CHAPTER 3
COMMON APPARATUS AND BASIC TECHNIQUES

3.1 INTRODUCTION

In this chapter the more important basic techniques and the apparatus commonly used in analytical operations will be described. It is essential that the beginner should become familiar with these procedures, and also acquire dexterity in handling the various pieces of apparatus. The habit of clean, orderly working must also be cultivated, and observance of the following points will be helpful in this direction.

1. The bench must be kept clean and a bench-cloth must be available so that any spillages of solid or liquid chemicals (solutions) can be removed immediately.
2. All glassware must be scrupulously clean (see Section 3.8), and if it has been standing for any length of time, must be rinsed with distilled or de-ionised water before use. The outsides of vessels may be dried with a lint-free glass-cloth which is reserved exclusively for this purpose, and which is frequently laundered, but the cloth should not be used on the insides of the vessels.
3. Under no circumstances should the working surface of the bench become cluttered with apparatus. All the apparatus associated with some particular operation should be grouped together on the bench; this is most essential to avoid confusion when duplicate determinations are in progress. Apparatus for which no further immediate use is envisaged should be returned to the locker, but if it will be needed at a later stage, it may be placed at the back of the bench.
4. If a solution, precipitate, filtrate, etc., is set aside for subsequent treatment, the container must be labelled so that the contents can be readily identified, and the vessel must be suitably covered to prevent contamination of the contents by dust: in this context, bark corks are usually unsuitable; they invariably tend to shed some dust. For temporary labelling, a 'Chinagraph' pencil or a felt tip pen which will write directly on to glass is preferable to the gummed labels which are used when more permanent labelling is required.
5. Reagent bottles must never be allowed to accumulate on the bench; they must be replaced on the reagent shelves immediately after use.
6. It should be regarded as normal practice that all determinations are performed in duplicate.
7. A stiff covered notebook of A4 size must be provided for **recording experimental observations as they are made**. A double page should be devoted

to each determination, the title of which, together with the date, must be clearly indicated. One of the two pages must be reserved for the experimental observations, and the other should be used for a brief description of the procedure followed, but with a full account of any special features associated with the determination, In most cases it will be found convenient to divide the page on which the experimental observations are to be recorded into two halves by a vertical line, and then to halve the right-hand column thus created with a second vertical line. The left-hand side of the page can then be used to indicate the observations to be made, and the data for duplicate determinations can be recorded side by side in the two right-hand columns.

The record must conclude with the calculation of the result of the analyses, and in this connection the equation(s) for the principal chemical reaction(s) involved in the determination should be shown together with a clear exposition of the procedure used for calculating the result. Finally, appropriate comments should be made upon the degree of accuracy and the precision achieved.

Many modern instruments used in the analytical laboratory are interfaced with a computer and a printer provides a permanent record of the experimental data and the final result may even be given. This printout should be permanently attached to the observations page of the laboratory record book, and it should be regarded as normal practice to perform a 'rough' calculation to confirm that the printed result is of the right order.

8. **Safety procedures must be observed in the laboratory at all times.** Many chemicals encountered in analysis are poisonous and must be carefully handled. Whereas the dangerous properties of concentrated acids and of widely recognised poisons such as potassium cyanide are well known, the dangers associated with organo-chlorine solvents, benzene and many other chemicals are less apparent.

   Many operations involving chemical reactions are potentially dangerous, and in such cases recommended procedures must be carefully followed and obeyed. All laboratory workers should familiarise themselves with local safety requirements (in some laboratories, the wearing of safety spectacles may be compulsory), and with the position of first-aid equipment.

   For further guidance it is recommended that some study should be made of books devoted to hazards and safe practices in chemical laboratories. Some institutions and organisations issue booklets dealing with these matters and further information will be found in citations 12–17 of the Bibliography, Section 3.39.

BALANCES

3.2 THE ANALYTICAL BALANCE

One of the commonest procedures carried out by the analyst is the measurement of mass. Many chemical analyses are based upon the accurate determination of the mass of a sample, and that of a solid substance produced from it (gravimetric analysis), or upon ascertaining the volume of a carefully prepared standard solution (which contains an accurately known mass of solute) which is required to react with the sample (titrimetric analysis). For the accurate

measurement of mass in such operations, an analytical balance is employed; the operation is referred to as weighing, and invariably reference is made to the weight of the object or material which is weighed.

The weight of an object is the force of attraction due to gravity which is exerted upon the object:

$$w = mg$$

where w is the weight of the object, m its mass, and g is the acceleration due to gravity. Since the attraction due to gravity varies over the earth's surface with altitude and also with latitude, the weight of the object is variable, whereas its mass is constant. It has however become the custom to employ the term 'weight' synonymously with mass, and it is in this sense that 'weight' is employed in quantitative analysis.

The analytical balance is thus one of the most important tools of the analytical chemist, and it is one which of recent years has undergone radical changes. These changes have been prompted by the desire to produce an instrument which is more robust, less dependent upon the experience of the operator, less susceptible to the environment, and above all, one which will hasten the weighing operation. In meeting these requirements, the design of the balance has been fundamentally altered, and the conventional free-swinging, equal-arm, two-pan chemical balance together with its box of weights is now an uncommon sight.

An important development was the replacement of the two-pan balance with its three knife edges by a **two-knife single-pan balance**. In this instrument one balance pan and its suspension is replaced by a counterpoise, and dial-operated ring weights are suspended from a carrier attached to the remaining pan support: see Fig. 3.1. In this system all the weights are permanently in position on the carrier when the beam is at rest, and when an object to be weighed is placed upon the balance pan, weights must be *removed* from the carrier to compensate for the weight of the object. Weighing is completed by allowing the beam to assume its rest position, and then reading the displacement of the beam on an optical scale which is calibrated to read weights below 100 mg. Weighing is thus accomplished by **substitution**; many such manually operated balances are still in service in analytical laboratories.

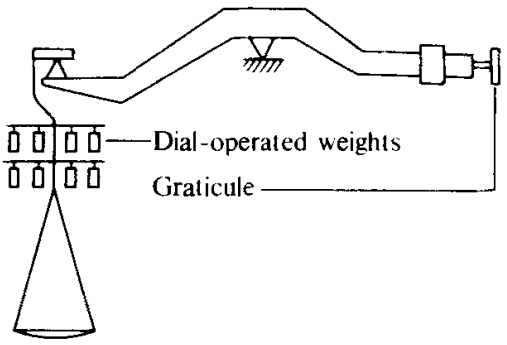

Fig. 3.1

The standard modern instrument however is the **electronic balance**, which provides convenience in weighing coupled with much greater freedom from mechanical failure, and greatly reduced sensitivity to vibration. The operations of selecting and removing weights, smooth release of balance beam and pan

support, noting the reading of weight dials and of an optical scale, returning the beam to rest, and replacing weights which have been removed, are eliminated. With an electronic balance, operation of a single on–off control permits the operator to read the weight of an object on the balance pan immediately from a digital display: most balances of this type can be coupled to a printer which gives a printed record of the weight. The majority of balances incorporate a **tare** facility which permits the weight of a container to be balanced out, so that when material is added to the container, the weight recorded is simply that of the material used. Many balances of this type incorporate a self-testing system which indicates that the balance is functioning correctly each time it is switched on, and also include a built-in weight calibration system. Operation of the calibration control leads to display of the weight of the standard incorporated within the balance, and thus indicates whether any correction is necessary. A more satisfactory calibration procedure is to check the balance readings against a series of calibrated analytical weights.

Electronic balances operate by applying an electromagnetic restoring force to the support to which the balance pan is attached, so that when an object is added to the balance pan, the resultant displacement of the support is cancelled out. The magnitude of the restoring force is governed by the value of the current flowing in the coils of the electromagnetic compensation system, and this is proportional to the weight placed on the balance pan: a microprocessor converts the value of the current into the digital display in grams.

The balance must of course be protected from draughts and from dust, and the balance pan is situated within an enclosure provided with glass doors which can be opened to provide access to the pan. The remainder of the balance, including the electrical components, is contained in a closed compartment attached to the rear of the pan compartment.

Electronic balances are available to cover weight ranges of

1. up to about 150 g and reading to 0.1 mg (macrobalance),
2. up to about 30 g and reading to 0.01 mg (semimicro balance),
3. up to about 20 g and reading to 1 μg (microbalance),
4. up to 5 g and reading to 0.1 μg (ultramicro balance).

Thus a wide variety of analytical balances is available.

3.3 OTHER BALANCES

For many laboratory operations it is necessary to weigh objects or materials which are far heavier than the upper weight limit of a macro analytical balance, or small amounts of material for which it is not necessary to weigh to the limit of sensitivity of such a balance: this type of weighing is often referred to as a 'rough weighing'. A wide range of electronic balances is available for such purposes with characteristics such as, for example,

Maximum capacity	Reading to
350 g	0.01 g
3500 g	0.1 g
6 kg	0.1 g

With these top pan balances it is not necessary to shield the balance pan from gentle draughts, and weighings can be accomplished very rapidly and with the usual facility of the results being recorded with a printer.

3.4 WEIGHTS, REFERENCE MASSES

Although with modern balances it is not necessary to make use of a box of weights in the weighing process, as indicated in Section 3.2 a set of weights is desirable for checking the accuracy of a balance.

For scientific work the fundamental standard of mass is the international prototype kilogram, which is a mass of platinum–iridium alloy made in 1887 and deposited in the International Bureau of Weights and Measures near Paris. Authentic copies of the standard are kept by the appropriate responsible authorities* in the various countries of the world; these copies are employed for the comparison of secondary standards, which are used in the calibration of weights for scientific work. The unit of mass that is almost universally employed in laboratory work, however, is the **gram**, which may be defined as the one-thousandth part of the mass of the international prototype kilogram.

An ordinary set of analytical weights contains the following: grams, 100, 50, 30, 20, 10, 5, 3, 2, 1; milligrams, 500–100 and 50–10 in the same 5, 3, 2, 1 sequence. The weights from 1 g upwards are constructed from a non-magnetic nickel–chromium alloy (80% Ni, 20% Cr), or from austenitic stainless steel; plated brass is sometimes used but is less satisfactory. The fractional weights are made from the same alloys, or from a non-tarnishable metal such as gold or platinum. For handling the weights a pair of forceps, preferably ivory-tipped, are provided and the weights are stored in a box with suitably shaped compartments.

Analytical weights can be purchased which have been manufactured to 'Class A' standard; this is the only grade of laboratory weights officially recognised in the United Kingdom. In 'Class A' weights the following tolerances are permitted: 100 g, 0.5 mg; 50 g, 0.25 mg; 30 g, 0.15 mg; 20 g, 0.10 mg; 10 g–100 mg, 0.05 mg; 50–10 mg, 0.02 mg.

The National Bureau of Standards at Washington recognises the following classes of precision weights:

Class M For use as reference standards, for work of the highest precision, and where a high degree of constancy over a period of time is required.

Class S For use as working reference standards or as high-precision analytical weights.

Class S-1 Precision analytical weights for routine analytical work.

Class J Microweight standards for microbalances.

3.5 CARE AND USE OF ANALYTICAL BALANCES

No matter what type of analytical balance is employed, due attention must be paid to the manner in which it is used. The following remarks apply particularly to electronic balances.

*The National Physical Laboratory (NPL) in Great Britain, the National Bureau of Standards (NBS) in USA, etc.

1. Never exceed the stated maximum load of the balance.
2. The balance must be kept clean. Remove dust from the pan and from the floor of the pan compartment with a camel hair brush.
3. Objects to be weighed should never be handled with the fingers; always use tongs or a loop of clean paper.
4. Objects to be weighed should be allowed to attain the temperature of the balance before weighing, and if the object has been heated, sufficient time must be allowed for cooling. The time required to attain the temperature of the balance varies with the size, etc., of the object, but as a rule 30–40 minutes is sufficient.
5. No chemicals or objects which might injure the balance pan should ever be placed directly on it. Substances must be weighed in suitable containers, such as small beakers, weighing bottles or crucibles, or upon watch glasses. Liquids and volatile or hygroscopic solids must be weighed in tightly closed vessels, such as stoppered weighing bottles.

   The addition of chemicals to the receptacle must be done outside the balance case. It is good practice to weigh the chosen receptacle on the analytical balance, to transfer it to a rough balance, to add approximately the required amount of the necessary chemical, and then to return the receptacle to the analytical balance for re-weighing, thus giving the exact weight of substance taken.
6. Nothing must be left on the pan when the weighing has been completed. If any substance is spilled accidentally upon the pan or upon the floor of the balance compartment, it must be removed at once.
7. Exposure of the balance to corrosive atmospheres must be avoided.

The actual weighing process will include the following steps.

1. Brush the balance pan lightly with a camel hair brush to remove any dust.
2. With the balance at rest, place the object to be weighed, which must be at or close to room temperature, on the pan, and close the pan compartment case.
3. Set the on/off control of the balance to the 'on' position and record the weight shown on the digital display: if the balance is linked to a printer, confirm that the printed result agrees with the digital display. Return the control to the 'off' position.
4. When all weighings have been completed, remove the object which has been weighed, clear up any accidental spillages, and close the pan compartment.

The above remarks apply particularly to analytical balances of the macrobalance range; microbalances and ultramicro balances must be handled with special care, particularly with regard to the temperature of objects to be weighed.

3.6 ERRORS IN WEIGHING

The chief sources of error are the following:

1. Change in the condition of the containing vessel or of the substance between successive weighings.
2. Effect of the buoyancy of the air upon the object and the weights.
3. Errors in recording the weights.

1. The first source of error is occasioned by change in weight of the containing vessel: (*a*) by absorption or loss of moisture, (*b*) by electrification of the

surface caused by rubbing, and (*c*) by its temperature being different from that of the balance case. These errors may be largely eliminated by wiping the vessel gently with a linen cloth, and allowing it to stand at least 30 minutes in proximity to the balance before weighing. The electrification, *which may cause a comparatively large error, particularly if both the atmosphere and the cloth are dry*, is slowly dissipated on standing; it may be removed by subjecting the vessel to the discharge from an antistatic gun. Hygroscopic, efflorescent, and volatile substances must be weighed in completely closed vessels. Substances which have been heated in an air oven or ignited in a crucible are generally allowed to cool in a desiccator containing a suitable drying agent. The time of cooling in a desiccator cannot be exactly specified, since it will depend upon the temperature and upon the size of the crucible as well as upon the material of which it is composed. Platinum vessels require a shorter time than those of porcelain, glass, or silica. It has been customary to leave platinum crucibles in the desiccator for 20–25 minutes, and crucibles of other materials for 30–35 minutes before being weighed. It is advisable to cover crucibles and other open vessels.

2. When a substance is immersed in a fluid, its true weight is diminished by the weight of the fluid which it displaces. If the object and the weights have the same density, and consequently the same volume, no error will be introduced on this account. If, however, as is usually the case, the density of the object is different from that of the weights, the volumes of air displaced by each will be different. If the substance has a lower density than the weights, as is usual in analysis, the former will displace a greater volume of air than the latter, and it will therefore weigh less in air than in a vacuum. Conversely, if a denser material (e.g. one of the precious metals) is weighed, the weight in a vacuum will be less than the apparent weight in air.

   Consider the weighing of 1 litre of water, first *in vacuo*, and then in air. It is assumed that the flask containing the water is tared by an exactly similar flask, that the temperature of the air is 20 °C and the barometric pressure is 101 325 Pa (760 mm of mercury). The weight of 1 litre of water *in vacuo* under these conditions is 998.23 g. If the water is weighed in air, it will be found that 998.23 g are too heavy. We can readily calculate the difference. The weight of 1 litre of air displaced by the water is 1.20 g. Assuming the weights to have a density of 8.0, they will displace $998.23/8.0 = 124.8$ mL, or $124.8 \times 1.20/1000 = 0.15$ g of air. The net difference in weight will therefore be $1.20 - 0.15 = 1.05$ g. Hence the weight in air of 1 litre of water under the experimental conditions named is $998.23 - 1.05 = 997.18$ g, a difference of 0.1 per cent from the weight *in vacuo*.

   Now consider the case of a solid, such as potassium chloride, under the above conditions. The density of potassium chloride is 1.99. If 2 g of the salt are weighed, the apparent loss in weight (= weight of air displaced) is $2 \times 0.0012/1.99 = 0.0012$ g. The apparent loss in weight for the weights is $2 \times 0.0012/8.0 = 0.000\,30$ g. Hence 2 g of potassium chloride will weigh $0.0012 - 0.000\,30 = 0.000\,90$ g less in air than *in vacuo*, a difference of 0.05 per cent.

