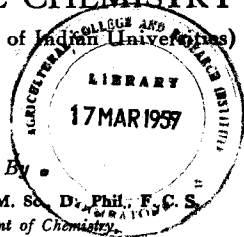


SENIOR  
PRACTICAL CHEMISTRY  
(For B. Sc. students of Indian Universities)



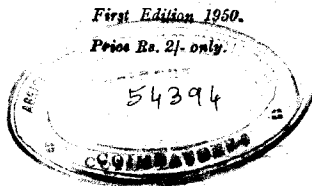
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## INTRODUCTION.

Practical chemistry is an important part in the curriculum of study for the B. Sc. student. During many years of teaching experience I have frequently found that students work in the practical class with fragmentary and not infrequently inadequate notes. The present book is an attempt to place in the hands of a B. Sc. student a reliable and accurate guide for practical work in chemistry. No attempt has been made to explain the theory underlying various processes. On the other hand, minute details are provided for manipulative skill. Frequently alternate methods have been provided to suit the conditions of every laboratory. Blank pages for notes have been attached at the end.

The unique feature of this book is that the student would find very complete and concrete instructions for work. The book contains answers to all the questions which students usually ask their guide in the practical class. It thus fulfils an important need of the student. It is written with the purpose that students would constantly use it in the practical class till they again mastery over the subject. It is hoped that if this book is intelligently used the student would find it to be a useful guide in later life.

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SAUGAR,

19TH MAY, 1950.

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SENIOR  
PRACTICAL CHEMISTRY  
FOR  
B. Sc. STUDENTS

PART I

QUALITATIVE INORGANIC ANALYSIS.

**Introductory** :—Qualitative analysis of a given mixture consists in identifying the basic and acidic radicals contained in it.

EXAMINATION OF BASIC RADICALS.

Basic radicals are identified by way of dry tests and tests carried out in solution. Dry tests are more useful in the case of single substances. In the case of mixtures they are better employed to individual basic radicals as they are separated in solution analysis. The more important of the dry tests are the flame, bead and charcoal tests.

## CHAPTER I

### DRY TESTS

**Flame Test** :—Clean the platinum wire by repeatedly dipping it in concentrated hydrochloric acid and heating in the Bunsen flame. When the wire becomes red hot without imparting colour to the flame it may be taken as clean. Substance is then moistened with pure concentrated hydrochloric acid and heated on the clean platinum wire in the non-luminous flame.

Flame colouration	Indication	Flame as seen through a blue (cobalt or didymium) glass.
Lavender violet	K	reddish violet.
Bluish white	Pb, As, Sb	
Blue (then green)	Cu	blue-green.
Green	Ba	
Golden yellow	Na	invisible.
Brick red	Ca	greenish-grey.
Crimson	Sr	purple.

In the case of substances such as barium sulphate the flame colouration is best obtained by first heating the substance in the reducing flame (i.e. approximately the lower half) then moistening with concentrated hydrochloric acid and performing the flame test.

In the presence of sodium the potassium flame is masked but is visible as reddish violet through a blue glass which cuts out the sodium flame. Presence of strontium and calcium also mask the potassium flame.

Traces of sodium are present in most compounds, and in testing for sodium the flame colouration should persist and should not be appreciably increased in intensity by mixing about 1% of sodium chloride with the original solid.

**Bead Test** :—Make a loop (1— $\frac{1}{2}$  m.m. diameter) at the end of a clean platinum wire and heat it to redness. Touch a small quantity of solid powdered borax with the red hot loop when some of it would adhere to the loop. Heat the wire again in the flame. The borax swells up and gives a

and heat. Notice the colour of the bead when heated in the oxidising (approximately upper half) and reducing (approximately lower half) flame. Also carefully observe the colour of the bead when hot and cold.

Coloured oxides impart characteristic colour to beads.

Oxides of:—	Colour imparted to bead in oxidising flame		Colour imparted to bead in reducing flame	
	Hot	Cold	Hot	Cold
Copper	green	bluish-green	colourless	brown to red (cloudy)
Iron	yellowish brown	yellow or colourless	bottle green	bottle green
Manganese	amethyst	reddish violet	colourless	colourless
Cobalt	blue	blue	blue	blue
Nickel	violet	reddish brown	grey (cloudy)	grey (cloudy)

*The colours of borax beads obtained with metallic sulphides and arsenides frequently differ from those given by other salts and the oxides, e.g., manganese sulphide gives a brown bead. In the case of sulphides and arsenides this difficulty is overcome by fusing with a fragment of sodium peroxide and then performing the bead test.*

**Charcoal tests** :—Substance is mixed with approximately twice the amount of sodium carbonate and heated in a clean cavity in a charcoal block in *reducing flame* of the blow pipe. Next it is moistened with a few drops of cobalt nitrate solution and heated in the *oxidising flame* of the blow pipe. Many substances impart colour to the fused mass thus obtained and the following are the more important amongst them.

Colour of the fused mass	Indication
Bright green	zinc
Dirty blue-green	tin
Pink	magnesium
Blue	aluminium or phosphate

## CHAPTER II

### SOLUTION ANALYSIS

The methods of solution analysis may be regarded as depending entirely on the chemistry of ions and not of the elements. The characteristic reactions of ions containing the elements are used for the identification of elements and the condition in which they are present. The methods of solution analysis depend upon the principle that the properties of a dilute solution of a salt are, in general, the sum of the properties of its ions.

**Preparation of the solution:**—For preparing the solution the following reagents may be tried in the order indicated below. A preliminary selection of the solvent should be made by taking about 0.1 gm. of the mixture and testing its solubility in 5 c.c. of the solvent before the solution of the mixture is actually prepared.

1. Water, cold and hot.
2. Dilute nitric acid, cold and hot — Treat a small amount (about 0.1 gm.) of the mixture with 5 c.c. of dilute nitric acid, warm and filter. In the filtrate add dilute hydrochloric acid. If no precipitate is obtained I-group is absent and in this case dilute nitric acid should never be used for solution. If a precipitate is obtained the presence of I-group is indicated and in this case dissolve about 1 gm. of the mixture in 20–25 c.c. of dilute nitric acid and proceed for group analysis.

3. Dilute hydrochloric acid cold and hot

4. Concentrated hydrochloric acid cold and warm.

(The solution should not be boiled for long as certain metallic chlorides are volatile with concentrated hydrochloric acid.)

5. Concentrated nitric acid cold and warm — Nitric acid should only be tried when the residue left undissolved in concentrated hydrochloric acid is coloured. If it has to be used the solution should be evaporated almost to dryness in a porcelain dish. This residue should be diluted with about 15 c.c. of water and some dilute hydrochloric acid added before proceeding for group analysis.



*It is usually advisable to try the first four solvents and if any part of the mixture remains undissolved then treat it as an insoluble substance. For the purposes of analysis an insoluble substance may be defined as that which is not soluble in single mineral acid. They are analysed separately.*

**Note:**—Only necessary minimum amounts of the acid should be used for preparing the solution. For about 1 gm. of the mixture 20—25 c.c. of dilute acid or 4—8 c.c. of concentrated acid is usually sufficient. Use of larger amounts of the acid causes a considerable increase in the bulk of the solution at a later stage in the analysis and causes a good deal of loss of time in concentrating the solution by evaporation.

All solutions in strong acids must be diluted with five to six times of their volume of water before proceeding to the group test. *If there is a white precipitate on dilution, soluble in concentrated hydrochloric acid, it indicates the presence of antimony or bismuth in the mixture.*

## CHAPTER III

### GROUP ANALYSIS

In carrying out the group analysis the presence of the group should always be tested first in a small amount of the solution of the mixture by adding the group reagent. Only if the presence of the group is indicated, the whole of the solution should be treated otherwise the presence of the next group should be tested for.

It should be noted that the colours of the precipitates formed are only indications of the nature of the radicals present as the presence of one metallic radical may cause the masking of the colour of the precipitate given by another metallic radical.

#### GROUP - I (Silver Group) Pb, Hg (ous), Ag

To the cold solution of the mixture add a few drops of dilute hydrochloric acid. If a white precipitate appears then add more hydrochloric acid to complete the precipitation. Filter and preserve the filtrate for group-II. Wash the precipitate twice with small amounts of cold water boil the precipitate with water and filter hot.

**Filtrate:—**Test for Pb

1. White crystals may separate on cooling.

2. To a portion of the solution add acetic acid and potassium chromate solution—**YELLOW PRECIPITATE.**

3. To another portion add potassium iodide solution—**YELLOW PRECIPITATE.**

**Residue:—**Wash 2 or 3 times with hot water to remove all lead chloride. Treat the residue with excess of ammonium hydroxide and filter quickly.

**Filtrate:—**  
Test for Ag.  
Acidify the solution with dilute nitric acid—**WHITE PRECIPITATE**

**Residue:—**If black, test for Hg(ous). Wash and dissolve in concentrated hydrochloric acid to which has been added a crystal of potassium chlorate. Evaporate the solution to 2 c. c. Filter if necessary. Add stannous chloride solution—**WHITE or GREY PRECIPITATE.** To a portion of the 2 c. c. solution add a clean copper turning—a grey deposit of metallic mercury on copper.

**Note** :—Owing to slight reducing action of mercurous chloride in presence of ammonia, a small amount of silver might not be detected in presence of a large amount of mercurous chloride, as it would remain insoluble as metallic silver. This may be prevented by oxidising the mixture of the two chlorides with bromine water when only the silver chloride remains undissolved. Mercury is detected in the filtrate by means of stannous chloride.

Warm the filtrate from group—I, pass a slow current of hydrogen sulphide gas, filter, dilute somewhat and again pass hydrogen sulphide gas till complete precipitation. Filter, if necessary, through the same filter paper and preserve the filtrate for group—III.

**Note** :—Care must be taken as to the acidity of the solution before passing hydrogen sulphide. If the solution is strongly acidic the precipitation of cadmium is prevented. On the other hand, the solution must contain a moderate amount of hydrochloric acid to prevent the formation of a colloidal suspension of arsenic sulphide and to keep bismuth and antimony in solution. Arsenic is most readily precipitated if the concentration of the acid is above 2N, whereas the concentration of the acid must be below N/2 to obtain complete precipitation of other members of this group notably cadmium, antimony and tin. To prevent metals of the later group being precipitated the concentration of the acid should be above N/8. To overcome this difficulty it is preferable to pass hydrogen sulphide gas in a comparatively stronger acid solution and filter. Dilute the filtrate with water and again pass hydrogen sulphide. Collect the precipitates together and analyse them for group—II.

*Only slight yellow precipitate of sulphur indicates the presence of an oxidising agent, e.g., ferric salt, and should not be confused with the precipitate of group—II.*

Wash the precipitate with a little water, then warm it with 5 to 10 c. c. of yellow ammonium sulphide. Filter, and preserve the filtrate for group-II-B. Examine the residue for group—II—A as follows.

#### GROUP-II-A (Pb, Hg<sub>2</sub>, Bi, Cd, Cu)

Wash the residue with water and then boil it with 5 to 10 c. c. of nitric acid (1:3) and filter.

**Residue:—** If black, test for Hg. Dissolve either in aqua regia or conc. HCl and a crystal of  $KClO_3$  and test for Hg as described in group-I

**Filtrate:—** Test for lead by adding to a small portion of the filtrate dilute sulphuric acid. If a white precipitate is obtained add dilute sulphuric acid to the whole of the filtrate and filter. If no white precipitate is formed then proceed to test as described under filtrate below.

**Residue:—** If white test for Pb  
Dissolve in acetic acid and test for Pb as described in group-I

**Filtrate:—** Add excess of ammonium hydroxide and filter. (If the solution becomes blue presence of Cu is indicated.)

**Residue:—** If white test for Bi  
Dissolve in HCl and dilute with a large volume of water—  
**WHITE PRECIPITATE**

**Filtrate:—** Test for Cu and Cd. If the filtrate is colourless Cu is absent. Test for Cd by passing  $H_2S$

**YELLOW PRECIPITATE**  
If the filtrate is blue test for Cu and Cd both. Acidify the blue solution with excess of conc. HCl and pass  $H_2S$ , Filter.

**Residue:—** If black Cu is present.

**Filtrate:—** Dilute with a large volume of water and pass  $H_2S$

again.  
**YELLOW PRECIPITATE** confirms the presence of Cd

**Alternate methods for the detection of cadmium in presence of copper:—**

1. To the blue filtrate containing copper and cadmium add excess of potassium cyanide solution (potassium cyanide is a deadly poison and no cuts and bruises should ever be exposed to the solution) and pass hydrogen sulphide gas. A yellow precipitate confirms the presence of cadmium.

2. Acidify the blue filtrate with dilute sulphuric acid and boil with clean iron nails or wire. Filter rapidly the precipitated copper, etc., dilute filtrate and pass hydrogen sulphide gas. Yellow precipitate—Cd.

## GROUP-II-B (As, Sb, Sn)

Acidify the filtrate for group II—B with dilute hydrochloric acid. A pure white precipitate indicates the absence of group-II-B. If a coloured precipitate is obtained then boil the acidified solution, allow the precipitate to settle, decant off as much liquid as possible, filter and wash the precipitate, rejecting the filtrate.

Boil the precipitate with 10 c.c. of concentrated hydrochloric acid and filter.

**Residue** :—If yellow—As, Confirm as follows :  
Boil the residue with about 4 c.c. of concentrated nitric acid. Dilute and filter if necessary. Add ammonium molybdate and boil.

—YELLOW PRECIPITATE

**Filtrate** :—Boil off hydrogen sulphide. Add 2 or 3 clean iron nails. Boil for 5 to 10 minutes and filter.

(Black scales indicate antimony)

**Residue** :—Black scales Sb Remove iron nails and collect black scales. Dissolve in concentrated hydrochloric acid containing a crystal of  $KClO_3$ . Dilute and pass  $H_2S$ . ORANGE.

**Filtrate** :—Add mercuric chloride solution. A WHITE or GREY PRECIPITATE —Sn

## PRECIPITATE

Alternately

Add ammonium hydroxide to the filtrate till the solution is just alkaline. Acidify the solution by adding 4 to 6 gms. of solid oxalic acid, boil, pass hydrogen sulphide and filter.

**Residue** :—IF ORANGE coloured  
Sb

**Filtrate** :—Add ammonium hydroxide till it becomes just alkaline. Acidify with acetic acid, boil, pass  $H_2S$

BROWNISH—YELLOW  
PRECIPITATE  
Sn

**Flame test for Sn** :—Take the precipitate containing tin in a porcelain dish. Add 3 c. c. of concentrated hydrochloric acid and a piece of pure zinc (free from tin). Agitate it with a test-tube half full of water and then put the test-tube in the flame—a blue flame mantle round the test-tube shows the presence of tin.

#### GROUP-III (Fe, Al, Cr)

Boil the filtrate from group -II to drive off all hydrogen sulphide (till a filter paper dipped in lead acetate solution and held in the vapours of the boiling solution does not turn black). Test for the presence of Fe(ous) ions by taking a portion of the solution and adding to it potassium ferricyanide solution when a blue precipitate indicates the presence of Fe(ous) ions. If iron is present oxidise the solution with 1 c.c. of concentrated nitric acid and boil for about five minutes. If iron is absent nitric acid need not be added. Test a portion of the solution for phosphate as follows.

**Test for phosphate** :—Add concentrated nitric acid to a portion of the solution, boil and add ammonium molybdate solution and boil. Formation of a **YELLOW PRECIPITATE** indicates the presence of Phosphate.

Before proceeding with the precipitation of elements of group—III the presence or absence of interfering acids should be noted. These interfering acids are phosphate, oxalate and fluoride. Phosphate is tested as above and oxalate and fluoride as described in the section dealing with acid radicals.

**When no interfering acid is present proceed as follows:—**

To the oxidised solution add about 10 c. c. of ammonium chloride solution and excess of ammonium hydroxide. Shake the solution well and filter. Reserve the filtrate for group -IV. Proceed with the precipitate as follows :—

Wash the precipitate into a boiling tube. Add caustic soda and boil till the smell of ammonia comes out no more. Add a further quantity of caustic soda and an excess of strong solution of hydrogen (or, solid sodium peroxide). boil for two to three minutes and filter.

<b>Residue</b> :—If brown test for Fe. Dissolve the precipitate in dilute hydrochloric acid and add potassium ferrocyanide solution <b>BLUE PRECIPITATE</b> <b>Fe</b>	<b>Filtrate</b> —Boil off excess of bromine and note the colour of the solution. <i>If the solution is yellow test for Cr and Al both. If the solution is colourless test for Al only.</i> Divide the solution in two parts.	
	To one part add excess of acetic acid and lead acetate solution. <b>--YELLOW PRECIPITATE</b> <b>Cr</b>	To the other part add nitric acid to acidify and then add excess of ammonium hydroxide <b>-WHITE GELATINOUS PRECIPITATE</b> <b>Al</b>

**Alternate test for Cr and Al** :—Take the filtrate after removing iron and boil off bromine. To the clear solution add solid ammonium sulphate and filter.

<b>Residue</b> :—If white gelatinous, it indicates the presence of Al. Confirm by charcoal test.	<b>Filtrate</b> :—Boil with excess of caustic soda until the solution is free from the smell of ammonia. Acidify with acetic acid and add silver nitrate solution <b>—RED PRECIPITATE</b> <b>Cr</b>
--	---

If interfering acids are present then the procedure has to be modified to eliminate them. Not more than one interfering acid is usually given to B.Sc. students. The procedures for eliminating these interfering acids are detailed below.

**Removal of phosphate** :—To the oxidised solution for group—III add sodium acetate and acetic acid and then add drop by drop ferric chloride solution (constantly stirring the solution with a glass rod) till it acquires a light red colour (the colour of prepared tea), boil for five minutes and filter. To the filtrate add excess of ammonium hydroxide, boil and filter. Add the two precipitates and test for chromium and aluminium in it according to the procedure described for the precipitate of the group—III. (Iron is tested in the original oxidised solution) Reserve the filtrate for group—IV.

