell, turns lime water milky (CO_2 gas)	From carbonate CO_3^{2-} and HCO_3^- bicarbonate
2) Colourless gas with a pungent and suffocating smell like burning sulphur, turns acidified $K_2Cr_2O_7$ paper green –SO_2 gas	From sulphite SO_3^{2-}
3) Colourless gas with a rotten egg- like smell, turns lead acetate paper black –H_2S gas	From sulphide S^{2-}
4) Colourless gas with a pungent and suffocating smell like burning sulphur, turn acidified dichromate paper green and gradual separation of sulphur – SO_2 and sulphur.	From thiosulphate $S_3O_3^{2-}$
5) Reddish brown vapour with strong smell like nitric acid turns ferrous sulphate solution black –NO_2 gas	From nitrite NO_2^-
6) A dark brown precipitate of iodine and brown vapours of NO_2 gas. On heating violet vapours of iodine are produced which turns starch paper blue – iodine and NO_2 gas.	From nitrite and iodide
7) A reddish brown coloured solution and brown vapours of NO_2 gas. On heating yellow brown vapours of bromine, which turn starch paper yellow – bromine and NO_2 gas.	From nitrite and bromide radicals
8) No action in cold.	Absence of carbonate, bicarbonate, sulphite, sulphide, thiosulphate, nitrite.

NOTE: Dilute hydrochloric acid can also be used in place of dilute sulphuric acid since it also decomposes the salts of weak acids.

2.1.6 Potassium Permanganate Test

Boil the reaction mixture of dilute sulphuric acid test to expel all gases and add more dilute sulphuric acid. Add potassium permanganate solution drop wise and note the changes as summarized below.

OBSERVATION	INFERENCE
1) Pink colour discharged:	
a) With a vigorous effervescence a gas with no colour, no smell, turns lime water milky – CO_2 gas	From oxalate and tartarate
b) A pale greenish yellow gas with a pungent, suffocating and irritating smell – Cl_2 gas	From chloride
c) The solution is turned reddish brown, on heating the solution yellowish brown vapours are produced which turn starch paper yellow – Br_2 gas	From bromide
d) The solution is turned dark brown. On heating violet vapours of iodine are produced which turn starch paper blue – I_2 gas	From iodide
2) Pink colour disappear with no evolution of gas	Presence of ferrous and stannous salts
3) Pink colour did not disappear	Absence of Cl^-, Br^-, I^-, oxalate, tartarate, Fe^{2+}, Su^{2+} and arsenite.

2.1.7 Concentrated Sulphuric Acid Test

Take a pinch of the mixture in a test tube and add 2-3 mL of concentrated sulphuric acid. An evolution of gas in the cold indicates the presence of acid radicals which decomposes with dilute sulphuric acid. Allow the evolution of gas to continue until it ceases. Shake the content of the tube and add more concentrated H_2SO_4 (1-2 mL) into the same test tube and heat gently at first and then strongly (do not boil). Further reactions will take place to liberate the following gases.

OBSERVATION	INFERENCE
1) Steamy fumes with pungent, irritating smell, form dense white fumes with a glass rod wetted with NH_4OH – HCl gas	Chloride present
2) Colourless vapours with a strong smell like that of vinegar no charring – acetic acid vapours	Acetate present
3) Colourless gases with no smell turn lime water milky, burns with a pale blue flame – CO and CO_2 gases.	Oxalate present
4) Charring takes place with the smell like burnt sugar, turns lime water milky and also burns with a blue flame – CO_2 and CO gases.	Tartarate present
5) Reddish brown vapours with pungent smell, colour becomes dense when copper chip is added, the vapour turn $FeSO_4$ solution dark brown -- HNO_3 and NO_2 vapours.	Nitrate present
6) A steamy yellowish brown vapours with pungent and irritating smell, turn moist starch paper yellow, turn filter paper soaked in flourescein solution red, dissolved in CS_2 to produce an orange solution – HBr and Br	Bromide present
7) Steamy violet vapours with pungent smell stain the skin brown, form brownish shining sublimate, turn moist starch paper blue, dissolve in CS_2 to from a violet solution – Hl and I_2	Iodide present
8) No action	Absence of Cl^-, Br^-, I^-, NO_3^-, acetate oxalate and tartarate.

2.1.8 Caustic Soda Test (Sodium Hydroxide Test)

Add sodium hydroxide solution to a pinch of the mixture in a test tube and heat gently and test the gas, which evolved as follows:

OBSERVATION	INFERENCE
Ammoniacal smell produced turns moist turmeric paper brown, form dense white fumes with HCl, turns Nessler's reagent reddish brown – ammonia gas	Presence of ammonium salt
No ammoniacal smell	Absence of ammonium salt

SHEDULE II

2.2 ANALYSIS OF GROUP I BASIC RADICALS

2.2.1 Preparation of Solution of the Mixture of substances.

Before proceeding to the study of the analysis of basic radicals by wet tests it is necessary to prepare the solution of the mixture. The following solvents should be tried out strictly in the order given but every attempt should be made to dissolve the mixture in one solvent before proceeding to the next.

a) Distilled water – first in cold and then hot.
b) Dilute hydrochloric acid – first in cold and then in hot.
c) Concentrated hydrochloric acid – first in cold and then hot
d) Dilute nitric acid
e) Concentrated nitric acid
f) Aqua regia

Procedure: Take a test tube half filled with distilled water and add a pinch of the mixture. Shake by tapping the bottom of test tube with the forefinger, if the solution does not become clear heat the test tube. Shake while heating. The resulting solution should become clear and transparent.