   It must be pointed out that for most analytical purposes where it is desired to express the results in the form of a percentage, the ratio of the weights in air, so far as solids are concerned, will give a result which is practically the same as that which would be given by the weights *in vacuo*. Hence no buoyancy

correction is necessary in these cases. However, where absolute weights are required, as in the calibration of graduated glassware, corrections for the buoyancy of the air must be made (compare Section 3.16). Although an electronic balance does not employ any weights, the above remarks apply to weights recorded by the balance because the balance scale will have been established by reference to metal (stainless steel) weights used in air.

Now consider the general case. It is evident that the weight of an object *in vacuo* is equal to the weight in air *plus* the weight of air displaced by the object *minus* the weight of air displaced by the weights. It can easily be shown that if W_v = weight *in vacuo*, W_a = apparent weight in air, d_a = density of air, d_w = density of the weights, and d_b = density of the body, then:

$$W_v = W_a + d_a\left(\frac{W_v}{d_b} - \frac{W_a}{d_w}\right)$$

The density of the air will depend upon the humidity, the temperature, and the pressure. For an average relative humidity (50 per cent) and average conditions of temperature and pressure in a laboratory, the density of the air will rarely fall outside the limits 0.0011 and 0.0013 g mL^{-1}. It is therefore permissible for analytical purposes to take the weight of 1 mL of air as 0.0012 g.

Since the difference between W_v and W_a does not usually exceed 1 to 2 parts per thousand, we may write:

$$W_v = W_a + d_a\left(\frac{W_a}{d_b} - \frac{W_a}{d_w}\right)$$

$$= W_a + W_a\left\{0.0012\left(\frac{1}{d_b} - \frac{1}{8.0}\right)\right\} = W_a + kW_a/1000$$

where

$$k = 1.20\left(\frac{1}{d_b} - \frac{1}{8.0}\right)$$

If a substance of density d_b weighs W_a grams in air, then $W_a.k$ milligrams are to be added to the weight in air in order to obtain the weight *in vacuo*. The correction is positive if the substance has a density lower than 8.0, and negative if the density of the substance is greater than 8.0.

3. The correct reading of weights is best achieved by checking weights as they are added to the balance *and* as they are removed from the balance. In the case of electronic balances any digital displays should be read at least twice.

GRADUATED GLASSWARE

3.7 UNITS OF VOLUME

For scientific purposes the convenient unit to employ for measuring reasonably large volumes of liquids is the cubic decimetre (dm^3), or, for smaller volumes, the cubic centimetre (cm^3). For many years the fundamental unit employed was the *litre*, based upon the volume occupied by one kilogram of water at 4 °C (the temperature of maximum density of water): the relationship between the litre

as thus defined and the cubic decimetre was established as

1 litre = 1.000 028 dm^3 or 1 millilitre = 1.000 028 cm^3.

In 1964 the *Conférence Générale des Poids et des Mésures* (CGPM) decided to accept the term **litre** as a special name for the cubic decimetre, and to discard the original definition. With this new meaning of the term litre (L), the millilitre (mL) and the cubic centimetre (cm^3) are identical.

3.8 GRADUATED APPARATUS

The most commonly used pieces of apparatus in titrimetric (volumetric) analysis are graduated flasks, burettes, and pipettes. Graduated cylinders and weight pipettes are less widely employed. Each of these will be described in turn.

Graduated apparatus for quantitative analysis is generally made to specification limits, particularly with regard to the accuracy of calibration. In the United Kingdom there are two grades of apparatus available, designated Class A and Class B by the British Standards Institution. The tolerance limits are closer for Class A apparatus, and such apparatus is intended for use in work of the highest accuracy: Class B apparatus is employed in routine work. In the United States, specifications for only one grade are available from the National Bureau of Standards at Washington, and these are equivalent to the British Class A.

Cleaning of glass apparatus. Before describing graduated apparatus in detail, reference must be made to the important fact that all such glassware must be perfectly clean and free from grease, otherwise the results will be unreliable. One test for cleanliness of glass apparatus is that on being filled with distilled water and the water withdrawn, only an unbroken film of water remains. If the water collects in drops, the vessel is dirty and must be cleaned. Various methods are available for cleaning glassware.

Many commercially available detergents are suitable for this purpose, and some manufacturers market special formulations for cleaning laboratory glassware; some of these, e.g. 'Decon 90' made by Decon Laboratories of Portslade, are claimed to be specially effective in removing contamination due to radioactive materials.

'Teepol' is a relatively mild and inexpensive detergent which may be used for cleaning glassware. The laboratory stock solution may consist of a 10 per cent solution in distilled water. For cleaning a burette, 2 mL of the stock solution diluted with 50 mL of distilled water are poured into the burette, allowed to stand for $\frac{1}{2}$ to 1 minute, the detergent run off, the burette rinsed three times with tap water, and then several times with distilled water. A 25 mL pipette may be similarly cleaned using 1 mL of the stock solution diluted with 25–30 mL of distilled water.

A method which is frequently used consists in filling the apparatus with 'chromic acid cleaning mixture' (**CARE**), a nearly saturated solution of powdered sodium dichromate or potassium dichromate in concentrated sulphuric acid, and allowing it to stand for several hours, preferably overnight; the acid is then poured off, the apparatus thoroughly rinsed with distilled water, and allowed to drain until dry. [It may be mentioned that potassium dichromate is not very soluble in concentrated sulphuric acid (about 5 g per litre), whereas

sodium dichromate ($Na_2Cr_2O_7,2H_2O$) is much more soluble (about 70 g per litre); for this reason, as well as the fact that it is much cheaper, the latter is usually preferred for the preparation of 'cleaning mixture'. From time to time it is advisable to filter the sodium dichromate–sulphuric acid mixture through a little glass wool placed in the apex of a glass funnel: small particles or sludge, which are often present and may block the tips of burettes, are thus removed. A more efficient cleaning liquid is a mixture of concentrated sulphuric acid and fuming nitric acid; this may be used if the vessel is very greasy and dirty, but must be handled with extreme caution.

A very effective degreasing agent, which it is claimed is much quicker-acting than 'cleaning mixture' is obtained by dissolving 100 g of potassium hydroxide in 50 mL of water, and after cooling, making up to 1 litre with industrial methylated spirit.[6a]

3.9 TEMPERATURE STANDARD

The capacity of a glass vessel varies with the temperature, and it is therefore necessary to define the temperature at which its capacity is intended to be correct: in the UK a temperature of 20 °C has been adopted. A subsidiary standard temperature of 27 °C is accepted by the British Standards Institution, for use in tropical climates where the ambient temperature is consistently above 20 °C. The US Bureau of Standards, Washington, in compliance with the view held by some chemists that 25 °C more nearly approximates to the average laboratory temperature in the United States, will calibrate glass volumetric apparatus marked either 20 °C or 25 °C.

Taking the coefficient of cubical expansion of soda glass as about 0.000 030 and of borosilicate glass about 0.000 010 per 1 °C, Part A of Table 3.1 gives the correction to be added when the sign is +, or subtracted when the sign is −, to or from the capacity of a 1000 mL flask correct at 20 °C in order to obtain the capacity at other temperatures.

In the use of graduated glassware for measurement of the volume of liquids, the expansion of the liquid must also be taken into consideration if temperature corrections are to be made. Part B of Table 3.1 gives the corrections to be added or subtracted in order to obtain the volume occupied at 20 °C by a volume of water which at the tabulated temperature is contained in an accurate 1000 mL flask having a standard temperature of 20 °C. It will be seen that the allowance for the expansion of water is considerably greater than that for the expansion

Table 3.1 Temperature corrections for a 1 L graduated flask

Temperature (°C)	(A) Expansion of glass		(B) Expansion of water	
	Correction (mL)		Correction (mL)	
	Soda glass	Borosilicate glass	Soda glass	Borosilicate glass
5	−0.39	−0.15	+1.37	+1.61
10	−0.26	−0.10	+1.24	+1.40
15	−0.13	−0.05	+0.77	+0.84
20	0.00	0.00	0.00	0.00
25	+0.13	+0.05	−1.03	−1.11
30	+0.26	+0.10	−2.31	−2.46

of the glass. For dilute (e.g. 0.1 *M*) aqueous solutions, the corrections can be regarded as approximately the same as for water, but with more concentrated solutions the correction increases, and for non-aqueous solutions the corrections can be quite large.[6b]

3.10 GRADUATED FLASKS

A graduated flask (known alternatively as a volumetric flask or a measuring flask), is a flat-bottomed, pear-shaped vessel with a long narrow neck. A thin line etched around the neck indicates the volume that it holds at a certain definite temperature, usually 20 °C (both the capacity and temperature are clearly marked on the flask); the flask is then said to be graduated *to contain.* Flasks with one mark are always taken *to contain* the volume specified. A flask may also be marked *to deliver* a specified volume of liquid under certain definite conditions; these are, however, not suitable for exact work and are not widely used. Vessels intended to contain definite volumes of liquid are marked C or TC or In, while those intended to deliver definite volumes are marked D or TD or Ex.

The mark extends completely around the neck in order to avoid errors due to parallax when making the final adjustment; the lower edge of the meniscus of the liquid should be tangential to the graduation mark, and both the front and the back of the mark should be seen as a single line. The neck is made narrow so that a small change in volume will have a large effect upon the height of the meniscus: the error in adjustment of the meniscus is accordingly small.

The flasks should be fabricated in accordance with BS 5898 (1980)* and the opening should be ground to standard (interchangeable) specifications and fitted with an interchangeable glass or plastic (commonly polypropylene) stopper. They should conform to either Class A or Class B specification BS 1792 (1982); examples of permitted tolerances for Class B grade are as follows:

Flask size	5	25	100	250	1000 mL
Tolerance	0.04	0.06	0.15	0.30	0.80 mL

For Class A flasks the tolerances are approximately halved: such flasks may be purchased with a works calibration certificate, or with a British Standard Test (BST) Certificate.

Graduated flasks are available in the following capacities: **1**, 2, 5, 10, 20, 50, 100, 200, 250, 500, 1000, 2000 and 5000 mL. They are employed in making up standard solutions to a given volume; they can also be used for obtaining, with the aid of pipettes, aliquot portions of a solution of the substance to be analysed.

3.11 PIPETTES

Pipettes are of two kinds: (i) those which have one mark and *deliver* a small, constant volume of liquid under certain specified conditions (transfer pipettes);

* Many modern British Standards are closely linked to the specifications laid down by the International Standardisation Organisation based in Geneva; in the above example the relevant reference is to ISO 384-1978.[7]

(ii) those in which the stems are graduated and are employed to deliver various small volumes at discretion (graduated or measuring pipettes).

The **transfer pipette** consists of a cylindrical bulb joined at both ends to narrower tubing: a calibration mark is etched around the upper (suction) tube, while the lower (delivery) tube is drawn out to a fine tip. The graduated or measuring pipette is usually intended for the delivery of pre-determined variable volumes of liquid: it does not find wide use in accurate work, for which a burette is generally preferred. Transfer pipettes are constructed with capacities of 1, 2, 5, 10, 20, 25, 50 and 100 mL; those of 10, 25 and 50 mL capacity are most frequently employed in macro work. They should conform to BS 1583 (1986); ISO 648-1984 and should carry a colour code ring at the suction end to identify the capacity [BS 5898 (1980)]: as a safety measure an additional bulb is often incorporated above the graduation mark. They may be fabricated from lime-soda or Pyrex glass, and some high-grade pipettes are manufactured in Corex glass (Corning Glass Works, USA). This is glass which has been subjected to an ion exchange process which strengthens the glass and also leads to a greater surface hardness, thus giving a product which is resistant to scratching and chipping. Pipettes are available to Class A and Class B specifications: for the latter grade typical tolerance values are:

Pipette capacity	5	10	25	50	100 mL
Tolerance	0.01	0.04	0.06	0.08	0.12 mL

whilst for Class A, the tolerances are approximately halved.

To use such pipettes, a suitable **pipette filler** is first attached to the upper or suction tube. These devices are obtainable in various forms, a simple version consisting of a rubber or plastic bulb fitted with glass ball valves which can be operated between finger and thumb: these control the entry and expulsion of air from the bulb and thus the flow of liquid into and out of the pipette. **Suction by mouth must never be used to fill a pipette with liquid chemicals or with a solution containing chemicals.**

The pipette is then rinsed with a little of the liquid to be transferred, and then filled with the liquid to about 1–2 cm above the graduation mark. Any adhering liquid is removed from the outside of the lower stem by wiping with a piece of filter paper, and then by careful manipulation of the filler, the liquid is allowed to run out slowly until the bottom of the meniscus just reaches the graduation mark: the pipette must be held vertically and with the graduation mark at eye-level. Any drops adhering to the tip are removed by stroking against a glass surface. The liquid is then allowed to run into the receiving vessel, the tip of the pipette touching the wall of the vessel. When the continuous discharge has ceased, the jet is held in contact with the side of the vessel for 15 seconds (**draining time**). At the end of the draining time, the tip of the pipette is removed from contact with the wall of the receptacle; the liquid remaining in the jet of the pipette must not be removed either by blowing or by other means.

A pipette will not deliver constant volumes of liquid if discharged too rapidly. The orifice must be of such size that the time of outflow is about 20 seconds for a 10 mL pipette, 30 seconds for a 25 mL pipette, and 35 seconds for a 50 mL pipette.

Graduated pipettes consist of straight, fairly narrow tubes with no central bulb, and are also constructed to a standard specification [BS 6696 (1986)];

they are likewise colour-coded in accordance with ISO 1769. Three different types are available:

Type 1 delivers a measured volume from a top zero to a selected graduation mark;

Type 2 delivers a measured volume from a selected graduation mark to the jet: i.e. the zero is at the jet;

Type 3 is calibrated to *contain* a given capacity from the jet to a selected graduation mark, and thus to *remove* a selected volume of solution.

For Type 2 pipettes the final drop of liquid remaining in the tip must be expelled, which is contrary to the usual procedure. Such pipettes are therefore distinguished by a white or sand-blasted ring near the top of the pipette.

For dealing with smaller volumes of solution, **micropipettes**, often referred to as **syringe pipettes**, are employed. These can be of a 'push-button' type, in which the syringe is operated by pressing a button on the top of the pipette: the plunger travels between two fixed stops and so a remarkably constant volume of liquid is delivered. Such pipettes are fitted with disposable plastic tips (usually of polythene or polypropylene) which are not wetted by aqueous solutions, thus helping to ensure constancy of the volume of liquid delivered. The liquid is contained entirely within the plastic tip and so, by replacing the tip, the same pipette can be employed for different solutions. Such pipettes are available to deliver volumes of 1 to 1000 μL, and the delivery is reproducible to within about 1 per cent.

Microlitre syringe pipettes are available with capacities ranging from 10 to 250 μL and with the body of the pipette calibrated. When fitted with a needle tip they are particularly useful for introducing liquids into gas chromatographs (Chapter 9).

Micrometer syringe pipettes are fitted with a micrometer head which operates the plunger of the syringe, and when fitted with a stainless steel needle tip can be used for the dropwise addition of liquid; the volume added is recorded by the micrometer.

Automatic pipettes. The Dafert pipette (Fig. 3.2) is an automatic version of a transfer pipette. One side of the two-way tap is connected to a reservoir containing the solution to be dispensed. When the tap is in the appropriate position, solution fills the pipette completely, excess solution draining away

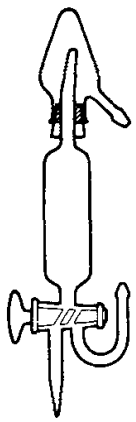

Fig. 3.2

through the overflow chamber. The pipette now contains a definite volume of solution which is delivered to the receiver by appropriate manipulation of the tap. These pipettes, are available in a range of sizes from 5–100 mL and are useful in routine work.

Autodispensers are also useful for measuring definite volumes of solutions on a routine basis. Solution is forced out of a container by depressing a syringe plunger: the movement of the plunger and hence the volume of liquid dispensed are controlled by means of a moveable clamp. The plunger is spring-loaded so that, when released, it returns to its original position and is immediately ready for operation again.

Tilting pipettes, which are attached to a reagent bottle, are only suitable for delivering approximate volumes of solution.

3.12 BURETTES

Burettes are long cylindrical tubes of uniform bore throughout the graduated length, terminating at the lower end in a glass stopcock and a jet; in cheaper varieties, the stopcock may be replaced by a rubber pinch valve incorporating a glass sphere. A diaphragm-type plastic burette tap is marketed: this can be fitted to an ordinary burette and provides a delicate control of the outflow of liquid. The merits claimed include: (*a*) the tap cannot stick, because the liquid in the burette cannot come into contact with the threaded part of the tap; (*b*) no lubricant is generally required; (*c*) there is no contact between ground glass surfaces; and (*d*) burettes and taps can be readily replaced. Burette taps made of polytetrafluoroethylene (PTFE or Teflon) are also available; these have the great advantage that no lubricant is required.