**Removal of oxalate** :—Take the precipitate of the group—III and ignite it dry for fifteen minutes on a piece of porcelain. Dissolve the ignited mass in dilute hydrochloric acid rejecting the small insoluble portion if any. Add ammonium chloride and excess of ammonium hydroxide and filter. Test the precipitate for radicals of group—III and add the filtrate thus obtained to the filtrate reserved for group—IV.

#### ALTERNATELY

Digest for three to five minutes the precipitate for group—III with boiling concentrated nitric acid containing a crystal of potassium chlorate. To the clear solution add ammonium chloride and excess of ammonium hydroxide and filter. Test the precipitate for radicals of group—III and add the filtrate thus obtained to the filtrate reserved for group—IV.

**Removal of fluoride** :—Digest repeatedly the precipitate of group—III with concentrated hydrochloric acid in a porcelain dish. (Take about 2 c. c. of concentrated hydrochloric acid with the precipitate and evaporate almost to dryness. Repeat the process three or four times.) Extract with dilute hydrochloric acid and neglect small amount of insoluble if any. To the clear solution add ammonium chloride and excess of ammonium hydroxide and filter. Test the precipitate for radicals of group—III and add the filtrate thus obtained to the filtrate reserved for group—IV.

#### GROUP—IV

Test a small portion of the filtrate by passing hydrogen sulphide gas. In case a precipitate is obtained warm the remainder of the filtrate and pass a current of hydrogen sulphide, filter and preserve the filtrate for group—V. Proceed with the precipitate as follows :—

Wash the precipitate with water and digest it with cold dilute hydrochloric acid and filter.



**Residue 1-** Pierce the filter paper and dissolve the precipitate in concentrated hydrochloric acid to which has been added crystal of potassium chlorate. Evaporate almost to dryness. Dissolve the residue in 5 c.c. of water, and proceed as follows :-

To the solution add solid bicarbonate in sufficient excess. Add bromine water, *cool and shake for some time*. Note the colour. Boil the solution and note change in colour. Draw conclusions as follows :-

- (1) Apple green colour in cold unaffected on boiling - COBALT  
 (2) No green colour in cold but blackening on boiling - NICKEL  
 (3) Green colour in cold and blackening on boiling - NICKEL and COBALT both present.

**Filtrate 1-** Boil to remove hydrogen sulphide gas, add an equal volume of caustic soda solution, boil and filter.

**Residue 1-** Test for Mn. Fuse the residue with sodium carbonate and potassium chlorate or potassium nitrate on a porcelain piece. A green mass would be obtained which when dissolved in water gives a pink coloured solution.

With a portion of the residue perform bead test -

A reddish-violet bead would be obtained.

**Filtrate 1-** Test for Zn. Pass hydrogen sulphide gas -  
**WHITE PRECIPITATE**  
 Perform charcoal test with cobalt nitrate solution.  
**GREEN MASS**

#### Alternate schemes for testing nickel and cobalt :

To the solution obtained in water (see under residue above) add an equal volume of ammonium chloride solution, add several drops of ammonium hydroxide and divide the solution into two parts.

To one portion add 1 c.c. of a sodium salt of  $\alpha$ -benziloxime or, an alcoholic solution of  $\alpha$ -dimethylglyoxime - a **PINK PRECIPITATE** confirms the presence of **NICKEL**.

To the other portion add 1 c.c. of a solution of the sodium salt of  $\alpha$ -nitroso- $\beta$ -naphthol - **ORANGE COLOURATION** or **PRECIPITATE** confirms the presence of **COBALT**.

Or

To the water solution (see above) add excess of potassium cyanide solution.

Add sodium hydroxid in excess and the bromine water, boil and filter.

**Residue 1-** If black  
**NICKEL**

**Filtrate 1-** Evaporate to dryness and perform bead test with the residue - **BLUE BEAD** confirms **COBALT**

## GROUP—V (Ba, Sr, Ca)

If the filtrate from group—IV is brown due to the presence of nickel, acidify with acetic acid, warm and filter.

Boil off hydrogen sulphide from the filtrate and concentrate it to about 20 to 30 c. c., filter if necessary. To the clear solution add an excess of ammonium hydroxide and then ammonium carbonate solution. Warm to about 60-70° C, (not more), filter and preserve the filtrate for group—VI.

Dissolve the precipitate as obtained above in acetic acid. To a portion of the solution add potassium chromate solution. If a yellow precipitate is obtained complete the precipitation of the remainder of the solution by adding excess of potassium chromate and filter. If no yellow precipitate is obtained proceed as described under filtrate below.

**Residue :—If YELLOW-BARIUM**  
Perform flame test with the precipitate—a persistent green flame.

**Filtrate :—**Add ammonium sulphate solution in excess, heat and scratch the sides of the test tube and allow to stand for several minutes and filter.

**Residue :—**  
**If WHITE**  
**STRONTIUM**  
Perform flame test with the precipitate—a persistent red flame.

**Filtrate :—**Add ammonium oxalate solution. If white precipitate is obtained the presence of CALCIUM is indicated.

Perform flame test with the precipitate—a non-persistent red flame.

(GROUP)—VI, Mg, Na, K, NH<sub>4</sub>

Treat the filtrate with an excess of ammonium chloride, ammonium sulphate and ammonium oxalate, boil for several minutes and filter.

To the clear filtrate add sodium phosphate, shake and scratch the insides of the test-tube by a glass rod. Formation of a white crystalline precipitate indicates the presence of **MAGNESIUM**.

With the above precipitate perform charcoal test with cobalt nitrate solution—a **PINK MASS** would be obtained.

**Sodium, Potassium, Ammonium**—These should be identified in the original mixture as they are often present as

shall invariably be found in the filtrate obtained after the precipitation of magnesium.

1. **Ammonium** :—Heat a portion of the original mixture with sodium hydroxide solution—evolution of ammonia confirms the presence of AMMONIUM in the mixture.

2. **Sodium** :—Perform flame test with the original mixture—a yellow flame invisible through blue glass confirms the presence of SODIUM.

3. **Potassium** :—Perform flame test with the original mixture—a lavender violet flame appearing reddish violet through a blue glass confirms the presence of POTASSIUM.

Since the flame of potassium is often masked it may be tested as follows in the mixture.

Boil the mixture with a solution of sodium carbonate (free from potassium) until free from ammonia, filter, add a slight excess of acetic acid to the filtrate and then add a *recently prepared* one percent solution of sodium cobaltinitrate. Formation of a **YELLOW PRECIPITATE** indicates potassium.

*Or*

After preparing the sodium carbonate extract as given above add excess of sodium acetate and then tartaric acid. Formation of a white crystalline precipitate indicates the presence of potassium. (The precipitate is best obtained by shaking in presence of alcohol.)

## CHAPTER IV

### EXAMINATION OF ACID RADICALS

Carefully observe the action of cold and warm dilute sulphuric acid, and hot concentrated sulphuric acid on the mixture. Also prepare a sodium carbonate extract of the mixture and test in it as indicated in the table.

**Preparation of sodium carbonate extract:**—Boil about 0.5 gms. of the mixture with 2 to 3 gms. of solid sodium carbonate add 10 to 15 c.c. of distilled water for about 10 minutes and filter. The filtrate is the sodium carbonate extract.

**Note:**—Commercial sodium carbonate frequently contains as impurities chlorides and sulphates, hence in testing for these radicals it is desirable that a blank test should be carried out with sodium carbonate and should be compared with the test obtained by the use of sodium carbonate extract.

Reagent	Observation	Indication	Confirmation
1. Dilute sulphuric acid.	Effervescence and evolution of a gas.	Carbonate	Pass the gas evolved in freshly prepared lime water— it would turn milky.
2. "	Evolution of sulphur-dioxide gas.	Sulphite	Expose a piece of filter paper moistened with potassium dichromate solution :— it would turn green.
3. "	Evolution of hydrogen Sulphide gas.	Sulphide	Expose a piece of a filter paper moistened with lead acetate solution :— it would turn black.
4. "	Evolution of brown fumes with pungent smell.	Nitrite	Expose a piece of filter paper moistened with potassium iodide, starch and a few drops of dilute sulphuric acid :— it would turn blue. Note :— A delicate test is to add 2 c.c. of an acetic acid solution of sulphamic acid and $\alpha$ -naphthylamine*, when within 5 to 10 minutes a mere trace of nitrite, will produce a red solution

\* The reagent is prepared as follows :—0.5 gm. sulphamic acid is dissolved in 150 c.c. of dilute acetic acid ; 0.2 gm. of  $\alpha$ -naphthylamine is extracted with 20 c.c. of water, the colourless solution decanted and mixed with 100 c.c. of dilute acetic acid. The two solutions are mixed and kept in dark.

Reagent	Observation	Indication	Confirmation
5. "	Evolution of SO <sub>2</sub> and white deposit of S.	Thio-sulphate	
6. Concentrated sulphuric acid.	Evolution of yellow gas with crackling sound.	Chlorate	
7. "	Evolution of white fumes having smell of vinegar.†	Acetate	Extract the substance with boiling water filter, cool and add ferric chloride solution :- it would turn blood red.
8. "	Evolution of brown fumes (enhanced by addition of copper (turnings) soluble in water.	Nitrate	Ring test :- To the solution of the mixture add ferrous sulphate solution, cool, add concentrated sulphuric acid drop by drop from the sides - a black ring would be formed. (The test is not applicable in presence of nitrite, bromide or iodide.) Note :- A sensitive test is to add dilute acetic acid solution of 'Nitron' ‡ which gives a quantitative white crystalline precipitate even with very dilute solution of a nitrate.
9. "	Evolution of gas which burns with a blue flame.	Oxalate	Acidify a portion of the sodium carbonate extract with excess of acetic acid and add calcium chloride solution - a white precipitate which decolorises dilute potassium permanganate solution in presence of dilute sulphuric acid would be obtained.

† Also often given by dilute sulphuric acid.

‡ Nitron is 1 : 4-Diphenyl-3, 5-oxadiazole-4, 5-dihydro-1: 2,4-triazole.

Reagent	Observation	Indication	Confirmation
10. "	Evolution of white fumes with pungent odour.	Chloride	Acidify a portion of the sodium carbonate extract with excess of nitric acid and add silver nitrate solution :- a white precipitate soluble in excess of ammonium hydroxide solution would be obtained.
11. "	Evolution of brown fumes soluble in water giving brown colour.	Bromide	Acidify sodium carbonate extract with nitric acid and add silver nitrate solution :- a yellow precipitate which is insoluble in ammonium hydroxide would be obtained.
12. "	Evolution of violet fumes with smell of iodine.	Iodide	Expose a piece of filter paper dipped in starch solution to the fumes :- it would turn blue.  Acidify a portion of the sodium carbonate extract with nitric acid and add silver nitrate :- a yellow precipitate insoluble in ammonium hydroxide would be obtained.

**Fluoride** :—Heat a portion of the mixture with concentrated sulphuric acid and a little sand in a dry test-tube and expose a moist glass rod to the white fumes evolved :- a white deposit on the rod would indicate the presence of fluoride.

Acidify a portion of the sodium carbonate extract with excess of acetic acid and add calcium chloride solution :- a white precipitate which does not decolorise dilute potassium permanganate solution acidified with sulphuric acid confirms the presence of fluoride. (*cf.* oxalate)

**Borate** :—Take in a porcelain dish a pinch of the mixture, moisten with concentrated sulphuric acid, add about 1 c.c. of ethyl alcohol, stir the whole with a glass

rod and apply flame:—alcohol vapours burn with a green flame indicating the presence of borate.

In case copper is present in the mixture it is advisable to evaporate a portion of the filtrate obtained after group—II and apply this test to the residue thus obtained.)

**Phosphate** :— Phosphate should always be tested in the filtrate obtained after group—II in the analysis of basic radicals. If however, arsenic is absent it can be tested as follows in the mixture.

Take a pinch of the mixture and boil it with 3 c.c. of concentrated nitric acid, filter if necessary, and then add ammonium molybdate solution and boil:— a yellow precipitate or a deep yellow colour indicates the presence of phosphate.

**Sulphate** :— Take a portion of the sodium carbonate extract and acidify it with excess of hydrochloric acid and then add barium chloride solution:— a white precipitate insoluble in nitric acid indicates the presence of sulphate. (Carry out a blank test with sodium carbonate and compare.)

Sometimes the presence of a particular acid radical interferes with the test carried out for another acid radical. Also, there are certain combinations of acid radicals which present some difficulty in their identification. Such cases can be tested as follows.

**Chloride, bromide and iodide** :— Acidify a portion of the sodium carbonate extract with excess of dilute sulphuric acid, warm and then add little by little solid sodium nitrite:— violet vapours of iodine pass out indicating the presence of IODIDE. Continue adding sodium nitrite till no more violet vapours come out, boil for 2 to 3 minutes, add solid sodium carbonate to render the solution alkaline, filter if necessary. To the clear solution add concentrated nitric acid:— the solution turns brown and brown fumes come out indicating the presence of BROMIDE. Continue adding concentrated nitric acid till all the bromine is expelled and the solution becomes colourless on cooling. Then add silver nitrate solution

a white precipitate soluble in excess of ammonium hydroxide indicates the presence of CHLORIDE.

**Sulphide, sulphite, sulphate (and thiosulphate)** :—If suitable reagents are available these present no difficulty. Take sodium carbonate extract and proceed to test as follows :—

- (i) To a portion add solid lead carbonate and shake :— formation of a black precipitate indicates SULPHIDE.
- (ii) To a portion add benzidine hydrochloride and hydrochloric acid :— a white precipitate would be formed indicating SULPHATE.
- (iii) To a portion add sodium nitroprusside :— a pink colouration which becomes red on addition of zinc sulphate indicates the presence of SULPHITE.
- (iv) To a portion add dilute hydrochloric acid in excess :— a white precipitate of sulphur indicates the presence of THIOSULPHATE.

or

In the absence of organic reagents proceed as follows  
Take the sodium carbonate extract add solid lead carbonate, shake well and filter.

Residue :— If black <b>SULPHIDE</b>	Filtrate :— Add barium chloride in excess and filter
	Filtrate :— Acidify with dilute hydrochloric acid a white precipitate indicates the presence of THIOSULPHATE.
	Residue :— Take in dilute hydrochloric acid and filter after shaking.
	Residue :— If white <b>SULPHATE</b>
	Filtrate :— Add bromine water and shake a white precipitate <b>SULPHITE</b>

**Nitrate in presence of nitrite** :— To a portion of the sodium carbonate extract add solid ammonium chloride or urea and dilute sulphuric acid, and boil. Continue boiling till no test for nitrite is obtained i. e. a piece of filter paper moistened



with potassium iodide, starch and a few drops of dilute sulphuric acid when exposed to the vapours does not turn blue. Add more dilute sulphuric acid and a piece of zinc metal. Brown fumes would be slowly produced. Expose a piece of filter paper moistened with potassium iodide, starch and a few drops of dilute sulphuric acid to these fumes :— it turns blue indicating the presence of NITRATE.

**Nitrate in presence of bromide** :—Acidify the sodium carbonate extract with excess of dilute sulphuric acid. Add a piece of zinc metal and boil. Brown fumes would be evolved slowly. Expose a piece of filter paper moistened with potassium iodide, starch and a few drops of sulphuric acid (*dilute*) to these fumes :—it turns blue indicating the presence of NITRATE.

**Nitrate in presence of iodide** :—Acidify a portion of the sodium carbonate extract with *dilute* sulphuric acid, add a piece of zinc metal and boil. Expose a piece of filter paper dipped only in starch solution to the fumes evolved :—it turns blue indicating the presence of NITRATE.

**Oxalate in presence of carbonate** :—Acidify a portion of the sodium carbonate extract with excess of acetic acid and to the clear solution thus obtained add calcium chloride solution :—a white precipitate which decolourises dilute potassium permanganate solution in presence of dilute sulphuric acid would indicate the presence of OXALATE.

## CHAPTER V

### ANALYSIS OF INSOLUBLE SUBSTANCES

Insoluble substances may be either white or coloured. The following is the list of insoluble substances which are usually included in the B.Sc. course.

**I. WHITE substances** :—Silver chloride ( $\text{AgCl}$ ), lead sulphate ( $\text{PbSO}_4$ ), barium sulphate ( $\text{BaSO}_4$ ), strontium sulphate ( $\text{SrSO}_4$ ), calcium fluoride ( $\text{CaF}_2$ ), tin oxide ( $\text{SnO}_2$ ), antimony oxide ( $\text{Sb}_2\text{O}_3$ ), aluminium oxide ( $\text{Al}_2\text{O}_3$ )

**II. YELLOW** :—Silver bromide ( $\text{AgBr}$ ), silver iodide ( $\text{AgI}$ ).  
**III. GREEN or VIOLET substances** :—Chromium oxide ( $\text{Cr}_2\text{O}_3$ ), chromium chloride ( $\text{CrCl}_3$ ), chromium sulphate  $\text{Cr}_2(\text{SO}_4)_3$ .

