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Chapter

# Introduction

## APPARATUS AND BASIC TECHNIQUES

The cleaning of glassware, equipment and bench is necessary before starting a chemistry experiment. The bench should be kept clean, free from any solid or liquid chemicals. Glassware are first washed with a detergent and then rinsed with distilled water before use. The outer surface may be dried with a cloth or filter paper. All the apparatus used in a particular experiment should be kept together on the bench to avoid confusion in determining duplicate experiments. Excess of apparatus, which are not in use, should be removed from the bench. All the solutions, precipitates and filtrates should be labelled to avoid confusion and covered to prevent contamination of the contents. Reagent bottles must be transferred on the reagent shelves immediately after use. Experimental observations must be recorded in a stiff covered notebook containing an index page and remaining one-sided line pages. The record must be concluded with calculations and the results.

## GLASSWARE

### Graduated Apparatus

Graduated flasks, burettes and pipettes are the most commonly used apparatus in volumetric analysis. All these glassware must be perfectly free from greasy matter to get exact results. Many detergents are available for cleaning the glass apparatus. Saturated solution of powdered sodium/potassium dichromate in concentrated sulphuric is also used for cleaning purpose. It is generally referred as ‘chromic acid’, cleaning mixture. It possesses powerful oxidizing and solvent properties. To prepare this, dissolve 5 g of sodium dichromate in 5 ml of water and then add sufficient concentrated sulphuric acid slowly with constant stirring to make up the volume 100 ml. The temperature will rise to 70–80°C. The mixture is allowed to cool to about 40°C and then transfer to a dry, glass stoppered bottle.

### (i) Volumetric Flask

A volumetric flask (Fig. 1.1) is flat-bottomed, pear-shaped apparatus with long narrow neck. A thin line mark around the neck indicates the volume which the flask holds at a certain definite temperature, usually 20°C. The capacity and temperature are clearly marked on the flask. Both the front and the back of the mark should be seen as a single line to avoid errors due to parallax while making the final adjustment. The lower edge of the miniscus should tangential to the graduation mark. A small change in the volume is detected easily in the long narrow neck.

Volumetric flasks are available in the capacities of 1, 2, 5, 10, 20, 50, 100, 200, 250, 500, 1000, 2000, 5000 $cm^3$. The standard solutions are obtained for analysis with the help of pipette in different analytical techniques.

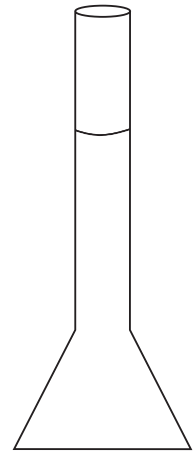

**Fig. 1.1:** Volumetric flask

### (ii) Pipettes

Pipettes are of two type:

(i) *Transfer pipettes*, which have one mark and withdraw a small and constant volume of the solutions.
(ii) *Measuring or graduated pipettes*, which are graduated and used to deliver various small volumes.

*The transfer pipette* is made up of a cylindrical bulb joined at both ends to narrower tubing. A calibration mark is present around the upper tube while the lower delivery tube is made to a fine tip. This type of pipette is used to deliver pre-determined variable volume of liquids. The transfer pipette are constructed with the capacities of 1, 2, 5, 10, 20, 25, 50 and 100 $cm^3$. The pipettes of the capacities of 10, 25, and 50 $cm^3$ are frequently used in macro work.

Before using, the pipettes are first rinsed with the liquid to be used, then filled with liquid by suction to about 2–3 cm above the mark and upper end of the pipette is closed with the tip of the finger. The liquid is allowed to run out slowly by slightly relaxing the pressure of the finger and rotating the pipette until the bottom of the meniscus just reached the graduation mark. The pipette is held vertically to fix the mark at the same level as the eye. The adhering drops at the tip are removed by stroking against a glass surface. Then the liquid is transferred into a flask keeping the tip of the pipette in contact with the wall of the flask. When all the solution is transferred, the upper end is closed with the tip of finger and the cylindrical bulb is closed with the fingers of other hand to discharge the last drop of the jet.

Corrosive or toxic liquids are drawn in the pipette with the help of rubber or plastic bulb with glass ball valves operated between finger and thumb. A piston-control is also attached to the suction end of the pipette.

Graduated pipettes are made up of straight, narrow tubes with no central bulbs. They deliver a measured volume from a top zero to a selected graduation mark or to the jet, i.e. the zero is at the set.