It is sometimes advantageous to employ a burette with an extended jet which is bent twice at right angles so that the tip of the jet is displaced by some 7.5–10 cm from the body of the burette. Insertion of the tip of the burette into complicated assemblies of apparatus is thus facilitated, and there is a further advantage, that if heated solutions have to be titrated the body of the burette is kept away from the source of heat. Burettes fitted with two-way stopcocks are useful for attachment to reservoirs of stock solutions.

As with other graduated glassware, burettes are produced to both Class A and Class B specifications in accordance with the appropriate standard [BS 846 (1985); ISO 385 (1984)], and Class A burettes may be purchased with BST Certificates. All Class A and some Class B burettes have graduation marks which completely encircle the burette; this is a very important feature for the avoidance of parallax errors in reading the burette. Typical values for the tolerances permitted for Class A burettes are:

Total capacity	5	10	50	100 mL
Tolerance	0.02	0.02	0.05	0.10 mL

For Class B, these values are approximately doubled. In addition to the volume requirements, limits are also imposed on the length of the graduated part of the burette and on the drainage time.

When in use, a burette must be firmly supported on a stand, and various types of burette holders are available for this purpose. The use of an ordinary

laboratory clamp is not recommended: the ideal type of holder permits the burette to be read without the need of removing it from the stand.

Lubricants for glass stopcocks. The object of lubricating the stopcock of a burette is to prevent sticking or 'freezing' and to ensure smoothness in action. The simplest lubricant is pure Vaseline, but this is rather soft, and, unless used sparingly, portions of the grease may readily become trapped at the point where the jet is joined to the barrel of the stopcock, and lead to blocking of the jet. Various products are available commercially which are better suited to the lubrication of burette stopcocks. **Silicone-containing lubricants must be avoided** since they tend to 'creep' with consequent contamination of the walls of the burette.

To lubricate the stopcock, the plug is removed from the barrel and two thin streaks of lubricant are applied to the length of the plug on lines roughly midway between the ends of the bore of the plug. Upon replacing in the barrel and turning the tap a few times, a uniform thin film of grease is distributed round the ground joint. A spring or some other form of retainer may be subsequently attached to the key to lessen the chance of it becoming dislodged when in use.

Reference is again made to the Teflon stopcocks and to the diaphragm type of burette tap which do not require lubrication.

Mode of use of a burette. If necessary, the burette is thoroughly cleaned using one of the cleaning agents described in Section 3.8 and is then well rinsed with distilled water. The plug of the stopcock is removed from the barrel, and after wiping the plug and the inside of the barrel dry, the stopcock is lubricated as described in the preceding paragraph. Using a small funnel, about 10 mL of the solution to be used are introduced into the burette, and then after removing the funnel, the burette is tilted and rotated so that the solution flows over the whole of the internal surface; the liquid is then discharged through the stopcock. After repeating the rinsing process, the burette is clamped *vertically* in the burette holder and then filled with the solution to a little above the zero mark. The funnel is removed, and the liquid discharged through the stopcock until the lowest point of the liquid meniscus is just below the zero mark; the jet is inspected to ensure that all air bubbles have been removed and that it is completely full of liquid. To read the position of the meniscus, the eye must be at the same level as the meniscus, in order to avoid errors due to parallax. In the best type of burette, the graduations are carried completely round the tube for each millilitre (mL) and half-way round for the other graduation marks: parallax is thus easily avoided. To aid the eye in reading the position of the meniscus a piece of white paper or cardboard, the lower half of which is blackened either by painting with dull black paint or by pasting a piece of dull black paper upon it, is employed. When this is placed so that the sharp dividing line is 1–2 mm below the meniscus, the bottom of the meniscus appears to be darkened and is sharply outlined against the white background; the level of the liquid can then be accurately read. A variety of 'burette readers' are available from laboratory supply houses, and a home-made device which is claimed to be particularly effective has been described by Woodward and Redman.[6c] For all ordinary purposes readings are made to 0.05 mL, but for precision work, readings should be made to 0.01–0.02 mL, using a lens to assist the estimation of the subdivisions.

To deliver liquid from a burette into a conical flask or other similar receptacle,

place the fingers of the left hand behind the burette and the thumb in front, and hold the tap between the thumb and the fore and middle fingers. In this way, there is no tendency to pull the plug out of the barrel of the stopcock, and the operation is under complete control. Any drop adhering to the jet after the liquid has been discharged is removed by bringing the side of the receiving vessel into contact with the jet. During the delivery of the liquid, the flask may be gently rotated with the right hand to ensure that the added liquid is well mixed with any existing contents of the flask.

3.13 WEIGHT BURETTES

For work demanding the highest possible accuracy in transferring various quantities of liquids, weight burettes are employed. As their name implies, they are weighed before and after a transfer of liquid. A very useful form is shown diagrammatically in Fig. 3.3(*a*). There are two ground-glass caps of which the lower one is closed, whilst the upper one is provided with a capillary opening; the loss by evaporation is accordingly negligible. For hygroscopic liquids, a small ground-glass cap is fitted to the top of the capillary tube. The burette is roughly graduated in 5 mL intervals. The titre thus obtained is in terms of weight loss of the burette, and for this reason the titrants are prepared on a weight/weight basis rather than a weight/volume basis. The errors associated with the use of a volumetric burette, such as those of drainage, reading, and change in temperature, are obviated, and weight burettes are especially useful when dealing with non-aqueous solutions or with viscous liquids.

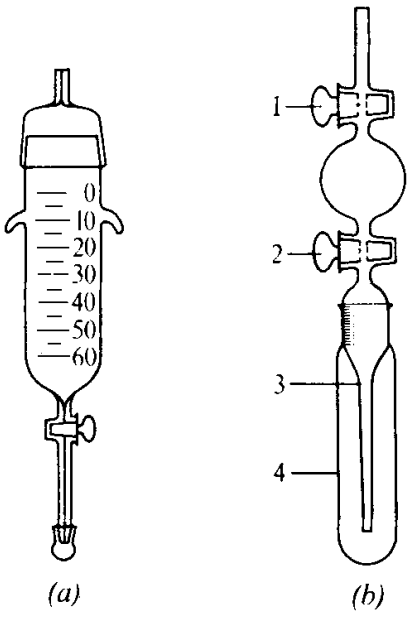

Fig. 3.3

An alternative form of weight burette due to Redman[6d] consists of a glass bulb, flattened on one side so that it will stand on a balance pan. Above the flattened side is the stopcock-controlled discharge jet, and a filling orifice which is closed with a glass stopper. The stopper and short neck into which it fits are pierced with holes, by alignment of which air can be admitted, thus permitting discharge of the contents of the burette through the delivery jet.

The **Lunge–Rey pipette** is shown in Fig. 3.3(*b*). There is a small central bulb (5–10 mL capacity) closed by two stopcocks 1 and 2; the pipette 3 below the stopcock has a capacity of about 2 mL, and is fitted with a ground-on test-tube 4. This pipette is of particular value for the weighing out of corrosive and fuming liquids.

3.14 PISTON BURETTES

In piston burettes, the delivery of the liquid is controlled by movement of a tightly fitting plunger within a graduated tube of uniform bore. They are particularly useful when the piston is coupled to a motor drive, and in this form serve as the basis of automatic titrators. These instruments can provide automatic plotting of titration curves, and provision is made for a variable rate of delivery as the end point is approached so that there is no danger of overshooting the end point.

3.15 GRADUATED (MEASURING) CYLINDERS

These are graduated vessels available in capacities from 2 to 2000 mL. Since the area of the surface of the liquid is much greater than in a graduated flask, the accuracy is not very high. Graduated cylinders cannot therefore be employed for work demanding even a moderate degree of accuracy. They are, however, useful where only rough measurements are required.

3.16 CALIBRATION OF VOLUMETRIC APPARATUS

For most analytical purposes, volumetric apparatus manufactured to Class A standard will prove to be satisfactory, but for work of the highest accuracy it is advisable to calibrate all apparatus for which a *recent* test certificate is unavailable. The calibration procedure involves determination of the weight of water contained in or delivered by the particular piece of apparatus. The temperature of the water is observed, and from the known density of water at that temperature, the volume of water can be calculated. Tables giving density values are usually based on weights *in vacuo* (Section 3.6), but the data given in Table 3.2 are based on weighings in air with stainless-steel weights, and these can be used to calculate the relevant volume directly from the observed weight of water. It is suggested that the data given in the table be plotted on a graph so that the volume of 1 gram of water at the exact temperature at which the calibration was performed can be ascertained. Fuller tables are given in BS 6696 (1986).

Table 3.2 Volume of 1 g of water at various temperatures

Temp. (°C)	Volume (mL)	Temp. (°C)	Volume (mL)
10.00	1.0013	22.00	1.0033
12.00	1.0015	24.00	1.0037
14.00	1.0017	26.00	1.0044
16.00	1.0021	28.00	1.0047
18.00	1.0023	30.00	1.0053
20.00	1.0027		

In all calibration operations, the apparatus to be calibrated must be carefully cleaned and allowed to stand adjacent to the balance which is to be employed, together with a supply of distilled or de-ionised water, so that they assume the temperature of the room. Flasks will also need to be dried, and this can be accomplished by rinsing twice with a little acetone and then blowing a current of air through the flask to remove the acetone.

Graduated flask. After allowing the clean dry flask to stand in the balance room for an hour it is stoppered and weighed. A small filter funnel, the stem of which has been drawn out so that it reaches below the graduation mark of the flask, is then inserted into the neck and de-ionised (distilled) water, which has also been standing in the balance room for an hour, is added slowly until the mark is reached. The funnel is then carefully removed, taking care not to wet the neck of the flask above the mark, and then, using a dropping tube, water is added dropwise until the meniscus stands on the graduation mark. The stopper is replaced, the flask re-weighed, and the temperature of the water noted. The true volume of the water filling the flask to the graduation mark can be calculated with the aid of Table 3.2.

Pipette. The pipette is filled with the distilled water which has been standing in the balance room for at least an hour, to a short distance above the mark. Water is run out until the meniscus is exactly on the mark, and the out-flow is then stopped. The drop adhering to the jet is removed by bringing the surface of some water contained in a beaker in contact with the jet, and then removing it without jerking. The pipette is then allowed to discharge into a clean, weighed stoppered flask (or a large weighing bottle) and held so that the jet of the pipette is in contact with the side of the vessel (it will be necessary to incline slightly either the pipette or the vessel). The pipette is allowed to drain for 15 seconds after the outflow has ceased, the jet still being in contact with the side of the vessel. At the end of the draining time the receiving vessel is removed from contact with the tip of the pipette, thus removing any drop adhering to the outside of the pipette and ensuring that the drop remaining in the end is always of the same size. To determine the instant at which the outflow ceases, the motion of the water surface down the delivery tube of the pipette is observed, and the delivery time is considered to be complete when the meniscus comes to rest slightly above the end of the delivery tube. The draining time of 15 seconds is counted from this moment. The receiving vessel is weighed, and the temperature of the water noted. The capacity of the pipette is then calculated with the aid of Table 3.2. At least two determinations should be made.

Burette. If it is necessary to calibrate a burette, it is essential to establish that it is satisfactory with regard to (*a*) leakage, and (*b*) delivery time, before undertaking the actual calibration process. To test for leakage, the plug is removed from the barrel of the stopcock and both parts of the stopcock are carefully cleaned of all grease; after wetting well with de-ionised water, the stopcock is reassembled. The burette is placed in the holder, filled with distilled (de-ionised) water, adjusted to the zero mark, and any drop of water adhering to the jet removed with a piece of filter paper. The burette is then allowed to stand for 20 minutes, and if the meniscus has not fallen by more than one scale division, the burette may be regarded as satisfactory as far as leakage is concerned.

To test the delivery time, again separate the components of the stopcock, dry, grease and reassemble, then fill the burette to the zero mark with distilled water, and place in the holder. Adjust the position of the burette so that the jet comes inside the neck of a conical flask standing on the base of the burette stand, but does not touch the side of the flask. Open the stopcock fully, and note the time taken for the meniscus to reach the lowest graduation mark of the burette: this should agree closely with the time marked on the burette, and in any case, must fall within the limits laid down by BS 846 (1985).

If the burette passes these two tests, the calibration may be proceeded with. Fill the burette with the distilled water which has been allowed to stand in the balance room to acquire room temperature: ideally, this should be as near to 20 °C as possible. Weigh a clean, dry stoppered flask of about 100 mL capacity, then, after adjusting the burette to the zero mark and removing any drop adhering to the jet, place the flask in position under the jet, open the stopcock fully and allow water to flow into the flask. As the meniscus approaches the desired calibration point on the burette, reduce the rate of flow until eventually it is discharging dropwise, and adjust the meniscus exactly to the required mark. Do not wait for drainage, but remove any drop adhering to the jet by touching the neck of the flask against the jet, then re-stopper and re-weigh the flask. Repeat this procedure for each graduation to be tested; for a 50 mL burette, this will usually be every 5 mL. Note the temperature of the water, and then, using Table 3.2, the volume delivered at each point is calculated from the weight of water collected. The results are most conveniently used by plotting a calibration curve for the burette.

WATER FOR LABORATORY USE

3.17 PURIFIED WATER

From the earliest days of quantitative chemical measurements it has been recognised that some form of purification is required for water which is to be employed in analytical operations, and with increasingly lower limits of detection being attained in instrumental methods of analysis, correspondingly higher standards of purity are imposed upon the water used for preparing solutions. Standards have now been laid down for water to be used in laboratories,[8] which prescribe limits for non-volatile residue, for residue remaining after ignition, for pH and for conductance. The British Standard 3978 (1987) (ISO 3696-1987) recognises three different grades of water.

(*a*) *Grade 3* is suitable for ordinary analytical purposes and may be prepared by single distillation of tap water, by de-ionisation, or by reverse osmosis: see below.

(*b*) *Grade 2* is suitable for more sensitive analytical procedures, such as atomic absorption spectroscopy and the determination of substances present in trace quantities. Water of this quality can be prepared by redistillation of Grade 3 distilled water, or by the distillation of de-ionised water, or of the product of reverse osmosis procedures.

(*c*) *Grade 1* water is suitable for the most stringent requirements including high-performance liquid chromatography and the determination of substances present in ultratrace amounts. Such water is obtained by subjecting

Grade 2 water to reverse osmosis or de-ionisation, followed by filtration through a membrane filter of pore size 0.2 μm to remove particulate matter. Alternatively, Grade 2 water may be redistilled in an apparatus constructed from fused silica.

The standards laid down for the three grades of water are summarised in Table 3.3.

Table 3.3 Standards for water to be used in analytical operations

	Grade of water		
Parameter	**1**	**2**	**3**
pH at 25 °C	*	*	5.0–7.5
Electrical conductance, mS m^{-1} at 25 °C	0.01	0.1	0.5
Oxidisable matter (equivalent to mg oxygen L^{-1})	†	0.08	0.4
Absorbance at 254 nm, 1 cm cell	0.001	0.01	‡
Residue after evaporation, mg kg^{-1}	†	1	2
SiO_2 content, mg L^{-1}	0.01	0.02	‡

* pH measurements in highly purified water are difficult; results are of doubtful significance.
† Not applicable.
‡ Not specified.

For many years the sole method of purification available was by distillation, and distilled water was universally employed for laboratory purposes. The modern water-still is usually made of glass and is heated electrically, and provision is made for interrupting the current in the event of failure of the cooling water, or of the boiler-feed supply; the current is also cut off when the receiver is full.

Pure water can also be obtained by allowing tap water to percolate through a mixture of ion exchange resins: a strong acid resin which will remove cations from the water and replace them by hydrogen ions, and a strong base resin (OH^- form) which will remove anions. A number of units are commercially available for the production of **de-ionised water**, and the usual practice is to monitor the quality of the product by means of a conductance meter. The resins are usually supplied in an interchangeable cartridge, so that maintenance is reduced to a minimum. A mixed-bed ion exchange column fed with distilled water is capable of producing water with the very low conductance of about $2.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ ($2.0\ \mu s\ cm^{-1}$), but in spite of this very low conductance, the water may contain traces of organic impurities which can be detected by means of a spectrofluorimeter. For most purposes, however, the traces of organic material present in de-ionised water can be ignored, and it may be used in most situations where distilled water is acceptable.

An alternative method of purifying water is by **reverse osmosis**. Under normal conditions, if an aqueous solution is separated by a semi-permeable membrane from pure water, osmosis will lead to water entering the solution to dilute it. If, however, sufficient pressure is applied to the solution, i.e. a pressure in excess of its osmotic pressure, then water will flow through the membrane *from* the solution; the process of reverse osmosis is taking place. This principle has been

adapted as a method of purifying tap water. The tap water, at a pressure of 3–5 atmospheres, is passed through a tube containing the semi-permeable membrane. The permeate which is collected usually still contains traces of inorganic material and is therefore not suitable for operations requiring very pure water, but it will serve for many laboratory purposes, and is very suitable for further purification by ion exchange treatment. The water produced by reverse osmosis is passed first through a bed of activated charcoal which removes organic contaminants, and is then passed through a mixed-bed ion exchange column and the resultant effluent is finally filtered through a sub-micron filter membrane to remove any last traces of colloidal organic particles.

