

Separation and Purification

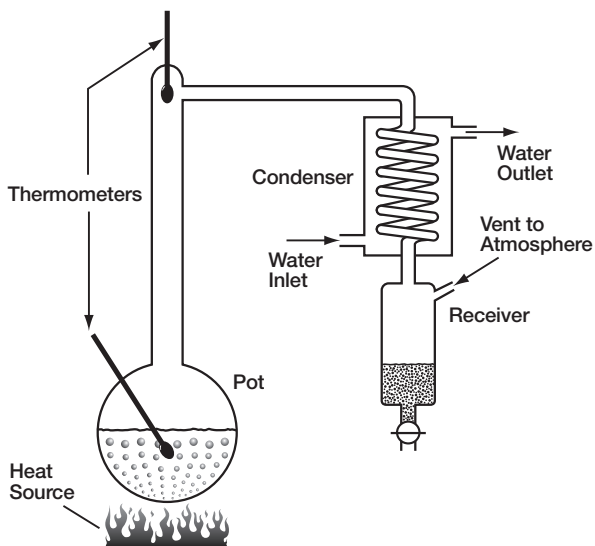
KEY TOPICS distillation, crystallization, solvent extraction, chromatography

In order to analyze and manipulate materials, it is important to be able to isolate them from mixtures and obtain them in pure form. The various methods by which purification can be achieved will be described in this chapter. In fragrance chemistry, the two principal properties we use to achieve separation of materials are volatility and solubility. The volatility of a material is its ability to become a gas rather than a solid or liquid. Distillation is a purification process which relies on volatility. Crystallization, solvent extraction and chromatography rely on a material's solubility.

Distillation

In the simplest application of distillation, liquids can be separated from the solids dissolved in them by heating the liquid above its boiling point so that it is removed as vapor, then condensing the vapor by contact with a cold surface so that it returns to the liquid state. An example of this might be the separation of water from brine. The liquid that distills is known as the distillate, and the material that remains in the still pot is known as the residue. So, in the case of brine distillation, the distillate would be pure water and the residue would be salt. The simplest form of still therefore comprises a pot (in which the liquid to be distilled is heated and evaporated), a condenser (in which the vapor is cooled to return it to the liquid state), and a receiver (in which the distillate is collected). **Figure 5.1** shows a drawing of such a still.

Figure 5.1 A simple still



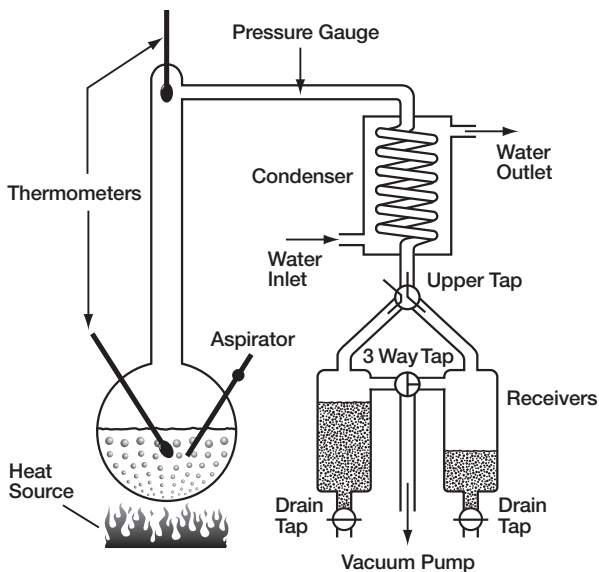
The heat source could be from an open flame or an electrical heater. Gas and electrical heaters sometimes use water or oil as a heat transfer medium. The heat source is applied to a thermally stable oil or to water, and the heated liquid is then brought into contact with the outer surface of the still pot. This system has the advantage that localized over-heating (or hot spots) is avoided. Hot spots on the pot surface can lead to uneven boiling, generating mechanical shocks and also to degradation of material in the pot. The condenser can be air-cooled or, more usually, has a supply of cold water running around it as shown in the figure. Even a simple still is usually equipped with two thermometers, one to measure the temperature in the pot and one to measure the temperature of the vapor at the top of the still before it comes into contact with the condenser (the head temperature). These thermometers give the operator valuable information about the progress of the distillation. It is also usual to provide a stirrer or some other means of helping vapor bubbles to form in the liquid. A piece of wood or boiling stones (small chips of porous ceramic material) will serve this purpose. If no such boiling aid is present, it is possible for the liquid to become super-heated, in other words, heated above its boiling point but remaining in the liquid phase. Super-heating can have disastrous consequences when something then triggers boiling since a large part of the liquid can suddenly enter the vapor phase, greatly increasing the pressure in the still and possibly causing mechanical damage and/or loss of hot liquid into the immediate environment.