### (iii) Burettes

Burettes are long cylindrical tubes with uniform bore throughout the graduated length, a narrow lower end with a glass stopcock and a jet. When in use, a burette must be firmly supported on a stand with a burette holder. The stopcock should be lubricated to prevent sticking or freezing and ensure smoothness in action. Vaseline may be used as a lubricant.

Before using, the burette is thoroughly cleaned with a cleansing agent, rinsed well with distilled water, the stopcock is lubricated and fixed in a burette holder. The solution is filled with the help of a small funnel up to zero mark. The liquid is discharged from a burette into a conical flask. The flask is gently rotated with the right hand for mixing the contents well.

### Purified water

Purified distilled water is used in analytical operations. Highly purifed water is obtained by allowing tap water to percolate through a mixture of ion-exchange resins. A strong acid resin will remove cations from the water and replace them by hydrogen ions, and a strong base resin will remove anions by hydroxyl ions. Various commercial unit are available for the preparation of de-ionized water.

### Wash bottles

A wash bottle is a flat-bottomed flask fitted up to withdraw a fine stream of distilled water. The thumb is kept over the tube and water is blown out.

A polythene wash bottle is cheap, fitted with a plastic cap and a plastic jet and has flexible sides. Pressure is applied by squeezing and jet of water is controlled.

### Filtration apparatus

A conical funnel fitted with a filter paper is usually used for filtration. The funnel should have an angle nearly 60° and a long stem.

Sintered glass crucibles are made of resistance glass and have porous disc fused into body of the crucible. The filter disc is made up of various pore diameters as indicated by numbers from 0 to 5. The numbers 3 and 4 are used for gravimetric analysis. The number '0' has largest pore size while number '5' has smallest pore size.

Buchner funnel and Buchner flask are used to filter large quantity of material. The Buchner flask consists of thick-walled conical flask (Fig. 1.2) with a short side-arm for connection to a water pump. Into the neck of the flask is fitted the Buchner funnel which is pierced by a number of small holes. Before filtration, a good quality of filter paper is placed in the funnel and moistened with a few drops of liquid to be filtered.

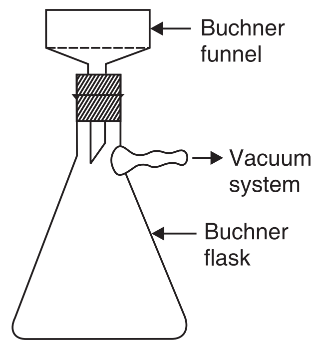


**Fig. 1.2:** Filtration assembly

## CALIBRATION OF PIPETTES, BURETTES AND GRADUATED FLASKS

The convenient unit to measure the large volume of liquid is 'litre'. The litre and millilitre are sufficiently precise for the requirements of titrimetric analysis.

The capacity of a glass vessel varies with temperature. Therefore, the temperature of the experiment should be recorded.

If high degree of accuracy is to be required, the correctness of all measuring apparatus must be tested. The process of testing is usually accomplished by comparing the actual weight of water contained in the apparatus with its apparatus volume. The weight of the water taken at a specified temperature will occupy only a definite volume at that temperature. The volumes of water for its definite weights at different specified temperatures may be known with the help of density table.

### (i) Pipette

Weigh an empty weighing bottle or a small conical flask. Fill the pipette to the mark with distilled water. Deliver the contents into the weighing bottle and reweigh. Repeat the process three times. Find out the temperature of water and with the help of density table calculate the volumes of observed weights of water. Tabulate the result as in Table1.1 and find out the correction constant of the pipette for that temperature.

### (ii) Burette

Fill a clean burette vertically clamped with distilled water. Record the temperature of this water which is same as that of room temperature. Adjust the level of the water to zero and carefully

**Table 1.1**
(temperature of water = 20°C, 1 ml = 0.9982 g)

| | Apparatus volume (ml) | Weight of empty bottle (g) | Weight of bottle + water (g) | Weight of water only (ml) | Real volume of water (ml) | Diff. | Mean |
|---|---|---|---|---|---|---|---|
| 1. | 20 | 35.5 | 55.5 | 20.0 | 20.04 | +0.04 | |
| 2. | 20 | -do- | 55.52 | 20.02 | 20.05 | +0.05 | +0.05 ml |
| 3. | 20 | -do- | 55.52 | 20.02 | 20.05 | +0.05 | |

run out a certain apparent volume into the flask which has been weighed earlier. Weigh the flask with water and find out the weight of water by difference. Carry out this process with different volumes, say 5, 10, 15, 20 ml, etc. taking always the zero mark as the starting point. Repeat the whole process and tabulate the result as in Table 1.2.