The **high-purity water** thus produced typically has a conductance of about $0.5 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ ($0.5\,\mu S\,cm^{-1}$) and is suitable for use under the most stringent requirements. It will meet the purity required for trace-element determinations and for operations such as ion chromatography. It must however be borne in mind that such water can readily become contaminated from the vessels in which it is stored, and also by exposure to the atmosphere. For the determination of organic compounds the water should be stored in containers made of resistant glass (e.g. Pyrex), or ideally of fused silica, whereas for inorganic determinations the water is best stored in containers made from polythene or from polypropylene.

3.18 WASH BOTTLES

A wash bottle is a flat-bottomed flask fitted up to deliver a fine stream of distilled water or other liquid for use in the transfer and washing of precipitates. A convenient size is a 500–750 mL flask of Pyrex or other resistant glass; it should be fitted up as shown in Fig. 3.4. A rubber bung is used, and the jet should deliver a fine stream of water; a suitable diameter of the orifice is 1 mm. Thick string, foam rubber, or other insulating material, held in place by copper wire, should be wrapped round the neck of the flask in order to protect the hand when hot water is used. In order to protect the mouth from scalding by the back rush of steam through the mouth-piece when the blowing is stopped, it is convenient to use a three-holed rubber stopper; a short piece of glass tubing open at both ends is inserted in the third hole. The thumb is kept over this tube whilst the water is being blown out, and is removed immediately before the mouth pressure is released. All-glass wash bottles, fitted with ground-glass joints, can be purchased. They should be used with organic solvents that attack rubber.

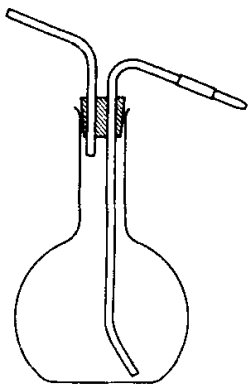

Fig. 3.4

A **polythene wash bottle** is available commercially and is inexpensive. It is fitted with a plastic cap carrying a plastic jet, and has flexible sides. The bottle can be held in the hand; application of slight pressure by squeezing gives an easily controllable jet of water. It is more or less unbreakable and is inert to many wash liquids. A polythene wash bottle should be used only for cool liquids.

Polythene wash bottles are sometimes charged with wash liquids other than water. Attention must be drawn to the fact that the components of some wash solutions may pass into the polythene and may be released into the space in the bottle when it is set aside: repeated fillings and rinsings may be required to remove the chemicals from the bottle. It is safer to label the wash bottle and to reserve it for the special wash liquid. Such wash solutions include a weakly acid solution saturated with hydrogen sulphide, dilute aqueous ammonia, saturated bromine water, and dilute nitric acid.

GENERAL APPARATUS

3.19 GLASSWARE, CERAMICS, PLASTIC WARE

In the following sections, a brief account of general laboratory apparatus relevant to quantitative analysis will be given. The commonest materials of construction of such apparatus are glass, porcelain, fused silica, and various plastics; the merits and disadvantages of these are considered below.

Glassware. In order to avoid the introduction of impurities during analysis, apparatus of resistance glass should be employed. For most purposes Pyrex glass (a borosilicate glass) is to be preferred. Resistance glass is very slightly affected by all solutions, but, in general, attack by acid solutions is less than that by pure water or by alkaline solutions; for this reason the latter should be acidified whenever possible, if they must be kept in glass for any length of time. Attention should also be given to watch, clock, and cover glasses; these should also be of resistance glass. As a rule, glassware should not be heated with a naked flame; a wire gauze should be interposed between the flame and the glass vessel.

For special purposes, Corning Vycor glass (96 per cent silica) may be used. It has great resistance to heat and equally great resistance to thermal shock, and is unusually stable to acids (except hydrofluoric acid), water, and various solutions.

The most satisfactory **beakers** for general use are those provided with a spout. The advantages of this form are: (*a*) convenience of pouring, (*b*) the spout forms a convenient place at which a stirring rod may protrude from a covered beaker, and (*c*) the spout forms an outlet for steam or escaping gas when the beaker is covered with an ordinary clock glass. The size of a beaker must be selected with due regard to the volume of the liquid which it is to contain. The most useful sizes are from 250 to 600 mL.

Conical (or Erlenmeyer's) flasks of 200–500 mL capacity find many applications, for example, in titrations.

Funnels should enclose an angle of 60°. The most useful sizes for quantitative analysis are those with diameters of 5.5, 7 and 9 cm. The stem should have an internal diameter of about 4 mm and should not be more than 15 cm long. For

filling burettes and transferring solids to graduated flasks, a short-stem, wide-necked funnel is useful.

Porcelain apparatus. Porcelain is generally employed for operations in which hot liquids are to remain in contact with the vessel for prolonged periods. It is usually considered to be more resistant to solutions, particularly alkaline solutions, than glass, although this will depend primarily upon the quality of the glaze. Shallow porcelain basins with lips are employed for evaporations. Casseroles are lipped, flat-bottomed porcelain dishes provided with handles; they are more convenient to use than dishes.

Porcelain crucibles are very frequently utilised for igniting precipitates and heating small quantities of solids because of their cheapness and their ability to withstand high temperatures without appreciable change. Some reactions, such as fusion with sodium carbonate or other alkaline substances, and also evaporations with hydrofluoric acid, cannot be carried out in porcelain crucibles owing to the resultant chemical attack. A slight attack of the porcelain also takes place with pyrosulphate fusions.

Fused-silica apparatus. Two varieties of silica apparatus are available commercially, the translucent and the transparent grades. The former is much cheaper and can usually be employed instead of the transparent variety. The advantages of silica ware are: (*a*) its great resistance to heat shock because of its very small coefficient of expansion, (*b*) it is not attacked by acids at a high temperature, except by hydrofluoric acid and phosphoric acid, and (*c*) it is more resistant to pyrosulphate fusions than is porcelain. The chief disadvantages of silica are: (*a*) it is attacked by alkaline solutions and particularly by fused alkalis and carbonates, (*b*) it is more brittle than ordinary glass, and (*c*) it requires a much longer time for heating and cooling than does, say, platinum apparatus. Corning Vycor apparatus (96 per cent silica glass) possesses most of the merits of fused silica and is transparent.

Plastic apparatus. Plastic materials are widely used for a variety of items of common laboratory equipment such as aspirators, beakers, bottles, Buchner

Table 3.4 Plastics used for laboratory apparatus

Material	Appearance†	Highest temperature (°C)	Chemical reagents‡				Attacking organic solvents§
			Acids		Alkalis		
			Weak	Strong	Weak	Strong	
Polythene (L.D.)	TL	80–90	R	R*	V	R	1, 2
Polythene (H.D.)	TL–O	100–110	V	R*	V	V	2
Polypropylene	T–TL	120–130	V	R*	V	V	2
TPX (Polymethylpentene)	T	170–180	V	R*	V	V	1, 2
Polystyrene	T	85	V	R*	V	V	Most
PTFE (Teflon)	O	250–300	V	V	V	V	V
Polycarbonate	T	120–130	R	A	F	A	Most
PVC [Poly(vinyl chloride)]	T–O	50–70	R	R*	R	R	2, 3, 4
Nylon	TL–O	120	R	A	R	F	V

† O = opaque; T = transparent; TL = translucent.
‡ A = attacked; F = fairly resistant; R = resistant; R* = generally resistant but attacked by oxidising mixtures; V = very resistant.
§ 1 = hydrocarbons; 2 = chlorohydrocarbons; 3 = ketones; 4 = cyclic ethers; V = very resistant.

funnels and flasks, centrifuge tubes, conical flasks, filter crucibles, filter funnels, measuring cylinders, scoops, spatulas, stoppers, tubing, weighing bottles, etc.; such products are often cheaper than their glass counterparts, and are frequently less fragile. Although inert towards many chemicals, there are some limitations on the use of plastic apparatus, not the least of which is the generally rather low maximum temperature to which it may be exposed: salient properties of the commonly used plastic materials are summarised in Table 3.4.

Attention is drawn to the extremely inert character of Teflon, which is so lacking in reactivity that it is used as the liner in pressure digestion vessels in which substances are decomposed by heating with hydrofluoric acid, or with concentrated nitric acid (see Section 3.31).

3.20 METAL APPARATUS

Crucibles and basins required for special purposes are often fabricated from various metals, amongst which platinum holds pride of place by virtue of its general resistance to chemical attack.

Platinum. Platinum is used mainly for crucibles, dishes and electrodes; it has a very high melting point (1773 °C), but the pure metal is too soft for general use, and is therefore always hardened with small quantities of rhodium, iridium, or gold. These alloys are slightly volatile at temperatures above 1100 °C, but retain most of the advantageous properties of pure platinum, such as resistance to most chemical reagents, including molten alkali carbonates and hydrofluoric acid (the exceptions are dealt with below), excellent conductivity of heat, and extremely small adsorption of water vapour. A 25 mL platinum crucible has an area of 80–100 cm^2 and, in consequence, the error due to volatility may be appreciable if the crucible is made of an alloy of high iridium content. The magnitude of this loss will be evident from Table 3.5, which gives the approximate loss in weight of crucibles expressed in mg/100 cm^2/hour at the temperature indicated. An alloy consisting of 95 per cent platinum and 5 per cent gold is referred to as a 'non-wetting' alloy and fusion samples are readily removed from crucibles composed of this alloy; removal is assisted by keeping the crucible tilted while the melt is solidifying. Crucibles made of this alloy are used in preparing samples for investigation by X-ray fluorescence.

A recent development is the introduction of ZGS (Zirconia Grain Stabilised) platinum. This is produced by the addition of a small amount of zirconia (zirconium(IV) oxide) to molten platinum, which leads to modification of the microstructure of the solid material with increased hot strength and greater resistance to chemical attack. Whereas the recommended operating temperature for pure platinum is 1400 °C, the ZGS material can be used up to 1650 °C.

Table 3.5 Weight loss of platinum crucibles

Temp. (°C)	Pure Pt	99% Pt–1% Ir	97.5% Pt–2.5% Ir
900	0.00	0.00	0.00
1000	0.08	0.30	0.57
1200	0.81	1.2	2.5

Apparatus can also be constructed from 'TRIM' which consists of palladium coated with ZGS platinum; this permits the production of stouter apparatus with the corrosion resistance of ZGS platinum at an appreciably cheaper price.

Platinum crucibles should be supported, when heated, upon a platinum triangle. If the latter is not available, a silica triangle may be used. Nichrome and other metal triangles should be avoided; pipe-clay triangles may contain enough iron to damage the platinum. Hot platinum crucibles must always be handled with platinum-tipped crucible tongs; unprotected brass or iron tongs produce stains on the crucible. Platinum vessels must not be exposed to a luminous flame, nor may they be allowed to come into contact with the inner cone of a gas flame; this may result in the disintegration of the surface of the metal, causing it to become brittle, owing, probably, to the formation of a carbide of platinum.

It must be appreciated that at high temperatures platinum permits the flame gases to diffuse through it, and this may cause the reduction of some substances not otherwise affected. Hence if a covered crucible is heated by a gas flame there is a reducing atmosphere in the crucible: in an open crucible diffusion into the air is so rapid that this effect is not appreciable. Thus if iron(III) oxide is heated in a covered crucible, it is partly reduced to metallic iron, which alloys with the platinum; sodium sulphate is similarly partly reduced to the sulphide. It is, advisable, therefore, in the ignition of iron compounds or sulphates to place the crucible in a slanting position with free access of air.

Platinum apparatus may be used without significant loss for:

1. Fusions with (*a*) sodium carbonate or fusion mixture, (*b*) borax and lithium metaborate, (*c*) alkali bifluorides, and (*d*) alkali hydrogensulphates (slight attack in the last case above 700 °C, which is diminished by the addition of ammonium sulphate).
2. Evaporations with (*a*) hydrofluoric acid, (*b*) hydrochloric acid in the absence of oxidising agents which yield chlorine, and (*c*) concentrated sulphuric acid (a slight attack may occur).
3. Ignition of (*a*) barium sulphate and sulphates of metals which are not readily reducible, (*b*) the carbonates, oxalates, etc., of calcium, barium and strontium, and (*c*) oxides which are not readily reducible, e.g. CaO, SrO, Al_2O_3, Cr_2O_3, Mn_3O_4, TiO_2, ZrO_2, ThO_2, MoO_3, and WO_3. (BaO, or compounds which yield BaO on heating, attack platinum.)

Platinum is *attacked* under the following conditions, and such operations must not be conducted in platinum vessels:

1. Heating with the following liquids: (*a*) aqua regia, (*b*) hydrochloric acid and oxidising agents, (*c*) liquid mixtures which evolve bromine or iodine, and (*d*) concentrated phosphoric acid (slight, but appreciable, action after prolonged heating).
2. Heating with the following solids, their fusions, or vapours: (*a*) oxides, peroxides, hydroxides, nitrates, nitrites, sulphides, cyanides, hexacyanoferrate(III), and hexacyanoferrate(II) of the alkali and alkaline-earth metals (except oxides and hydroxides of calcium and strontium); (*b*) molten lead, silver, copper, zinc, bismuth, tin, or gold, or mixtures which form these metals upon reduction; (*c*) phosphorus, arsenic, antimony, or silicon, or mixtures which form these elements upon reduction, particularly phosphates, arsenates,

and silicates in the presence of reducing agents; (*d*) sulphur (slight action), selenium, and tellurium; (*e*) volatile halides (including iron(III) chloride), especially those which decompose readily; (*f*) all sulphides or mixtures containing sulphur and a carbonate or hydroxide; and (*g*) substances of unknown composition: (*h*) heating in an atmosphere containing chlorine, sulphur dioxide, or ammonia, whereby the surface is rendered porous.

Solid carbon, however produced, presents a hazard. It may be burnt off at low temperatures, with free access to air, without harm to the crucible, but it should never be ignited strongly. Precipitates in filter paper should be treated in a similar manner; strong ignition is only permissible after *all* the carbon has been removed. Ashing in the presence of carbonaceous matter should not be conducted in a platinum crucible, since metallic elements which may be present will attack the platinum under reducing conditions.

Cleaning and preservation of platinum ware. All platinum apparatus (crucibles, dishes, etc.) should be kept clean, polished, and in proper shape. If, say, a platinum crucible becomes stained, a little sodium carbonate should be fused in the crucible, the molten solid poured out on to a dry stone or iron slab, the residual solid dissolved out with water, and the vessel then digested with concentrated hydrochloric acid: this treatment may be repeated, if necessary. If fusion with sodium carbonate is without effect, potassium hydrogensulphate may be substituted; a slight attack of the platinum will occur. Disodium tetraborate may also be used. In some cases, the use of hydrofluoric acid or potassium hydrogenfluoride may be necessary. Iron stains may be removed by heating the covered crucible with a gram or two of pure ammonium chloride and applying the full heat of a burner for 2–3 minutes.

All platinum vessels must be handled with care to prevent deformation and denting. Platinum crucibles must on no account be squeezed with the object of loosening the solidified cake after a fusion. Box-wood formers can be purchased for crucibles and dishes; these are invaluable for re-shaping dented or deformed platinum ware.

Platinum-clad stainless steel laboratory ware is available for the evaporation of solutions of corrosive chemicals. These vessels have all the corrosion-resistance properties of platinum up to about 550 °C. The main features are: (1) much lower cost than similar apparatus of platinum; (2) the overall thickness is about four times that of similar all-platinum apparatus, thus leading to greater mechanical strength; and (3) less susceptible to damage by handling with tongs, etc.

Silver apparatus. The chief uses of silver crucibles and dishes in the laboratory are in the evaporation of alkaline solutions and for fusions with caustic alkalis; in the latter case, the silver is slightly attacked. Gold vessels (m.p. 1050 °C) are more resistant than silver to fused alkalis. Silver melts at 960 °C, and care should therefore be taken when it is heated over a bare flame.

Nickel ware. Crucibles and dishes of nickel are employed for fusions with alkalis and with sodium peroxide (**CARE!**). In the peroxide fusion a little nickel is introduced, but this is usually not objectionable. No metal entirely withstands the action of fused sodium peroxide. Nickel oxidises in air, hence nickel apparatus cannot be used for operations involving weighing.

Iron ware. Iron crucibles may be substituted for those of nickel in sodium peroxide fusions. They are not so durable, but are much cheaper.

Stainless-steel ware. Beakers, crucibles, dishes, funnels, etc., of stainless steel are available commercially and have obvious uses in the laboratory. They will not rust, are tough, strong, and highly resistant to denting and scratching.