**IV. BLACK substances** —Mercury sulphide ( $\text{HgS}$ ).

Not more than one insoluble substance is usually given to the B.Sc. class. The acid radical in these substances is generally tested by preparing a sodium carbonate extract and testing the acid radical in the extract. Substances amenable to such treatment are lead sulphate, barium sulphate, strontium sulphate, silver chloride, silver bromide and silver iodide. Basic radicals in these substances may be tested as follows :—

Substance	Detection of Basic Radical
$\text{PbSO}_4$	Digest a portion of the insoluble residue in concentrated solution of ammonium acetate and acetic acid, filter and to the filtrate add potassium chromate solution :—a yellow precipitate indicates LEAD.
$\text{BaSO}_4, \text{SrSO}_4$	Perform flame test (see under flame test). GREEN flame :—BARIUM CRIMSON flame :—STRONTIUM.
$\text{AgCl}$	Dissolve a portion of the residue in ammonium

Substance	Detection of Basic Radical
AgBr, AgI	<p>hydroxide and to the clear solution add dilute nitric acid :—a white precipitate indicates the presence of SILVER (the precipitate gradually changes to violet on exposure to light),</p> <p>Treat a portion of the residue with dilute sulphuric acid and a piece of zinc metal and boil. Brisk evolution of hydrogen takes place and silver halides are reduced to metallic silver. Filter, wash the residue with water, and dissolve it in concentrated nitric acid. To the clear solution add dilute hydrochloric acid :—a white precipitate soluble in ammonium hydroxide indicates the presence of SILVER.</p>

**Chromium oxide** ( $\text{Cr}_2\text{O}_3$ ), **Chromium chloride** ( $\text{CrCl}_3$ ), **Chromium sulphate**  $\text{Cr}_2(\text{SO}_4)_3$ . In testing these fuse a portion of the insoluble residue with equal weights of potassium carbonate and potassium nitrate (or, *potassium chlorate*) on a porcelain piece. Extract the fused mass with water, divide into two parts and test as follows :—

1. To one part add acetic acid and lead acetate :—a yellow precipitate indicates the presence of CHROMIUM.
2. In the other part test for acid radical such as chloride or sulphate.

**Tin oxide** ( $\text{SnO}_2$ ), **Antimony oxide** ( $\text{Sb}_2\text{O}_3$ ) :—In testing them fuse a portion of the insoluble residue with an equal weight of sodium carbonate and twice its weight of powdered sulphur on a porcelain piece. Add powdered sulphur from time to time. Take the fused mass in water and add dilute hydrochloric acid :—

Orange precipitate indicates the presence of ANTIMONY.

Grayish yellow precipitate indicates the presence of TIN.

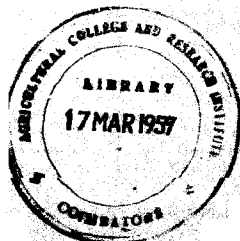
**Calcium fluoride** ( $\text{CaF}_2$ ) :—Test for fluoride as usual with concentrated sulphuric acid and acid. For the basic radical evaporate a portion of the residue with concentrated sulphuric acid. Repeat the process 3 or 4 times. Perform same

test with the residue thus obtained :—a non-persistent brick red flame indicates the presence of CALCIUM.

**Aluminium oxide ( $Al_2O_3$ )** :—Heat a portion of the residue with solid sodium carbonate in a charcoal cavity, cool and moisten the fused mass with a couple of drops of cobalt nitrate solution. Heat again :—a blue fused mass indicates the presence of ALUMINIUM.

**Mercury sulphide ( $HgS$ )** :—For the acid radical treat a portion of the residue with zinc metal and dilute sulphuric acid :—hydrogen sulphide gas would be evolved which would turn a lead acetate paper held in the vapours black indicating the presence of SULPHIDE.

For testing the basic radical digest a portion of the residue in aqua regia (3 parts concentrated hydrochloric acid + 1 part concentrated nitric acid), dilute the solution with water and add stannous chloride solution :—white or grey precipitate indicates the presence of MERCURY.



## CHAPTER VI

### APPENDIX TO QUALITATIVE INORGANIC ANALYSIS

While carrying out qualitative inorganic analysis the testing of the following radicals requires special attention. Presence of these radicals often causes confusion in the mind of the worker during the course of analysis.

1. **Testing of Pb** :—Sometimes the mixture which is soluble in hot dilute hydrochloric acid may throw down the precipitate of lead chloride on cooling. In this case the white precipitate should immediately be tested for lead.

The mixture may contain some sulphate and when it is brought in solution some lead sulphate may be thrown out as insoluble substance. But there may not be sufficient amount of sulphate present to precipitate all the lead in the mixture. Under these conditions the worker is likely to find lead in the insoluble portion, in the precipitate of the group-I and may be in the precipitate of the group-II as well. This should not cause confusion.

2. **Mercury (ic)** :—After the precipitate of the group-II has been divided into A and B groups by the help of yellow ammonium sulphide test for mercury is made in the portion which is not dissolved by yellow ammonium sulphide. This should be washed with water thoroughly. In the absence of thorough washing if the precipitate is treated with dilute nitric acid sulphur would be liberated from the adhering yellow ammonium sulphide and some particles of the precipitate would adhere to the sulphur particles tenaciously. The result would be that a portion of precipitate that would appear to remain insoluble in dilute nitric acid. This residue which if it is black is often confused with the precipitate of mercuric sulphide. Remember that the density of mercury salts is pretty high and if the residue contains mercuric sulphide as a rule it would not float on the surface of dilute nitric acid. In such cases a full confirmatory test must be carried out before declaring the presence of mercury in the mixture.

3. **Testing Cd in presence of Cu by iron nails** :—In this test the solution containing cadmium and copper should

not be boiled for a long time with iron nails. If the boiling is continued for a long time some iron is likely to dissolve which would give a black precipitate of iron sulphide on passing hydrogen sulphide.

**4. Dissolving mixture in dilute nitric acid when tin is present:**—The tin which is present originally in the form of a soluble salt may on boiling with diluted nitric acid be converted into insoluble tin oxide ( $\text{SnO}_2$ ) and a white insoluble residue may be obtained.

**5. Dissolving mixture in dilute nitric acid when sulphite is present:**—In this case sulphite is likely to be converted into a sulphate and consequently if the mixture contains lead, barium or strontium they may be partly thrown out as insoluble sulphates. Under these circumstances the presence of these radicals is likely to be encountered both in the insoluble portion and in the regular analysis for basic radicals.

**6. Removal of phosphate when iron is present in the mixture:**—In this case while the removal of the phosphate is being carried out by the addition of sodium acetate and acetic acid a red colour may be obtained. Under these circumstances it is obviously unnecessary to add any ferric chloride solution. However, if need be only slight amounts of ferric chloride solution be added to obtain the necessary colour.

**7. Removal of oxalate in presence of aluminium:**—If the oxalate is removed by igniting the precipitate of the group-III the heating should not be carried too long as there is likelihood of aluminium hydroxide being converted into insoluble aluminium oxide ( $\text{Al}_2\text{O}_3$ ).

**8. Testing of chromium:**—If chromium is present in the mixture a greenish or bluish precipitate is usually obtained in the group-III. The method for testing chromium is based on oxidising the chromium ion to chromate ion. This oxidation is not accomplished if the bromine water used is very dilute. In any case if oxidation is to be carried out by bromine water the addition of the bromine water followed by boiling should at least be repeated thrice. If, however, sodium peroxide is used for oxidation there is no such

9. **Precipitation of manganese in group-III** :—Manganese hydroxide may sometimes be precipitated along with the hydroxides of iron, aluminium and chromium. As usual boil the precipitate with caustic soda and bromine water. Manganese would remain in the residue along with iron. They may be tested as follows :—

**BOIL THIS RESIDUE WITH DILUTE NITRIC ACID AND  
FILTER**

**Residue** :—Test for manganese.

- (i) Perform borax bead test—a brown or amethyst bead confirms MANGANESE.
- (ii) Fuse with sodium carbonate and potassium nitrate—a green mass would be obtained which would give pink colour when dilute sulphuric acid is added indicating the presence of MANGANESE.

**Filtrate** :— Test for iron.

Add potassium ferrocyanide solution— a prussian blue precipitate would be obtained confirming the presence of IRON.

PART--II  
QUANTITATIVE INORGANIC ANALYSIS.  
CHAPTER VII  
INTRODUCTION

Quantitative estimations may be carried out either volumetrically or gravimetrically. Below are given some useful hints on quantitative estimations.

1. All apparatus to be used must be scrupulously clean. Glass apparatus soon becomes dirty for no apparent reason must be frequently cleaned. Usually clean it with alkali clay or quick lime using a brush if necessary. Wash thoroughly with water. If this fails, fill the apparatus with sulphuric—chromic acid mixture and leave over night. Wash thoroughly with water. Graduated apparatus for quantitative work e. g. burette, pipette, measuring flask, etc., should never be heated as on cooling they do not return to the original volume and may take months or years to do so. When not in use it is a good practice to keep your graduated flasks stoppered, ends of a burette covered with a test-tube and jets protected by a piece of India rubber tubing. Remember that water will not run evenly down dirty glass ware, but will form drops.

2. Never place a substance directly on the scale pan of a balance, but put it in a weighing tube or other suitable vessels. Clean pieces of metal may, however be weighed directly. Do not leave weights on the scale-pan after a weighing has been done and weights recorded. Always close the balance case as soon as weighing is completed. It is bad practice to jot down weighings and quantities on loose sheet of paper. All rough notes even should be recorded on the practical note-book.

3. Carry out the quantitative processes calmly and patiently. Undue haste often ruins an otherwise nicely carried out experiment.

4. Do not forget that cleanliness is the essential prerequisite for carrying out accurate quantitative analysis.



## CHAPTER VIII

### VOLUMETRIC ANALYSIS

All apparatus to be used must be thoroughly clean.

It is highly desirable to calibrate all the measuring apparatus such as the burette, pipette and the graduated flask. The method of calibration is given in the appendix to this section.

Pipettes generally in use in the B. Sc. class are those which are required to deliver a known volume of the liquid. It is recommended that a standard technique be adopted for draining the pipette. One good way is to hold the tip against the side of a receiving vessel while the bulk of the liquid is being delivered, and to continue holding it still for a further *fifteen seconds* to allow it to drain after the rapid flow has ceased. It is a bad practice to blow through or warm the pipette to remove the last drop.

**Normal Solutions** :— The term normal (N) is used to indicate a solution of which one litre contains the gram equivalent weight of the dissolved substance. Semi-normal (N/2), deci-normal (N/10), centi-normal (N/100) etc., solutions contain 1/2, 1/10, 1/100, etc., of the gram equivalent per litre.

Substance	Formula	Eq. wt.	Remarks
Hydrochloric acid	HCl	36.46	Concentrated hydrochloric acid has a density of 1.2 and contains 39.1% acid which corresponds to 11 N.
Sulphuric acid	H <sub>2</sub> SO <sub>4</sub>	49.04	Concentrated sulphuric acid has a density of 1.84 and contains 95.6% acid which corresponds to 37 N.
Oxalic acid	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> 2H <sub>2</sub> O	63.04	
Sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>	53.00	For a standard work it is prepared by washing thoroughly with ice cold water a pure sample of sodium bicarbonate and then heating it to 180-200°C. until constant in weight. It is heated in the air oven each time before use.

Substance	Formula	Eq. Wt.	Remarks
Sodium bi-carbonate	$\text{NaHCO}_3$	84.00	
Sodium hydroxide	$\text{NaOH}$	40.00	
Barium hydroxide	$\text{Ba}(\text{OH})_2$ $8\text{H}_2\text{O}$	157.55	The clear solution must be kept protected from atmospheric carbon dioxide.
Potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	49.03	
Ferrous-ammonium sulphate	$\text{FeSO}_4$ $(\text{NH}_4)_2\text{SO}_4$ $6\text{H}_2\text{O}$	392.13	Add about a 100 c.c. of dilute sulphuric acid to a litre of the solution to keep it clear.
Potassium permanganate	$\text{KMnO}_4$	31.61	52.68 in alkaline solution.
Iodine	I	126.92	It is preferable to weigh iodine in a small glass stoppered bottle. Add about $1\frac{1}{2}$ times the weight of iodine potassium iodide and dissolve in a few c.c. of water. When dissolved dilute with water up to the required volume.
Sodium-thio-sul-phate	$\text{Na}_2\text{S}_2\text{O}_3$ $5\text{H}_2\text{O}$	248.19	
Potassium chloride	$\text{KCl}$	74.55	
Sodium chloride	$\text{NaCl}$	58.45	
Silver nitrate	$\text{AgNO}_3$	169.81	
	$\text{KCN}$	65.17	

Substance	Formula	Eq. wt.	Remarks
Copper Sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.71	
Arsenious oxide	$\text{As}_2\text{O}_3$	49.45	To make a standard N/10 solution in 100 c.c. weigh accurately 0.4945 gm. of pure arsenious oxide, dissolve in a few c.c. of water containing about 0.4 gm. caustic soda. Add a drop of phenolphthalein and titrate with dilute sulphuric acid until the indicator is just colourless. Transfer the whole to the flask. Add 10 c.c. of a saturated solution of sodium bicarbonate, and make up to 100 c.c. by adding distilled water.

**Indicators** :— Only a few drops of the indicators should be used. It is recommended that at first a trial titration be carried out which indicates approximately the end point. In the next titration add the indicator a little before the end point and find the end-point accurately. This process is specially advocated in iodometry. In the case of acidimetry and alkalimetry the following indicators should be used.

Titration.	Indicator.	Remarks.
1. Strong alkali-weak acid	Phenolphthalein	<i>e. g.</i> caustic soda-acetic acid
2. Strong acid-weak alkali	Methyl orange	<i>e. g.</i> sulphuric acid-sodium carbonate
3. Strong acid-strong alkali	any	<i>e. g.</i> caustic soda-hydrochloric acid

The following table gives suitable indicators for different types of titrations.

Titration	Indicator	Remarks
1. Oxalic acid—potassium permanganate	Colour of the solution	At the neutral point the colour of the solution would be discharged.
2. Ferrous ammonium sulphate-potassium permanganate	„	
3. Ferrous ammonium sulphate-potassium dichromate	A freshly prepared solution of potassium ferriocyanide (used externally)	Place on a piece of glazed porcelain (e.g. inverted dish) a drop of the indicator. Dip the tip of the glass rod in the solution and touch the drop of indicator with it. When no more blue colour appears, the whole of ferrous salt has been converted into ferric. The starch solution must be added only a little before the end point.
4. Iodometry	A freshly prepared starch solution.	
5. Silver nitrate sodium or potassium chloride	No more formation of precipitate.	
6. Silver nitrate-potassium thiocyanate	Ferric salt	The indicator is prepared by boiling a saturated solution of ferric ammonium sulphate (alum) with a small quantity of concentrated nitric acid until all nitrous fumes have been expelled.

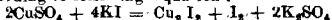
**Note on iodometry:**—The iodine solution is usually standardised against arsenious oxide solution. With the help of standardised iodine solution the strength of a sodium thiosulphate (hypo) solution can be determined. Various estimations of liberated iodine are carried out with standardised sodium thiosulphate solution e.g.,

(a) Potassium dichromate in presence of dilute sulphuric acid liberates iodine from potassium iodide according to the following equation:—



The amount of iodine liberated from potassium iodide is proportional to the amount of potassium dichromate present. The liberated iodine can be titrated against hypo. Taking advantage of this, hypo solution can also be standardised by taking a standard potassium dichromate solution. For carrying out such estimation 10 c. c. of a 10% potassium iodide solution should be added to 10 c. c. of about N/20 potassium dichromate solution containing a little dilute sulphuric acid. The liberated iodine should then be titrated with hypo solution.

(b) Copper sulphate liberates iodine from potassium iodide according to following equation :—



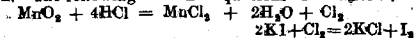
The amount of iodine liberated from potassium iodide is proportional to the amount of copper sulphate present. The liberated iodine can be titrated against hypo as described in (a) above.

Chlorine can liberate iodine from potassium iodide solution according to the equation



liberated iodine can be titrated against hypo using starch as indicator (use above).

Based on the above principle is the method of estimating manganese dioxide in a sample of pyrolucite. A known weight of pyrolucite is treated with concentrated hydrochloric acid and boiled. The liberated chlorine is then passed into an excess of potassium iodide solution. Iodine is liberated which can be titrated against a standard hypo solution. The following are the equations of reactions :—



Thus 86.9 gms. of manganese dioxide would give rise to 253.8 gms. of iodine.

**Calculations in volumetric analysis** :— All calculations in volumetric analysis depend on the principle that equinormal solutions contain equivalent amounts of different substances. This can be expressed in the form of a formula

strength ( $S_1$ )  $\times$  volume ( $V_1$ ) of one solution = strength ( $S_2$ )  $\times$  volume ( $V_2$ ) of the other solution

$$\text{i. e. } S_1 \times V_1 = S_2 \times V_2$$

When the strengths are being expressed in terms of normality.

Suppose  $S_1, V_1$  refer to the known and  $S_2, V_2$  refer to the unknown solution at the neutral point then, the strength of the unknown solution ( $S_2$ ) will be as follows:—

$$S_2 = S_1 \times \frac{V_1}{V_2}$$

This will give the strength of the solution in terms of normality, say  $N/x$ , which to express in terms of grams per litre would be equivalent weight grams per litre.

If calculation for the weight of an element is to be made use of chemical factors is recommended as it simplifies the process (see calculation under gravimetric analysis).

## CHAPTER IX

### APPENDIX TO VOLUMETRIC ANALYSIS

The volumetric apparatus (burette, pipette, graduated flask, measuring cylinder) is meant to measure the volume of liquid contained in it. The National Physical Laboratory has recommended that litre and the millilitre (ml.) and not the cubic centimeter (C. C.), be used as units of volume, and most volumetric glass ware is now marked in these units. This followed the discovery of a slight error in the weight of the standard kilograms, originally defined as the weight of a cubic decimeter of water at 4°C. In 1901 the litre was defined as the volume occupied by a mass of one kilogram of pure water at its maximum density point and under standard atmospheric pressure. As a result of extensive experiments it has been shown that

$$1 \text{ Litre} = 1000.28 \text{ c. c.}$$

For practical purposes this small difference is negligible, but it cannot be ignored in experiments of high accuracy.

**Calibration of apparatus:**—By this term is meant the measurement of the error, if any, in the graduation of volumetric apparatus. For ordinary volumetric work relative calibration is sufficient. By relative calibration is meant that the pipette, burette and the graduated flask deliver the volume marked on them as measured by these instruments. For this purpose a pipette may be regarded a standard. To calibrate the burette with respect to the pipette proceed as follows.

