

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, then an intimate mixture of the flux and the finely divided substance added; the crucible should not be 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 min, has been completed, the crucible is grasped by means of the crucible tongs and gently rotated and tilted so 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 cooled 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). Acid digestion vessels comprise a stainless steel pressure vessel (capacity 50 mL) with a screw-on lid fitted with a Teflon liner. They may be heated to 150–180°C and will withstand pressures of 80–90 atm (8–9 MPa); under these conditions it is possible to decompose refractory materials in about 45 min. Apart from the time saving and the cost saving – there is no need for expensive platinum ware – other advantages are that no losses can occur during the treatment, and the resulting solution is free from the heavy loading of alkali metal which follows the usual fusion procedures. Digestions of this type can now be carried out in microwave ovens using vessels specially constructed from Teflon. A full discussion of decomposition techniques is given in the literature.<sup>[7]</sup>

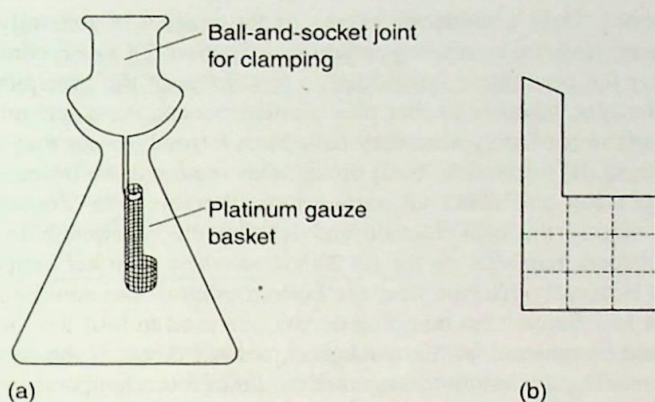
### 3.29 Decomposing organic compounds

Analysis of organic compounds for elements such as halogens, phosphorus or sulphur is achieved by 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<sup>[8,9]</sup> and is usually known as the Schöniger oxygen flask method. A number of reviews have been published giving considerable detail on all aspects of the procedure.

In outline the procedure consists of carefully weighing about 5–10 mg of sample on a shaped piece of paper (Figure 3.10(b)) 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 L flask. The flask, containing a few millilitres of absorbing solution (e.g. aqueous sodium hydroxide), is filled with oxygen then sealed using the stopper with the platinum basket attached.

The wick of the sample paper can either be ignited before the stopper is placed in the neck of the flask, or better still ignited by remote electrical control or an infrared lamp.

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**Figure 3.10** Decomposing organic compounds: (a) safety oxygen flask, (b) paper shape for wrapping samples

Combustion is rapid and usually complete within 5–10 s. After standing for a few minutes until any combustion cloud has disappeared, the flask is shaken for 2–3 min to ensure 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 argentimetric potentiometric titration,<sup>[12]</sup> whereas for bromides it is mercurimetric titration.<sup>[13]</sup>

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 17.35). Procedures have also been devised for determining metallic constituents. Mercury is absorbed in nitric acid and titrated with sodium diethyldithiocarbamate, and zinc is absorbed in hydrochloric acid and determined by an EDTA titration (Section 13.77).

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 to give a solution which can be analysed by appropriate procedures. This technique is known 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 is given in the literature.<sup>[14]</sup>

### 3.30 Precipitation

The conditions for precipitation of inorganic substances are given in Section 11.2. Precipitations are usually carried out in resistance-glass beakers, and the solution of the precipitant is added slowly (e.g. by 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 large excess may lead to increasing solubility (Section 2.13) 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; unless they are definitely colloidal, such as iron(III) hydroxide, most precipitates require more or less digestion to complete the precipitation and make all particles of filterable size. Sometimes 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 h; and where a higher temperature is permissible, digestion is usually effected near the boiling point of the solution. Hotplates, water baths, or even a low flame if no bumping occurs, are used to heat the mixture; in all cases the beaker should be covered with a clockglass, convex down. If the solubility of the precipitate is appreciable, the solution may need to attain room temperature before filtration.

### 3.31 Filtration

Filtration is the separation of the precipitate from the mother liquor; the object is to get the precipitate and the filtering medium quantitatively free from the solution. The systems employed for filtration are (1) filter paper; (2) porous fritted plates made of resistant glass, e.g. Pyrex (sintered-glass filtering crucibles), of silica (Vitreosil filtering crucibles) or made of porcelain (porcelain filtering crucibles); see Section 3.21. The choice of the filtering medium will be controlled by the nature of the precipitate (filter paper is especially suitable for gelatinous precipitates) and the cost. The limitations of the various filtering media are given below.