3.21 HEATING APPARATUS

Various methods of heating are required in the analytical laboratory ranging from gas burners, electric hot plates and ovens to muffle furnaces.

Burners. The ordinary Bunsen burner is widely employed for the attainment of moderately high temperatures. The maximum temperature is attained by adjusting the regulator so as to admit rather more air than is required to produce a non-luminous flame; too much air gives a noisy flame, which is unsuitable.

Owing to the differing combustion characteristics and calorific values of the gaseous fuels which are commonly available [natural gas, liquefied petroleum (bottled) gas], slight variations in dimensions, including jet size and aeration controls, are necessary: for maximum efficiency it is essential that, unless the burner is of the 'All Gases' type which can be adjusted, the burner should be the one intended for the available gas supply.

Hot plates. The electrically heated hot plate, preferably provided with three controls — 'Low', 'Medium' and 'High' — is of great value in the analytical laboratory. The heating elements and the internal wiring should be totally enclosed; this protects them from fumes or spilled liquids. Electric hot plates with 'stepless' controls are also marketed; these permit a much greater selection of surface temperatures to be made. A combined electric hot plate and magnetic stirrer is also available. For some purposes a steam bath may be used.

Electric ovens. The most convenient type is an electrically heated, thermostatically controlled drying oven having a temperature range from room temperature to about 250–300 °C; the temperature can be controlled to within ± 1–2 °C. They are used principally for drying precipitates or solids at comparatively low controlled temperatures, and have virtually superseded the steam oven.

Microwave ovens. These also find application for drying and heating operations. They are particularly useful for determining the moisture content of materials since the elimination of water takes place very rapidly on exposure to microwave radiation.

Muffle furnaces. An electrically heated furnace of muffle form should be available in every well-equipped laboratory. The maximum temperature should be about 1200 °C. If possible, a thermocouple and indicating pyrometer should be provided; otherwise the ammeter in the circuit should be calibrated, and a chart constructed showing ammeter and corresponding temperature readings. Gas-heated muffle furnaces are marketed; these may give temperatures up to about 1200 °C.

Air baths. For drying solids and precipitates at temperatures up to 250 °C in which acid or other corrosive vapours are evolved, an electric oven should not be used. An air bath may be constructed from a cylindrical metal (copper, iron,

or nickel) vessel with the bottom of the vessel pierced with numerous holes. A silica triangle, the legs of which are appropriately bent, is inserted inside the bath for supporting an evaporating dish, crucible, etc. The whole is heated by a Bunsen flame, which is shielded from draughts. The insulating layer of air prevents bumping by reducing the rate at which heat reaches the contents of the inner dish or crucible. An air bath of similar construction but with special heat-resistant glass sides may also be used; this possesses the obvious advantage of visibility inside the air bath.

Infrared lamps and heaters. Infrared lamps with internal reflectors are available commercially and are valuable for evaporating solutions. The lamp may be mounted immediately above the liquid to be heated: the evaporation takes place rapidly, without spattering and also without creeping. Units are obtainable which permit the application of heat to both the top and bottom of a number of crucibles, dishes, etc., at the same time; this assembly can char filter papers in the crucibles quite rapidly, and the filter paper does not catch fire.

Immersion heaters. An immersion heater consisting of a radiant heater encased in a silica sheath, is useful for the direct heating of most acids and other liquids (except hydrofluoric acid and concentrated caustic alkalis). Infrared radiation passes through the silica sheath with little absorption, so that a large proportion of heat is transferred to the liquid by radiation. The heater is almost unaffected by violent thermal shock due to the low coefficient of thermal expansion of the silica.

Heating mantles. These consist of a flexible 'knitted' fibre glass sheath which fits snugly around a flask and contains an electrical heating element which operates at black heat. The mantle may be supported in an aluminium case which stands on the bench, but for use with suspended vessels the mantle is supplied without a case. Electric power is supplied to the heating element through a control unit which may be either a continuously variable transformer or a thyristor controller, and so the operating temperature of the mantle can be smoothly adjusted.

Heating mantles are particularly designed for the heating of flasks and find wide application in distillation operations. For details of the distillation procedure and description of the apparatus employed, a textbook of practical organic chemistry should be consulted.[9]

Crucibles and beaker tongs. Apparatus such as crucibles, evaporating basins and beakers which have been heated need to be handled with suitable tongs. Crucible tongs should be made of solid nickel, nickel steel, or other rustless ferro-alloy. For handling hot platinum crucibles or dishes, platinum-tipped tongs must be used. Beaker tongs are available for handling beakers of 100–2000 mL capacity. The tongs have jaws: an adjustable screw with locknut limits the span of these jaws and enables the user to adjust them to suit the container size.

3.22 DESICCATORS AND DRY BOXES

It is usually necessary to ensure that substances which have been dried by heating (e.g. in an oven, or by ignition) are not unduly exposed to the atmosphere, otherwise they will absorb moisture more or less rapidly. In many cases, storage

in the dry atmosphere of a desiccator, allied to minimum exposure to the atmosphere during subsequent operations, will be sufficient to prevent appreciable absorption of water vapour. Some substances, however, are so sensitive to atmospheric moisture that all handling must be carried out in a 'dry box'.

A **desiccator** is a covered glass container designed for the storage of objects in a dry atmosphere; it is charged with some drying agent, such as anhydrous calcium chloride (largely used in elementary work), silica gel, activated alumina, or anhydrous calcium sulphate ('Drierite'). Silica gel, alumina and calcium sulphate can be obtained which have been impregnated with a cobalt salt so that they are self-indicating: the colour changes from blue to pink when the desiccant is exhausted. The spent material can be regenerated by heating in an electric oven at 150–180 °C (silica gel); 200–300 °C (activated alumina) 230–250 °C (Drierite); and it is therefore convenient to place these drying agents in a shallow dish which is situated at the bottom of the desiccator, and which can be easily removed for baking as required.

The action of desiccants can be considered from two points of view. The amount of moisture that remains in a closed space, containing incompletely exhausted desiccant, is related to the vapour pressure of the latter, i.e. the vapour pressure is a measure of the extent to which the desiccant can remove moisture, and therefore of its efficiency. A second factor is the weight of water that can be removed per unit weight of desiccant, i.e. the drying capacity. In general, substances that form hydrates have higher vapour pressures but also have greater drying capacities. It must be remembered that a substance cannot be dried by a desiccant of which the vapour pressure is greater than that of the substance itself.

The relative efficiencies of various drying agents will be evident from the data presented in Table 3.6. These were determined by aspirating properly conditioned air through **U**-tubes charged with the desiccants; they are applicable, strictly, to the use of these desiccants in absorption tubes, but the figures may reasonably be applied as a guide for the selection of desiccants for desiccators. It would appear from the table that a hygroscopic material such as ignited alumina should not be allowed to cool in a covered vessel over 'anhydrous' calcium chloride; anhydrous magnesium perchlorate or phosphorus pentoxide is satisfactory.

Table 3.6 Comparative efficiency of drying agents

Drying agent	Residual water (mg per L of air)	Drying agent	Residual water (mg per L of air)
$CaCl_2$ (gran. 'anhyd.' tech.)	1.5	Al_2O_3	0.005
NaOH (sticks)	0.8	$CaSO_4$	0.005
H_2SO_4 (95%)	0.3	Molecular sieve	0.004
Silica gel	0.03	H_2SO_4	0.003
KOH (sticks)	0.014	$Mg(ClO_4)_2$	0.002
		P_2O_5	0.00002

The normal (or Scheibler) desiccator is provided with a porcelain plate having apertures to support crucibles, etc.: this is supported on a constriction situated roughly halfway up the wall of the desiccator. For small desiccators, a silica triangle, with the wire ends suitably bent, may be used. The ground edge of the

desiccator should be lightly coated with white Vaseline or a special grease in order to make it air-tight; too much grease may permit the lid to slide.

There is however controversy regarding the effectiveness of desiccators. If the lid is briefly removed from a desiccator then it may take as long as two hours to remove the atmospheric moisture thus introduced, and to re-establish the dry atmosphere: during this period, a hygroscopic substance may actually gain in weight while in the desiccator. It is therefore advisable that any substance which is to be weighed should be kept in a vessel with as tightly fitting a lid as possible while it is in the desiccator.

The problem of the cooling of hot vessels within a desiccator is also important. A crucible which has been strongly ignited and immediately transferred to a desiccator may not have attained room temperature even after one hour. The situation can be improved by allowing the crucible to cool for a few minutes before transferring to the desiccator, and then a cooling time of 20–25 minutes is usually adequate. The inclusion in the desiccator of a metal block (e.g. aluminium), upon which the crucible may be stood, is also helpful in ensuring the attainment of temperature equilibrium.

When a hot object, such as a crucible, is placed in a desiccator, about 5–10 seconds should elapse for the air to become heated and expand before putting the cover in place. When re-opening, the cover should be slid open very gradually in order to prevent any sudden inrush of air due to the partial vacuum which exists owing to the cooling of the expanded gas content of the desiccator, and thus prevent material being blown out of the crucible.

A desiccator is frequently also employed for the thorough drying of solids for analysis and for other purposes. Its efficient operation depends upon the condition of the desiccant; the latter should therefore be renewed at frequent intervals, particularly if its drying capacity is low. For dealing with large quantities of solid a vacuum desiccator is advisable.

Convenient types of **'vacuum' desiccators** are illustrated in Fig. 3.5. Large surfaces of the solid can be exposed; the desiccator may be evacuated, and drying is thus much more rapid than in the ordinary Scheibler type. These desiccators are made of heavy glass, plastics, or even metal, and are designed to withstand reduced pressure; nevertheless, no desiccator should be evacuated unless it is surrounded by an adequate guard in the form of a stout wire cage.

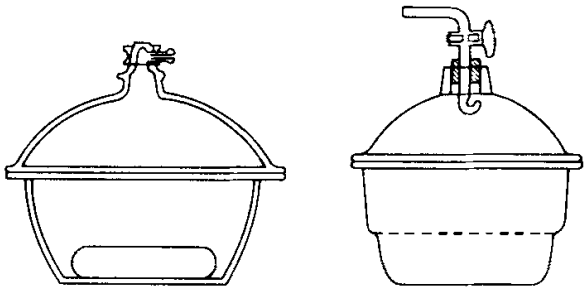

Fig. 3.5

For most purposes the 'vacuum' produced by an efficient water pump (20–30 mm mercury) will suffice; a guard tube containing desiccant should be inserted between the pump and the desiccator. The sample to be dried should

be covered with a watch or clock glass, so that no mechanical loss ensues as a result of the removal or admission of air. Air must be admitted slowly into an exhausted desiccator: if the substance is very hygroscopic, a drying train should be attached to the stopcock. In order to maintain a satisfactory vacuum within the desiccator, the flanges on both the lid and the base must be well lubricated with Vaseline or other suitable grease. In some desiccators an elastomer ring is incorporated in a groove in the flange of the lower component of the desiccator: when the pressure is reduced, the ring is compressed by the lid of the desiccator, and an air-tight seal is produced without the need for any grease. The same desiccants are used as with an ordinary desiccator.

Dry boxes (glove boxes) which are especially intended for the manipulation of materials which are very sensitive to atmospheric moisture (or to oxygen), consist of a plastic or metal box provided with a window (of glass or clear plastic) on the upper side, and sometimes also on the side walls. A pair of rubber or plastic gloves are fitted through air-tight seals through the front side of the box, and by placing the hands and forearms into the gloves, manipulations may be carried out inside the box. One end of the box is fitted with an air-lock so that apparatus and materials can be introduced into the box without disturbing the atmosphere inside. A tray of desiccant placed inside the box will maintain a dry atmosphere, but to counter the unavoidable leakages in such a system, it is advisable to supply a slow current of dry air to the box; inlet and outlet taps are provided to control this operation. If the box is flushed out before use with an inert gas (e.g. nitrogen), and a slow stream of the gas is maintained while the box is in use, materials which are sensitive to oxygen can be safely handled. For a detailed discussion of the construction and uses of glove boxes, see Ref. 10.

3.23 STIRRING APPARATUS

Many operations involving solutions of reagents require the thorough mixing of two or more reactants, and apparatus suitable for this purpose ranges from a simple glass stirring rod to electrically operated stirrers.

Stirring rods. These are made from glass rod 3–5 mm in diameter, cut into suitable lengths. Both ends should be rounded by heating in the Bunsen or blowpipe flame. The length of the stirring rod should be suitable for the size and the shape of the vessel for which it is employed, e.g. for use with a beaker provided with a spout, it should project 3–5 cm beyond the lip when in a resting position.

A short piece of Teflon or of rubber tubing (or a rubber cap) fitted tightly over one end of a stirring rod of convenient size gives the so-called '**policeman**'; it is used for detaching particles of a precipitate adhering to the side of a vessel which cannot be removed by a stream of water from a wash bottle: it should not, as a rule, be employed for stirring, nor should it be allowed to remain in a solution.

Boiling rods. Boiling liquids and liquids in which a gas, such as hydrogen sulphide, sulphur dioxide etc., has to be removed by boiling can be prevented from superheating and 'bumping' by the use of a boiling rod (Fig. 3.6). This consists of a piece of glass tubing closed at one end and sealed approximately 1 cm from the other end; the latter end is immersed in the liquid. When the rod

Fig. 3.6

is removed, the liquid in the open end must be shaken out and the rod rinsed with a jet of water from a wash bottle. This device should not be used in solutions which contain a precipitate.

Stirring may be conveniently effected with the so-called **magnetic stirrer**. A rotating field of magnetic force is employed to induce variable-speed stirring action within either closed or open vessels. The stirring is accomplished with the aid of a small cylinder of iron sealed in Pyrex glass, polythene, or Teflon, which is caused to rotate by a rotating magnet.

The usual type of glass paddle stirrer is also widely used in conjunction with an electric motor fitted with either a transformer-type, or a solid-state, speed controller. The stirrer may be either connected directly to the motor shaft or to a spindle actuated by a gear box which forms an integral part of the motor housing; by these means, wide variation in stirrer speed can be achieved.

Under some circumstances, e.g. the dissolution of a sparingly soluble solid, it may be more advantageous to make use of a **mechanical shaker**. Various models are available, ranging from 'wrist action shakers' which will accommodate small-to-moderate size flasks, to those equipped with a comparatively powerful electric motor and capable of shaking the contents of large bottles vigorously.

3.24 FILTRATION APPARATUS

The simplest apparatus used for filtration is the filter funnel fitted with a filter paper. The funnel should have an angle as close to 60° as possible, and a long stem (15 cm) to promote rapid filtration. Filter papers are made in varying grades of porosity, and one appropriate to the type of material to be filtered must be chosen (see Section 3.34).

In the majority of quantitative determinations involving the collection and weighing of a precipitate, it is convenient to be able to collect the precipitate in a crucible in which it can be weighed directly, and various forms of **filter crucible** have been devised for this purpose. Sintered glass crucibles are made of resistance glass and have a porous disc of sintered ground glass fused into the body of the crucible. The filter disc is made in varying porosities as indicated by numbers from 0 (the coarsest) to 5 (the finest); the range of pore diameter for the various grades is as follows:

Porosity	0	1	2	3	4	5
Pore diameter μm	200–250	100–120	40–50	20–30	5–10	1–2

Porosity 3 is suitable for precipitates of moderate particle size, and porosity 4 for fine precipitates such as barium sulphate. These crucibles should not be heated above about 200 °C.

Silica crucibles of similar pattern are also available, and, although expensive, have certain advantages in thermal stability.

Filter crucibles with a porous filter base are available in porcelain (porosity 4), in silica (porosities 1, 2, 3, 4), and in alumina (coarse, medium and fine porosities): these have the advantage as compared with sintered crucibles, of being capable of being heated to much higher temperatures. Nevertheless, the heating must be gradual otherwise the crucible may crack at the join between porous base and glazed side.

For filtering large quantities of material, a **Buchner funnel** is usually employed; alternatively, one of the modified funnels shown diagrammatically in Fig. 3.7 may be used. Here (*a*) is the ordinary porcelain Buchner funnel, (*b*) is the 'slit sieve' glass funnel. In both cases, one or (better) two good-quality filter papers are placed on the plate; the glass type is preferable since it is transparent and it is easy to see whether the funnel is perfectly clean. Type (*c*) is a Pyrex funnel with a sintered glass plate; no filter paper is required so that strongly acidic and weakly alkaline solutions can be readily filtered with this funnel. In all cases the funnel of appropriate size is fitted into a filter flask (*d*), and the filtration conducted under the diminished pressure provided by a filter pump or vacuum line.