Take some water in the burette and take the reading. Fill the pipette with water up to the mark. Deliver the liquid from the pipette into the burette and take the reading. Record as

Volume delivered from the pipette	= 10 c. c.
First reading of burette	= 20.0 c. c.
Second reading of burette	= 10.1 c. c.

This shows that 10 c. c. of the pipette correspond to 9.9 c. c. of the burette. This fact is taken into account when the burette readings are used for calculations.

This graduated flask is calibrated with respect to the already calibrated burette. The flask is completely dried and filled with water from the burette. The capacity upto the mark is noted. It may be found that a 100 c. c. flask might be containing 101 c. c. of the liquid as measured by the calibrated burette.

When, however, the volumetric apparatus is to be used for the purpose of preparing solutions of definite concentration or for other purposes where the different measures are used independently, independent calibration must be carried out to check their graduation. The method of calibration generally adopted is to fill the instrument to the mark with distilled water at a known temperature and find the weight of this water. Measuring flasks are weighed empty, then filled with water and weighed again. The pipette is calibrated by running the water into a weighing bottle, emptying the pipette in the manner which is to be adhered to afterwards, and then weighing the water. In the case of the burette, the water is run out into the weighing bottle 5 c.c. or 10 c.c. at a time, and each quantity carefully weighed. The error at each 5 or 10 c.c. can then be calculated, and it may be assumed to vary proportionally at the intermediate points. A curve may be drawn to obtain the errors at these points. Below is given the density and volume of water at different temperatures :—

Water  
(DENSITY AND VOLUME AT DIFFERENT  
TEMPERATURES)

Temperature in °C.	Wt. of 1 c.c. water in gm.	Volume of 1 gm. water in c.c.
10	0.999739	1.000291
11	0.999650	1.000350
12	0.999544	1.000456
13	0.999420	1.000570



Temperature in °C.	Wt. of 1 c.c. water in gm.	Volume of 1 gm. water in c.c.
14	0.999297	1.000703
15	0.999154	1.000847
16	0.999004	1.000997
17	0.998839	1.001162
18	0.998663	1.001339
19	0.998475	1.001527
20	0.998272	1.001731
21	0.998065	1.001939
22	0.997849	1.002156
23	0.997623	1.002383
24	0.997386	1.002621
25	0.997140	1.002868
30	0.99577	1.00425
35	0.99417	1.00586

## CHAPTER X

### GRAVIMETRIC ANALYSIS

**Introduction** :—All apparatus to be used should be perfectly clean. In weighing the crucible a standard technique should be adopted. It is preferable to cool down very hot crucibles (loaded or unloaded) in the air to a temperature of about 100°C. before transferring to the desiccator. This is advocated as very hot crucibles cool comparatively slowly when enclosed in a glass vessel. The crucible kept in the desiccator should not require more than 26 minutes for reaching the room temperature. Every time before use the crucible should be heated for a short time, cooled in the desiccator and weighed.

Care should be taken in properly fitting the filter paper in the funnel. Filter papers which are in common use are 9 or 11 cms. in diameter. For such filter paper choose a funnel which is symmetrical and has a stem of 8 to 10 cms. length with an internal diameter of about 0.5 cms., the cross-section of the end of the stem ground to an angle of 45°. Fold the filter paper firmly across the centre and then double the paper again, but this time making the fold with only slight pressure. Open the paper at the larger division and fit it to the dry funnel. Now fill up the paper with hot distilled water, close stem with a finger and raise the paper slightly. See that the stem and the lower part of the funnel are completely full of water, and fit the paper to the glass as tightly as possible. Remove the finger from the stem and allow the water to flow away, meanwhile pressing especially near the folds to the glass. No air should leak between the paper and the glass to collect in a bubble at the top of the stem. It is important to choose the filter paper rather smaller than the funnel; a centimeter of the glass should be exposed round the top edge as it is then easier to wash the precipitate efficiently. Remember that time spent on correctly folding and fitting the filter paper is never wasted.

The precipitation should always be carried out slowly

With constant stirring. The precipitate should be washed first by decantation. Allow the precipitate to settle, decant off most of the supernatant liquid through the filter paper. Add a fresh quantity of washing liquid, stir or boil, allow the precipitate to subside and decant off the clear washing liquid through the same filter paper. Repeat the process. Next transfer the precipitate to the filter paper. If the precipitate is reluctant to leave the beaker, the latter may be inclined over the funnel at an angle of  $45^\circ$ . A glass rod should be so held over the mouth of the beaker that any liquid runs along it into the funnel. A fast jet of washing liquid is then directed not at but above the precipitate. The greater part of a heavy precipitate can be transferred by this method. Sometimes the precipitate sticks to the glass of the beaker. In such cases it is often best to dissolve the precipitate in the least possible quantity of some suitable solvent and to reprecipitate it using only a corner of the beaker. If this plan is not feasible a police man (a glass rod tipped with a  $\frac{1}{4}$  inch piece of India rubber) can be used for rubbing out the precipitate from the sides of the beaker.

When all the precipitate has been transferred to the filter paper it should be washed. At each washing care should be taken not to fill the filter more than  $\frac{2}{3}$ rd at a time. At each washing the liquid in the filter paper should be allowed to drain out almost completely before further washing liquid is added.

After the precipitate has been washed it is dried over a chimney, the top of the funnel being covered by a piece of clean paper containing a few holes. When the precipitate is thoroughly dry separate as much of the precipitate as possible from the filter paper and keep it in a clock glass on a glazed sheet of paper, and cover it with an inverted funnel. Fold the filter paper and hold that end which does not contain the precipitate by a clean pair of tongs. Hold it over a weighed crucible placed on a glazed sheet of paper and burn it by a flame from a Bunsen burner held horizontally, allowing the ash to fall directly into the crucible. Collect the fallen ash from the glazed paper by a dry camel's hair brush or a dry clean feather, into the crucible. Heat the ash, and treat it with appropriate chemicals if necessary.

The average weight of the ash of the filter paper is always given on the packet.

When all the carbon in the ash has been burnt out, cool the crucible and carefully add the precipitate. Heat the precipitate till a constant weight is obtained. The crucible should always be gradually heated in a non-luminous flame. It frequently happens that some black specs of carbon either inside or outside the crucible remain and are often difficult to remove. In such cases cool the crucible and carefully moisten the spot with saturated solution of ammonium nitrate. Heat gently till no more fumes are evolved. Gradually raise the temperature. If these specs persist, repeat the process. Not more than one attempt is usually necessary.

Always heat the pair of tongs before touching a hot crucible with it.

### SOME SIMPLE ESTIMATIONS

Estimation of :--	As	Precipitant	Remarks
Iron in a solution of ferrous ammonium sulphate.	$\text{Fe}_2\text{O}_3$	Ammonium hydroxide	Oxidise the solution by adding 1 c.c. of concentrated nitric acid and boiling before precipitating with ammonium hydroxide. The precipitate is washed with hot water till free from sulphate ion.
Copper in a solution of copper sulphate.	$\text{CuO}$	Fairly strong solution of caustic soda.	Wash precipitate with hot water till free from sulphate ion. Treat ash* with nitric acid.
Silver in a solution of silver nitrate.	$\text{AgCl}$	Solution of hydrochloric acid	Either the whole operation should be carried out in cold or the precipitation may be carried out in hot solution but the whole must be thoroughly cool when washing or transferring precipitate to

Estimation of:—	As	Precipitant	Remarks
			<p>the filter paper as silver chloride is appreciably soluble in hot water. Wash the precipitate with cold water acidulated with dilute nitric acid till free from chloride ion. The crucible containing the precipitate of silver chloride be preferably heated by hot air (i.e. flame kept not in direct contact with the crucible but a little below it) till a small portion of the precipitate just melts. Cool and weigh as usual.</p> <p>The precipitate becomes light violet in colour when exposed to light, but the change is such as usually does not effect the result.</p>
Chloride in a solution of chloride.	AgCl	Solution of Silver nitrate	See estimation of silver as silver chloride.
Barium in a solution of barium chloride.	BaSO <sub>4</sub>	Dilute sulphuric acid.	Add about 5 c.c. of dilute hydrochloric acid before precipitation. Wash precipitate with hot water till free from chloride ion. Treat ash* with two drops of dilute hydrochloric acid and a drop of dilute sulphuric acid.
Sulphate in a solution of sulphate.	BaSO <sub>4</sub>	Solution of barium chloride.	Wash precipitate with hot water till free from barium and chloride ions. Treat ash* as in estimation of barium.
Lead in a solution of lead nitrate.	PbSO <sub>4</sub>	Dilute sulphuric acid.	Add alcohol to complete the precipitation. Wash the precipitate with water and then with alcohol till free from sulphate ion.

Estimation of —	As	Precipitant	Remarks
Zinc in a solution of zinc chloride or zinc sulphate.	ZnO	Solution of sodium carbonate.	To the hot solution add hot sodium carbonate solution till a permanent precipitate is obtained. Add a drop of phenolphthalein, and add a further quantity of sodium carbonate solution till just a faint colouration (pink) is obtained as in titration. Boil and allow the precipitate to settle. Filter and wash the precipitate with hot water till free from chloride or sulphate according as the original solution was a chloride or sulphate.  Soak the dried filter paper with a strong solution of ammonium nitrate before ignition.
Aluminium in a solution of alum.	Al <sub>2</sub> O <sub>3</sub>	Ammonium hydroxide	Add 20 c.c. of a 10 % solution of ammonium chloride to the solution and boil. Add ammonium hydroxide till it is just in excess. Wash the precipitate with hot water preferably containing a little ammonium nitrate, till it is free from sulphate ion.
Calcium in a solution of calcium chloride.	CaO	Ammonium oxalate	Warm the solution, add a slight excess of ammonium hydroxide and then add slowly ammonium oxalate. Wash the precipitate with hot water till free from chloride ion. Ignite strongly in a blow pipe flame and weigh quickly as CaO is hygroscopic.

Estimation of—	As	Precipitant	Remarks
Chromium in a solution of potassium dichromate.	$\text{Cr}_2\text{O}_3$	Ammonium hydroxide	Acidify with 5 c. c. of dilute sulphuric acid and add 2 c. c. of alcohol. Dilute with about 50 c. c. of water and boil till free from aldehyde vapours. Add ammonium hydroxide in slight excess. Wash the precipitate with hot water till free from sulphate.
Magnesium in a solution of magnesium sulphate.	$\text{Mg}_2\text{P}_2\text{O}_7$	Microcosmic salt	Add about 10 c. c. of ammonium chloride to the hot solution and then ammonium hydroxide till the solution is clear. Add solution of microcosmic salt. Allow the precipitate to stand overnight. Wash the precipitate with water containing a little ammonium hydroxide till free from chloride ion.

**Treatment of ash**—The crucible should be cooled down to room temperature ash treated and the crucible is again slowly heated till no more fumes comes out. It can then be heated strongly.

Microcosmic salt is Sodium-ammonium-hydrogen phosphate



## CALCULATIONS

Suppose the weight of the precipitate of silver chloride is 0.2324 gm. and the weight of silver is required. Multiply this weight for the factor for silver that is 0.7526 (of table) and you get the weight of silver, namely,  $0.2324 \times 0.7526 = 0.1749$  gm. In the following Table are given some factors together with their logarithms.

Radical sought A	Weighed as or equivalent to B	Factor (wt. of A represented by 1 gm. of B. C	Log. C
Ag	AgCl	0.7526	1.8766
	AgNO <sub>3</sub>	0.6350	1.8028
Al	Al <sub>2</sub> O <sub>3</sub>	0.5291	1.7236
As	As <sub>2</sub> O <sub>3</sub>	0.7574	1.8793
Ba	BaSO <sub>4</sub>	0.5885	1.7697
	BaCl <sub>2</sub> ·2H <sub>2</sub> O	0.5623	1.7499
oxalate	CaO	1.5695	0.1958
	KMnO <sub>4</sub>	1.392	0.1436
Ca	CaO	0.7147	1.8541
Cl	AgCl	0.2474	1.3934
Cr <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.5167	1.7132
Cu	CuO	0.7989	1.9025
	CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.2546	1.4056
Fe	Fe <sub>2</sub> O <sub>3</sub>	0.6994	1.8447
	FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	0.1424	1.1535



Radical sought A	Weighed as or equivalent to B	Factor (wt. of A represented by 1 gm. of B.) C	Log. C
Mg	$Mg_2P_2O_7$	0.2184	13.393
$Na_2CO_3$	HCl	1.453	0.1624
	$H_2SO_4$	1.081	0.0337
NaOH	HCl	1.097	0.0402
	$H_2SO_4$	0.8158	1.9916
$Na_2S_2O_3$	1	1.246	0.0951
$PO_4$	$Mg_2P_2O_7$	0.8534	1.9312
Pb	$PbSO_4$	0.7380	1.8669
$SO_4$	$BaSO_4$	0.4115	1.6144
Zn	ZnO	0.8034	1.9049
CuO	Cu	1.252	0.0975
$Fe_2O_3$	Fe	1.430	0.1563
HCl	$Na_2CO_3$	0.6880	1.8376
	NaOH	0.9115	1.9598
$H_2SO_4$	$NaCO_3$	0.9252	1.9683
	NaOH	1.226	0.0885
I	$Na_2S_2O_3$	0.8027	1.9046
$KMnO_4$	$H_2C_2O_4 \cdot 2H_2O$	0.5014	1.7002

CHAPTER XI  
APPENDIX TO QUANTITATIVE INORGANIC  
ANALYSIS

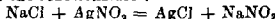
NUMERICAL QUESTIONS

1. How would you prepare and standardise a N/10 solution of silver nitrate? 0.22 gm. of a mixture of NaCl

and KCl were titrated with  $\frac{0.992}{10}$  N solution of AgNO<sub>3</sub>,

and required 33 c.c. for complete reaction. What are the percentages of NaCl and KCl in the mixture? (I.C.S., 1932) (Ans. NaCl 39.36 %; KCl 60.4 %)

*Hint*—For the first part see standardised solutions. For the second part let  $x$  represent the quantity of sodium chloride, then KCl would be  $0.22 - x$  gm. The equations of the reactions are:—



From these equations calculate the amount of AgNO<sub>3</sub> required to neutralise  $x$  gms. of NaCl and  $(0.22 - x)$  gm. of KCl. Equate this silver nitrate present in 33 c.c. of 0.0992 N solution. Evaluate  $x$ . Find the percentage.

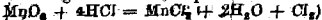
2. 0.2 gm. of a sample of pyrolucite, when warmed with excess of hydrochloric acid, and the evolved chlorine passed into excess of potassium iodide solution, required for the liberated iodine 30 c.c. of N/10 thiosulphate solution. What is the percentage of pure manganese dioxide.

(Agr. University, B.Sc. 1932)

(Ans. 30.10 %)

*Hint*:—First calculate the amount of iodine neutralised by thiosulphate solution. This gives the amount of iodine liberated from KI. From the equation given below calculate the amount of chlorine evolved.

$2\text{KI} + \text{Cl}_2 = 2\text{KCl} + \text{I}_2$ ; then calculate the amount of manganese dioxide present from the equation:—



3. One gram of pyrolucite is treated with excess of concentrated hydrochloric acid and the chlorine evolved is passed through KI solution in bulbs. This solution

together with the liberated iodine is diluted to 250 c.c. and on titration with N/50 thiosulphate solution 25 c.c. of the former are found equivalent to 31 c.c. of the latter. Calculate the percentage of manganese dioxide in the mineral.

(Allahabad University, B.Sc., 1935) (Ans 26.94 %)

*Hint* :— The amount of N/50 thiosulphate solution required by 250 c.c. of diluted solution would be 310 c.c. From this calculate the amount of liberated iodine. For the rest proceed as indicated in question no. 2.

4. Indicate the uses of sodium thiosulphate in analytical chemistry. 0.2915 gm. of manganese ore was heated with hydrochloric acid and the chlorine evolved was passed into a solution of potassium iodide. The liberated iodine required 20.5 c.c. of 0.1 N sodium thiosulphate solution. Calculate the percentage of manganese dioxide in the ore.

(Agra University, B.Sc., 1935) (Ans 15.3 %)

*Hint* :— Same as in question no. 2.

5. Calculate in grams per litre the amount of ferrous and ferric iron present in a solution containing both from the following data :

25 c.c. of the iron solution, required for titration 24 c.c. of standard  $\text{KMnO}_4$  solution. 100 c.c. of the same solution were reduced completely by zinc and sulphuric acid, and the reduced solution was diluted to 250 c.c. 50 c.c. of this dilute solution required 36.75 c.c. of the same  $\text{KMnO}_4$  solution.

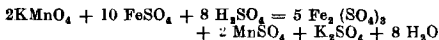
The solution of  $\text{KMnO}_4$  was titrated against N/10 oxalic acid and it was found that 25 c.c. of N/10 oxalic acid were equivalent to 37.5 c.c. of  $\text{KMnO}_4$ .

(B.H.U., B.Sc., 1936)

(Ans. Ferrous 3.57 gm. and

Ferric 3.266 gm.)

*Hint* :— First find the strength of the permanganate solution from the titration data with oxalic acid. The estimation of ferrous salt with permanganate is based on the fact that permanganate oxidises ferrous iron to ferric state. The equation is :—

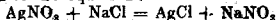


From this equation we find the equivalence of permanganate and ferrous iron. It is given that 25 c.c. of the iron solution required 24 c.c. of permanganate solution i.e. 1 litre would require 960 c.c. of permanganate solution. Calculate the amount of ferrous iron equivalent to 960 c.c. of permanganate solution. This would give the amount of ferrous iron in the mixture. Next in the same way calculate the amount of ferrous iron present in 1 litre of solution after reduction. The increase in the amount of ferrous iron is due to the reduction of ferric iron. From the data of the reduced solution find the total iron content of the solution, subtract the amount of ferrous iron, the rest would give the ferric iron content of the mixture.

