

## Common Apparatus and Basic Techniques

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 3.32. Take care that the liquid level in the crucible is never less than 1 cm from the top of the crucible.

With both sintered-glass and porous-base crucibles, avoid filtering materials that may clog the filter plate. A new crucible should be washed with concentrated hydrochloric acid 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, 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 encountered in analysis, except metallic sulphides and hexacyanoferrates(III). These include barium sulphate, calcium oxalate, calcium phosphate, calcium oxide, lead carbonate, lead iodate, lead oxalate and ammonium magnesium phosphate. The crucible may be completely immersed in the hot reagent, or the hot reagent may be drawn by suction through the crucible.

### 3.34 Washing precipitates

Most precipitates are produced in the presence of one or more soluble compounds. Since the soluble compounds are frequently not volatile at the drying temperature of the precipitate, it is necessary to wash the precipitate to remove impurities 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 removal of the impurities should be made on small volumes of the filtered washing solution. 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 (Section 11.5).

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

1. It should have no solvent action on 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 drying temperature 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 it will not dissolve appreciable amounts of the precipitate. 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 2.15); calcium oxalate may be washed with dilute ammonium oxalate solution. 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 (Section 11.5). The nature of the electrolyte is immaterial, provide it has no action on the precipitate during washing and



is volatilised during the final heating. Ammonium salts are usually selected for this purpose; ammonium nitrate solution is used for washing iron(III) hydroxide.

Sometimes it is possible to select a solution which will both reduce the solubility of the precipitate and prevent peptisation; for example, dilute nitric acid is used with silver chloride. Some precipitates tend to oxidise during washing; then the precipitate cannot be allowed to run dry, and a special washing solution which reconverts 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 precipitates, 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 minimise any disturbance of the precipitate. Some 20–50 mL 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 be higher. 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 transferred to the filter with the aid of a wash bottle as described in Section 3.31, 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 a 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 adaptor.

### 3.35 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, drying or igniting the precipitate will depend on the nature of the precipitate and the nature of the filtering medium. The choice of drying or igniting depends on the temperature to which the precipitate is heated. In general, drying applies when the temperature is below 250 °C (the maximum temperature which is readily reached in the usual thermostatically controlled, electric drying oven) and ignition applies from 250 to 1200 °C. Precipitates for drying should be collected on filter paper, or in sintered-glass or porcelain filtering crucibles. Precipitates for igniting should be collected on filter paper, porcelain filtering crucibles, or silica filtering crucibles. Igniting is simply effected by placing in a special ignition dish and heating with the appropriate burner; alternatively, these crucibles (indeed, any type of crucible) may be placed in an electrically heated muffle furnace equipped with a pyrometer and a means for controlling the temperature.

Thermogravimetry (TG) provides information on the temperature range to which a precipitate should be heated for a particular composition.<sup>[15,16]</sup> In general, TG curves seem to suggest that, in the past, precipitates were heated for too long and at too high



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temperature. But remember that the TG curve is sometimes 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, TG curves do provide valuable data concerning the range of temperature over which a precipitate has a constant composition under the conditions that the analysis was made; at the very least, they 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 times when filter paper is used, then the ignition method will be somewhat different. The exact technique depends on whether or not the precipitate may be safely ignited in contact with the filter paper. Some precipitates, e.g. barium sulphate, may be reduced or changed in contact with filter paper or its decomposition products.

### 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 the precipitate ultimately reaches. 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 taking care not to tear the paper. The packet is placed point-down in the weighed crucible, which is supported on a pipeclay, 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 it does catch fire, the flame should be extinguished by momentarily placing the cover on the mouth of the crucible with the aid 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, this may be done with the crucible in a vertical position) and heated to the required temperature by means of a Bunsen burner. Usually it takes about 20 min to char the paper, and 30–60 min to complete the ignition.

When the ignition is ended, the flame is removed and, after 1–2 min, the crucible and lid are placed in a desiccator containing a suitable desiccant (Section 3.19) and allowed to cool for 25–30 min. The crucible and lid are then weighed. The crucible and contents are then ignited at the same temperature for 10–20 min, 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. Remember that 'heating to constant weight' has no real significance unless the periods of heating, cooling of the **covered** crucible, and weighing are duplicated.

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



### Incineration of the filter paper apart from the precipitate

This method is used whenever the ignited substance is reduced by the burning paper. For example, barium sulphate, lead sulphate, bismuth oxide and copper oxide. The filter paper containing the precipitate is covered by a piece of qualitative filter paper, made secure by crumpling its edges over the rim of the funnel so they 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 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 paper is removed from the funnel, then as much as possible of the precipitate is removed and allowed to drop onto a clockglass resting on the glazed paper. This should be done by very gently rubbing the sides of the filter paper together, when the bulk of the precipitate becomes detached and drops onto the clockglass. Any small particles of precipitate which may have fallen onto the glazed paper are brushed into the clockglass with a small camel-hair brush.

The clockglass containing the precipitate is covered with a larger clockglass or with a beaker. The filter paper is then carefully folded and placed inside a weighed porcelain or silica crucible. The crucible is placed on a triangle and the filter paper incinerated as 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 crucible is then placed on 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 explained in the previous section.

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