In case the mixture dissolves, more of the mixture should be added into it pinch by pinch at a time and shake to get a concentrate solution termed as Original solution. The original solution prepared contains basic radicals for the identification and confirmation by west tests.

The basic radicals are divided to six groups for their systematic analysis. The division is based upon the difference in the solubility of their chlorides, sulphides, hydioxides,and carbonates in water. The basic radicals belonging to each are precipitated by the addition of a common known solution, which is called group reagent. The basic radicals belonging to a particular group resemble each other in certain properties but differ from the basis radicals of other groups. If the mixture did not dissolve, repeat the procedure with the next solvent.

2.2.2 Group I Table

To a portion of the original solution prepared, add a few drops of dilute HCl. If a white precipitate is produced add more dilute HCl slowly with shaking till the precipitation is complete. Filter or decant the precipitate and wash with cold water. Analyze the precipitate for the basic radical of group I as indicated below. Keep filtrate for analyze of subsequent groups.

White precipitate: - Due to AgCl, $PbCl_2$ and black precipitate due to Hg_2Cl_2. Transfer into a test tube and add distilled water and boil, filter or decant while hot if necessary.

Filtrate or clear solution: May contain lead chloride. Divide the solution into three different portions and confirm Lead [Pb^{2+}].

1) Cool portion of the filtrate in water. White crystalline precipitate due to $PbCl_2$

2) Potassium chromate test: To another portion of the filtrate add potassium chromate solution, a yellow precipitate appears.

$PbCl_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2KCl$

3) Potassium iodide test. To another portion add Potassium iodide solution, a yellow precipitate of Lead iodide is produced

$PbCl_2 + 2KI \rightarrow PbI_2 + 2KCl$

Residue or Precipitate: Due to AgCl, Hg_2Cl_2. Add NH_4OH solution and warm, shake and filter or decant if necessary.

Filtrate or clear solution: May contain complex compound of AgCl in NH_4OH divide into different portion and confirm silver [Ag^+].

1) Nitric acid test

adds nitric acid to a portion of the clear solution, a white precipitate of AgCl appears

$Ag(NH_3)_2Cl + 2HNO_3 \rightarrow AgCl + 2NH_4NO_3$

2) Potassium iodide test

add potassium iodide to another portion, a yellow precipitate of Agl is formed.

$Ag(NH_3)_2Cl + KI + 2H_2O \rightarrow AgI + KCl + 2NH_4OH$

3) White precipitate of AgCl when exposed to light turns grey.

Residue or precipitate: Which is black is Hg_2Cl_2 to the black precipitate in a test tube add zinc of aqua regia and boil. The black precipitate will dissolve, boil off excess nitric acid and dilute with water. Divide into two portions and confirm Mercury [Mercurous Hg^+].

1) Stannous chloride test: Add Stannous chloride solution, a white precipitate which turns grey on adding excess of Stannous chlorideis due to separation of Mercury.

2) NaOH solution test: Add NaOH solution, a yellow precipitate of Mercuric oxide is produced.

$HgCl_2 + 2NaOH \rightarrow HgO + 2NaCl + H_2O$

SCHEDULE III

2.3 ANALYSIS OF GROUP II BASIC RADICALS

To portion of the filtrate of group I or the original solution of the mixture, add dilute HCl into it. Heat the solution and pass H_2S into it. If no precipitate is formed proceed to the analysis of the radicals of group III. If a coloured precipitate is obtained pass more H_2S gas into the remaining solution and ensure complete precipitation. Filter or decant if necessary.

<table>
<tr><th>Filtrate</th><th colspan="2">Residue or precipitate</th></tr>
<tr><td rowspan="2">May contain radicals of subsequent groups</td><td colspan="2">May contain the sulphide of group II radicals. Wash the precipitate with distilled water. Add yellow Ammonium sulphide solution and warm, shake while heating. Filter or decant if necessary</td></tr>
<tr><td><u>Filtrate or clear solution</u>
May contain radicals of group II-B which are As_2S_3, Sb_2S_3, SnS analyse the solution for group II-B basic radicals.</td><td><u>Residue or precipitate</u>
May contain radicals of group II-A which are HgS, PbS, Bi_2S_3, CuS, CdS. Analyse the precipitate by group II-A basic radicals</td></tr>
</table>

NOTE

1) Thioacetamide solution in the presence of dilute HCl can be used to generate sulphide radical for the reaction.
2) NaOH or KOH in the presence of little yellow ammonium sulphide. Or NaOH or KOH in the presence of a H_2S gas can also be used.
3) Yellow ammonium sulphide should be freshly prepared.

2.3.1 Group II-A Basic Radicals

Dark brown or black coloured precipitate due to HgS, PbS, Bi_2S_3, CuS, CdS. Wash with hot water and add dilute Nitric acid and boil. Filter or decant if necessary. The precipitate of Mercuric sulpide is insolube while those of Pb, Bi, Cu and Cd go into solution as soluble nitrates.

$$HgS + 2HCl + 3[O] \rightarrow HgCl_2 + H_2O + SO_2$$

<u>Residue or precipitate</u>: Due to HgS. Dissolve the precipitate in aqua regia and boil. Divide the resulting solution in to different portion and confirm mercuric [Hg^{2+}]

(1) Stannous chloride test

Add Stannous chloride to a portion,

White precipitate is formed which turns

Grey on standing

(2) NaOH test:

To another portion add NaOH solution

a yellow precipitate is produced

mercury oxide

$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$. $HgCl_2 + 2NaOH \rightarrow HgO + 2NaCl + H_2O$

$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$

Filtrate or clear solution: May contain Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+} as nitrates. Add dilute H_2SO_4 small portion of the solution. Pb^{2+} goes into solution as lead sulphate.

$Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4\downarrow + 2HNO_3$

It is separated by filtration and the filtrate may contain $Bi^{2+,}$ Cu^{2+} and Cd^{2+} radicals. If there was no precipitate formed reject it and proceed with the rest solution for $Bi^{2+,}$ Cu^{2+} and Cd^{2+} radicals.

Residue or precipitate: white precipitate due to $PbSO_4$. Add excess ammonium acetate solution to the precipitate. The precipitate dissolves to form a clear solution, divide the resulting solution into two to confirm lead [Pb^{2+}].

$PbSO_4 + 2CH_3COONH_4 \rightarrow (CH_3COO)_2Pb + (NH4)_2SO_4$

1) Potassiun chromate test

To a portion of the above solution add potassium chromate solution, a yellow precipitate is produced.

$(CH_3COO)_2Pb + K_2CrO_4 \rightarrow 2CH_3COOK + PbCrO_4$

2) Potassium iodide test

To second portion of the above solution add potassium iodide solution, a yellow precipitate is produced.

$(CH_3COO)_2Pb + 2KI \rightarrow PbI_2 + 2CH_3COOK$

Clear solution or filtrate: May contain Bi^{3+}, Cu^{2+} and Cd^{2+} as the sulphate or nitrate. Add NH_4OH solution in excess into it till the solution becomes alkaline, filter or decant if necessary.

Residue or precipitate: White precipitate due to $Bi(OH)_3$. Add dilute HCl to dissolve the precipitate and divide into two different portions to confirm Bismuth [Bi^{3+}].

$Bi_2(SO_4)_3 + 6NH_4OH \rightarrow 2Bi(OH)_3 + 3(NH_4)_2SO_4$

1) Dilution test

To a portion of the solution add water to dilute, a milkiness is produced

$BiCl_2 + H_2O \rightarrow BiOCl + 2HCl$

2) Sodium stannate solution test

To another portion add sodium stannite solution, a black precipitate is produced

$2BiCl_2 + 3Na_2SnO_2 \rightarrow 2Bi + 2Na_2SnO_3 + 2NaCl + SnCl_4$

Filtrate or clear solution: May contain Cu^{2+} or Cd^{2+} as complex compounds.

Note the colour of the solution.

Blue coloured solution due to Cu^{2+} or Cu^{2+} and Cd^{2+} Colourless solution Cu^{2+} is absent

Divide into the solution two portions to confirm Cupper [Cu^{2+}] or and Cadmium [Cd^{2+}] and Cd^{2+} may be present.

1) Potassium ferrocyanide solution test

To a portion of the solution add acetic acid and Potassium ferrocyanide solution. A chocolate precipitate is produced.

$2Cu^{2+} + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + 4K^+$

2) Potassium iodide test

To another portion add acetic acid and potassium iodide solution. A white precipitate of cuprous iodide is produced. Iodine is set free

$Cu^{2+} + 2KI \rightarrow CuI_2\downarrow + 2K^+$

$2CuI_2 \rightarrow Cu_2I_2 + I_2$

Using colourless solution: Add ammouium sulphide. A yellow precipitate of CdS is produced. Dissolve the precipitate in small quantity of dilute HCI and boil. Divide different portions to confirm Cd^{2+}.

1) NaOH solution test:

To a portion of the above solution a white precipitate is produced.

$CdCl_2 + 2NaOH \rightarrow Cd(OH)_2 + 2NaCl$

2) Potassium ferrocyanide test:

To another portion, add potassium ferrocyanide solution, a white a precipitate is produced

$2CdCl_2 + K_4[Fe(CN)_6] \rightarrow Cd_2[Fe(CN)_6]\downarrow + 4KCl$

2.3.2 Group II-B Basic Radicals

To the filtrate or clear solution containing the radicals for group II-B, add dilute HCl till the solution is acidic. A coloured precipitate indicates the presence of As, Sb, Sn radicals. Add H_2S gas or thioacetamide solution to complete the precipitation. Filter or decant and wash precipitate with distilled water. Boil the precipitate with concentrated HCl and filter or decant if necessary.

Residue or precipitate: Yellow colour precipitate due to As_2S_3 wash the precipitate with distilled water dissolve it in concentrated HNO_3 and boil. Divide the resultant solution into different portions and confirm Arsenic (As^{3+}).

1) Ammonium Molybdate test:

To a portion of the above solution add dilute HNO_3 boil and add ammonium molybdate solution. A yellow precipitate

2) Magnesia mixture test

To another portion of the above solution add NH_4OH to make it alkaline. Add magnesia mixture (a solution of $MgCl_2$,

produced.

chloride NH_4Cl and $NH_4(OH)$, a white precipitate is produced.

$H_2AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3[AsMo_{12}O_{4O}] + 21NH_4NO_3 + 12H_2O$

$(NH_4)_3ASO_4 + MgCl_2 \rightarrow Mg(NH_4)ASO_4 + 2NH_4Cl$

3) To the above precipitate in 2) above
add silver nitrate solution containing acetic acid.
Brownish red precipitate is produced.