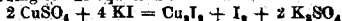
6. How is decinormal solution of "hypo" prepared ?  
100 c.c. of a solution of NaCl and copper sulphate gave 1.434 gm. of AgCl in a quantitative experiment. Another 100 c.c. of the same solution on addition of excess of KI consumed 100 c.c. of N/10 hypo. Find the amounts of NaCl and crystallised copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in grams per litre.  
(Allahabad University, B.Sc., 1937)

(Ans. NaCl 58.45 gm.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  - 24.97 gm.)

Hint:— For the first part see normal solutions. 1 litre of the solution would give 14.34 gm. of silver chloride according to the equation:—



Calculate the amount of NaCl which would give 14.34 gm. of AgCl. Copper sulphate liberates iodine from KI according to the equation:—



Calculate the amount of copper sulphate.

7. 0.261 gm. of a sample of pyrolucite was heated with an excess of HCl, and the chlorine evolved was passed into a solution of KI. The liberated iodine required 90 c.c. of N/30 hypo. Calculate percentage of pure  $\text{MnO}_2$  in the

(Agra University, B.Sc., 1942)

(Ans. 50 %)

*Hint* :— Same as in question no. 2.

8. How many grams of iodine will be liberated from a strong solution of KI when 100 c.c. of copper sulphate solution containing 24.96 gm. of the crystallised salt ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) per litre are added to it. Give full equations of reactions

(Agra University, B.Sc. 1944)

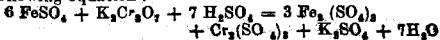
(Ans. 1.2692 gm.)

*Hint* :— For equation see question no. 6.

9. 1.137 gm. of pure iron was dissolved in an acid and raised to 250 c.c. 25 c.c. of this ferrous solution, when titrated with a dichromate solution ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) required 21.1 c.c. of the dichromate solution. Find out the strength of the dichromate solution in grams per litre.

(Agra University, B.Sc., 1945)

Ans. 4.73 gms.)

*Hint* :— The oxidation reaction is represented by the following equation :—

## PART III—ORGANIC

### CHAPTER XII

#### QUALITATIVE ORGANIC ANALYSIS

Qualitative organic analysis consists of detection of organic compounds. For this purpose the compounds usually prescribed for the B. Sc. course may be classified as follows—

- I. **Calcium chloride group** —oxalic, tartaric and citric acids and their salts.
- II. **Ferric chloride group** —formic acid, acetic acid, carbonic acid, resorcinol, salicylic acid, pyrogallol, benzoic acid and succinic acid and their salts.
- III. **Fehling solution group** —formaldehyde, acetaldehyde, chloral hydrate, chloroform, resorcinol, glucose and pyrogallol.
- IV. **Caustic soda group** —acetamide, ammonium salts of acids, aniline salts, chloral hydrate, resorcinol, glucose, acetaldehyde, pyrogallol, benzamide, acetanilide.
- V. **Iodoform group** —Ethyl alcohol and acetone
- VI. **Miscellaneous group** —Phthalic acid, methyl alcohol, urea, glycerine, aniline, nitrobenzene, iodoform, ether, benzene, cane sugar, starch, naphthalene and benzaldehyde.

This classification is quite arbitrary. Some substances would be found to occur in more than one group. Further, the group—VI is a heterogeneous group.

These substances may be given in the pure form, water solution or in alcoholic solution. Usually substances are given

in solution. Below is given a list of substances which are usually given either in water solution or in alcoholic solution :—

**Substances usually given in water solution :—**oxalic acid, succinic acid, succinates, tartaric acid, tartrates, citric acid, citrates, formic acid, formates, acetic acid, acetates, sodium benzoate, sodium salicylate, sodium phthalate, formaldehyde, acetone, methyl alcohol, ethyl alcohol, glycerine, pyrogallol, resorcinol, glucose, cane sugar, chloral hydrate, acetamide, starch, urea, aniline salt.

**Substances usually given in alcoholic solution—**benzoic acid, phthalic acid, salicylic acid, benzamide, acetanilide, naphthalene, iodoform, aniline, nitrobenzene, carbolic acid, benzaldehyde, chloroform, benzene, ether.

**N. B.** When substances are given in alcoholic solution the student would be asked to neglect alcohol.

If the substances are given in solutions the student should prepare a residue as follows. Take five c. c. of the solution in a beaker, cover and place it over a beaker half full of water. Boil the water in the beaker by placing it over the flame on a wire gauze. The solvent would evaporate and usually a residue would be obtained. Acetic acid, formic acid, acetone, formaldehyde, acetaldehyde, methyl alcohol, ethyl alcohol, chloroform, ether and benzene do not leave any residue. Liquid and solid residues would be given by the following:

**Liquid residues :—** glycerine, nitrobenzene, aniline, carbolic acid, benzaldehyde (often leaves a solid residue because of oxidation to benzoic acid; during evaporation).

**Solid residues :—** oxalic acid, oxalates, succinic acid, succinates, tartaric acid, tartrates, citric acid, citrates, sodium benzoate, benzoic acid, sodium salicylate, salicylic acid, sodium phthalate, phthalic acid, sodium formate, sodium acetate, pyrogallol, resorcinol, glucose, cane sugar, acetamide, chloral hydrate,

starch, urea, aniline salt, benzamide, acetanilide, naphthalene, iodoform.

Of these residues the most characteristic are the following familiar to students.

1. **White glistening plates** :— benzoic acid, salicylic acid, salicylates.
2. **Transparent sticky** :— cane sugar, tartaric acid (web like), citric acid (with stars at places), starch.
3. **White translucent** :— The residue is easily scratched by nails and is soapy in touch— urea, (sodium salt containing free alkali)
4. **Reddish or brownish coloured** :— resorcinol, pyrogallol, aniline salts, impure glucose (raw sugar, gur).
5. **Syrupy liquid** :— glycerine.
6. **White solid with blisters** :— acetanilide.

**Note** :— Certain substances which are volatile with steam may not leave any residue. These are — naphthalene, aniline, iodoform, nitrobenzene, acetamide, carbolic acid, chloral hydrate and benzaldehyde. It may also be pointed out that acetaldehyde and formaldehyde may polymerise and may leave slight residue.

Some of the organic substances prescribed in the B. Sc. course possess characteristic smell. The students should be familiar with the smell of the following substances particularly of those which are printed in italics :—

Acetic acid, formic acid, carbolic acid, acetaldehyde, benzaldehyde, formaldehyde, methyl alcohol, ethyl alcohol, chloroform, acetone, *benzene, naphthalene, ether, iodoform, nitrobenzene.*

#### Identification of Compounds in Various Groups



neutral solution as follows. Take 5 c. c. of the solution in beaker and drop a little piece of litmus paper in it. Add sodium carbonate solution to it in small amounts till it becomes slightly alkaline. (Litmus paper turns blue) No add a few drops of dilute hydrochloric acid till the solution becomes just acidic. (Litmus paper turns red). Finally add slight excess of ammonium hydroxide to this solution (Litmus paper turns blue). Boil the solution to drive off ammonia completely. This is the neutral solution.

From 5 c. c. of the solution start preparing the residue.

Take a portion of the neutral solution and add to calcium chloride solution. Observe the change if any. Shake the solution vigorously and scratch the insides of the test tube with a glass rod. Notice any change. Next boil the solution and continue scratching the insides of the test tube with a glass rod.

Observation	Indication and confirmation
Immediate white precipitate.	<p><b>Oxalic acid (oxalate)</b>. Confirm as follows:-</p> <p>(1) The precipitate is insoluble in acetic acid but soluble in hydrochloric acid.</p> <p>(2) Add to the precipitate dilute potassium permanganate solution and a few drops of dilute sulphuric acid, shake. The permanganate solution will be decolorized. (Warm a little if necessary)</p>
White precipitate on shaking and scratching	<p><b>Tartaric acid (tartrate)</b>. Confirm as follows:-</p> <p>(1) The precipitate is soluble in acetic acid. (cf. Oxalic acid)</p> <p>(2) To a portion of the neutral solution add ammoniacal silver nitrate solution (2 c. c. of silver nitrate + one drop of ammonium hydroxide) Heat. Redden take place (black deposit).</p> <p>(3) Take a portion of the residue add twice amount of resorcinol and a few drops of concentrated sulphuric acid and warm. A red colour would be developed. (cf. citric acid)</p>
White precipitate on boiling and scratching	<p><b>Citric acid (citrate)</b>. Confirm as follows:-</p> <p>(1) To a portion of the neutral solution add ammoniacal silver nitrate solution. A white precipitate will be obtained. The precipitate is soluble in ammonium</p>

Observation	Indication and confirmation
	hydroxide. No reduction takes place. ( <i>cf.</i> tartaric acid) (2) The residue formed is transparent and sticky with stars at places.

**Note** — Sometimes succinic acid or succinates give a white precipitate on boiling with calcium chloride solution. Presence of succinic acid or succinates can be confirmed as follows:—

(1) To a portion of the neutral solution add ferric chloride solution. A buff or brown coloured precipitate would be obtained.

(2) **Fluorescein test** — Take a portion of the dry residue, add twice the amount of resorcin and a couple of drops of concentrated sulphuric acid in a dry test tube. Heat it carefully till the whole becomes orange red. Pour the contents of the test tube in a beaker containing 100 c. c. of water to which has been added about 15 to 20 c. c. of caustic soda solution. The liquid in the beaker shows yellow-green fluorescence.

**II. Ferric chloride group** :— To a portion of the neutral solution add a dilute solution of neutral ferric chloride in cold. The ferric chloride solution supplied on the shelf may be diluted slightly and should be made almost neutral by the addition of a trace of ammonium hydroxide solution. This dilute neutral ferric chloride solution should then be added to the neutral solution of the compound. Note the change if any.

Observation	Indication and confirmation
Red colour developed	Formic acid (formates), Acetic acid (acetates). These may be confirmed as follows :— Formic acid (formates) :— (1) The red colour is discharged by the addition of dilute hydrochloric acid.

Observation	Indication and confirmation
Violet or blue colour is developed	<p>To a portion of the neutral solution add ammoniacal silver nitrate solution and heat. A white precipitate would be obtained which would turn black on heating.</p> <p>(3) Note the characteristic smell.</p> <p>Acetic acid (acetates) :- (1) To a portion of the neutral solution add ammoniacal silver nitrate solution. A white precipitate would be obtained which would dissolve on heating. (<i>cf.</i> formic acid)</p> <p>(2) Note the characteristic vinegar smell. (If acetate is given add dilute sulphuric acid and heat when the characteristic smell would be obtained).</p> <p>Carbolic acid, resorcinol, salicylic acid (salicylates)]. These may be confirmed as follows:</p> <p>Carbolic acid :- (1) The colour is discharged on the addition of acetic acid.</p> <p>Liebermann's nitroso reaction - Dissolve a little sodium nitrite in a few c. c. of concentrated sulphuric acid by gently warming and add a small quantity of the given solution. A brown colouration, rapidly changing to blue, would be produced. Pour the liquid into water; the colour would become red, would again change to blue on addition of alkali.</p> <p>(3) Note the characteristic odour.</p> <p>Resorcinol :- (1) Heat the given solution with caustic soda solution. A characteristic greenish-yellow colour would be produced.</p> <p>(2) Heat the residue with phthalic acid and 3 drops of concentrated sulphuric acid till a reddish colour is obtained. Pour the contents into a beaker containing water and caustic soda solution. A characteristic greenish-yellow fluorescent colour would be obtained.</p> <p>(3) It does not reduce ammoniacal silver nitrate solution. (<i>cf.</i> pyrogallol)</p> <p>Salicylic acid (salicylates) :- (1) Violet colour is not discharged on addition of acetic acid.</p> <p>(2) Heat a portion of the solid residue with methyl alcohol and concentrated sulphuric acid. A sweet characteristic smell of oil of winter green would be obtained.</p> <p>(3) Heat a portion of the residue with concentra-</p>

Observation	Indication and confirmation
Dark colour	<p>ted nitric acid. A yellow colour is obtained which is intensified on addition of alkali.</p> <p><b>Pyrogallol</b> :- (1) To a portion of the solution add ammoniacal silver nitrate solution and heat. The solution would be reduced giving a black deposit.</p> <p>(2) To a portion of the solution add ferrous sulphate solution. A blue or violet colour would be obtained</p> <p>(3) The fresh solution is colourless but becomes brown on exposure to air.</p>
Buff or brown precipitate	<p><b>Benzoate (benzoic acid), succinate (succinic acid)</b> . They may be tested as follows:</p> <p><b>Benzoate (benzoic acid)</b> :- (1) The buff coloured precipitate is soluble in dilute hydrochloric acid and ammonium hydroxide.</p> <p>(2) To a portion of the neutral solution add a few drops of dilute sulphuric acid, shake and cool. A white precipitate of benzoic acid would be obtained.</p> <p>(3) The neutral solution gives no precipitate with calcium chloride solution nor the residue gives fluorescein test. (cf. succinic acid)</p> <p><b>Succinate (succinic acid)</b> :- See note under calcium chloride group.</p>

**III. Fehling solution group** :- Fehling solution is obtained by adding a solution of sodium-potassium tartrate in caustic soda solution (Solution no. 2) to copper sulphate solution (Solution no.1) till the blue precipitate first formed dissolves giving an intense blue colour. To about three c. c. of the given solution add about 2 c. c. of the Fehling solution and boil. The formation of green, yellow, orange or red coloured precipitate indicates that the solution is reduced by the substance. Substances which reduce Fehling solution are formaldehyde, acetaldehyde, chloral hydrate, chloroform, resorcinol, glucose and pyrogallol. The presence of these may be confirmed as follows :-

Substance	Confirmatory tests
Formaldehyde	<p>(1) Add Schiff's reagent to the cold solution. A pink colour would be obtained.</p> <p>(2) To a portion of the solution add ammoniacal silver nitrate solution and heat. The solution is reduced and a black precipitate would be obtained.</p> <p>(3) Note the characteristic odour. The colour or the smell of the substance is not changed on heating with caustic soda. (cf. acetaldehyde)</p>
Acetaldehyde	<p>(1) Add Schiff's reagent to the cold solution. A pink colour would be obtained.</p> <p>(2) To a portion of the solution add ammoniacal silver nitrate solution and heat. The solution is reduced and a black precipitate would be obtained.</p> <p>Note the characteristic smell. Heat a portion of the solution with caustic soda. A buggy odour would be obtained and the colour of the solution would become yellow. (cf. formaldehyde)</p>
Chloral hydrate	<p>(1) Heat a portion of the solution with caustic soda solution. An emulsion would be formed and the characteristic sweet smell of chloroform would be obtained.</p> <p>(2) To a portion of the solution add resorcinol and caustic soda solution and warm. A red colour would be produced.</p> <p>(3) To a portion of the solution add ammoniacal silver nitrate solution and heat. The solution is reduced and a black precipitate would be obtained.</p>
Chloroform	<p>(1) Note the sweet pleasant characteristic odour</p> <p>(2) To a portion of the substance add resorcinol and caustic soda solution and warm. A red colour would be obtained.</p> <p>(3) To a portion add ammoniacal silver nitrate solution and heat. The solution would be reduced.</p> <p>(4) To a portion of the solution add a drop of aniline and caustic soda solution. Warm if necessary. A characteristic bad odour of phenyl isocyanate would be produced. (The odour is poisonous and the whole should be thrown into the sink immediately)</p>
Resorcinol	See under Ferric chloride group.
Glucose	(1) Heat the solution with caustic soda. A yellow

Substance	Confirmatory tests
	<p>colour would be obtained. To this add a few drops of Fehling solution. Reduction would take place.</p> <p>(2) To a portion of the solid residue add concentrated sulphuric acid. A yellow-brown colour would be obtained but no charring would take place. (<i>cf.</i> cane sugar)</p> <p>(3) To a portion of the solution add ammoniacal silver nitrate solution and warm. A shining deposit of silver would be produced.</p>
Pyrogallol	See under Ferric chloride group.

**IV. Caustic soda group** :—Heat a portion of the water solution or solid residue with strong caustic soda solution. Note any change in smell or colour.

Observation	Inference
1. Smell of ammonia	Ammonium salts of acids and acetamide, benzamide
2. Smell of chloroform	Chloral hydrate
3. Yellow colour	Glucose
4. Yellow colour with buggy smell	Acetaldehyde
5. Yellowish green colour	Resorcinol
6. Brown colour	Pyrogallol
7. Oily drops and smell of aniline	Acetanilide

The confirmatory tests for acetamide, benzamide and acetanilide are given below. The tests for the rest of them have already been given.

Substance	Confirmatory tests
Acetamide	<p>(1) Boil the solution with excess of caustic soda for five minutes. Add excess of concentrated sulphuric acid and warm. A smell of acetic acid would be obtained.</p> <p>(2) To a portion of the solution add ferric chloride solution and observe that no change occurs. (<i>cf.</i> ammonium acetate)</p>

Substance	Confirmatory tests
Benzamide	(1) Boil the solution with excess of caustic soda a smell of ammonia would be obtained. Take a portion of the solid residue and boil it for five minutes with excess of caustic soda. Add excess of concentrated sulphuric acid. Cool. White precipitate of benzoic acid would be obtained. The precipitate can be tested for benzoic acid. (2) The solution gives no colour or precipitate with ferric chloride. (cf. benzoate)
Acetanilide	(1) Note the characteristic residue. (2) Take a portion of the given solid or solid residue, add caustic soda and boil when oily globules of aniline would be obtained which can be identified with their characteristic smell. (or, test the liberated aniline as described under aniline.)

V. Iodoform group :— Heat a portion of the solution with strong caustic soda solution and iodine. If the solution becomes yellow and characteristic smell of iodoform is obtained with sometimes a deposit of yellow substance the presence of ethyl alcohol or acetone is indicated. These may be distinguished as follows.

