

done by recrystallisation from water. Using a conical flask, a known weight of the solid dissolved in a volume of water sufficient to give a saturated or nearly saturated solution at the boiling point. 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 any insoluble material present. If the substance crystallises out in the funnel, it should be filtered through a heated or jacketed 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 should be constantly stirred in order to promote the formation of small crystals and to prevent the trapping of mother liquor. The solid is then separated from the mother liquor by filtration, using one of the funnels shown in Figure 3.6. 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, then washed with small portions of the original solvent to remove the adhering mother liquor. The recrystallised solid is dried in an oven above the laboratory temperature with the exclusion of dust. The dried solid is preserved in glass stoppered bottles. When the solid is removed from the funnel, take great care to avoid introducing fibres from the filter paper, or small particles of glass from the glass filter disc.

Some inorganic 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 a concentrated aqueous solution by the addition of a liquid, miscible with water, in which it is less soluble. Many inorganic compounds are almost insoluble in ethanol, so ethanol is generally used. Take care that the amount of ethanol or other solvent 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. Liquids can be purified by fractional distillation.

Sublimation

Sublimation is used 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

Zone refining was originally developed to refine certain metals; it 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 m. 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, and the substance travels slowly down the tube with the heater. Since impurities normally lower the melting point of a substance, the impurities tend to flow down the column in step with the heater, becoming concentrated in the lower part of the tube. The process is

usually repeated several times (the apparatus may be programmed to reproduce automatically a given number of cycles) until the required degree of purification has been achieved.

3.25 Standard solutions

In any analytical laboratory it is essential to maintain stocks of various reagents in solution. Standard solutions of accurately known concentration need to be stored correctly. They may be classified into four types:

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) (IUPAC primary standard solutions).
4. Standard titrimetric solutions which have a known concentration (determined either by weighing or by standardisation) of a substance other than a primary standard (IUPAC secondary standard solutions).

For **reagent solutions** (item 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** use the following procedure. 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 the required amount of substance is then transferred from the weighing bottle to the funnel, taking care that no particles are lost. After the weighing bottle has been reweighed, 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, use a dropping tube drawn out to form a very fine jet.

If a watchglass 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 watchglass. If the weighing scoop (Figure 3.8) is used, then a funnel is not needed, provided the flask is big enough to allow the end of the scoop easily into its 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 deionised 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 deionised water, added to the contents of the flask, and finally the solution is made up to the mark. To ensure the solution is at room temperature, it may be necessary to allow the flask to stand for a while before making the final adjustment to the mark. **Never heat the graduated flask.**

It is also possible to prepare the standard solution by using one of the commercial volumetric solutions supplied in sealed ampoules; all they require is 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 L or 2.5 L bottles. For work requiring the highest accuracy, the bottles should be Pyrex, or other resistance glass, and fitted with ground-glass stoppers; this considerably reduces the solvent action of the solution. For alkaline solutions, a plastic stopper is

preferable to a glass stopper, and a polythene container may often replace glass vessels. But some solutions, e.g. iodine and silver nitrate, can be stored only in glass containers and for iodine and silver nitrate the bottle should be made of dark (brown) glass. Solutions of EDTA (Section 10.38) are best stored in polythene containers.

Bottles for storing standard solutions should initially be clean and dry. They should be rinsed with a small amount of the standard solution then allowed to drain before the bulk of the solution is poured in and the bottle stoppered. Bottles which have been washed and are still wet with water will require rinsing and draining with at least three small volumes of the standard solution, and they should be well drained between each rinse; then they can be filled with the standard solution. Immediately after the solution has been transferred to the stock bottle, it should be labelled with the name of the solution, its concentration, the date of preparation and 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 are not usually expressed now in normalities, although they are still used by some people and their relationship is explained briefly in Appendix 18.

Some standard solutions are likely to be affected by air (e.g. alkali hydroxides which absorb carbon dioxide; iron(II) and titanium(III) salts which are readily oxidised). Ideally they should be kept under an inert atmosphere, such as nitrogen, in bottles fitted with automatic dispensers or burettes. A simple apparatus for storage and use of standard solutions is shown in Figure 3.9. 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 (D), the tap (C) is opened and the liquid pumped in using the small bellows (E). A small guard tube (F) is fitted to the top of the burette.

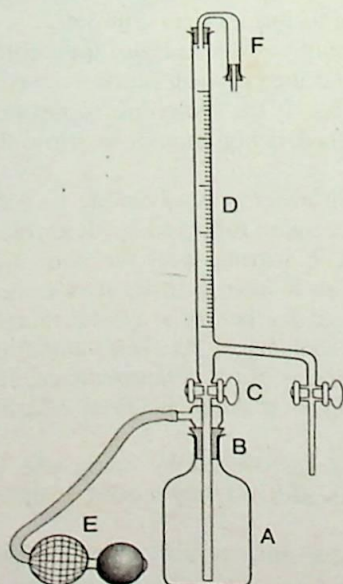


Figure 3.9 How to store a standard solution: A = storage bottle, B = ground-glass joint, C = burette tap, D = burette, E = small bellows, F = small guard tube

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guard tube (F) is filled with soda-lime or Carbosorb when caustic alkali is contained in the storage bottle. Bottles with a capacity up to 2 L 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. Many fixed volumes of standard solution for multiple analyses can be dispensed by automatic syringe pipettes of the type used in automatic analysers.