Filtrate or clear solution: May contain chloride of Sb and Sn. Boil off H_2S gas and add NH_4OH solution to make it alkaline and add solid oxalic acid and boil. Cool and add H_2S gas or thioacetamide solution. Filter if a precipitate is formed.

Residue or precipitate: Orange colour precipitate due to Sb_2S_3. Dissolve in small quantity of concentrated HCl boil to expel H_2S gas. Divide into different portion to confirm antimony Sb^{3+}

1) Dilution test:
To a portion of the above solution add NH_4OH solution to neutralize the excess acid. Dilute the solution
A white precipitate is produced.

$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$

2) Tin metal test:
To another portion add a piece of tin metal. A black deposit is formed on the surface of the metal.

$4SbCl_2 + 3Sn \xrightarrow{HCl} 4Sb + 3SnCl_4\downarrow$

Filtrate or clear solution: May contain complex compound of tin. Boil of H_2S gas add a piece of zinc metal and conc HCl. Filter and divide the solution into different portions to confirm Tin (Sn^{2+}).

1) Mercuric Chloride test:
To a portion of the above solution add mercuric chloride solution, a white-precipitate which turns grey is produced.

$SnCl_4 + 2HgCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

2) Ammonium Molybdate test
To another portion add Ammonium molybdate
A blue colour or precipitate is produced.

$3(NH_4)_2MoO_4 + 2[H] + 6HCl \rightarrow Mo_3O_4 + 6NH_4Cl + 4H_2O$

QUESTIONS

1) Why was Pb detected in both group I & II analysis?
2) What are the pharmaceutical and medicinal applications of the radicals?

SCHEDULE IV

2.4 ANALYSIS OF GROUP III BASIC RADICALS

To a solution of the mixture for group III analysis, add a few drops of conc nitric acid, to oxidise any ferrous salt (Fe^{2+}) to ferric salt (Fe^{3+}). Add about 1g of solid Ammonium chloride and boil for 5 minutes. Cool the solution until bearable to touch. Add ammonium hydroxide solution slowly with constant shaking. Continue the addition of NH_4OH until the solution gives a strong smell of ammonia. Filter or decant if necessary.

Residue or precipitate: Brown or brownish precipitate due to $Fe(OH)_3$, $MnO.(OH)_2$, $Cr(OH)_3$ and a white gelatinuous precipitate due to $Al(OH)_3$. Wash the precipitate with NH_4Cl solution and with hot water. Boil with water and a little (Na_2O_2) sodium peroxide until evolution of oxygen ceases. Cool and filter or decant if necessary.

<table>
<tr><td colspan="2">Residue of precipitate: Reddish brown due to $Fe(OH)_3$ and $MnO.(OH)_2$. Divide into 2 parts to confirm Iron (Fe^{3+}) and Manganese (Mn^{2+}).</td></tr>
<tr><td>To one part add dilute HCl to dissolve the precipitate. Divide into two parts to confirm Fe^{3+}.
1) To one part add potassium sulphocyanide, a blood red colour is produced.
$FeCl_3 + 3KCNS \rightarrow Fe(CNS)_3 + 3KCl$

2) To another portion add potassium ferrocyanide. A deep blue colour or precipitate produced.</td><td>Divide the remaining precipitate into two portions to confirm Mn^{2+}.

1) To one portion add lead peroxide and concentrated HNO_3 boil, cool and dilute the reaction mixture. A pink or purple colour is formed.
$2MnO.(OH)_2 + 3[O] \rightarrow 2HMnO_4 + H_2O$

2) To another portion of the precipitate add concentrated HNO_3 and sodium bismuthate and shake. Dilute the solution, a pinkish or purple colour is formed.
$NaBiO_3 + 4HNO_2 \rightarrow NaNO_2 + Bi(NO_3)_3 + H_2O + [O]$
Nascent
$2MnO(OH)_2 + 3[O] \rightarrow 2HMnO_4 + H_2O$</td></tr>
</table>

Filtrate or clear solution: Yellow colour solution due to Na_2CrO_4 and $NaAlO_2$, acidify with HCl, add NH_4OH solution to make it just alkaline and boil. Filter if precipitate is produced.

Filtrate or solution: Yellow solution due to sodium chromate. Divide the solution into different portions to confirm chromium (Cr^{2+}).

1) Lead acetate test:
To one portion acidify with acetic acid solution and add lead acetate solution yellow precipitate of lead chromate is produced.

$(CH_3COO)_2Pb + Na_2CrO_4 \rightarrow PbCrO_4 + 2CH_2COONa$

2) Silver nitrate test:
To another portion acidify with nitric acid, add $CaCO_3$ powder to neutralize the acid and add $AgNO_3$ solution. A brick red precipitate of silver chromate is produced.

$Na_2CrO_4 + 2AgNO_3 \rightarrow AgCrO_4 + 2NaNO_3$

Residue or precipitate: Gelatinous white precipitate due to $Al(OH)_3$. Aluminum [Al^{3+}] is confirmed using Lake test.

Lake test: Dissolve a portion of the above precipitate in mm quantity of dilute HCl, add a drop or two or blue litmus solution. The solution becomes pink. Add NH_4OH slowly with shaking till it becomes just alkaline. A blue precipitate in colourless solution is produced.

Note: * An alternate reagent is Sodium hydoxide (NaOH) and Hydrogen peroxide (H_2O_2).