**Table 1.2**
(temperature of water = 20°C, 1 ml = 0.9982 g)

| | Burette readings apparent volume (ml) | Weight of water delivered (g) | True volume (ml) | Correction at each mark (ml) |
|---|---|---|---|---|
| 1. | 0.0 – 15.00 = 15.00 | 15.04 | 15.07 | + –0.07 |
| 2. | 15.00 – 30.00 = 15.00 | 15.00 | 15.02 | + –0.02 |
| 3. | 30.00 – 50.00 = 20.00 | 19.95 | 19.98 | + –0.02 |

The apparent volume should be substracted from the true volume and a plus correction should be added to and a minus correction should be substracted from the corresponding burette reading.

### (iii) Graduated Flask

The procedure of standardizing a measuring flask is practically same as that applied to pipette. It is only necessary to weigh the water delivered by or contained in the flask, as the case may be. Sometimes, the measuring flasks are also standardized in reference to a standardized flask knowing exactly the difference of volumes with the help of other standard apparatus such as a burette or a pipette.

## DRYING OF ORGANIC SOLUTIONS

The process of synthesizing and isolating an organic compound often results in an organic compound or solution contaminated with traces of water. For instance, in aqueous extractions some water will be transferred into the organic phase because of the partial miscibility of the organic phase and water. Also, many reactions themselves are performed in an aqueous solution. This water must be removed before the required compound can be properly characterized.

The following two methods for drying the organic solutions are commonly used:

- Saturated aqueous sodium chloride
- Solid drying agents

These two methods are described below.

### 1. Saturated Aqueous Sodium Chloride Solution

The bulk of the water can often be removed by shaking or "washing" the organic layer with saturated aqueous sodium chloride (also called brine). The salt water works to pull the water from the organic layer to the water layer. This is because the concentrated salt solution wants to become more dilute and because salts have a stronger attraction to water than to organic solvent. Traces of water are removed by treating the organic solution with a drying agent.

#### *Procedure*

(i) Place the organic solution in a separatory funnel. The organic solvent might be methylene chloride, diethyl ether, hexanes, etc., as long as it is not, of course, water.
(ii) Add an amount of saturated aqueous sodium chloride, less than or equal to the amount of organic solution you have.
(iii) Stopper the funnel and shake as in an extraction. Allow the layers to separate. The rules as to which layer is on top are the same as for extraction. Since there is a lot of salt dissolved in the water, the density of the saturated aqueous sodium chloride solution is 1.2 g/ml.

### 2. Solid Drying Agents

Some anhydrous inorganic salts like calcium chloride ($CaCl_2$), calcium sulphate ($CaSO_4$), magnesium sulphate ($MgSO_4$), potassium carbonate ($K_2CO_3$), sodium sulphate ($Na_2SO_4$), etc., which readily takes up water to become hydrated, are used routinely for drying organic solvents.

Of the five drying agents in the above table, magnesium sulphate is a fine powder and the rest are of a larger particle size. Calcium chloride, magnesium sulphate, and sodium sulphate are the three most commonly used drying agents.

#### *Procedure*

(i) Add a smaller amount of the solid drying agent directly to the organic solution. Swirl the solution.
(ii) Observe the drying agent; if it is all clumped together, add more.
(iii) Continue swirling and observing the solution for 5–15 minutes, adding more drying agent only until a fresh addition no longer forms clumps.

Each drying agent adopt a slightly different appearance when "clumped" on absorbing water and practice will make you better at judging whether the inorganic salt is wet or dry. There is no set "rule" as to how much drying agent needs to be added. The amount required depends on the amount of water in the solvent solution which you are drying, and this amount varies from experiment to experiment. Use as much as it takes to dry the solution. In most cases, drying process is completed in 20 minutes. When drying is complete, you need to remove the dried organic solution from the drying agent. There are several methods by which you can do this.

You can filter the solution by gravity filtration. If the powder is quite fine (as when using magnesium sulphate) or if the volume is large, gravity filtration is the method of choice. If the drying agent is of larger particle size (e.g. sodium sulphate or calcium chloride), decanting is the method of choice. An alternative to decanting is to remove the liquid from the drying agent simply by drawing it off with a pipet attached with rubber bulb. Squeeze the bulb of the pipet, carefully and slowly draw liquid into the pipet, leaving the solid drying agent behind.

**Note:** Sodium hydroxide (solid) is also used for drying the organic solvent. For example, pyridine becomes moisture free on distillation under anhydrous condition after adding NaOH pellets.