Most fragrance materials have boiling points well above that of water and contain less robust molecules. Heating them to their boiling point can therefore cause decomposition. Even a small amount of decomposition is very likely to have an adverse effect on the odor of the distillate, since traces of volatile decomposition products will often significantly affect the odor of the whole. In the previous chapter, we looked at a typical phase diagram (**Figure 4.7**) and saw how the boiling point of a liquid could be altered by changing the pressure. Lowering the pressure above a liquid reduces its boiling point and so makes it possible to distill the liquid at a lower temperature. Therefore most fragrance ingredients are distilled at reduced pressure in order to lower the possibility of decomposition or degradation. Of course, it also has the beneficial effect of reducing the amount of heat required and hence the energy consumed in the process. For example, α -pinene, the major component of turpentine, boils at 156°C at atmospheric pressure (760 mmHg or 101.3 kPa) (1mmHg is the pressure exerted by a column of mercury 1mm high, kPa = 1,000 Pascals, 1 Pascal is a pressure of 1 Newton per square metre, 1 Newton is the force required to impart an acceleration of 1 metre per second to an object weighing 1 kg. Both mmHg and kPa are used as units of pressure in distillation.) but, when the pressure is reduced to 100 mmHg (equal to 13.33 kPa), the boiling point is 89°C.

The reduced pressure is achieved by connecting a vacuum pump to the still and this, in turn, means that several other additions or modifications to the still construction are necessary. A stirrer is often used to ensure even boiling, but usually an aspirator or bleed is also added. The bleed allows a small continuous flow of a gas to enter the still, with the rate of flow controlled by a valve. The gas needs to be non-reactive and so nitrogen is usually used for this purpose as it is the least expensive gas which will not react with the still contents. The gas flow promotes boiling and also allows the operator to return the pressure inside the still to atmospheric pressure when the distillation is over. A pressure gauge is used to measure the pressure in the still.

In order to be able to remove distillate from the still while it is running under vacuum, it is necessary to install a device known as a Perkin triangle. A Perkin triangle can be constructed various ways; one example is shown in **Figure 5.2**. In this case, it has two receivers. The upper tap connects one receiver at a time to the condenser and simultaneously connects the other to the atmosphere. The lower tap is a three way tap which connects one receiver at a time to the vacuum pump. Thus, while one reservoir is filling with distillate from the still, the other is open to the atmosphere and can be drained out through the drain tap. When the second receiver is full, the taps can be reversed so that the distillate now flows into the first receiver and the second can be drained. Each batch of distillate is known as a fraction and, using the set up in **Figure 5.2**, as many fractions as desired can be collected without having to shut the still down between them. Obviously, the total volume of the fractions will be no more than the volume charged to the pot.

Figure 5.2 Distillation under reduced pressure



Liquids exist in equilibrium with their vapors. In the space above a mixture of two liquids, the vapors of the two will be present in the ratio of their vapor pressures. Therefore, there will be more of the vapor of the liquid with the higher vapor pressure, and hence, lower boiling point. So if a mixture of two liquids is distilled, the distillate will initially contain more of the lower boiling component. The degree of separation will depend on the difference between the boiling points. If the difference is sufficiently large, one single distillation could be sufficient to separate the two mixtures. However, if the boiling points are closer together, only a partial separation will be achieved in a single evaporation/condensation cycle. If this initial distillate is condensed and then brought to boiling again, the lower boiling component will be further enriched in the vapor of the second distillation. Thus, with repeated distillations, it is possible to separate even liquids which have very similar boiling points.

In practice, this separation is achieved using a fractionating still. In such a still, the ascending vapor is taken through a column packed with an inert material shaped so that as high a surface area as possible is presented to the vapor. In the laboratory, glass rings or glass helices are often used. Custom designed ceramic or stainless steel packings are used in commercial scale stills. As the vapor ascends through the packed column, it meets a flow of condensate running back down over the surface of the packing. This process enables re-equilibration to take place with more of the lower boiling component entering the vapor phase and more of the

higher boiling component condensing and joining the flow back down towards the pot. The longer the column and the more efficient the liquid vapor exchange, the better the separation will be. The efficiency of a column is measured in units called theoretical plates. One theoretical plate will achieve one complete equilibration between ascending vapor and descending condensate. The efficiency of the packing in a column is expressed as the height equivalent per theoretical plate (HETP); in other words, the height of column necessary to achieve separation equivalent to one theoretical plate. Columns are very well insulated to keep the liquid/vapor equilibria going throughout the length of the column. Efficient operation of a commercial scale fractionating scale requires considerable skill, as factors such as the rate of boil up (i.e. the rate at which liquid is boiled and fed into the bottom of the still) and the reflux ratio (i.e. the ratio between the amount of material being taken off at the top of the still and passed into the condenser to the amount of material being returned down the column) all play a part in the degree of separation that will be achieved. Of course, all of these parameters are also affected by the temperature and pressure in the various parts of the still.

Figure 5.3 A fractionating still