### 3.32 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 chosen are circles of 7.0, 9.0, 11.0 and 12.5 cm diameter; 9.0 and 11.0 cm are most widely used. The ash of an 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; this may also be determined by igniting several filter papers in a crucible. Quantitative filter paper is made in various degrees of porosity. The texture of the filter paper must allow rapid filtration while retaining the smallest particles of the precipitate. Three textures are generally made, one for very fine precipitates, one for the average precipitate containing medium-sized particles, and one for gelatinous precipitates and coarse particles. The speed of filtration depends on the porosity of the paper.

'Hardened' filter papers are made by further treatment of quantitative filter papers with acid; they 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. Table 3.5 gives the characteristics for the Whatman series of hardened ashless filter papers. The size of the filter paper selected for a particular operation is determined by the bulk of the precipitate, not by the volume of the liquid to be filtered. The entire precipitate should occupy about one-third of the filter's capacity 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.

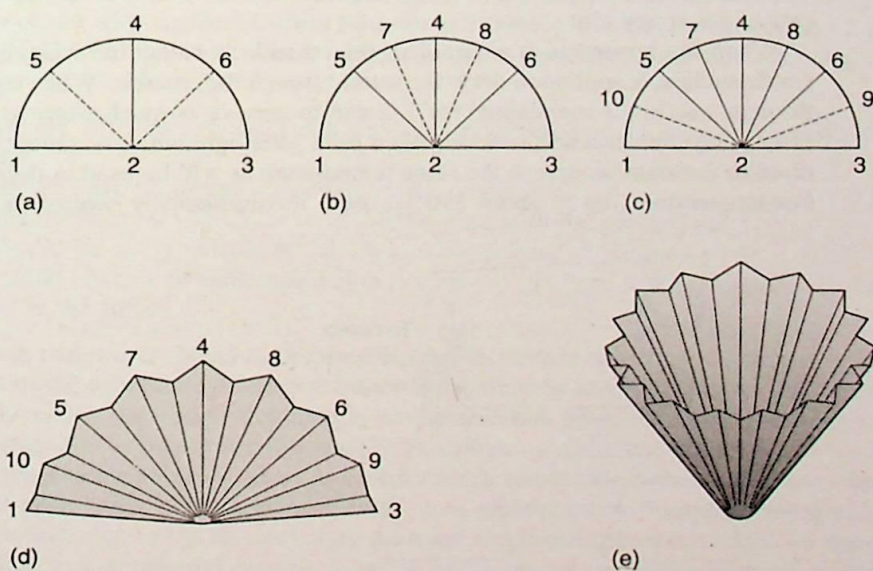
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**Table 3.5** Whatman quantitative filter papers

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

To promote rapid filtration, use a funnel with an angle as near as possible to  $60^\circ$  and a stem of length about 15 cm. The filter paper must be carefully fitted into the funnel so 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  $60^\circ$  cone is formed with three thicknesses of paper on 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, then filled with water. If the paper fits properly, the stem of the funnel will remain filled with liquid during the filtration. Sometimes filtration may be achieved more rapidly using a fluted filter paper (Figure 3.11).

To carry out a filtration, the funnel containing the properly fitted paper is placed in a funnel stand (or supported vertically in some other way) and a clean beaker is placed so 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, not into the apex; the lower end of the stirring rod should be very close to the



**Figure 3.11** How to make a fluted filter paper

filter paper, but not quite touching, 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 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 the precipitate is rinsed into the filter funnel. This procedure may also be used 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 3.20).

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.

### 3.33 Crucibles with permanent porous plates

Section 3.21 has already mentioned crucibles with porous plates. In use they are supported in a special holder, known as a crucible adaptor, by means of a wide rubber tube (Figure 3.12). The bottom of the crucible should be quite free from the side of the funnel and free from the rubber gasket; this ensures the filtrate does not come into contact with the rubber. The adaptor 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 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 which is 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 Figure 3.12; 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.

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 min to remove as much water as possible from the filter plate. The crucible is then placed on a small ignition dish, saucer or watchglass and dried to constant weight at the same temperature as will be used in drying the precipitate. For temperatures up to about 250 °C, use a thermostatically controlled electric oven. For

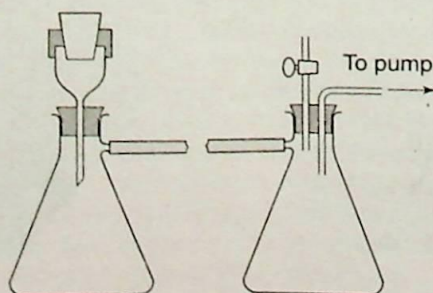


Figure 3.12 How to support crucibles using a wide rubber tube