Experiment	Observation	
	Ethyl alcohol	Acetone
Solution + ammonium hydroxide + iodine and heat	No smell of iodoform	Smell of iodoform
Solution + ammonium hydroxide + sodium nitroprusside solution (fresh)	No action	Violet colour
Solution + solid potassium dichromate + concentrated sulphuric acid and warm	Smell of acetaldehyde	No action

VI. Miscellaneous group :— This includes phthalic acid, methyl alcohol, urea, glycerine, aniline, nitrobenzene, iodoform, ether, benzene, cane sugar, starch, naphthalene and benzaldehyde. These can be tested as given below :

- Phthalic acid**— (1) Heat a portion of the dry residue or the solid substance in a dry test tube when vapours having choking smell are given out (*cf.* succinic acid)
- (2) To the neutral solution add calcium chloride or ferric chloride solution. No colour or precipitate would be obtained (*cf.* succinic acid)
- (3) Take in a dry test tube a portion of the residue or the dry substance with solid resorcinol and concentrated sulphuric acid and heat. Pour the dark coloured contents of the test tube into a beaker half full of water containing caustic soda solution. A yellow green fluorescent solution would be obtained. (The test is also given by succinic acid but tests given above can distinguish phthalic acid from it.)

- Methyl alcohol**— (1) Note the characteristic smell.
- (2) Heat a portion of the solution with solid sodium salicylate or salicylic acid and concentrated sulphuric acid. A smell of methyl salicylate (oil of winter green) would be obtained.
- (3) Heat a portion of the solution with potassium dichromate and sulphuric acid. A smell of formaldehyde would be obtained.

- Urea**— (1) Note the characteristic residue with soapy touch.
- (2) **Biuret reaction**— Take a portion of the residue in a dry test tube and heat it slowly. The substance first melts and smell of ammonia is given. Stop heating at this stage. Add to the melt two to three drops of a dilute copper sulphate solution and a drop of caustic soda solution and shake. A violet or pink colour is



**Glycerine** :— (1) **Dunstan's test**— Take a dilute solution of borax in water and add to it one or two drops of phenolphthalein solution till a light pink colour is obtained. Gradually add to a portion of this solution glycerine solution. The colour of the solution would be discharged. Heat the solution. The colour would reappear.

**Note** : The colour of borax solution would also be discharged by glucose and free acids. Glycerine does not reduce Fehling solution. (cf. glucose) The colour discharged by free acids does not reappear on heating. (cf. glycerine).

**Aniline** :— (1) **Diazo reaction** — Take a portion of the solution, add dilute hydrochloric acid and then solid sodium nitrite little by little cooling the test tube all the time under the tap. Prepare in another test tube a solution of  $\beta$ -naphthol in caustic soda. To solution add the first solution drop by drop. A red colour would be obtained.

**Note** : The acid solution should be added to the  $\beta$ -naphthol solution in caustic soda and not vice-versa.

**Nitrobenzene** :— (1) Note the characteristic smell.

(2) Heat a portion of the solution with zinc and dilute sulphuric acid. Nitrobenzene is thus reduced to aniline. With this reduced solution perform the diazo reaction. (See aniline)

**Iodoform** :— (1) yellow in colour with characteristic smell.

**Ether** :— (1) Note the characteristic smell.

(2) Pour a small quantity of the liquid on the palm of your hand. The liquid would eva-

ports very rapidly and cooling sensation would be felt.

**Benzene** :— (1) Note the characteristic odour.  
(2) Take a few c. c. of the liquid and apply flame. It would burn with a very smoky flame.

**Cane sugar and starch** :— To a portion of the solution add 1 c. c. of dilute sulphuric acid solution and boil. To this solution add excess of caustic soda solution. A yellowish coloured solution would be obtained. To this solution add about 3 c. c. of Fehling solution and boil. A red or green precipitate would be obtained indicating the presence of cane sugar or starch. Distinguish between them as follows:

Experiment	Observation	
	Cane sugar	Starch
To a portion of the residue add concentrated sulphuric acid and shake	Charring takes place in cold	No action in cold
To a portion of the given solution add a drop of iodine solution	No action	Blue colour
Taste	Sweet	Tasteless

**Naphthalene** :— (1) Note the characteristic odour.  
(2) The residue or solid sublimes on heating.

**Benzaldehyde** :— (1) Characteristic smell.  
(2) To a portion of the liquid add a few c. c. of ammoniacal silver nitrate solution and heat. Reduction takes place.  
(3) To a portion of the solution add Fehling solution and warm. No reduction takes place.  
(4) To a portion of the solution add strong caustic soda solution and boil. Acidify this solution with dilute sulphuric acid. White precipitate of benzoic acid would be obtained (test

## PART IV

### PREPARATION OF SOME COMPOUNDS

#### INTRODUCTION

In the preparation of Compounds separation of solid from liquid and the separation of liquid from liquid is frequently required. Methods of such separation are discussed below.

(i) **Separation of solid from liquid** :—This separation is most commonly carried out by filtration. A useful device for carrying out filtration efficiently and rapidly is to use a Buchner funnel with a filter pump.

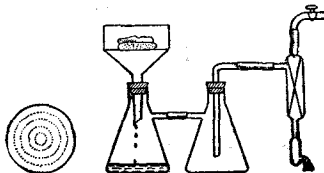


Fig. 1.—Use of Buchner funnel with suction

In Fig. 1 is illustrated the assembly required for the use of Buchner funnel with suction. Buchner funnel is a porcelain or glass funnel which carries a perforated disc, usually fused or cinked. Cut a filter paper only slightly bigger than the size of the disc. Wet the filter paper and press it gently but firmly on to the disc. Pour a little liquid on the filter paper and open the tap to which the suction pump is connected. As the liquid drains out in the Buchner funnel press gently but firmly the ends of the filter paper which are touching the sides of the funnel just a little above the perforated disc. The assembly is now ready for filtration. The mixture containing the solid to be separated from the liquid is now poured with the help of a glass rod in the centre of the

**Buchner funnel.** When all the mixture has been filtered, the solid on the filter, if required, can be washed by throwing a jet of the washing liquid from a wash bottle. It can then be left for five minutes to drain out. The solid can now be pressed by a flat stopper and further liquid would drain out. Remove the Buchner funnel from filtering flask and tap it for removing the solid.

(ii) **Separation of liquid from liquid** :—If the liquids are not miscible then they can be easily separated by the use of separating funnels.

Separating funnels are available with various shapes, sizes and designs. Two of the common types are shown in Fig 2. A convenient size of the separating funnel is chosen for the separation of a mixture of immiscible liquids. The mixture is placed inside the separating funnel and the funnel is usually stoppered. It is thoroughly shaken and then allowed to stand when the liquid separates into two layers. By gently opening the lower stopcock the lower layer of the liquid can be completely drained off without disturbing the upper layer. Before opening the lower stopcock the stopper of the separating funnel should be removed,

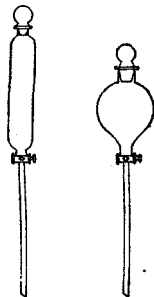


Fig. 2.—Separating funnels

When the liquids to be separated are miscible liquids then recourse is taken to distillation for their separation. Various methods of distillation are :—

1. Simple distillation.
2. Fractional distillation using a fractionating column
3. Distillation under reduced pressure.
4. Steam distillation.

Of these only the simple distillation and steam distillation are usually required for the preparation of compounds commonly prescribed for the B. Sc. course of Indian universities.

Assembly for simple distillation is shown in Fig. 3A.

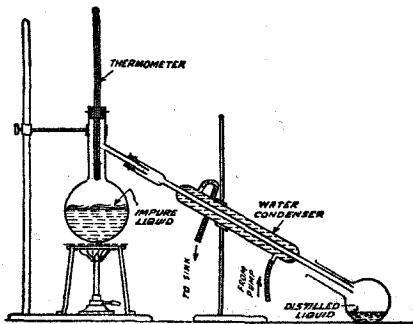


Fig. 3A— Common distillation assembly

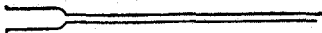


Fig. 3B— Air condenser

The diagram in Fig. 3A shows simple distillation using a downward water condenser. If the liquid to be distilled has a B. P. lower than  $100^{\circ}$  then the distilling flask should be heated on a water bath and a water condenser should be employed. For liquids having B. P. above  $100^{\circ}$  an air condenser (Fig. 3B) should be used and the distilling flask should be heated, as a rule, on a sand bath. Unless otherwise required, the thermometer should be placed well above the boiling liquid.

In Fig. 4 is given the arrangement for steam distillation.

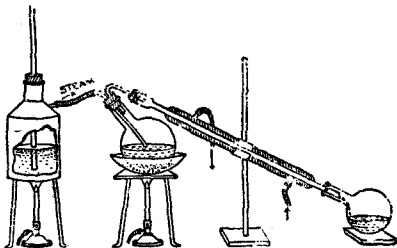


Fig. 4.—Steam distillation.

The steam from the boiler is led into the distilling flask which is kept inclined to prevent splashing of its contents. The liquid or the solid present in the distilling mixture, being volatile in steam, distils over and is collected in the receiver. When the bulk of the steam collected in the distilling flask is increased, it is heated to distil off excess water. Once the generation of steam has started it should be kept up till the whole of the substance has passed over. If it is required to disconnect the assembly then first the rubber tubing connecting the steam generator to the distilling flask should be removed and only then the burner under the steam generator should be extinguished otherwise the liquid in the distilling flask would be sucked back. Steam distillation is only used for substance which are volatile in steam.

Substances as they are usually prepared in the laboratory require purification. For purifying liquids distillation is usually required and solids are commonly purified by crystallisation. Methods of distillation have already been described. Crystallisation should be carried out as follows.

For crystallisation a suitable solvent is selected. The properties of the solvent should be such that it should dissolve more substance while hot than when cold. The solution

of the substance to be crystallised in minimum of the hot solvent should be prepared as follows. Take the substance in a round bottomed flask and add a small amount of the solvent just sufficient to moisten the substance. Fit up a reflux condenser and heat the flask. If the solvent has B. P. lower than  $100^{\circ}$  it should be heated on a water bath using a water condenser. For solvents having B. P. above  $100^{\circ}$  air

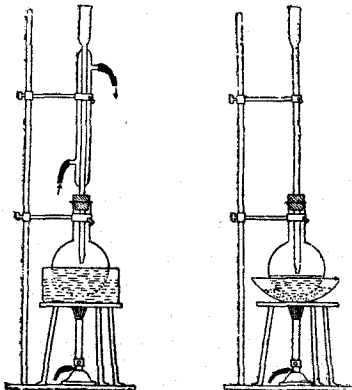


Fig. 5— Preparation of saturated solution

condenser should be used and heating should be carried out on sand bath. Fig. 5 shows the necessary assemblies for refluxing the solvent.

As the heating is continued more of the solvent, if needed, is poured from the top of the condenser without disturbing the assembly. In this way the amount of the solvent can be controlled and a saturated solution easily prepared.

The saturated solution thus obtained should be filtered hot to remove insoluble impurities. Sometimes even during the course of filtration there is sufficient cooling and the substance crystallises out. To avoid this difficulty a hot water funnel may conveniently be used for filtering the solution hot.

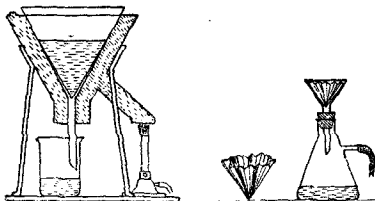


Fig. 6.—Hot water funnel in use.

In Fig. 6 is shown a hot water funnel in use. This funnel has a water jacket which can be heated. This enables a hot solution to be filtered without much cooling.

After filtration the saturated solution is allowed to stand when crystallisation takes place. Crystals are usually filtered out on a Buchner funnel which is connected to a filter pump. Depending upon the nature of the substance, the crystals can be dried between the folds of a filter paper at room temperature, in a steam oven or in an air oven.

To judge the purity of the product a few of its constants should be determined. In the case of inorganic substances purity of a product can, as a rule, only be judged by carrying out a gravimetric or volumetric estimation. On the other hand, in the case of organic solids the melting point, and in the case of organic liquids the boiling point gives a very good idea about the purity of a substance, as these constants are readily influenced by impurities. The melting point of an organic solid is determined as follows:—



**Determination of melting point:**—For determining the melting point, the substance should be powdered. Take a fine capillary tube of about 6 cms. in length and close one of its end by heating for a short time in the Bunsen flame. Fill the capillary tube to a length of about 4 mm with the powdered substance. A good way to do this is to take the substance in a watch glass and scrape a little of the solid into the capillary tube. By gently tapping the capillary against the table-top the substance can easily be shifted to the bottom. A typical melting point assembly is shown in Fig. 7. In place of the beaker a Kjeldahl flask or a small

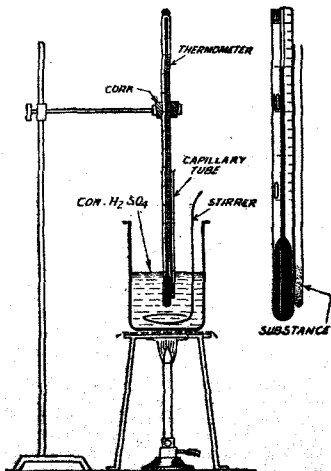


Fig. 7.—Determination of melting point.

distilling flask can also be employed. Concentrated sulphuric acid is usually employed in the heating bath as its boiling point is high. Moisten the capillary tube with concentrated sulphuric acid and stick it to the side of the thermometer bulb. The correct position for placing the capillary tube is indicated in the figure. Heat the bath gently and note the temperature when the substance has melted. Pure substances always give a sharp melting point.

Boiling point of an organic liquid is determined by the methods given below :—



Fig. 8—Determination of boiling point.

**Determination of boiling point :—**  
When sufficient liquid is available, the boiling point determination can be carried out by distilling it. A convenient and easily assembled apparatus for this purpose is shown in Fig. 8.

Place about 8 c. c. of the liquid in the boiling tube. Note that the thermometer is kept well above the surface of the liquid. Gently heat the liquid from below till it begins to boil. When the thermometer records a steady temperature note it. This is the boiling point of the liquid. Pure liquids give a constant boiling point.

If the quantity of the liquid available is very small its boiling point should be determined by the capillary tube method. The experimental assembly for this method is shown in Fig. 9.

Fit a small test-tube to the thermometer by rubber bands. Place in this test-tube about 1 c.c. of the liquid whose boiling point is to be determined. Next take a capill-

ary tube and seal it about one cm. from one end by gently rotating it in the flame. In this way a constriction in the capillary tube is created. Arrange the capillary tube in the

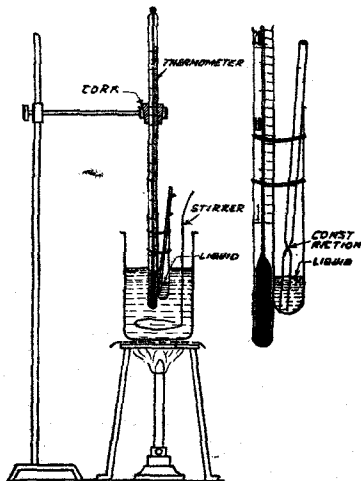


Fig. 9.—Capillary tube method for determination of boiling point.

small test-tube as shown in the figure. Now heat the sulphuric acid bath slowly and carefully stir the acid. At first a bubble or two would escape at the end of the capillary and when the boiling point is reached a steady stream of

bubbles would arise from the end of the capillary tube. Note the temperature at this stage. This would be the boiling point of the liquid.

**Note :—** Previously described methods of determining the M. P. and the B. P. give uncorrected values for these constants. For all routine purposes, however, the uncorrected values are quite sufficient to give an idea of the purity of the substance under investigation.

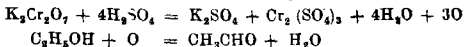
## CHAPTER XIV.

### ORGANIC PREPARATIONS.

#### Preparation No. 1.

#### ACETALDEHYDE.

It is prepared by the oxidation of ethyl alcohol. The oxidation is usually carried out by a mixture of potassium dichromate and sulphuric acid. The equations are:—



**Required** :— 15 gms. Potassium dichromate.  
18 c. c. absolute ethyl alcohol.  
11 c. c. Concentrated sulphuric acid.  
60 c. c. water.

**Procedure** :—Powdered potassium dichromate and water are taken in a litre flask. The flask is fitted with a dropping funnel carrying a mixture of alcohol and concentrated sulphuric acid and is also fitted with a condenser. Heat the flask on water bath and add with constant shaking drop by drop alcohol-acid mixture from the dropping funnel. A vigorous reaction would set up and a mixture of acetaldehyde, acetal, alcohol and water would distil over. The distillate should be collected in a receiver surrounded by ice.

Now fit up a distilling apparatus in such a way that the condenser is inclined upwards and the receiver is surrounded by ice. Water at a temperature of 25° should be circulated in the condenser.

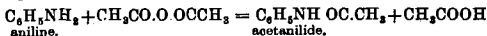
Pour the contents of the last receiver in distilling flask and gently heat the flask on water bath. The acetaldehyde passes over and is collected in the receiver. Fractionally distil the aldehyde thus collected and collect the fraction between 20-22°.

Yield = 3 gms.

B. P. 21°

**Preparation No. 2.****ACETANILIDE.**

It is prepared by acetylating aniline. The common acetylating agents are acetic acid, acetic anhydride and acetyl chloride. The use of acetic anhydride is recommended. The equation is:—



**Required:**— 20 gms. Aniline.  
25 gms. Acetic anhydride  
water and a pinch of animal charcoal.

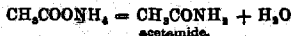
**Procedure:**—To the aniline add with constant shaking acetic anhydride. When the addition is complete pour the whole into 500 c. c. of water. Heat to boiling and add more water if necessary to dissolve the acetanilide. It should be noted that acetanilide melts under boiling water and sufficient water should be used to dissolve all the oil thus formed. Add a pinch of animal charcoal and continue boiling for five minutes. Filter hot through a fluted filter paper or better use a hot water funnel. Crystals of acetanilide separate on cooling. Filter and dry.