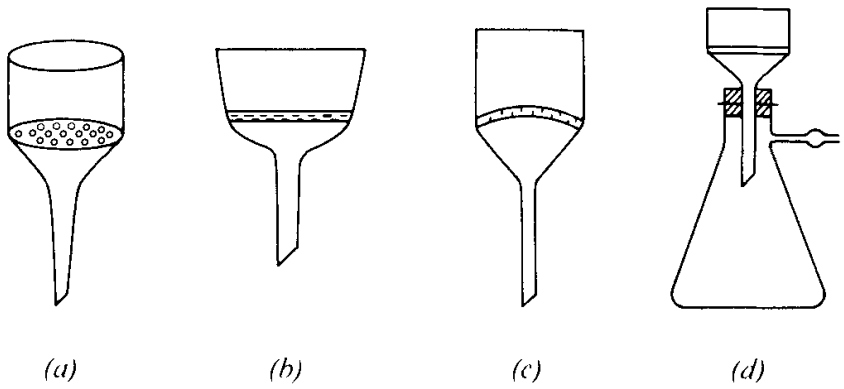

Fig. 3.7

One of the disadvantages of the porcelain Buchner funnel is that, being of one-piece construction, the filter plate cannot be removed for thorough cleaning and it is difficult to see whether the whole of the plate is clean on both sides. In a modern polythene version, the funnel is made in two sections which can be unscrewed, thus permitting inspection of both sides of the plate.

In some circumstances, separation of solid from a liquid is better achieved by use of a **centrifuge** than by filtration, and a small, electrically driven centrifuge is a useful piece of equipment for an analytical laboratory. It may be employed for removing the mother liquor from recrystallised salts, for collecting difficultly filterable precipitates, and for the washing of certain precipitates by decantation. It is particularly useful when small quantities of solids are involved; centrifuging, followed by decantation and re-centrifuging, avoids transference losses and yields the solid phase in a compact form. Another valuable application is for the separation of two immiscible phases.

3.25 WEIGHING BOTTLES

Most chemicals are weighed *by difference* by placing the material inside a stoppered weighing bottle which is then weighed. The requisite amount of substance is shaken out into a suitable vessel (beaker or flask), and the weight of substance taken is determined by re-weighing the weighing bottle. In this way, the substance dispensed receives the minimum exposure to the atmosphere during the actual weighing process: a feature of some importance if the material is hygroscopic.

The most convenient form of weighing bottle is one fitted with an external cap and made of glass, polythene or polycarbonate. A weighing bottle with an *internally* fitting stopper is not recommended; there is always the danger that small particles may lodge at the upper end of the bottle and be lost when the stopper is pressed into place.

If the substance is unaffected by exposure to the air, it may be weighed on a watch glass, or in a disposable plastic container. The weighing funnel (Fig. 3.8) is very useful, particularly when the solid is to be transferred to a flask: having weighed the solid into the scoop-shaped end which is flattened so that it will stand on the balance pan, the narrow end is inserted into the neck of the flask and the solid washed into the flask with a stream of water from a wash bottle.

Fig. 3.8

Woodward and Redman[6c] have described a specially designed weighing bottle which will accommodate a small platinum crucible: when a substance has been ignited in the crucible, the crucible is transferred to the weighing bottle and subsequently weighed in this. This device obviates the need for a desiccator.

If the substance to be weighed is a liquid, it is placed in a weighing bottle fitted with a cap carrying a dropping tube.

REAGENTS AND STANDARD SOLUTIONS

3.26 REAGENTS

The purest reagents available should be used for quantitative analysis; the analytical reagent quality is generally employed. In Great Britain 'AnalaR' chemicals from BDH Chemicals conform to the specifications given in the handbook '*AnalaR' Standards for Laboratory Chemicals.*[11] In the USA the American Chemical Society committee on Analytical Reagents has established standards for certain reagents, and manufacturers supply reagents which are labelled 'Conforms to ACS Specifications'. In addition, certain manufacturers market chemicals of high purity, and each package of these analysed chemicals has a label giving the manufacturer's limits of certain impurities.

With the increasingly lower limits of detection being achieved in various types of instrumental analysis, there is an ever growing demand for reagents of

correspondingly improved specification, and some manufacturers are now offering a range of specially purified reagents such as the BDH Ltd 'Aristar' chemicals, specially purified solvents for spectroscopy (e.g. BDH Ltd 'Spectrosol') and specially prepared reagents for chromatography.

In some instances, where a reagent of the requisite purity is not available, it may be advisable to weigh out a suitable portion of the appropriate *pure* metal (e.g. the Johnson, Matthey 'Specpure' range), and to dissolve this in the appropriate acid.

It must be remembered that the label on a bottle is not an infallible guarantee of the purity of a chemical, for the following reasons:

(*a*) Some impurities may not have been tested for by the manufacturer.
(*b*) The reagent may have been contaminated after its receipt from the manufacturers either by the stopper having been left open for some time, with the consequent exposure of the contents to the laboratory atmosphere or by the accidental return of an unused portion of the reagent to the bottle.
(*c*) In the case of a solid reagent, it may not be sufficiently dry. This may be due either to insufficient drying by the manufacturers or to leakage through the stoppers during storage, or to both of these causes.

However, if the analytical reagents are purchased from a manufacturing firm of repute, the instructions given (*a*) that no bottle is to be opened for a longer time than is absolutely necessary, and (*b*) that no reagent is to be returned to the bottle after it has been removed, the likelihood of any errors arising from some of the above possible causes is considerably reduced. Liquid reagents should be poured from the bottle; a pipette should never be inserted into the reagent bottle. Particular care should be taken to avoid contamination of the stopper of the reagent bottle. When a liquid is poured from a bottle, the stopper should never be placed on the shelf or on the working bench; it may be placed upon a clean watchglass, and many chemists cultivate the habit of holding the stopper between the thumb and fingers of one hand. The stopper should be returned to the bottle immediately after the reagent has been removed, and all reagent bottles should be kept scrupulously clean, particularly round the neck or mouth of the bottle.

If there is any doubt as to the purity of the reagents used, they should be tested by standard methods for the impurities that might cause errors in the determinations. It may be mentioned that not all chemicals employed in quantitative analysis are available in the form of analytical reagents; the purest commercially available products should, if necessary, be purified by known methods: see below. The exact mode of drying, if required, will vary with the reagent; details are given for specific reagents in the text.

3.27 PURIFICATION OF SUBSTANCES

If a reagent of adequate purity for a particular determination is not available, then the purest available product must be purified: this is most commonly done by recrystallisation from water. A known weight of the solid is dissolved in a volume of water sufficient to give a saturated or nearly saturated solution at the boiling point: a beaker, conical flask or porcelain dish may be used. The hot solution is filtered through a fluted filter paper placed in a short-stemmed funnel, and the filtrate collected in a beaker: this process will remove insoluble

material which is usually present. If the substance crystallises out in the funnel, it should be filtered through a hot-water funnel. The clear hot filtrate is cooled rapidly by immersion in a dish of cold water or in a mixture of ice and water, according to the solubility of the solid; the solution is constantly stirred in order to promote the formation of small crystals, which occlude less mother liquor than larger crystals. The solid is then separated from the mother liquor by filtration, using one of the Buchner-type funnels shown in Fig. 3.7 (Section 3.24). When all the liquid has been filtered, the solid is pressed down on the funnel with a wide glass stopper, sucked as dry as possible, and then washed with small portions of the original solvent to remove the adhering mother liquor. The recrystallised solid is dried upon clock glasses at or above the laboratory temperature according to the nature of the material; care must of course be taken to exclude dust. The dried solid is preserved in glass-stoppered bottles. It should be noted that unless great care is taken when the solid is removed from the funnel, there is danger of introducing fibres from the filter paper, or small particles of glass from the glass filter disc: scraping of the filter paper or of the filter disc must be avoided.

Some solids are either too soluble, or the solubility does not vary sufficiently with temperature, in a given solvent for direct crystallisation to be practicable. In many cases, the solid can be precipitated from, say, a concentrated aqueous solution by the addition of a liquid, miscible with water, in which it is less soluble. Ethanol, in which many inorganic compounds are almost insoluble, is generally used. Care must be taken that the amount of ethanol or other solvent added is not so large that the impurities are also precipitated. Potassium hydrogencarbonate and antimony potassium tartrate may be purified by this method.

Many organic compounds can be purified by recrystallisation from suitable organic solvents, and here again, precipitation by the addition of another solvent in which the required compound is insoluble, may be effective; while liquids can be purified by fractional distillation.

Sublimation. This process is employed to separate volatile substances from non-volatile impurities. Iodine, arsenic(III) oxide, ammonium chloride and a number of organic compounds can be purified in this way. The material to be purified is gently heated in a porcelain dish, and the vapour produced is condensed on a flask which is kept cool by circulating cold water inside it.

Zone refining. This is a purification technique originally developed for the refinement of certain metals, and is applicable to all substances of reasonably low melting point which are stable at the melting temperature. In a zone refining apparatus, the substance to be purified is packed into a column of glass or stainless steel, which may vary in length from 15 cm (semimicro apparatus) to 1 metre. An electric ring heater which heats a narrow band of the column is allowed to fall slowly by a motor-controlled drive, from the top to the bottom of the column. The heater is set to produce a molten zone of material at a temperature 2–3 °C above the melting point of the substance, which travels slowly down the tube with the heater. Since impurities normally lower the melting point of a substance, it follows that the impurities tend to flow down the column in step with the heater, and thus to become concentrated in the lower part of the tube. The process may be repeated a number of times (the

apparatus may be programmed to reproduce automatically a given number of cycles), until the required degree of purification has been achieved.

3.28 PREPARATION AND STORAGE OF STANDARD SOLUTIONS

In any analytical laboratory it is essential to maintain stocks of solutions of various reagents: some of these will be of accurately known concentration (i.e. standard solutions) and correct storage of such solutions is imperative.

Solutions may be classified as:

1. reagent solutions which are of approximate concentration;
2. standard solutions which have a known concentration of some chemical;
3. standard reference solutions which have a known concentration of a primary standard substance (Section 10.6);
4. standard titrimetric solutions which have a known concentration (determined either by weighing or by standardisation) of a substance other than a primary standard.

The IUPAC Commission on Analytical Nomenclature refers to (3) and (4) respectively as Primary Standard Solutions and Secondary Standard Solutions.

For **reagent solutions** as defined above (i.e. 1) it is usually sufficient to weigh out approximately the amount of material required, using a watchglass or a plastic weighing container, and then to add this to the required volume of solvent which has been measured with a measuring cylinder.

To prepare a **standard solution** the following procedure is followed. A short-stemmed funnel is inserted into the neck of a graduated flask of the appropriate size. A suitable amount of the chemical is placed in a weighing bottle which is weighed, and then the required amount of substance is transferred from the weighing bottle to the funnel, taking care that no particles are lost. After the weighing bottle has been re-weighed, the substance in the funnel is washed down with a stream of the liquid. The funnel is thoroughly washed, inside and out, and then removed from the flask; the contents of the flask are dissolved, if necessary, by shaking or swirling the liquid, and then made up to the mark: for the final adjustment of volume, a dropping tube drawn out to form a very fine jet is employed.

If a watch glass is employed for weighing out the sample, the contents are transferred as completely as possible to the funnel, and then a wash bottle is used to remove the last traces of the substance from the watch glass. If the weighing scoop (Fig. 3.8; Section 3.25) is used, then of course a funnel is not needed provided that the flask is of such a size that the end of the scoop is an easy fit in the neck.

If the substance is not readily soluble in water, it is advisable to add the material from the weighing bottle or the watchglass to a beaker, followed by distilled water; the beaker and its contents are then heated gently with stirring until the solid has dissolved. After allowing the resulting concentrated solution to cool a little, it is transferred through the short-stemmed funnel to the graduated flask, the beaker is rinsed thoroughly with several portions of distilled water, adding these washings to the flask, and then finally the solution is made up to the mark: it may be necessary to allow the flask to stand for a while before making the final adjustment to the mark to ensure that the solution is at room temperature. **Under no circumstances may the graduated flask be heated.**

In some circumstances it may be considered preferable to prepare the standard solution by making use of one of the concentrated volumetric solutions supplied in sealed ampoules which only require dilution in a graduated flask to produce a standard solution.

Solutions which are comparatively stable and unaffected by exposure to air may be stored in 1 litre or 2.5 litre bottles; for work requiring the highest accuracy, the bottles should be Pyrex, or other resistance glass, and fitted with ground-glass stoppers: the solvent action of the solution being thus considerably reduced. It is however necessary to use a rubber bung instead of a glass stopper for alkaline solutions, and in many instances a polythene container may well replace glass vessels. It should be noted, however, that for some solutions as, for example, iodine and silver nitrate, glass containers only may be used, and in both these cases the bottle should be made of dark (brown) glass: solutions of EDTA (Section 10.49) are best stored in polythene containers.

The bottle should be clean and dry: a little of the stock solution is introduced, the bottle well rinsed with this solution, drained, the remainder of the solution poured in, and the bottle immediately stoppered. If the bottle is not dry, but has recently been thoroughly rinsed with distilled water, it may be rinsed successively with three small portions of the solution and drained well after each rinsing; this procedure is, however, less satisfactory than that employing a clean and dry vessel. Immediately after the solution has been transferred to the stock bottle, it should be labelled with: (1) the name of the solution; (2) its concentration; (3) the data of preparation; and (4) the initials of the person who prepared the solution, together with any other relevant data. Unless the bottle is completely filled, internal evaporation and condensation will cause drops of water to form on the upper part of the inside of the vessel. For this reason, the bottle must be thoroughly shaken before removing the stopper.

For expressing concentrations of reagents, the molar system is universally applicable, i.e. the number of moles of solute present in 1 L of solution. Concentrations may also be expressed in terms of normality if no ambiguity is likely to arise (see Appendix 17).

Solutions liable to be affected by access of air (e.g. alkali hydroxides which

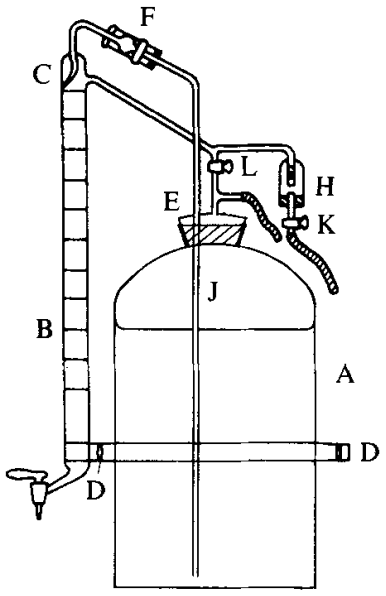

Fig. 3.9

absorb carbon dioxide; iron(II) and titanium(III) which are oxidised) may be stored in the apparatus shown diagrammatically in Fig. 3.9. A is a large storage bottle of 10–15 litres capacity. B is a 50 mL burette provided with an automatic filling device at C (the point of the drawn-out tube is adjusted to be exactly at the zero mark of the burette), D is the burette–bottle clamp, E is a two-holed ground-glass joint, F is a ground-glass tension joint, a rubber tube is connected to a hydrogen cylinder and to the T-joint below L, H is a Bunsen valve, and J is hydrogen. The burette is filled by closing tap K and passing hydrogen through the rubber tube attached to the T-piece (below tap L) with tap L closed; taps L and K are opened, and the excess of liquid allowed to siphon back.

Another apparatus for the storage of standard solutions is shown in Fig. 3.10 which is self-explanatory. The solution is contained in the storage bottle A, and the 50 mL burette is fitted into this by means of a ground-glass joint B. To fill the burette, tap C is opened and the liquid pumped into the burette by means of the small bellows E. F is a small guard tube; this is filled with soda-lime or 'Carbosorb' when caustic alkali is contained in the storage bottle. Bottles with a capacity up to 2 litres are provided with standard ground-glass joints; large bottles, up to 15 L capacity, can also be obtained. With both of these storage vessels, for strongly alkaline solutions, the ground-glass joints should be replaced by rubber bungs or rubber tubing.

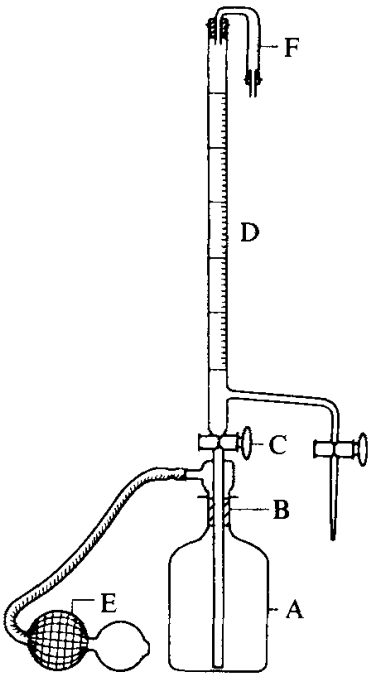

Fig. 3.10

The Dafert pipette (Fig. 3.2; Section 3.11) is a convenient apparatus for dispensing fixed volumes of a standard solution, as are also the various liquid dispensers which are available.

SOME BASIC TECHNIQUES

3.29 PREPARATION OF THE SUBSTANCE FOR ANALYSIS

Presented with a large quantity of a material to be analysed, the analyst is immediately confronted with the problem of selecting a representative sample

for the analytical investigations. It may well be that the material is in such large pieces that comminution is necessary in order to produce a specimen suitable for handling in the laboratory. These important factors are considered in Chapter 5 (Sections 5.2; 5.4), and as explained therein, the material is usually dried at 105–110 °C before analysis.

3.30 WEIGHING THE SAMPLE

If necessary refer to Section 3.5 dealing with the operation of a chemical balance, and to Sections 3.25 and 3.22 which are concerned with the use of weighing bottles and desiccators respectively.

The material, prepared as above, is usually transferred to a weighing bottle which is stoppered and stored in a desiccator. Samples of appropriate size are withdrawn from the weighing bottle as required, the bottle being weighed before and after the withdrawal, so that the weight of substance is obtained by difference.

Attention is drawn to vibro-spatulas which are useful adjuncts to the weighing-out of powders. The spatula is connected to the electric mains, and the powder is placed on the blade of the spatula. When the current is switched on, the blade is caused to vibrate and to deposit solid gradually into the beaker or other container over which it is held: the intensity of the vibration may be adjusted.

3.31 SOLUTION OF THE SAMPLE

Most organic substances can be dissolved readily in a suitable organic solvent and some are directly soluble in water or can be dissolved in aqueous solutions of acids (basic materials) or of alkalis (acidic materials). Many inorganic substances can be dissolved directly in water or in dilute acids, but materials such as minerals, refractories, and alloys must usually be treated with a variety of reagents in order to discover a suitable solvent: in such cases the preliminary qualitative analysis will have revealed the best procedure to adopt. Each case must be considered on its merits; no attempt at generalisation will therefore be made. It is however of value to discuss the experimental technique of the simple process of solution of a sample in water or in acids, and also the method of treatment of insoluble substances.

For a substance which dissolves readily, the sample is weighed out into a beaker, and the beaker immediately covered with a clockglass of suitable size (its diameter should not be more than about 1 cm larger than that of the beaker) with its convex side facing downwards. The beaker should have a spout in order to provide an outlet for the escape of steam or gas. The solvent is then added by pouring it carefully down a glass rod, the lower end of which rests against the wall of the beaker; the clockglass is displaced somewhat during this process. If a gas is evolved during the addition of the solvent (e.g. acids with carbonates, metals, alloys, etc.), the beaker must be kept covered as far as possible during the addition. The reagent is then best added by means of a pipette or by means of a funnel with a bent stem inserted beneath the clockglass at the spout of the beaker; loss by spirting or as spray is thus prevented. When the evolution of gas has ceased and the substance has completely dissolved, the underside of the clockglass is well rinsed with a stream of water from a wash bottle, care being taken that the washings fall on to the side of the beaker and not directly into

the solution. If warming is necessary, it is usually best to carry out the dissolution in a conical flask with a small funnel in the mouth; loss of liquid by spirting is thus prevented and the escape of gas is not hindered. When using volatile solvents, the flask should be fitted with a reflux condenser.

It may often be necessary to reduce the volume of the solution, or sometimes to evaporate completely to dryness. Wide and shallow vessels are most suitable, since a large surface is thus exposed and evaporation is thereby accelerated. Shallow beakers of resistance glass, Pyrex evaporating dishes, porcelain basins or casseroles, silica or platinum basins may be employed; the material selected will depend upon the extent of attack of the hot liquid upon it and upon the constituents being determined in the subsequent analysis. Evaporations should be carried out on the steam bath or upon a low-temperature hot plate; slow evaporation is preferable to vigorous boiling, since the latter may lead to some mechanical loss in spite of the precautions to be mentioned below. During evaporations, the vessel must be covered by a Pyrex clockglass of slightly larger diameter than the vessel, and supported either on a large all-glass triangle or upon three small **U**-rods of Pyrex glass hanging over the rim of the container. Needless to say, at the end of of the evaporation the sides of the vessel, the lower side of the clockglass and the triangle and glass hooks (if employed) should be rinsed with distilled water into the vessel.

For evaporation at the boiling point either a conical flask with a short Pyrex funnel in the mouth or a round-bottomed flask inclined at an angle of about 45° may be employed; in the latter the drops of liquid, etc., thrown up by the ebullition or by effervescence will be retained by striking the inside of the flask, while gas and vapour will escape freely. When organic solvents are employed the flask should be fitted with a 'swan-neck' tube and a condenser so that the solvent is recovered.

Consideration must be given to the possibility of losses occurring during the concentration procedure; for example, boric acid, halogen acids and nitric acid are lost from boiling aqueous solutions.

Substances which are insoluble (or only slightly soluble) in water can often be dissolved in an appropriate acid, but the possible loss of gaseous products must be borne in mind. The evolution of carbon dioxide, hydrogen sulphide and sulphur dioxide from carbonates, sulphides and sulphites respectively will be immediately apparent, but less obvious are losses of boron and silicon as the corresponding fluorides during evaporations with hydrofluoric acid, or loss of halogen by the treatment of halides with a strong oxidising agent such as nitric acid.

Concentrated hydrochloric acid will dissolve many metals (generally those situated above hydrogen in the electrochemical series), as well as many metallic oxides. Hot concentrated nitric acid dissolves most metals, but antimony, tin and tungsten are converted to slightly soluble acids thus providing a separation of these elements from other components of alloys. Hot concentrated sulphuric acid dissolves many substances and many organic materials are charred and then oxidised by this treatment.

A mixture of hydrochloric and nitric acids (3:1 by volume) known as *aqua regia* is a very potent solvent largely due to its oxidising character, and the addition of oxidants such as bromine or hydrogen peroxide frequently increases the solvent action of acids.

Hydrofluoric acid is mainly used for the decomposition of silicates; excess

hydrofluoric acid is removed by evaporation with sulphuric acid leaving a residue of metallic sulphates. Complexes of fluoride ions with many metallic cations are very stable and so the normal properties of the cation may not be exhibited. It is therefore essential to ensure complete removal of fluoride, and to achieve this, it may be necessary to repeat the evaporation with sulphuric acid two or three times. **Hydrofluoric acid must be handled with great care**; it causes serious and painful burns of the skin.

Perchloric acid attacks stainless steels and a number of iron alloys that do not dissolve in other acids. **Perchloric acid must be used with great care**; the hot concentrated acid gives explosive reactions with organic materials or easily oxidised inorganic compounds, and it is recommended that if frequent reactions and evaporations involving perchloric acid are to be performed, a fume cupboard which is free from combustible organic materials should be used. A mixture of perchloric and nitric acids is valuable as an oxidising solvent for many organic materials to produce a solution of inorganic constituents of the sample. For safety in such operations, the substance should be treated first with concentrated nitric acid, the mixture heated, and then careful additions of small quantities of perchloric acid can be made until the oxidation is complete. Even then, the mixture should not be evaporated because the nitric acid evaporates first allowing the perchloric acid to reach dangerously high concentrations. If a mixture of nitric, perchloric and sulphuric acids (3:**1**:1 by volume) is used, then the perchloric acid is also evaporated leaving a sulphuric acid solution of the components to be analysed. In this operation the organic part of the material under investigation is destroyed and the process is referred to as '**wet ashing**'.

Substances which are insoluble or only partially soluble in acids are brought into solution by fusion with the appropriate reagent. The most commonly used fusion reagents, or **fluxes** as they are called, are anhydrous sodium carbonate, either alone or, less frequently, mixed with potassium nitrate or sodium peroxide; potassium pyrosulphate, or sodium pyrosulphate; sodium peroxide; sodium hydroxide or potassium hydroxide. *Anhydrous* lithium metaborate has found favour as a flux, especially for materials containing silica;[12] when the resulting fused mass is dissolved in dilute acids, no separation of silica takes place as it does when a sodium carbonate melt is similarly treated. Other advantages claimed for lithium metaborate are the following.

1. No gases are evolved during the fusion or during the dissolution of the melt, and hence there is no danger of losses due to spitting.
2. Fusions with lithium metaborate are usually quicker (15 minutes will often suffice), and can be performed at a lower temperature than with other fluxes.
3. The loss of platinum from the crucible is less during a lithium metaborate fusion than with a sodium carbonate fusion.
4. Many elements can be determined directly in the acid solution of the melt without the need for tedious separations.

Naturally, the flux employed will depend upon the nature of the insoluble substance. Thus acidic materials are attacked by basic fluxes (carbonates, hydroxides, metaborates), whilst basic materials are attacked by acidic fluxes (pyroborates, pyrosulphates, and acid fluorides). In some instances an oxidising medium is useful, in which case sodium peroxide or sodium carbonate mixed with sodium peroxide or potassium nitrate may be used. The vessel in which fusion is effected must be carefully chosen; platinum crucibles are employed for

sodium carbonate, lithium metaborate and potassium pyrosulphate; nickel or silver crucibles, for sodium hydroxide or potassium hydroxide; nickel, gold, silver, or iron crucibles for sodium carbonate and/or sodium peroxide; nickel crucibles for sodium carbonate and potassium nitrate (platinum is slightly attacked).

For the preparation of samples for X-ray fluorescence spectroscopy, lithium metaborate is the preferred flux because lithium does not give rise to interfering X-ray emissions. The fusion may be carried out in platinum crucibles or in crucibles made from specially prepared graphite: these graphite crucibles can also be used for the vacuum fusion of metal samples for the analysis of occluded gases.

To carry out the fusion, a layer of flux is placed at the bottom of the crucible, and then an intimate mixture of the flux and the finely divided substance added; the crucible should be not more than about half-full, and should, generally, be kept covered during the whole process. The crucible is very gradually heated at first, and the temperature slowly raised to the required temperature. The final temperature should not be higher than is actually necessary; any possible further attack of the flux upon the crucible is thus avoided. When the fusion, which usually takes 30–60 minutes, has been completed, the crucible is grasped by means of the crucible tongs and gently rotated and tilted so that the molten material distributes itself around the walls of the container and solidifies there as a thin layer. This procedure greatly facilitates the subsequent detachment and solution of the fused mass. When cold, the crucible is placed in a casserole, porcelain dish, platinum basin, or Pyrex beaker (according to the nature of the flux) and covered with water. Acid is added, if necessary, the vessel is covered with a clockglass, and the temperature is raised to 95–100 °C and maintained until solution is achieved.

Many of the substances which require fusion treatment to render them soluble will in fact dissolve in mineral acids if the digestion with acid is carried out under pressure, and consequently at higher temperatures than those normally achieved. Such drastic treatment requires a container capable of withstanding the requisite pressure, and also resistant to chemical attack: these conditions are met in **acid digestion vessels** (bombs). These comprise a stainless-steel pressure vessel (capacity 50 mL) with a screw-on lid and fitted with a Teflon liner. They may be heated to 150–180 °C and will withstand pressures of 80–90 atmospheres; under these conditions decomposition of refractory materials may be accomplished in 45 minutes. Apart from the saving in time which is achieved, and the fact that the use of expensive platinum ware is obviated, other advantages of the method are that no losses can occur during the treatment, and the resulting solution is free from the heavy loading of alkali metals which follows the usual fusion procedures. A recent modification is the construction of vessels made entirely of Teflon which can be heated in a microwave oven, with even more rapid reaction times. A full discussion of decomposition techniques is given in Ref. 13.

A decomposition procedure applicable to organic compounds containing elements such as halogens, phosphorus or sulphur, consists in combustion of the organic material in an atmosphere of oxygen; the inorganic constituents are thus converted to forms which can be determined by titrimetric or spectrophotometric procedures. The method was developed by Schöniger[14,15] and is usually referred to as the Schöniger Oxygen Flask Method. A number

of reviews of the procedures have been published[16,17] giving considerable details of all aspects of the subject.

In outline the procedure consists of carefully weighing about 5–10 mg of sample on to a shaped piece of paper (Fig. 3.11*c*) which is folded in such a way that the tail (wick) is free. This is then placed in a platinum basket or carrier suspended from the ground-glass stopper of a 500 mL or 1 litre flask. The flask, containing a few millilitres of absorbing solution (e.g. aqueous sodium hydroxide), is filled with oxygen and then sealed with the stopper with the platinum basket attached.

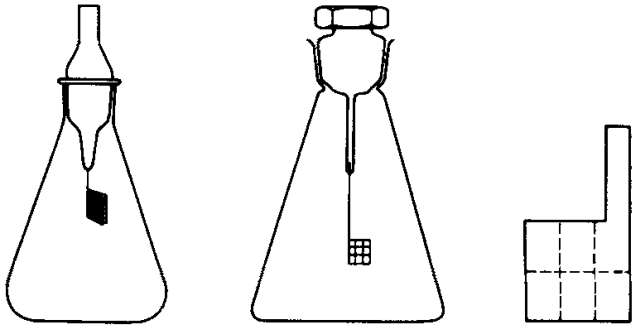

Fig. 3.11 Conventional flasks for microdeterminations: (*a*) air leak design; (*b*) stopper design; (*c*) filter paper for wrapping sample. Reproduced by permission from A. M. B. Macdonald, in *Advances in Analytical Chemistry and Instrumentation*, C. N. Reilly (Ed.), Vol. 4, Interscience, New York, 1965, p. 75.

The wick of the sample paper can either be ignited before the stopper is placed in the flask neck, or better still ignited by remote electrical control, or by an infrared lamp. In any case combustion is rapid and usually complete within 5–10 seconds. After standing for a few minutes until any combustion cloud has disappeared, the flask is shaken for 2–3 minutes to ensure that complete absorption has taken place. The solution can then be treated by a method appropriate to the element being determined.

Organic sulphur is converted to sulphur trioxide and sulphur dioxide by the combustion, absorbed in hydrogen peroxide, and the sulphur determined as sulphate.

The combustion products of organic halides are usually absorbed in sodium hydroxide containing some hydrogen peroxide. The resulting solutions may be analysed by a range of available procedures. For chlorides the method most commonly used is that of argentimetric potentiometric titration[18] (see Section 15.20), whilst for bromides a mercurimetric titration[19] is comparable with the argentimetric method.

Phosphorus from organophosphorus compounds, which are combusted to give mainly orthophosphate, can be absorbed by either sulphuric acid or nitric acid and readily determined spectrophotometrically either by the molybdenum blue method or as the phosphovanadomolybdate (Section 17.39).

Procedures have also been devised for the determination of metallic constituents. Thus, mercury is absorbed in nitric acid and titrated with sodium diethyldithiocarbamate, whilst zinc is absorbed in hydrochloric acid and determined by an EDTA titration (see Section 10.65).

The simplest method for decomposing an organic sample is to heat it in an open crucible until all carbonaceous matter has been oxidised leaving a residue of inorganic components, usually as oxide. The residue can then be dissolved in dilute acid giving a solution which can be analysed by appropriate procedures. This technique is referred to as **dry ashing**; it is obviously inapplicable when the inorganic component is volatile. Under these conditions the wet ashing procedure described under perchloric acid must be used. A full discussion of the destruction of organic matrices is given in Ref. 20.

3.32 PRECIPITATION

The conditions for precipitation of inorganic substances are given in Section 11.6. Precipitations are usually carried out in resistance-glass beakers, and the solution of the precipitant is added slowly (for example, by means of a pipette, burette, or tap funnel) and with efficient stirring of the suitably diluted solution. The addition must always be made without splashing; this is best achieved by allowing the solution of the reagent to flow down the side of the beaker or precipitating vessel. Only a moderate excess of the reagent is generally required; a very large excess may lead to increasing solubility (compare Section 2.6) or contamination of the precipitate. After the precipitate has settled, a few drops of the precipitant should always be added to determine whether further precipitation occurs. As a general rule, precipitates are not filtered off immediately after they have been formed; most precipitates, with the exception of those which are definitely colloidal, such as iron(III) hydroxide, require more or less digestion (Section 11.5) to complete the precipitation and make all particles of filterable size. In some cases digestion is carried out by setting the beaker aside and leaving the precipitate in contact with the mother liquor at room temperature for 12–24 hours; in others, where a higher temperature is permissible, digestion is usually effected near the boiling point of the solution. Hot plates, water baths, or even a low flame if no bumping occurs, are employed for the latter purpose; in all cases the beaker should be covered with a clockglass with the convex side turned down. If the solubility of the precipitate is appreciable, it may be necessary to allow the solution to attain room temperature before filtration.

3.33 FILTRATION

This operation is the separation of the precipitate from the mother liquor, the object being to get the precipitate and the filtering medium quantitatively free from the solution. The media employed for filtration are: (1) filter paper; (2) porous fritted plates of resistance glass, e.g. Pyrex (sintered-glass filtering crucibles), of silica (Vitreosil filtering crucibles), or of porcelain (porcelain filtering crucibles): see Section 3.24.

The choice of the filtering medium will be controlled by the nature of the precipitate (filter paper is especially suitable for gelatinous precipitates) and also by the question of cost. The limitations of the various filtering media are given in the account which follows.

3.34 FILTER PAPERS

Quantitative filter papers must have a very small ash content; this is achieved during manufacture by washing with hydrochloric and hydrofluoric acids. The

sizes generally used are circles of 7.0, 9.0, 11.0, and 12.5 cm diameter, those of 9.0 and 11.0 cm being most widely employed. The ash of a 11 cm circle should not exceed 0.0001 g; if the ash exceeds this value, it should be deducted from the weight of the ignited residue. Manufacturers give values for the average ash per paper: the value may also be determined, if desired, by igniting several filter papers in a crucible. Quantitative filter paper is made of various degrees of porosity. The filter paper used must be of such texture as to retain the smallest particles of precipitate and yet permit of rapid filtration. Three textures are generally made, one for very fine precipitates, a second for the average precipitate which contains medium-sized particles, and a third for gelatinous precipitates and coarse particles. The speed of filtration is slow for the first, fast for the third, and medium for the second. 'Hardened' filter papers are made by further treatment of quantitative filter papers with acid; these have an extremely small ash, a much greater mechanical strength when wet, and are more resistant to acids and alkalis: they should be used in all quantitative work. The characteristics of the Whatman series of hardened ashless filter papers are shown in Table 3.7.

Table 3.7 'Whatman' quantitative filter papers

Filter paper	Hardened ashless		
Number	540	541	542
Speed	Medium	Fast	Slow
Particle size retention	Medium	Coarse	Fine
Ash (%)	0.008	0.008	0.008

The size of the filter paper selected for a particular operation is determined by the bulk of the precipitate, and not by the volume of the liquid to be filtered. The entire precipitate should occupy about a third of the capacity of the filter at the end of the filtration. The funnel should match the filter paper in size; the folded paper should extend to within 1–2 cm of the top of the funnel, but never closer than 1 cm.

A funnel with an angle as nearly 60° as possible should be employed; the stem should have a length of about 15 cm in order to promote rapid filtration. The filter paper must be carefully fitted into the funnel so that the upper portion beds tightly against the glass. To prepare the filter paper for use, the dry paper is usually folded exactly in half and exactly again in quarters. The folded paper is then opened so that a 60° cone is formed with three thicknesses of paper on the one side and a single thickness on the other; the paper is then adjusted to fit the funnel. The paper is placed in the funnel, moistened thoroughly with water, pressed down tightly to the sides of the funnel, and then filled with water. If the paper fits properly, the stem of the funnel will remain filled with liquid during the filtration.

To carry out a filtration, the funnel containing the properly fitted paper is placed in a funnel stand (or is supported vertically in some other way) and a clean beaker placed so that the stem of the funnel just touches the side; this will prevent splashing. The liquid to be filtered is then poured down a glass rod into the filter, directing the liquid against the side of the filter and not into the apex; the lower end of the stirring rod should be very close to, but should not quite touch, the filter paper on the side having three thicknesses of paper. The

paper is never filled completely with the solution; the level of the liquid should not rise closer than to within 5–10 mm of the top of the paper. A precipitate which tends to remain in the bottom of the beaker should be removed by holding the glass rod across the beaker, tilting the beaker, and directing a jet of water from a wash bottle so that the precipitate is rinsed into the filter funnel. This procedure may also be adopted to transfer the last traces of the precipitate in the beaker to the filter. Any precipitate which adheres firmly to the side of the beaker or to the stirring rod may be removed with a rubber tipped rod or 'policeman' (Section 3.23).

Filtration by suction is rarely necessary: with gelatinous and some finely divided precipitates, the suction will draw the particles into the pores of the paper, and the speed of filtration will actually be reduced rather than increased.

3.35 CRUCIBLES WITH PERMANENT POROUS PLATES

Reference has already been made in Section 3.24 to these crucibles and to crucibles with a porous base. In use, the crucible is supported in a special holder, known as a crucible adapter, by means of a wide rubber tube (Fig. 3.12); the bottom of the crucible should be quite free from the side of the funnel and from the rubber gasket, the latter in order to be sure that the filtrate does not come into contact with the rubber. The adapter passes through a one-holed rubber bung into a large filter flask of about 750 mL capacity. The tip of the funnel must project below the side arm of the filter flask so that there is no risk that the liquid may be sucked out of the filter flask. The filter flask should be coupled with another flask of similar capacity, and the latter connected to a water filter pump; if the water in the pump should 'suck back', it will first enter the empty flask and the filtrate will not be contaminated. It is advisable also to have some sort of pressure regulator to limit the maximum pressure under which filtration is conducted. A simple method is to insert a glass tap in the second filter flask, as in the figure; alternatively, a glass **T**-piece may be introduced between the receiver and the pump, and one arm closed either by a glass tap or by a piece of heavy rubber tubing ('pressure' tubing) carrying a screw clip.

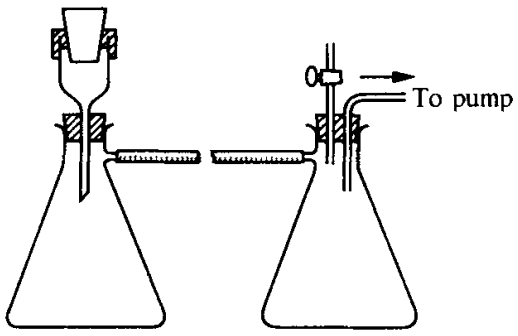

Fig. 3.12

When the apparatus is assembled, the crucible is half-filled with distilled water, then gentle suction is applied to draw the water through the crucible. When the water has passed through, suction is maintained for 1–2 minutes to remove as much water as possible from the filter plate. The crucible is then placed on a small ignition dish or saucer or upon a shallow-form Vitreosil

capsule and dried to constant weight at the same temperature as that which will be subsequently used in drying the precipitate. For temperatures up to about 250 °C a thermostatically controlled electric oven should be used. For higher temperatures, the crucible may be heated in an electrically heated muffle furnace. In all cases the crucible is allowed to cool in a desiccator before weighing.

When transferring a precipitate into the crucible, the same procedure is employed as described in Section 3.34 referring to the use of filter papers: care must be taken that the liquid level in the crucible is never less than 1 cm from the top of the crucible.

Care must be taken with both sintered glass and porous base crucibles to avoid attempting the filtration of materials that may clog the filter plate. A new crucible should be washed with concentrated hydrochloric acid and then with distilled water. The crucibles are chemically inert and are resistant to all solutions which do not attack silica; they are attacked by hydrofluoric acid, fluorides, and strongly alkaline solutions.

Crucibles fitted with permanent porous plates are cleaned by shaking out as much of the solid as possible, and then dissolving out the remainder of the solid with a suitable solvent. A hot 0.1 *M* solution of the tetrasodium salt of the ethylenediaminetetra-acetic acid is an excellent solvent for many of the precipitates [except metallic sulphides and hexacyanoferrates(III)] encountered in analysis. These include barium sulphate, calcium oxalate, calcium phosphate, calcium oxide, lead carbonate, lead iodate, lead oxalate, and ammonium magnesium phosphate. The crucible may either be completely immersed in the hot reagent or the latter may be drawn by suction through the crucible.

3.36 WASHING PRECIPITATES

Most precipitates are produced in the presence of one or more soluble compounds. Since the latter are frequently not volatile at the temperature at which the precipitate is ultimately dried, it is necessary to wash the precipitate to remove such material as completely as possible. The minimum volume of the washing liquid required to remove the objectionable matter should be used, since no precipitate is absolutely insoluble. Qualitative tests for the removal of the impurities should be made on small volumes of the filtered washing solution. Furthermore, it is better to wash with a number of small portions of the washing liquid, which are well drained between each washing, than with one or two large portions, or by adding fresh portions of the washing liquid while solution still remains on the filter (see Section 11.8).

The ideal washing liquid should comply as far as possible with the following conditions.

1. It should have no solvent action upon the precipitate, but dissolve foreign substances easily.
2. It should have no dispersive action on the precipitate.
3. It should form no volatile or insoluble product with the precipitate.
4. It should be easily volatile at the temperature of drying of the precipitate.
5. It should contain no substance which is likely to interfere with subsequent determinations in the filtrate.

In general, pure water should not be used unless it is certain that it will not dissolve appreciable amounts of the precipitate or peptise it. If the precipitate

is appreciably soluble in water, a common ion is usually added, since any electrolyte is less soluble in a dilute solution containing one of its ions than it is in pure water (Section 2.7); as an example the washing of calcium oxalate with dilute ammonium oxalate solution may be cited. If the precipitate tends to become colloidal and pass through the filter paper (this is frequently observed with gelatinous or flocculent precipitates), a wash solution containing an electrolyte must be employed (compare Section 11.3). The nature of the electrolyte is immaterial, provided it has no action upon the precipitate during washing and is volatilised during the final heating. Ammonium salts are usually selected for this purpose: thus ammonium nitrate solution is employed for washing iron(III) hydroxide. In some cases it is possible to select a solution which will both reduce the solubility of the precipitate and prevent peptisation; for example, the use of dilute nitric acid with silver chloride. Some precipitates tend to oxidise during washing; in such instances the precipitate cannot be allowed to run dry, and a special washing solution which re-converts the oxidised compounds into the original condition must be employed, e.g. acidified hydrogen sulphide water for copper sulphide. Gelatinous precipitates, like aluminium hydroxide, require more washing than crystalline ones, such as calcium oxalate.

In most cases, particularly if the precipitate settles rapidly or is gelatinous, **washing by decantation** may be carried out. As much as possible of the liquid above the precipitate is transferred to the prepared filter (either filter paper or filter crucible), observing the usual precautions, and taking care to avoid, as far as possible, disturbing the precipitate. Twenty to fifty millilitres of a suitable wash liquid is added to the residue in the beaker, the solid stirred up and allowed to settle. If the solubility of the precipitate allows, the solution should be heated, since the rate of filtration will thus be increased. When the supernatant liquid is clear, as much as possible of the liquid is decanted through the filtering medium. This process is repeated three to five times (or as many times as is necessary) before the precipitate is transferred to the filter. The main bulk of the precipitate is first transferred by mixing with the wash solution and pouring off the suspension, the process being repeated until most of the solid has been removed from the beaker. Precipitate adhering to the sides and bottom of the beaker is then transferred to the filter with the aid of a wash bottle as described in Section 3.34, using a 'policeman' if necessary to transfer the last traces of precipitate. Finally, a wash bottle is used to wash the precipitate down to the bottom of the filter paper or to the plate of the filter crucible.

In all cases, tests for the completeness of washing must be made by collecting a small sample of the washing solution after it is estimated that most of the impurities have been removed, and applying an appropriate qualitative test. Where filtration is carried out under suction, a small test-tube is placed under the crucible adapter.

3.37 DRYING AND IGNITING PRECIPITATES

After a precipitate has been filtered and washed, it must be brought to a constant composition before it can be weighed. The further treatment will depend both upon the nature of the precipitate and upon that of the filtering medium; this treatment consists in drying or igniting the precipitate. Which of the latter two terms is employed depends upon the temperature at which the precipitate is heated. There is, however, no definite temperature below or above which the

precipitate is said to be dried or ignited respectively. The meaning will be adequately conveyed for our purpose if we designate *drying* when the temperature is below 250 °C (the maximum temperature which is readily reached in the usual thermostatically controlled, electric drying-oven), and *ignition* above 250 °C up to, say 1200 °C. Precipitates that are to be dried should be collected on filter paper, or in sintered-glass or porcelain filtering crucibles. Precipitates that are to be ignited are collected on filter paper, porcelain filtering crucibles, or silica filtering crucibles. Ignition is simply effected by placing in a special ignition dish and heating with the appropriate burner; alternatively, these crucibles (and, indeed, any type of crucible) may be placed in an electrically heated muffle furnace, which is equipped with a pyrometer and a means for controlling the temperature.

Attention is directed to the information provided by thermogravimetric analysis[21,22] concerning the range of temperature to which a precipitate should be heated for a particular composition. In general, thermal gravimetric curves seem to suggest that in the past precipitates were heated for too long a period and at too high a temperature. It must, however, be borne in mind that in some cases the thermal gravimetric curve is influenced by the experimental conditions of precipitation, and even if a horizontal curve is not obtained, it is possible that a suitable weighing form may be available over a certain temperature range. Nevertheless, thermograms do provide valuable data concerning the range of temperature over which a precipitate has a constant composition under the conditions that the thermogravimetric analysis was made; these, at the very least, provide a guide for the temperature at which a precipitate should be dried and heated for quantitative work, but due regard must be paid to the general chemical properties of the weighing form.

Although precipitates which require ignition will usually be collected in porcelain or silica filtering crucibles, there may be some occasions where filter paper has been used, and it is therefore necessary to describe the method to be adopted in such cases. The exact technique will depend upon whether the precipitate may be safely ignited in contact with the filter paper or not. It must be remembered that some precipitates, such as barium sulphate, may be reduced or changed in contact with filter paper or its decomposition products.

A. Incineration of the filter paper in the presence of the precipitate. A silica crucible is first ignited to constant weight (i.e. to within 0.0002 g) at the same temperature as that to which the precipitate is ultimately heated. The well-drained filter paper and precipitate are carefully detached from the funnel; the filter paper is folded so as to enclose the precipitate completely, care being taken not to tear the paper. The packet is placed point-down in the weighed crucible, which is supported on a pipe-clay, or better, a silica triangle resting on a ring stand. The crucible is slightly inclined, and partially covered with the lid, which should rest partly on the triangle. A *very small flame* is then placed under the crucible lid; drying thus proceeds quickly and without undue risk. When the moisture has been expelled, the flame is increased slightly so as to carbonise the paper *slowly*. The paper should not be allowed to inflame, as this may cause a mechanical expulsion of fine particles of the precipitate owing to the rapid escape of the products of combustion: if, by chance, it does catch fire, the flame should be extinguished by momentarily placing the cover on the mouth of the crucible with the aid of a pair of crucible tongs. When the paper has completely

carbonised and vapours are no longer evolved, the flame is moved to the back (bottom) of the crucible and the carbon slowly burned off while the flame is gradually increased.* After all the carbon has been burned away, the crucible is covered completely (if desired, the crucible may be placed in a vertical position for this purpose) and heated to the required temperature by means of a Bunsen burner. Usually it takes about 20 minutes to char the paper, and 30–60 minutes to complete the ignition

When the ignition is ended, the flame is removed and, after 1–2 minutes, the crucible and lid are placed in a desiccator containing a suitable desiccant (Section 3.22), and allowed to cool for 25–30 minutes. The crucible and lid are then weighed. The crucible and contents are then ignited at the same temperature for 10–20 minutes, allowed to cool in a desiccator as before, and weighed again. The ignition is repeated until constant weight is attained. Crucibles should always be handled with clean crucible tongs and preferably with platinum-tipped tongs.

It is important to note that 'heating to constant weight' has no real significance unless the periods of heating, cooling of the *covered* crucible, and weighing are duplicated.

B. Incineration of the filter paper apart from the precipitate. This method is employed in all those cases where the ignited substance is reduced by the burning paper; for example, barium sulphate, lead sulphate, bismuth oxide, copper oxide, etc. The funnel containing the precipitate is covered by a piece of qualitative filter paper upon which is written the formula of the precipitate and the name of the owner; the paper is made secure by crumpling its edges over the rim of the funnel so that they will engage the outer conical portion of the funnel. The funnel is placed in a drying oven maintained at 100–105 °C, for 1–2 hours or until completely dry. A sheet of glazed paper about 25 cm square (white or black, to contrast with the colour of the precipitate) is placed on the bench away from all draughts. The dried filter is removed from the funnel, and as much as possible of the precipitate is removed from the paper and allowed to drop on a clockglass resting upon the glazed paper. This is readily done by very gently rubbing the sides of the filter paper together, when the bulk of the precipitate becomes detached and drops upon the clockglass. Any small particles of the precipitate which may have fallen upon the glazed paper are brushed into the clockglass with a small camel-hair brush. The clockglass containing the precipitate is then covered with a larger clockglass or with a beaker. The filter paper is now carefully folded and placed inside a weighed porcelain or silica crucible. The crucible is placed on a triangle and the filter paper incinerated as detailed above. The crucible is allowed to cool, and the filter ash subjected to a suitable chemical treatment in order to convert any reduced or changed material into the form finally desired. The cold crucible is then placed upon the glazed paper and the main part of the precipitate carefully transferred from the clockglass to the crucible. A small camel-hair brush will assist in the transfer. Finally, the precipitate is brought to constant weight by heating to the necessary temperature as detailed under A.

* If the carbon on the lid is oxidised only slowly, the cover may be heated separately in a flame. It is, of course, held in clean crucible tongs.

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