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$$

QUESTIONS

1) Why did you boil the filtrate of group III analysis with concentrated HNO_3. Write the reaction involved using chemical equations.
2) What is the function of ammonium chloride before adding ammonium hydroxide in group III analysis?
3) Write the acid radicals that can interfere in group III analysis.
4) Explain what can be done to prevent the precipitation of Manganese in group III analysis.

SHEDULE V

2.5 ANALYSIS OF GROUP IV BASIC RADICALS

To a small portion of the solution for group IV analysis add NH_4OH and pass H_2S gas from Kipp's apparatus steady and at constant pressure if a precipitate appears, then pass more H_2S gas through the rest of the solution to precipitate completely the cations of group IV as sulphides. Note the colour of the precipitate.

<table>
<tr><td colspan="2">Black precipitate: Due to CoS and NiS may also contain MnS and ZnS. Wash with hot water, add dilute HCl and boil, filter or decant.</td><td colspan="2">Brownish precipitate: Due to MnS and ZnS. Dissolve in dilute HCl.</td></tr>
<tr><td colspan="2">Residue or precipitate: Black in colour due to CoS or NiS. Dissolve in conc HCl and conc HNO_3 (Aqua regia) evaporate to nearly dryness. Divide into portions.</td><td colspan="2">Solution or filtrate: Contain $MnCl_2$ and $ZnCl_2$. Boil the solution to expel the H_2S, add NaOH solution and filter or decant if necessary.</td></tr>
<tr><td>Confirmatory tests for Cobalt
1) Evaporate a portion to dryness; a blue or bluish green colour is produced.
2) Add a pinch of Na_2CO_3 to neutralize the acid and acidify with Acetic acid and add concentrated solution of potassium nitrite and warm, a yellow precipitate is produced.

$Co(NO_2)_3 + 3KNO_2 \rightarrow K_3[Co(NO_3)_6]$

Cobalt $[Co^{2+}]$ is confirmed</td><td>Confirmatory test for Nickel
1) Evaporate to dryness, a portion of the above solution, a yellow precipitate is produced.
2) To another portion add sod. Hydroxide solution and bromine water and boil, a black precipitate is produced.
$2NaOH + Br_2 \rightarrow 2NaBrO + NaBr + H_2O$
$2K_2[Ni(CN)_2] + 4NaOH + 9Na(BrO) + H_2O \rightarrow 2Ni(OH)_3 + 4KCNO + 4NaCNO + 9NaBr$
3) To another portion add NH_4OH solution and a few drops of dimethyl glyoxime solution, a bright pinkish colour is</td><td>Precipitate or residue
Brownish colour precipitate due to $MnOH_2.XH_2O$.

1) To a portion of the precipitate add bromine water and NaOH and boil. A black is produced.
$Mn(OH)_2 + [O] \rightarrow MnO.(OH)_2$
2) To another portion of the precipitate add lead peroxide and con HNO_3. Boil and cool, dilute and allow to settle. A pink colour is produced.
$2MnO.(OH)_2 + 3[O] \rightarrow 2HMnO_4 + H_2O$</td><td>Filtrate or clear solution
Contain sod. Zincate. Divide into different parts.
1) Pass H_2S gas into one part of the solution, a white precipitate of zinc sulphide is produced.
$Na_2ZnO_2 + H_2S \rightarrow ZnS + 2\ NaOH$.
To another portion add dilute HCl and potassium ferrocyanide solution, a white or bluish white precipitate is /produced.

$K_4[Fe(CN)_4] + 2ZnCl \rightarrow Zn_2[Fe(CN)_4] + 4KCl$</td></tr>
</table>

	produced. Nickel [Ni^{2+}] is confirmed.	Manganese [Mn^{2+}] is confirmed.	Zinc [Zn^{2+}] is confirmed.

Note: Thioacetamide solution can be used in place of H_2S gas.

QUESTIONS

1) What is aqua regia?
2) What is the function of NH_4OH added before passing H_2S gas?

SCHEDULE VI

2.6 ANALYSIS OF GROUP V BASIC RADICALS

A small portion of the solution for the analysis of group V is evaporated to concentrate it, add ammonium chloride and ammonium hydroxide solution into the solution, then add ammonium carbonate solution, warm and allow to stand. If precipitate is formed it indicates the presence of group V radical. Filter or decant if necessary.

<table>
<tr><td colspan="2">White precipitate: Due to $BaCO_3$, $SrCO_3$ and $CaCO_3$ wash the precipitate with hot water. Dissolve the precipitate in minimum quantity of acetic acid boil to expel CO_2 gas. To a test portion add potassium chromate solution, a yellow precipitate indicates barium, add more to the remaining solution to complete precipitation of barium. If no precipitate, test the remaining solution for Sr and Ca.</td></tr>
<tr><td rowspan="2">Yellow precipitate: Due to barium chromate. Dissolve precipitate in conc HCl and divide into two to confirm Barium [Ba^{2+}].
1) To one portion of the solution add dilute H_2SO_4. A white precipitate of $BaSO_4$ is produced.
$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
greenish
2) Flame test: A grassy flame is produced.
Barium is confirmed.</td><td>Clear solution or filtrate which is yellow colour solution may contain Sr^{2+} and Ca^{2+} add ammonium sulphate solution and filter or decant if necessary.</td></tr>
<tr><td>Residue or precipitate: which is white is due to $SrSO_4$. perform flame test with the precipitate. A crimson colour flame visible through the blue glass is observed.

Strontium is confirmed.</td></tr>
</table>

<u>Filtrate or clear solution</u>: May contain calcium sulphate. Divide into different portion.

1) To one portion add Ammonium oxalate solution: a white precipitate of calcium oxalate is produced.

$$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4\downarrow + 2CH_3COONH_4$$

2) Flame test with above precipitate gives a brick red colour flame.
3) Dissolve the precipitate in conc HCl, add NH4OH to neutralize the acid and add NH4Cl and potassium ferrocyanide solution, a white precipitate is produced.

$$CaCl_2 + NH_4Cl + K_4[Fe(CN)_4] \longrightarrow Ca(NH_4)K[Fe(CN)_6]\downarrow + 3KCl$$

4) Calcium is confirmed.

QUESTIONS

1) What is the function of Ammonium carbonate in group V analysis?
2) Explain in detail giving chemical equations to show the ionization of NH_4Cl and $(NH_4)_2CO_3$.

SHEDULE VII

2.7 ANALYSIS OF GROUP VI BASIC RADICALS

To a portion of the solution for group VI analysis, add NH_4OH solution and add ammonium hydrogen phosphate solution. Titurate the side of the glass tube with a glass rod. Filter or decant if a precipitate is produced.

<table>
<tr><td colspan="2">White precipitate: Due to $Mg(NH_4)PO_4$. Disssolve the precipitate in dilute HCl and divide into two.
$MgCl_2 + (NH_4)_2HPO_4 + NH_4OH \rightarrow MgNH_4PO_4 + 2NH_4Cl + H_2O$
1) To a portion, add a few drops of Cobalt nitrate, soak a filter paper with the solution and ignite its edge in the flame. A pinkish ash is produced (CoO.MgO).
2) Magneson reagent test. To another portion add a few drops of magneson reagent and excess NaOH solution. A sky-blue precipitate is produced. (Mg) Magnesium is confirmed.</td></tr>
<tr><td colspan="2">Filtrate or solution: boil the solution to concentrate and to expel all ammonia. Divide into two parts and test for sodium and potassium radicals.</td></tr>
<tr><td>For sodium $[Na^{2+}]$
1) Potassium Pyro-antimonate test
To one portion of the solution add solid KOH, boil till ammonia gas ceases (test using Wessler's reagent). Add Potassium pyroantimonate solution. Titrate the sides of tube, a milkiness is produced.
$2NaCl + K_2H_2Sb_2O_7 \rightarrow Na_2H_2Sb_2O_2 + 2KCl$
2) Flame test:
Evaporate a portion of the solution to dryness and perform the flame test. A golden yellow colour invisible through blue glass is produced.

(Na) Sodium is confirmed.</td><td>For potassium $[K^{+}]$
1) Sodium cobalt nitrite test
To one portion of the solution add solid NaOH, boil till ammonia ceases (test using Nessler's reagent). Add sodium cobalt nitrate solution. A yellow precipitate is produced.
$NH_4Cl + NaOH \rightarrow NaCl + NH_3\uparrow + H_2O$
2) Picric acid test
To another portion of the solution add picric acid solution, a yellow precipitate is produced.
3) Tartaric acid test
To another portion of the solution add saturated solution of tartaric acid. Rub the sides of the glass tube with glass tube and add alcohol, a white precipitate is produced.
4) Flame test
Perform flame test on evaporated mass, a violet colour in the flame which is pink through blue glass is produced.
Potassium is confirmed.</td></tr>
</table>

For Ammonium (NH_4^+)

Caustic soda test: To the pinch of the mixture add sodium hydroxide solution and heat. Ammonia gas evolved which turns Nessler's reagent reddish brown.

$(NH_4)_2\ SO_4\ +\ 2NaOH \longrightarrow Na_2SO_4 +\ \ 2NH_3\ \ + 2H_2O$

Ammonium is confirmed.

QUESTIONS

1) Why is there no common reagent for cations of group VI?
2) Give the structure of Magneson reagent.

SCHEDULE VIII

2.8 EXAMINATION OF ACID RADICALS

2.8.1 Preparation of Solution of the Mixture

For the analysis of acid radicals, the first step is to prepare a solution of the mixture using the following procedure:

a) Preparation of water extract: Certain salts are soluble in water and thus their solutions in water can be used to detect the acid radicals.

b) Preparation of sodium carbonate extract: In the analysis of acid radicals certain basic radical interferes with the detection of some acid radicals and thus have to be removed from solution. This is achieved by boiling the mixture of salts with concentrated solution of sodium carbonate which will precipitate out the heavy metals as carbonates. The filtrate or clear solution obtained can then be used for the analysis of the acid radicals.

2.8.2 Analysis of Carbonate and Bicarbonate Radicals

The presence of carbonate and bicarbonate can be confirmed by performing the following test. To a pinch of the mixture in a test tube add distilled water, shake, filter or decant if necessary.

Residue or precipitate: may be due to insoluble carbonate. To a portion of the precipitate add dilute HCl, an effervescence with evolution of a colourless gas with no smell and turn lime water milky is due to CO_2 gas. $MgCO_3 + 2HCl \rightarrow MgCl_2 + CO_2 + H_2O$ Confirms presence of insoluble carbonate.
Filtrate or clear solution: May be soluble carbonate or bicarbonate. Divide into two portions. 1) <u>Dilute HCl test</u>: Add dilute HCl to a portion of the above solution, an effervescence with evolution of colourless gas which turn lime water milky is due to CO_2. $K_2CO_3 + 2HCl \rightarrow 2KCl + H_2O + CO_2$ $Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O + 2CO_2$ Confirms presence of soluble carbonate and bicarbonate. 2) <u>$MgSO_4$ solution test</u>: To another portion, add $MgSO_4$ solution, shake, filter or decant if necessary.

White precipitate: In the cold, which is due to presence of soluble carbonate. $Na_2CO_3 + MgSO_4 \rightarrow MgCO_3\downarrow + Na_2SO_4$ Presence of soluble carbonate confirmed.	Clear solution or filtrate: Heat the clear solution to boil- white precipitate indicated the presence of bicarbonate. $Ca(HCO_3)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(HCO_3)_2$ Soluble $Mg(HCO_3)_2 \xrightarrow{\text{Boiling}} MgCO_3\downarrow + CO_2 + H_2O$ Presence of bicarbonate confirmed.

2.8.3 Analysis of Nitrite and Nitrate Radicals

a) For Nitrite radical

i. Ferrous sulphate test: To a portion of the water extract, add acetic acid solution and ferrous

sulphate solution A dark brown or black solution is produced.

$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$

$3HNO_2 \rightarrow HNO_2 + H_2O + 2NO$

$FeSO_4 + NO \rightarrow FeSO_4.NO$

ii. Potassium iodide solution test: To a portion of water extract, add potassium iodide solution and acetic acid solution – iodine is set free and the solution turn brown.

iii Potassium permanganate solution test: To a portion of the water extract, add potassium permanganate solution acidified with sulphuric acid – the pink colour is discarded.

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$KNO_2 + [O] \rightarrow KNO_3$

b) For Nitrate radical

i. Copper turning test: To a pinch of the mixture in a test tube add conc H_2SO_4 and few pieces of copper turnings. Heat the tube – evolution of reddish-brown fumes that turn ferrous sulpahte solution dark brown.

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$3HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$

iii. Brown ring test: Take a portion of the sodium carbonate extract, acidify with acetic acid solution, boil to expel CO_2 gas. Add ferrous sulphate solution and warm. Pour concentrated H_2SO_4 slowly down the side of the tube without allowing the acid to mix with the solution – a black ring is produced at the junction of the two layers.

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe(SO_4)_3 + 2NO + 4H_2O$

$FeSO_4 + NO \rightarrow FeSO_4.NO$

Brown Ring

2.8.4 Analysis of Sulphide, Sulphite, Thiosulphate and Sulphate Radicals

a) For Sulphide radical

i. Cadmium carbonate solution test: Take a portion of sodium carbonate extract and add a suspension of cadmium carbonate in water – a yellow precipitate is produced.

$CdCO_3 + Na_2S \rightarrow CdS\downarrow + Na_2CO_3$

ii. Sodium nitroprusside solution test: Take a portion of sodium carbonate extract in a test tube

and add a few drops of sodium nitroprusside solution – a purple or violet colour is produced.

$Na_2S + Na_2[Fe(CN)_2NO] \rightarrow Na_4[Fe(CN)_5NOS]$

Sodium nitroprusside — violet colouration

iii. Lead acetate solution test: Take a portion of sodium carbonate extract in a test tube and add drop by drop of acetic acid solution to neutralize sodium carbonate boil to expel CO_2 gas and add lead acetate solution into it – a black precipitate is produced.

$CH3(COO)_2Pb + Na_2S \rightarrow PbS\downarrow + 2CH_3COONa$

b) For Sulphite radical

i. Barium chloride test: Take a portion of sodium carbonate extract in a test tube and acidify with acetic acid solution, boil to expel CO_2 gas. Add barium chloride solution into it – a white precipitate, which is soluble in dilute HCl, is produced.

$Na_2SO_4 + BaCl_2\downarrow \rightarrow BaSO_3 + 2NaCl$

ii. Potassium dichromate solution test: Take a portion of sodium carbonate extract in a test tube and add drops of acidified solution of potassium dichromate – orange colour solution changes to green colour.

$K_2Cr2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

$SO_2 + [O] + H_2O \rightarrow H_2SO_4$

c) For Thiosulphate radical

i. Iodine solution test: Take a portion of water extract of the sample in a test tube and add drops of iodine solution into it – the brown colour of iodine is discharged.

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

ii. Silver nitrate solution test: Take about 8 mL of water extract of sample in a test tube and dilute to 15 mL with water and add silver nitrate solution into it – a white precipitate is formed which changes to pale yellow, yellow, orange, brown and finally black.

$Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3\downarrow + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$

iii. Lead acetate solution test: Take a portion of water extract in a test tube and add lead acetate solution, a white precipitate is produced which turned black on boiling.

d) For Sulphate radical

i. Barium chloride solution test: To a portion of sodium carbonate extract, add acetic acid, boil to expel CO_2 gas. Add barium chloride solution into it – a white precipitate is produced which is insoluble in dilute HCl or dilute nitric acid

$Na_2C_2O_4 + BaCl_2 \longrightarrow BaC_2O_4\downarrow + 2NaCl$

$Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow BaSO_4\downarrow + 2NaCl$

ii. Lead acetate solution test: To a portion of sodium carbonate extract, add acetic acid boil to expel CO2 gas, add lead acetate solution, a white precipitate is produced which is soluble in excess ammonium acetate solution

$Na_2SO_4 + (CH_3COO)_2Pb \rightarrow PbSO_4 + 2CH_3COONa$

2.8.5 Analysis of Chloride, Bromide and Iodide Radicals

a) For Chloride radical

i. Silver nitrate solution test: Take a portion of sodium carbonate extract in a test tube and acidify with dilute nitric acid and boil to expel CO_2 gas, add silver nitrate solution, a white precipitate is produced which is soluble in ammonium hydroxide solution but insoluble in nitric acid.

$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$

ii. Manganese dioxide test: Take a pinch of the mixture add concentrated Sulphuric acid in a test tube, add manganese dioxide and heat, a greenish yellow gas is produced with a pungent irritating smell, which turns moist starch iodide paper blue.

$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$

$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + [O]$

$2HCl + [O] \rightarrow H_2O + Cl_2\uparrow$

b) For Bromide radical

i. Silver nitrate solution test: Take a portion of sodium carbonate extract and acidify with dilute nitric acid and boil to expel CO_2 gas. Add silver nitrate solution into it, a pale-yellow precipitate, which is insoluble in dilute nitric acid but soluble in excess NH_4OH solution, is produced.

$$NaBr + AgNO_3 \rightarrow AgBr\downarrow + NaNO_3$$

ii. Manganese dioxide test: Take a pinch of the mixture in a test tube and add manganese dioxide and con H_2SO_4 shake and heat gently – a yellowish brown vapours are evolved with pungent irritating smell, turn moist starch paper yellow.

$$SrBr_2 + H_2SO_4 \rightarrow SrSO_4 + 2HBr$$

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + [O]$$

$$2HBr + [O] \rightarrow H_2O + Br_2$$

c) For Iodide radical

i) Silver nitrate solution test: Take a portion of sodium carbonate extract in a test tube and acidify with dilute nitric acid and boil to expel CO_2 gas. Add silver nitrate solution into it, a yellow precipitate is produced which is insoluble in dilute nitric acid and in ammonium hydroxide solution.

$$NaI + AgNO_3 \rightarrow AgI\downarrow + NaNO_3$$

ii) Lead acetate solution test: Take a portion of sodium carbonate extract in a test tube and acidify with acetic acid and boil to expel CO_2 gas. Cool the solution and add lead acetate solution into it – yellow precipitate is produced which is soluble when boiled with water and cooled to produce golden yellow shinning plates.

$$2NaI + (CH_3COO)_2Pb \rightarrow 2CH_3COONa + PbI_2\downarrow$$

2.8.6 Analysis of Oxalate, Chromate, Phosphate, Borate, Arsenate and Arsenite Radicals

a) Oxalate radical

Barium chloride solution test: Take a portion of the sodium carbonate extracts of the mixture acidified with dilute acetic acid solution, boil to expel CO_2 gas. Add barium chloride solution – a white precipitate is produced which is soluble in dilute nitric acid.

b) Chromate radical

Barium chloride solution test: Take a portion of sodium carbonate extract acidify with acetic acid solution and boil to expel CO_2 gas, add barium chloride solution – a yellow precipitate is produced which is insoluble in dilute nitric acid to form a yellow solution.

$$NaCrO_4 + BaCl \rightarrow BaCrO_4\downarrow + 2NaCl$$

c) Phosphate radical

Calcium chloride test: Take a portion of sodium carbonate extract acidify with acetic acid solution boil to expel CO_2 gas. Add ammonium hydroxide solution and calcium chloride solution into it – a white precipitate of calcium phosphate is produced which is soluble in acid solution but insoluble in ammoniacal solution.

$2Na_2PO_4 + 3CaCl_2 \rightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$

d) Borate radical

Calcium fluoride test: A paste of the mixture and fluoride with few drops of concentrated sulphuric acid impart a greenish colour in Bunsen flame due to the formation of boron trifluoride.

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

$2Na_3BO_3 + 3H_2SO_4 \rightarrow 3Na_2SO_4 + 2H_3BO_3$

$2HF + H_3BO_3 \rightarrow BF_3 + 3H_2O$

e) Arsenate radical

Silver nitrate solution test: Acidify a portion of sodium carbonate extract with acetic acid and boil to expel all gases. On adding silver nitrate solution, a brick red precipitate of silver arsenate is produced.

$NaAsO_4 + 3AgNO_3 \rightarrow AgAsO_4\downarrow + 3NaNO_3$

f) Arsenite radical

Silver nitrate solution test: Acidify a portion of sodium carbonate extract with dilute nitric acid, boil to expel carbon dioxide gas completely.

$Na_3AsO_3 + 3AgNO_3 \rightarrow Ag_3AsO_3\downarrow + 3NANO_3$

SCHEDULE IX

2.9 IDENTIFICATION OF UNKNOWN SUBSTANCE

Identify the radicals in the following inorganic samples A, B and C.

NOTE: The following method should be used:

2.9.1 Preliminary Tests for Acid and Basic Radicals

a) Action of dilute and concentrated sulphuric acid
b) Flame test
c) Borax bead test (for coloured salts)

2.9.2 Confirmatory Test for Acid and Basic Radicals

2.9.3 Analysis of Mixtures of Substances

Identify the radicals in the each of the inorganic mixtures D and E.

NOTE: The following methods should be used:

2.9.4 Preliminary Tests for Acid and Basic Radicals

a) Action of dilute and conc H_2SO_4.
b) Flame test
c) Borax bead test (for coloured salt).
d) Test for ammonium salts.

2.9.5 Confirmatory Tests for Acid and Basic Radicals

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