Yield = 23 gms.

M. P. 114°

**Preparation No. 3.****ACETAMIDE.**

Acetamide is usually obtained by distilling ammonium acetate. The equation is:—



**Required:**— 25 gms. Ammonium acetate

**Procedure:**—Melt the ammonium acetate in a porcelain dish. Take the melt in a distilling flask fitted with an air

condenser and a thermometer. Heat the flask over sand bath. The distillate that comes over consists chiefly of water and acetic acid upto the temperature 180°. The molten mass in the distilling flask usually solidifies at this temperature and consists mainly of acetamide. Change the receiver. Continue heating the flask and collect distillate between 220-224°. The air condenser used should be a wide bore pyrex glass tube. If any distillate solidifies in the condenser it can be removed by gentle scraping. The distillate in the receiver would solidify on cooling. Dry it on a porous plate or on filter paper. If need be recrystallise from ether.

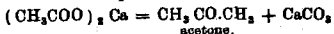
Yield = 15 gms.

M. P. 82° ; B. P. 222°

#### Preparation No. 4.

#### ACETONE.

It is usually prepared in the laboratory by heating calcium acetate. The equation is:—



**Required:**— 50 gms. calcium acetate.

**Procedure:**—Place dry calcium acetate in a distilling flask connected with a water condenser. Heat gently at first and strongly afterwards. A slightly brown coloured liquid would distil over and is collected in a receiver. This is acetone mixed with impurities.

Shake the distillate with a saturated solution of sodium bisulphite, warm slightly and allow to cool. The bisulphite compound of acetone would crystallise out. Filter the crystals and dry them on filter paper. Add to the crystals a saturated solution of sodium carbonate and distil. Collect the fraction between 55-57°. Dry this fraction over anhydrous calcium chloride and redistil.

Yield = 20 gms.

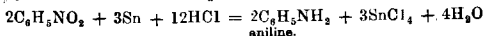
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**Preparation No. 5.****ANILINE.**

Aniline is prepared by the reduction of nitrobenzene. The reduction can be carried out by either tin and hydrochloric acid or iron and hydrochloric acid.

**Method I.**

In this method the reduction is carried out by tin and hydrochloric acid. The equation is:—



**Required** :— 25 gms. Nitrobenzene (21 c.c.)  
 45 gms granulated tin.  
 85 c. c. concentrated hydrochloric acid  
 (sp.gr. 1.16).  
 70 gms, caustic soda.  
 45 c. c. Chloroform.

**Procedure** :—Take tin and nitrobenzene into a round bottomed one litre flask fitted with an upright air condenser. Heat the mixture for a few minutes on the water bath. Remove the flask and add small quantities of concentrated hydrochloric acid (5 c. c. at a time) and shake repeatedly. If the reaction becomes very violent it should be moderated by cooling the flask in cold water. The addition of acid should require 30-35 minutes. After the addition of acid replace the flask on water bath without air condenser and heat for an hour or more until the reduction is complete (i. e. when there is absence of any smell of nitrobenzene). Cool the flask slightly and add 50 c c of water and then run in strong caustic soda solution (70 gms. in 100 c. c. of water) until the stannic oxide which is first precipitated, nearly redissolves and the liquid has a strong alkaline reaction. If during the addition of caustic soda the mixture begins to boil it must be cooled by immersing the flask in cold water. The aniline separates out as a dark coloured oil and is steam distilled. On steam distillation aniline and water collect in the receiver. When the distillate as it comes over, appears clear instead of milky, the distillation is stopped. The distillate is taken in a



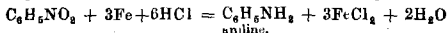
separating funnel and is extracted three times with small quantities (15 c. c.) of chloroform. The separated chloroform solution of aniline is dehydrated by adding a little solid potassium carbonate. The clear liquid is decanted into a distilling flask and the chloroform removed by distillation until the temperature reaches 100°, when the receiver should be changed. Raise the temperature and collect the distillate between 182-183°. The aniline thus obtained has usually a faint amber colour.

Yield = 15 gms.

B. P. 183°

### Method II

In this method the reduction of nitrobenzene is carried out by iron borings and hydrochloric acid. The equation is :-



**Required** :— 22 gms. Nitrobenzene.  
 22 gms. clean fine iron borings,  
 2.5 c. c. concentrated hydrochloric acid  
 (in 5 c. c. of water)  
 5 gms. anhydrous sodium carbonate.

**Procedure** :—The nitrobenzene and iron borings are mixed together in a 250 c. c. round bottomed flask. The hydrochloric acid is added in portions of 2 to 3 c. c. at a time and the whole is well shaken. Vigorous reaction would take place and the temperature would rise. The temperature should be kept at nearly 70° by cooling the flask if necessary. When the reaction is over (i. e. when no smell of nitrobenzene comes out) add 25 c. c. of water and 5 gms. of anhydrous sodium carbonate, in small quantities at a time, and subject the resulting alkaline mixture to steam distillation. The aniline along with water distils over. The rest of the process is just like the one given in method I.

Yield = 14 gms.

B. P. 183°



the flask frequently. Filter off the precipitated benzamide, wash with a little cold water, and recrystallise from hot water. Dry upon the filter paper in air.

Yield = 9 gms.

M. P. 129°

**Note** :—Benzamide should not be dried in oven having a temperature of 100° or more. It undergoes partial decomposition at 100° into benzonitrile.

### Preparation No. 8.

#### BENZANILIDE.

In the laboratory the benzylation of aromatic amines is usually carried out by the method of Schotten-Baumann. Benzamide is prepared by the action of benzoyl chloride on aniline in presence of caustic soda. The equation is :—



**Required** :— 5.2 gms (5 c. c.) aniline.  
8.5 gms. (7 c. c.) benzoyl chloride.  
45 c. c. caustic soda solution (10%).

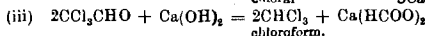
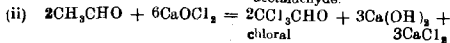
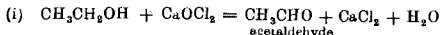
**Procedure** :—Take aniline and caustic soda solution in a conical flask and add to it benzoyl chloride, stopper and shake vigorously for ten to fifteen minutes. Heat would be evolved in the reaction. The crude benzoyl derivative would separate as a white powder. When the reaction is complete (*i. e.*, when the odour of benzoyl chloride is not detectable) make sure that the reaction mixture is alkaline. Dilute with water and filter off the product with suction on a Buchner funnel. Wash well with water and drain. Recrystallise from hot alcohol or methylated spirit. Dry the crystals in air or steam oven.

Yield = 9 gms.

M. P. = 162°

**Preparation No. 9.****CHLOROFORM.**

Chloroform is usually prepared by the action of bleaching powder on ethyl alcohol. The equations of the reaction are :—



**Required** :— 20 c. c. Absolute alcohol.  
80 gms. bleaching powder.

**Procedure** :—Take the bleaching powder in a mortar, add 120 c. c. of water and grind the whole to a cream like consistency. Transfer it to a flask of about one and a half litre capacity. Add more water (150 c. c.) and all the alcohol. Place the flask on the hot water bath and attach to it a water condenser. Heat the water bath till the reaction commences and then remove the burner. Once the reaction starts the heat of the reaction would be sufficient to distil over the chloroform. When the reaction slackens the water bath may again be gently warmed to complete the reaction.

Take the distillate in a separating funnel and shake it with alkali solution. Separate the lower layer of chloroform, dry it over fused calcium chloride and redistil.

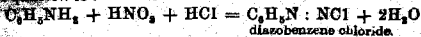
Yield = 20 gms.

B. P. 60-62°

**Preparation No. 10.****DIAZOBENZENE CHLORIDE.**

It is prepared by the action of aniline and nitrous acid.

The equation is :—



**Required** :— 15 gms. aniline.  
160 c. c. absolute alcohol.  
70 gms. concentrated hydrochloric acid.  
24 gms. amyl nitrite.

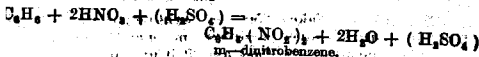
**Procedure** :—Mix aniline and alcohol and add concentrated hydrochloric acid in a slow stream with constant shaking. The precipitate of hydrochloride, which first appears, redissolves. Cool the mixture to 30° and keep at 30-35° and out of direct sunlight whilst the amyl nitrite is dropped from a tap-funnel. Then cool in ice water and leave for half an hour. Crystals of diazobenzene chloride would separate out. They may be filtered at the pump, washed with alcohol and ether and dried in the air at room temperature.

**Note** :—On drying diazobenzene chloride may decompose with violence. The substance can be used for further reactions in a state of solution.

### Preparation No. 11.

#### META DINITROBENZENE.

The nitration of benzene can be easily controlled to give either mono- or dinitrobenzene. The dinitration is accomplished by using larger amount of nitric and sulphuric acids and by heating the reaction mixture to 120° instead of 60° (of nitrobenzene). The equation is:—



**Required** :— 225 c.c. concentrated sulphuric acid.  
75 c.c. nitric acid.  
30 gms. benzene.

**Procedure** :—Take 75 c.c. nitric acid in a liter flask and add to it cautiously and with cooling 75 c.c. of concentrated sulphuric acid. To the cooled mixture add 30 gms. of benzene in small portions with vigorous shaking. After the addition of all benzene shake the whole for several minutes. Add 150 c.c. of concentrated sulphuric acid in small portions with agitation. Introduce a thermometer into the mixture which is then heated on an oil bath to 120° for five minutes. A few drops of the liquid is removed on a glass rod and added to a test tube filled with acid water. If the nitration is complete the dinitrobenzene will separate as a lead, pale

yellow solid. If the nitration is not complete, an oil will be formed, and the heating must be continued.

The reaction mixture is finally cooled to about 80° and poured with stirring, into two litres of cold water. The dinitrobenzene that separates is filtered by suction and washed thoroughly with water. It is purified by recrystallisation from dilute alcohol.

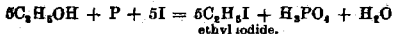
Yield = 50-60 gms.

M. P. 90°

#### Preparation No. 12.

#### ETHYL IODIDE.

It is prepared by the action of phosphorus and iodine on ethyl alcohol. The equation of the reaction is:—

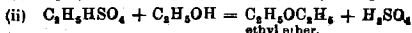


**Required** :— 100 gms. iodine,  
50 gms. absolute alcohol (63 c. c.)  
10 gms. red phosphorus.

**Procedure** :—Take a 250 c. c. distilling flask and close its side tube with a stopper of rubber and glass rod. Take the iodine and alcohol in the flask and fit it up with a reflux condenser. Keep the flask surrounded by cold water and gradually add phosphorus by detaching the flask from the condenser. Attach to the upper end of the condenser a bent tube dipping to a stout and narrow glass cylinder containing mercury. Heat the flask for 2-3 hours on water bath. It is advisable to stand the mercury vessel in a basin in the event of mercury being splashed over. The ethyl iodide is then distilled in the ordinary way from a brine bath (a saturated solution of salt). The distillate is purified by shaking with a solution of sodium carbonate, then with a solution of sodium thiosulphate to remove free iodine and finally with water. The liquid separated as far as possible from water is dehydrated over calcium chloride and distilled.

**Preparation No. 13.**  
**ETHYL ETHER.**

The most important method for the preparation of simple aliphatic ethers is the dehydration of the corresponding alcohols, usually by means of concentrated sulphuric acid. When ethyl alcohol is in excess and the reaction takes place at about 140° ethyl ether is produced. The equations of the reaction are :—



**Required** :— 50 c. c. concentrated sulphuric acid.  
150 c. c. absolute alcohol.

**Procedure** :—50 c. c. of concentrated sulphuric acid is added with shaking and cooling to an equal volume of alcohol in a distilling flask. The flask is fitted with a thermometer extending below the surface of the liquid and with a dropping funnel, to the end of which is attached a glass tube leading below the surface of the liquid in the flask. The distilling flask is connected with a downward water condenser. The receiver should be a flask with a side tube. The receiver should be connected with the condenser by rubber stopper and the side tube of the receiver is connected to a rubber tube which is lead down into the sink. The receiver is kept immersed in ice.

The flask is heated on a wire gauze over a small flame until the thermometer registers 140 to 145°. While this temperature is maintained 100 c. c. of alcohol is added from the dropping funnel at the same rate as that at which the ether distils over. Toward the end of the reaction it may be necessary to raise the temperature somewhat. When the reaction is complete, the distillate is washed successively with dilute sodium hydroxide and saturated sodium chloride. The ether is dried over powdered calcium chloride in a flask fitted with a calcium chloride tube. The ether is finally decanted from the drying agent and distilled on a water bath the temperature of which does not exceed 45°.





The dilute acid collected in the receiver is neutralised with lead carbonate, heated, filtered hot and allowed to cool. About 140 gms of crystals of lead formate would separate out. The powdered lead salt is introduced in a long layer into a slopping wide tube, loosely stopped at the lower end by a plug of glass wool. To the lower end of the tube a receiver, in the form of a distilling flask, is attached, which is protected from moisture by a calcium chloride drying tube. The salt is heated gently by moving a flame along the tube whilst hydrogen sulphide, washed through water, and dried by passing through a U-tube containing calcium chloride, is led over the salt in not too rapid a stream. The lead formate blackens, and is slowly converted into lead sulphide and formic acid, which drops into the receiver. The acid which retains the smell of hydrogen sulphide, is freed from the latter by distillation over a little dry lead formate.

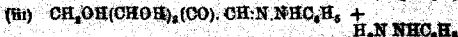
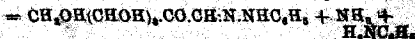
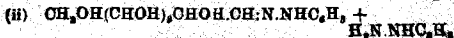
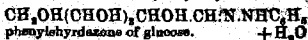
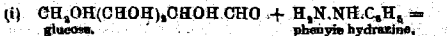
Yield is practically theoretical.

B. P. 100°

### Preparation No. 15.

#### GLUCOSAZONE.

The osazone of glucose is prepared by heating it with phenyl hydrazine in presence of dilute acetic acid. The equations of the reaction are:—





**Procedure** :—Place potassium iodide in a litre flask and add acetone. Slowly add, with frequent shaking, solution of sodium hypochlorite as long as any precipitate of iodoform is formed. Allow the mixture to stand for about ten minutes, then filter at the pump, wash the crystals two or three times with water, and drain the crystals thoroughly. Recrystallise this crude iodoform from methylated or rectified spirit.

Yield = 7 gms.

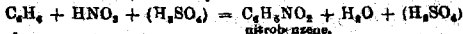
M. P. 119°

**Note** :—Iodoform may similarly be prepared by substituting an equal volume of rectified spirit in place of acetone.

#### Preparation No. 17.

#### NITROBENZENE.

Nitration of benzene is carried out by a mixture of concentrated nitric acid and concentrated sulphuric acid. (of m-dinitrobenzene). The equation is :—



**Required** :— 80 c. c. concentrated sulphuric acid,  
70 c. c. concentrated nitric acid.  
50 gms. benzene.

**Procedure** :—Sulphuric acid is added cautiously with cooling to nitric acid and thus a nitrating mixture is prepared. To this mixture 50 gms. of benzene is added in small portions with shaking, the temperature of the liquid being held between 50-60°. After the benzene has been added, the shaking is continued for about 30 minutes and the temperature kept at 60°. The mixture is then cooled and taken in a separating funnel. The lower acid layer is removed. The nitrobenzene (heavier than water) is once washed with water, once with 10% sodium hydroxide, and finally with water. It is dried over anhydrous calcium chloride and purified by distillation using an air condenser. The product which passes between 205-215° is first collected. It is redistilled, and the fraction between 208-212° is collected.

Yield = 40 gms.

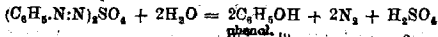
B. P. 211°

**Note** :—In distilling nitrobenzene the temperature should never be allowed to go beyond 215°.

### Preparation No. 19.

#### PHENOL.

In the laboratory phenol is usually prepared from aniline via diazobenzene sulphate which on boiling with water gives phenol. The equation is :—



**Required** :— 49 gms. concentrated sulphuric acid  
 23 gms. aniline (22.5 c.c.) (27 c.c.)  
 18 gms. sodium nitrite.  
 150 gms. ether.

**Procedure** :—Take a litre flask and pour in it 200 c. c. of water. To this water add cautiously, small amounts at a time, 27 c.c. concentrated sulphuric acid. To the resulting hot solution add 23 gms. of aniline and warm it till all aniline dissolves. Dilute the whole with more water (200 c. c.) and cool the mixture in ice till the temperature falls to 3-4°. Add an ice cold solution of 18 gms. of sodium nitrite in 30-35 c. c. of water slowly with constant shaking till a drop of solution when placed over potassium-iodide-starch paper gives just a faint blue colour. Allow the solution to stand at room temperature for about half an hour. Heat the flask on water bath at 50-55° for about 20 minutes. Steam distil the reaction mixture and collect about 500 c.c. distillate. Add to this distillate about 22 gms. of common salt and shake till all the salt dissolves. Take this solution in a separatory funnel and extract 2 to 4 times with ether (use in all 150 c. c. ether). Add 4 gms. of anhydrous potassium carbonate to the ethereal solution for dehydration. Remove the ether by distillation (use all precautions mentioned under distillation of ether). Distil the remaining liquid from wire gauze using an air condenser and collect the fraction coming over between 179-183°. Cool the receiver in ice and scratch the sides of the receiver with glass rod when phenol would usually crystallise out.

Yield = 13-14 gms.  
 M. P. 43° ; B. P. 182°

CHAPTER XV  
INORGANIC PREPARATIONS.

Preparation No. 1.