Some basic techniques

3.26 Preparing substances for analysis

In many instances the analyst is presented with the problem of selecting a representative sample from a large quantity of available material. Sometimes this may also mean that a large bulky material has to be broken into smaller more uniform pieces in order to obtain a sample suitable for laboratory work. This is considered in Sections 5.3 and 5.4. Before analysis most samples are dried at 105–110 °C to remove moisture.

3.27 Weighing the sample

Section 3.3 explains the operation of a chemical balance, and Sections 3.22 and 3.19 cover 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 is weighed before and after the withdrawal, so the weight of substance is obtained by difference.

3.28 Dissolving the sample

Most organic substances can be readily dissolved in a suitable organic solvent, and some are directly soluble in water or can be dissolved in aqueous solutions of acids or alkalis. Many inorganic substances can be dissolved directly in water or in dilute acids, but materials such as minerals, refractories and alloys must usually be tested with a variety of reagents in order to discover a suitable solvent; the preliminary qualitative analysis will have revealed the best procedure to adopt. Each case must be considered on its merits, but it is worth considering how to dissolve a sample in water or in acids, and how to treat 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 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 added by pouring it carefully down a glass rod, the lower end of which rests against the wall of the beaker, with the clockglass slightly displaced. If a gas is evolved during addition of the solvent (e.g. acids with carbonates, metals, alloys), the beaker must be kept covered as far as possible during the addition. The reagent is then best added by pipette or by funnel with a bent stem inserted beneath the clockglass at the spout of the beaker; loss by spurting 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 spurting 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, shallow vessels are most suitable, since a large surface is thus exposed and evaporation is thereby accelerated. Pyrex evaporating dishes, porcelain basins or casseroles, and silica or platinum basins may be employed; the material selected will depend on the extent of attack by the hot liquid, and on the constituents being determined in the subsequent analysis. Evaporations should be carried out on the steam bath or on a low-temperature hotplate; slow evaporation is preferable to vigorous boiling, since boiling may lead to some mechanical loss in spite of the precautions mentioned above. 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 three suitable U-rods of Pyrex glass hanging over the rim of the container. At the end of the evaporation the sides of the vessel, the lower side of the clockglass and the triangle and glass rods (if employed) should be rinsed with distilled water into the vessel.

For evaporation at the boiling point, use a conical flask with a short Pyrex funnel in the mouth or a round-bottomed flask inclined at an angle of about 45° ; with the round-bottomed flask the drops of liquid, etc., thrown up by ebullition or effervescence, will be retained by striking the inside of the flask, whereas gas and vapour will escape freely. When organic solvents are used the flask should be fitted with a swan neck and a reflux condenser, so the solvent is recovered, or a rotary evaporator may be used. Consider the possibility of losses 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 respective evolution of carbon dioxide, hydrogen sulphide and sulphur dioxide from carbonates, sulphides and sulphites will be immediately apparent; 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. The following more powerful reagents may be used to dissolve difficult materials.

Concentrated acids 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, providing a separation of these elements from other components of alloys. Hot concentrated sulphuric acid dissolves many metals, and many organic materials are charred and then oxidised by this treatment.

Aqua regia Aqua regia is 75 vol% hydrochloric acid and 25 vol% nitric acid. Largely due to its oxidising character, it is a very potent solvent; and the effectiveness of the mixture is frequently increased by adding other oxidants, e.g. bromine and hydrogen peroxide.

Hydrofluoric acid 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, 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 re-

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the evaporation with sulphuric acid two or three times. Hydrofluoric acid causes serious and painful skin burns. Use **hydrofluoric acid with great care**.

Perchloric acid Perchloric acid attacks stainless steels and a number of iron alloys that do not dissolve in other acids. 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, 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. When using a mixture of 60 vol% nitric acid, 20 vol% perchloric acid and 20 vol% sulphuric acid, the perchloric acid is also evaporated to leave a sulphuric acid solution of the components for analysis. The organic part of the material under investigation is destroyed and the process is known as **wet ashing**. Hot concentrated perchloric acid gives explosive reactions with organic materials or easily oxidised inorganic compounds; if frequent reactions and evaporations involving perchloric acid are to be performed, it is wise to use a fume cupboard free from combustible organic materials. Use **perchloric acid with great care**.

Fusion reagents Fusion reagents, commonly known as **fluxes**, are used to solubilise substances that are not soluble in normal solvents or acids. Typical fluxes include anhydrous sodium carbonate, either alone or mixed with potassium nitrate or sodium peroxide; potassium pyrosulphate or sodium pyrosulphate; sodium peroxide; sodium hydroxide or potassium hydroxide. Anhydrous lithium metaborate is especially suitable for materials containing silica;^[7] 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. Here are some other advantages claimed for lithium metaborate:

1. No gases are evolved during the fusion or during the dissolution of the melt, hence there is no danger of losses due to spitting.
2. Fusions with lithium metaborate are usually quicker (15 min 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.

The flux employed will depend on the nature of the insoluble substance. Acidic materials are attacked by basic fluxes (carbonates, hydroxides and metaborates), whereas 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 fusion vessel 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).

To prepare 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