BORIC ACID FROM BORAX

Boric acid is obtained from borax by the action of hydrochloric acid. The equation is:—



**Required:**—10 gms. borax  
Concentrated hydrochloric acid  
water

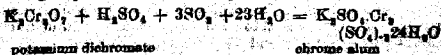
**Procedure:**—Prepare a concentrated solution of borax in water in a beaker. Add to this a small piece of litmus paper. Now add concentrated hydrochloric acid to the hot solution in small amounts till the solution becomes strongly acidic to litmus. On cooling the solution, crystals of boric acid would separate out. Filter the crystals at pump, wash with a little ice cold water and recrystallise from hot water.

Yield = 12 gms.

Preparation No. 2.

CHROME ALUM

Chrome alum is usually prepared in the laboratory by passing sulphur dioxide in potassium dichromate solution containing sulphuric acid. The equation is:—



**Required:**— 5 gms. potassium dichromate  
1 c.c. concentrated sulphuric acid  
sulphur dioxide gas  
water

**Procedure** :— Dissolve the potassium dichromate in about 38 c.c. of hot water. Cool the solution and add 1 c.c. of concentrated sulphuric acid. Again cool the solution. Keep the vessel containing this solution surrounded by cold water and pass through it a slow stream of sulphur dioxide (can be conveniently prepared by the action of dilute sulphuric acid on sodium sulphite). The colour of the solution would change from red to greenish blue in the sequence red-brown-olive green-greenish blue. Cut off the supply of sulphur dioxide at this stage and set aside the solution in a loosely covered dish until crystals form.

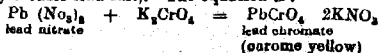
Yield = 16 gms.

**Note** :— An alternate method which also gives good results is to add 10 c.c. of absolute alcohol with constant stirring to a solution of 30 gms. of potassium dichromate and 25 c.c. of concentrated sulphuric acid in 200 c.c. of water, the liquid being cooled in ice.

### Preparation No. 3.

#### CHROME YELLOW

Chrome yellow is the name given to lead chromate which is the least soluble of all lead salts. It can be prepared by the action of potassium chromate on lead nitrate (or, any soluble lead salt). The equation is :—



**Required** :— 6.62 gms. lead nitrate  
4 gms. potassium chromate  
distilled water

**Procedure** :— Dissolve separately the lead nitrate and potassium chromate in minimum quantity of hot distilled water. Mix the two solutions in a beaker. Immediately a yellow precipitate of lead chromate would be obtained. Cool the solution and filter. Wash the precipitate with water till free from chromate ion (test the wash by adding a drop of silver nitrate solution, non-formation of red precipitate indicated the absence of chromate ions). Dry the precipitate in air oven.

Yield = 3.4 gms.

## INORGANIC PREPARATIONS

### Preparation No. 4.

#### CUPROUS OXIDE

Cuprous oxide can be readily prepared by the reduction of Fehling's solution by glucose.

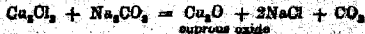
**Required:**—6.9 gms. copper sulphate crystals ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ )  
35 gms. Rochelle salt (sodium-potassium-tartrate),  
10 gms. caustic soda  
15 gms. glucose  
water

**Procedure:**— Dissolve copper sulphate (6.9 gms.) in 100 c.c. of water and add to it one drop of dilute sulphuric acid to keep the solution clear (Solution-A). In a separate beaker dissolve Rochelle salt (35 gms.) in 100 c.c. of water and add to this caustic soda (10 gms.) (Solution-B). When equal volumes of solution A and solution B are mixed we get Fehling solution.

Mix the two solutions in a 600 c.c. pyrex beaker. Add glucose in small amounts at a time while keeping the solution almost boiling. Constantly stir the solution. At first a yellow precipitate would be deposited which would turn to bright red cuprous oxide quickly. Cool the solution and filter. Wash the filtrate first with plenty of boiling water and then with alcohol. Dry the precipitate in steam oven.

Yield = 2 gms.

**Note:**—It can also be prepared in the dry way by heating a mixture of cuprous chloride and sodium carbonate in a crucible. The cooled mass is treated with water and the solution filtered. The residue is cuprous oxide. The equation is:—

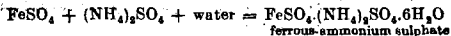


### Preparation No. 5.

#### FERROUS AMMONIUM SULPHATE

Ferrous ammonium sulphate is prepared by taking equimolecular proportions of ferrous sulphate and ammo-

mium sulphate and mixing their saturated solutions in water. The equation is :—



**Required** :— 27.8 gms. ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )  
13.2 gms. ammonium sulphate  
distilled water.

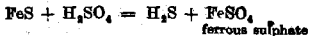
**Procedure** :—Dissolve separately ferrous sulphate and ammonium sulphate in minimum quantity of hot water. Filter the hot solutions through a hot water funnel and mix the filtered solution together. On cooling bluish green monoclinic crystals of ferrous sulphate would separate out. Chill the solution with ice and add a little alcohol. Filter the precipitate and wash it with cold aqueous alcohol. Dry the crystals in air oven at  $60^\circ$ .

Yield = 38 gms.

#### Preparation No. 6.

#### FERROUS SULPHATE FROM KIPP-WASTE

In Kipp's apparatus hydrogen sulphide gas is usually prepared by the action of sulphuric acid on iron sulphide. The equation is :—



**Required** :— 500 c.c. Kipp-waste

**Procedure** :—Concentrate the waste solution from Kipp's apparatus, with constant stirring to about one-fourth its bulk by boiling. Filter hot and leave the filtrate preferably over night for cooling. On cooling crystals of ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) would be formed. Filter off the crystals, wash with a little acetone and dry them between the folds of filter paper at room temperature.

Yield = Depends on the nature of Kipp-waste



**Preparation No. 7****POTASSIUM CHLORATE**

Potassium chlorate is prepared by passing chlorine gas into caustic potash solution. The equation is :—



**Required :—** 11.2 gms. caustic potash  
water  
chlorine gas

**Procedure**—Dissolve 11.2 gms. of caustic potash in 22 c.c. of water. Chlorine gas, washed with water, is passed into this solution, the gas being delivered through an inverted funnel to prevent choking of the delivery tube by crystals. When caustic potash solution is thoroughly saturated by chlorine and smells strongly of chlorine, the reaction is complete. Chill the solution by surrounding it with ice cold water or ice when all the potassium chlorate formed would crystallise out. Decant off the mother liquor and wash the crystals with a little cold water. Recrystallise potassium chlorate from hot water.

Yield = 3—4 gms.

**Preparation No. 8.****SODIUM CHLORIDE FROM SEA-SALT**

**Required :—** 25 gms. sea salt

**Procedure** :—Prepare a saturated solution of the sea salt in water. Pass hydrochloric acid gas into it through an inverted funnel to avoid suction. As the concentration of hydrochloric acid gas increases in the solution sodium chloride would be precipitated. Filter off the precipitated sodium chloride, wash it with a little alcohol and dry in an air oven.

Yield = 22 gms.

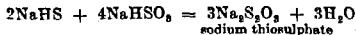
**Note** :—(1) The sodium chloride thus obtained would still contain some impurities of potassium chloride. Potassium chloride can only be removed by repeated crystallisation (fractional) from water.

- (2) Hydrogen chloride gas may conveniently be generated by dropping concentrated sulphuric acid on concentrated hydrochloric acid,

### Preparation No. 9

#### SODIUM THIOSULPHATE

Sodium thiosulphate is best prepared by the interaction of sodium hydrogen sulphide and sodium hydrogen sulphite in water. The equation is :—

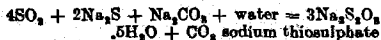


**Required** :— 5.6 gms. sodium hydrogen sulphide (NaHS)  
20.8 gms. sodium hydrogen sulphite  
(NaHSO<sub>3</sub>) water

**Procedure** :— Prepare saturated solutions, separately, of sodium hydrogen sulphide and sodium hydrogen sulphite in minimum of boiling water. Mix the two solutions while hot. On cooling crystals of sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O) would be deposited. Filter the crystals and wash with a little acetone and finally dry between the folds of filter paper at room temperature.

Yield = 26—28 gms.

**Note** :— Sodium thiosulphate may also be prepared by passing sulphur dioxide into a solution containing sodium sulphide and sodium carbonate. The equation is :—



It can also be prepared by heating sodium sulphite crystals with flowers of sulphur.

APPENDIX I  
SPECIMEN OF RECORD OF WORK

In an examination a B.Sc. student is usually given the following exercises :—

1. A mixture for qualitative inorganic analysis.
2. A Volumetric estimation.
3. A gravimetric estimation.
4. Identification of three organic compounds.

The following methods are recommended to indicate the way a student should record his work.

1. Suppose the no. of the mixture given is 25 and it has been found that it contains Cu, As, Mg, PO<sub>4</sub>, SO<sub>4</sub>. Record it as follows :—

Mixture No. 25

Date :

Experiment	Observation	Inference
1. Mixture in dil. HNO <sub>3</sub> + dil. HCl	no ppt.	I-group absent
2. Mixture in dil. HCl + H <sub>2</sub> S and filter	black ppt.	II-group present
3. Ppt. (2) + (NH <sub>4</sub> ) <sub>2</sub> S <sub>x</sub> and filter	black residue	II—A group present
4. Black residue (3) + dil. HNO <sub>3</sub> boil	residue dissolves	Hg absent
5. Solution (4) + dil. H <sub>2</sub> SO <sub>4</sub>	no ppt.	Pb absent
6. Solution (4) + NH <sub>4</sub> OH	no ppt. but blue colour	Bi absent
7. Solution (4) + conc. HCl + H <sub>2</sub> S and filter	black ppt.	Cu indicated
8. Filtrate (7) + water + H <sub>2</sub> S	no ppt.	Cu confirmed
9. Filtrate (3) + dil. HCl and filter	coloured ppt.	Cd absent
10. Ppt. (9) + conc. HCl and boil	ppt. dissolves	II—B group present
11. Solution (10) + conc. HNO <sub>3</sub> + ammonium molybdate, boil	yellow ppt.	Hg absent
12. Solution (10) + iron nail, boil and filter. Filtrate + HgCl <sub>2</sub>	no black scales	As present
13. Filtrate (2), boil off H <sub>2</sub> S	no ppt.	Sb absent
14. Solution (13) + K <sub>2</sub> Fe(CN) <sub>6</sub>	no blue ppt.	Sn absent
15. Solution (13) + Conc. HNO <sub>3</sub> + ammonium molybdate and boil	yellow ppt.	Fe absent
16. Solution (13) + NH <sub>4</sub> Cl + NH <sub>4</sub> OH	white ppt.	PO <sub>4</sub> present
		PO <sub>4</sub> or III-group

Experiment	Observation	Inference
17. Solution (16) + $\text{CH}_3\text{COOH}$ + $\text{CH}_3\text{COONa}$ + $\text{FeCl}_3$ , boil and filter	brown ppt.	
18. Filtrate (17) + $\text{NH}_4\text{OH}$ and filter	brown ppt.	
19. Ppt (18+17) + $\text{NaOH}$ + Br water, boil, filter. Boil off $\text{Br}_2$	Colourless solution	Cr absent
20. Solution (19) + dil. $\text{HNO}_3$	no ppt.	Al absent
21. Filtrate (18) + $\text{H}_2\text{S}$	no ppt.	IV-group absent
22. Filtrate (18) + $\text{NH}_4\text{Cl}$ + $\text{NH}_4\text{OH}$ + $(\text{NH}_4)_2\text{CO}_3$	no ppt.	V-group absent
23. Filtrate (18) + soda phosphate	white ppt.	Mg present
24. $\text{Na}_2\text{CO}_3$ extract + dil. $\text{HCl}$ + $\text{BaCl}_2$	white ppt.	$\text{SO}_4$ present

**Result:**—Mixture no. 25 contains Cu, As, Mg,  $\text{PO}_4$ ,  $\text{SO}_4$ .

2. Determine the strength of the given copper sulphate solution (No. 25) using potassium iodide and sodium thiosulphate solution (supplied) iodometrically. The approximate strength both in terms of normality and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  gms. per litre.

### Observations —

I. Wt. of the known  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution—

Wt. of weighing tube +  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ..... = 8.8764 gms.

Wt. of empty weighing tube ..... = 6.3802 ,,

Wt. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  taken ..... = 2.4962 ,,

The solution was prepared in a 100 c.c. flask.

II. Standardisation of the supplied thiosulphate solution. The amount of thiosulphate required for 10 c.c. of known  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution.

Ist. reading	IInd. reading	Amount of Thiosulphate used
0.00	9.50	9.50 c.c.
9.50	18.90	9.40 c.c.
18.90	28.30	9.40 c.c.

III. Titration of unknown  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution with standardised thiosulphate solution.

The amount of thiosulphate required for 10 c.c. of unknown  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution.

Ist. reading	IInd. reading	Amount of thiosulphate used
0.00	9.80	9.80 c.c.
9.80	19.40	9.60 c.c.
19.40	29.00	9.60 c.c.

Calculations :—

The strength of the prepared solution of copper sulphate in 100 c.c. is =  $\frac{N \times 2.462}{24.971}$

10 c.c. of known copper sulphate solution requires 9.40 c.c. of thiosulphate solution. Hence the strength of thiosulphate solution is ..... =  $\frac{N \times 2.462 \times 10}{24.971 \times 9.40}$

10 c.c. of unknown copper sulphate solution requires 9.60 c.c. of thiosulphate solution. Hence the strength of unknown copper solution is .....

$$= \frac{N \times 2.462 \times 10}{24.971 \times 9.40} \times \frac{9.60}{10}$$

$$= \frac{N \times 2.462 \times 9.60}{24.971 \times 9.40}$$

$$= \frac{N}{9.836}$$

$$= \frac{249.71}{9.836} \text{ gms. per litre}$$

$$= 25.39 \text{ gms. per litre}$$

**Result** :— The amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  present in the given solution No. 25 is 25.39 gms. per litre or  $\frac{N}{0.836}$  is the strength of the given solution.

3. Estimate the amount of barium in the given solution of barium chloride gravimetrically. The number of the supplied solution is 25.

**Observations** :—

- |  |                |
|--|----------------|
| 1. Wt. of the empty crucible.....                  | = 10.4398 gms. |
| 2. Wt. of crucible + ppt. of $\text{BaSO}_4$ ..... | = 10.7580 "    |
| 3. " " " " " " " .....                             | = 10.7572 "    |
| 4. " " " " " " " .....                             | = 10.7572 "    |

**Calculations** :— The amount of  $\text{BaSO}_4$  obtained from the given solution is  $10.7572 - 10.4398 = 0.3174$  gms.

Hence the amount of Ba present in the given solution is  $0.3174 \times 0.5886$  gms. i.e. 0.1773 gms.

**Result** :— The amount of Ba present in the given solution No. 25 is 0.1773 gms.

4. Identify the given organic compounds numbered 25-A, 25-B and 25-C.

Experiment	Observation	Inference
<i>Substance 25—A</i>		
i. Solution + litmus paper	turns red	acid
ii. Neutral solution + $\text{CaCl}_2$	immediate white ppt.	indication oxalic acid
iii. Ppt. (ii) + $\text{CH}_3\text{COOH}$	insoluble	
iv. Ppt. (ii) + $\text{KMnO}_4$ + dil. $\text{H}_2\text{SO}_4$	Solution becomes colourless	oxalic acid confirmed
<i>Substance 25—B</i>		
i. Neutral solution + $\text{FeCl}_2$	violet colour	indication phenol
ii. Blue solution (i) + $\text{CrCl}_3$ COOH	Solution becomes colourless	"
iii. Odour	characteristic	phenol
iv. Solution + $\text{NaNO}_2$ in $\text{H}_2\text{NO}_4$ warm	brown colour	
v. Solution (iv) poured in water	red colour	} phenol confirmed
vi. Solution (v) + alkali	blue colour	
<i>Substance 25—C</i>		
i. Solution + Schiff's reagent in cold	pink colour	aldehyde
ii. Solution + ammoniacal $\text{AgNO}_3$ , heat	black ppt.	formaldehyde
iii. Solution + $\text{NaOH}$ , heat	no change	formaldehyde confirmed
iv. Odour	characteristic	formaldehyde

**Result** :—Substance No. 25—A is oxalic acid,  
 " " 25—B " phenol,  
 " " 25—C " formaldehyde.

## APPENDIX II

## STRENGTHS OF COMMON BENCH REAGENTS.

Reagent.	Approximate normality	Approximate concentration in grams per litre
<b>Acids :—</b>		
Sulphuric (Conc.)	37 N	1840
Sulphuric (dil)	4 N	200
Hydrochloric (conc.)	11 N	400
Hydrochloric (dil.)	4 N	150
Nitric (Conc.)	15 N	1000
Nitric (dil.)	4 N	250
Acetic (dil.)	4 N	240
<b>Bases :—</b>		
Caustic soda	4 N	160
Ammonium hydroxide	4 N	140
Lime water	0.04 N	1.7 (saturated solution)
<b>Salts etc. :</b>		
Ammonium chloride	4 M	214
Ammonium oxalate	0.25 M	31
Ammonium sulphate	2 N	132
Barium chloride	0.5 M	104
Bromine water	0.4 M	32 (saturated solution)
Ferric chloride	0.33 M	54
Lead acetate	0.5 M	162
Mercuric chloride	0.1 M	27
Potassium chromate	0.125 M	25
Potassium ferrocyanide	0.25 M	92
Potassium iodide	16 %	-
Potassium permanganate	0.2 M	32
Cobalt nitrate	0.5 N	72.5
Silver nitrate	0.1 M	17
Sodium acetate	2 M	160 (anhydrous)
Sodium phosphate	0.17 M	24 (60gm. $\text{Na}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ )
Stannous chloride	0.5 M	95 (110 gm $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ )
Calcium chloride	M	91.0 (60gm. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ )