ANALYTICAL APPLICATIONS: DISTILLATION

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Distillation is a widely used technique in chemical analysis for characterizing materials by establishing an index of purity and for separating selected components from a complete matrix. The technique is even more widely used in preparative chemistry and throughout manufacturing industry as a means of purifying products and chemical intermediates. Distillation operations differ enormously in size and complexity from the semi-micro scale to the 'thousands of tonnes per annum' production operations. For analytical purposes the scale employed is usually bench-level.

Numerous quoted standard specifications refer to distillation ranges as criteria of purity or suitability for use, or as indicators of performance. Published standards for analytical reagents in the AnalaR range and similar documentation by the American Chemical Society refer to distillation ranges as criteria of purity for appropriate materials.

Distillation is the process that occurs when a liquid sample is volatilized to produce a vapour that is subsequently condensed to a liquid richer in the more volatile components of the original sample. The volatilization process usually involves heating the liquid but it may also be achieved by reducing the pressure or by a combination of both. This can be demonstrated in a simple laboratory distillation apparatus comprising a flask, distillation head, condenser and sample collector (**Figure 1**). A thermometer is included in the apparatus as shown to monitor the progress of the operation. In its simplest form this procedure results in a separation into a volatile fraction collected in the receiver flask and a nonvolatile residue in the distillation flask. When a distillation column is incorporated in the equipment (**Figure 2**), the evaporation and condensation processes occur continuously. This results in a progressive fractionation of the volatiles as they pass up the column. The most volatile components emerge from the top of the column initially and the less volatile components emerge later. By changing the receivers throughout the course of the distillation a separation or fractionation is effected. Eventually, all the volatiles will have passed over into the sample collectors and any involatile residue present will remain in the distillation flask.

Principles

The underlying principles are conveniently illustrated by reference to a vapour–liquid equilibrium diagram (**Figure 3**). The diagram relates to a binary mixture containing components P and Q. The lower curve gives the composition of the liquid boiling at various temperatures whilst the upper curve gives the composition of the vapour in equilibrium with the boiling liquid. Points x and y therefore give the boiling points of the individual components P and Q respectively. For example, point A shows that at X degrees the vapour has a composition of approximately 90% P, whilst point B shows that the boiling liquid with which it is in equilibrium, has a composition of approximately 80% P. In a continuous distillation process, such as occurs in a distillation column, liquid of composition C (90% Q, 10% P) vaporizes to vapour of composition D which condenses to liquid of composition E. Subsequently liquid E becomes vapour F and liquid G (composition: 50% Q, 50% P). This continuous process of vaporization and condensation occurs in the distillation column until a volatile fraction leaves the top of the column and is removed from the process by being collected in the collection flask. At the same time the liquid in the distillation flask becomes progressively more concentrated in the involatile component.

Distillation techniques may be classified into several different types including:

- Distillation at atmospheric pressure
- Distillation under reduced pressure
- Steam distillation
- Molecular distillation (short-path distillation)
- Azeotropic distillation
- Isopiestic distillation

Distillation at atmospheric or reduced pressure produces a separation according to the general principles discussed in the introduction.

Steam distillation is a means of distilling that part of a sample that is volatile in steam at a lower temperature than would otherwise be the case. This method is typically used for removing phenols from an aqueous sample. A means of introducing steam into the distillation flask must be provided.

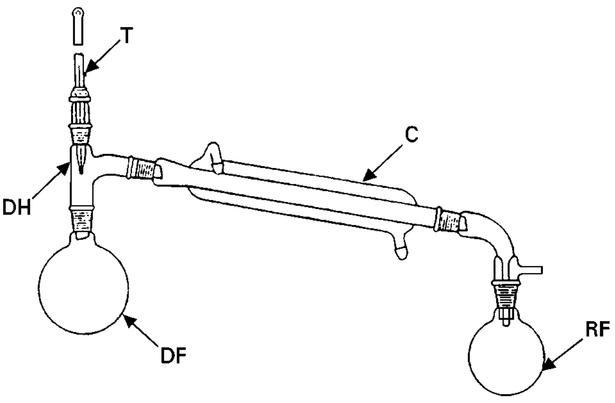

Figure 1 Simple distillation apparatus comprising distillation flask (DF), distillation head (DH), thermometer (T), condenser (C) and receiver(or collection) flask (RF). (Reproduced by permission of Longman Scientific & Technical from Furniss *et al.*, 1989.)

Molecular distillation, sometimes termed short-path distillation, is used principally for compounds normally having high boiling points. In such cases, very low pressures are needed to achieve the desired low boiling points. The apparatus is constructed such that the condensing surface is located only a short distance from the distilling liquid and the pressure is reduced so that the process is governed to a large extent by the mean free path of the molecules involved. Hence the terms short-path distillation and molecular distillation.

Azeotropic distillation occurs when a mixture of two materials distils at constant composition. This technique is commonly used to remove water from samples. As an example, toluene may be added to a complex sample containing water, the distillation process results in the toluene–water azeotrope distilling. The distillate can then be examined to determine the water content of the original sample.

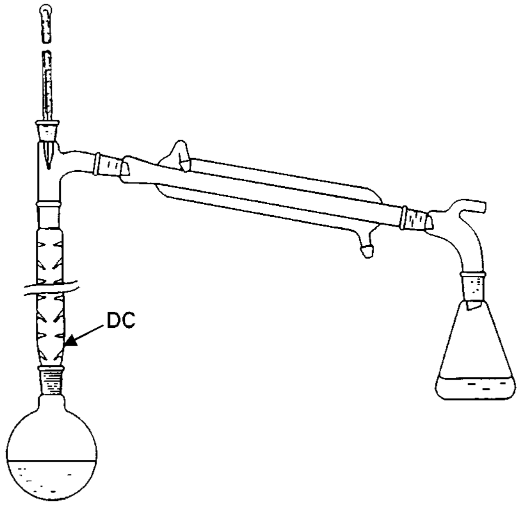

Figure 2 Distillation apparatus including distillation column (DC). (Reproduced by permission of Longman Scientific & Technical from Furniss *et al.*, 1989.)

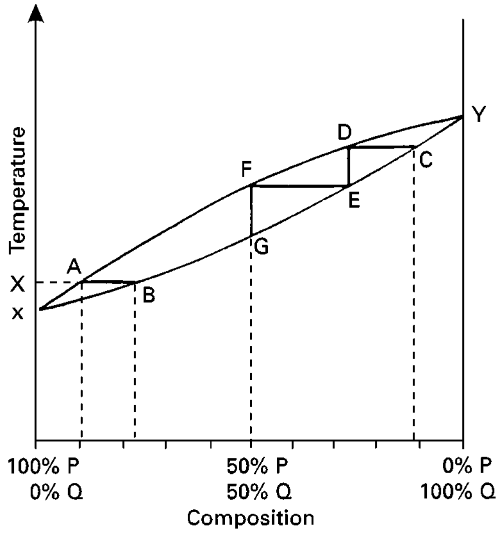

Figure 3 Vapour–liquid diagram for a binary mixture of components 'P' and 'Q', illustrating the principles of distillation (see text for details).

Isopiestic distillation is a convenient way of producing metal-free aqueous samples of volatile acids. The 'crude' acid is placed in an open container, such as a beaker, in a desiccator containing also an open beaker of pure water. The acid vaporizes and subsequent condensation in the pure water produces an aqueous sample of the volatile acid without any of the involatile contaminants such as metals.

The alternative terms 'flash' distillation and 'fractional' distillation are sometimes used to describe some of the above procedures carried out in a particular way. Flash distillation effects a crude separation into volatiles and residue, whilst fractional distillation produces a series of 'cuts' of different volatility (or boiling point) ranges.

Additionally, there are other forms of sample purification and separation that are either a type of distillation or are related to a distillation process:

- Simultaneous distillation/extraction (see application section)
- Dean and Stark distillation (see application section)
- Simulated distillation (gas chromatographic technique)

Analytically, distillation is used for two principal purposes, firstly as a criterion of purity and secondly as a means of preparing a sample for analysis. Many specification tests include reference to a distillation range within the limits of which a stated percentage of the material of interest distils. Alternative distillation may be used to separate volatiles from a sample prior to a suitable analytical technique being employed on the distillate or on the residue. Standard tests are documented that involve distillation as a sample pretreatment method prior to titrimetry, potentiometry and spectrophotometry.

It is of course essential, if meaningful comparative results are to be obtained, that the design and use of the apparatus are standardized for such determinations.

Apparatus

A wide variety of apparatus is available to satisfy the different distillation techniques. The appropriate design of apparatus depends upon the type of distillation to be performed, considering, for example, whether a vacuum is required or steam is needed. Descriptions of apparatus are to be found in a number of different texts (see the Further Reading). Standards referring to the design and use of distillation apparatus have been published by the British Standards Institute and the American Society for Testing and Materials. Simulated distillation, which is a gas chromatographic technique, is dealt with in a [recent] review by Robillard *et al.* and referred to in several standards.

Apparatus may be discussed in terms of the distillation flask, the distillation column, the condenser and the collecting flask(s). By far the most effort has been expended in the design and operation of the distillation column, which is at the heart of the separation efficiency. The form of the column, its size and the packing used are very influential upon the results that are achievable. A summary of some different types of columns is given in **Table 1** and of packings in **Table 2**.

Once apparatus has been chosen carefully to compare with previously used apparatus or to conform to standards, the operation of the equipment must be considered. The following factors are among the most important to be controlled:

- The heating of the distillation flask must be carefully controlled.
- The distillation column must be operated so that it does not become flooded.
- The reflux ratio, that is the ratio of material returning via reflux to the distillation column or the distillation flask compared to the amount presented to the condenser in unit time must be carefully controlled. The higher the reflux ratio, the purer the material collected from the distillation. Reflux ratios are controlled in simple distillation apparatus by adjustment of the heating rate and by maintaining stable thermal conditions throughout the apparatus.

Table 1 Types of distillation column

Column type	*Description/comments*
Dufton	An open tube into which a glass spiral fits closely
Hempel	A simple tube normally filled with a suitable packing (rings/helices) and having a side-arm near the top
Oldershaw	A column with fixed but perforated plates that maintains a fixed amount of liquid on each plate
Podbielniak	A simple tube with a wire packing to provide large contact area between liquid and vapour to effect high efficiencies
Spinning band	A tube fitted with a closely fitting spiral of PTFE or metal gauze that can be rotated at typical speeds of 600 to 3000 rev min^{-1} as the vapour–liquid equilibrium is maintained in the column
Vigreux	A tube having pairs of indentations down its length that slope downwards and provide a large and designed surface area to enhance the liquid–vapour equilibrium

Applications

Documentation of analytical applications of distillation is widely dispersed. However, there are numerous references to distillation as a means of characterizing materials and as means of sample pretreatment in the lists of BSI standards, the ASTM methods documentation, the analytical methods of the Institute of Petroleum and those of other worldwide standards organizations. **Table 3** gives a selection of standards involving distillation originating from various standards organizations.

Table 2 Distillation column packings

Packing	*Description*
Balls	Mostly made of glass. Columns have a tendency to flood easily
Helices	Made from metal or glass, although metal may be packed mechanically to produce a more uniform column
Rings	Usually made of glass of an appropriate size for the column but can be made of porcelain, stainless steel, aluminium, copper or nickel. Depending upon design they can be termed Raschig, Lessing or Dixon rings
Wire packings	Produced as ‘Heli-Grid’ and ‘Heli-Pak’ packings especially for use with Podbielniak columns

Table 3 Applications of distillation in analysis

Application	*Standards*[a]
Water/moisture determination	
Petroleum products	AASHTO T55; ASTM D95; BS 4385; CNS K6339
Crude oil	ASTM D4006
Wool	ASTM D2462
Wood/wood products	TAPPI T208 OM
Coal/coke	BS 1016
Spices	BS 4585; ISO 939
Animal feeds/feedstuffs	AACCH 44–50
Fats/oils	AACCH 44–51; BS 684; ISO 934
Paints and pigments	CGSB 1-GP-71 Meth 24-1
Fruits/vegetables	SASO 436
Soaps/detergents	CGSB 2-GP-d11M Meth 13-2; ISO 4318
Tobacco	CNS N4133; ISO 6488
Pulp and paper	CNS P3025
Plastic moulding materials	DIN 53713
Water quality assessment	
Phenol index	BS 6068 Sect. 2.12; ISO 6439
Ammonium content	BS 6068 Sect. 2.7; ISO 5664
Hydrocarbons, purity	
Road tars	ASTM D20; IP27
Petroleum products	AASHTO T115; ASTM D86; BS 7392; CNS K6109; IP 123
Creosote/creosote oil	AASHTO T62; ASTM D246; CNS K6070
Bituminous coatings	AASHTO T78 & T110; ASTM D255
Aromatic hydrocarbons	ASTM D580; CNS K6255
Volatile organic liquids	ASTM D1078
Organic liquids, distillation range and characterization	
Amyl acetate	BS 552
Analytical reagents	Anala standards for laboratory chemicals
Butyl acetate	BS 551
Chloroform	BS 4774
Diethyl ether	BS 579
Perchlorethylene	BS 1593
Isopropyl acetate	BS 1834
4-Methylpentan-2-one	BS 1941
2-Ethoxyethanol	BS 2713
Oil of lime	CNS K5089
Citronella oil	CNS K6063
Formic acid	ISO 731 Part VII
Phenols	ISO 1897 Parts 12 & 13
Caprolactam	ISO 8661
Miscellaneous application of distillation	
Ethyl acetate	BS 553
White spirit	IP 123
N-determination	
Sulfuric acid/oleum	ISO 914
Urea	ISO 1592
Ammonium nitrate	ISO 3330, 3331
Fertilizers	BS 5551; ISO 5314 & 5315
Available fluorine in:	
Hexafluorosilicic acid	BS 6445; ISO 6677
Fluorspar	ISO 5439
Arsenic in ores	CNS M3094
Volatiles content	
Aerosols	CNS Z6052
Fire residues	ASTM E1385

[a] *Sources*: AASHTO, American Association of State Highway Transport Offices; ASTM, American Society for Testing and Materials; BS, British Standards Institution; CGSB, Canadian General Standard Board; CNS, Chinese National Standards; DIN, Deutsche Institut für Normung; ISO, International Organization for Standardization; SASO, Saudi Arabian Standards Organization; TAPPI, Technical Association of the Pulp and Paper Industry; IP, Institute of Petroleum.

Distillation is used widely to determine the moisture or water content of a variety of samples from petroleum products to cereal feeds. The technique used is one of azeotropic distillation using a codistillate such as toluene. **Table 3** includes a selection of the available methods. Dean and Stark provided a particular design of apparatus that can be used for determining water content following azeotropic distillation with an immiscible organic solvent. As the azeotropic distillate condenses, the water separates from the immiscible organic and can be estimated directly in a specially graduated collection arm.

Some methods for the determination of water quality involve distillation, for example the determination of a 'phenol index', nitrate content or ammonium content.

The determination of nitrogen by the Kjeldahl method involves a preliminary distillation of the sample. Thus methods for the determination of ammoniacal and total nitrogen in ammonium nitrate, urea, sulfuric acid and fertilizers for industrial purposes involve a preliminary distillation followed by titrimetry.

Methods for the determination of available fluorine involve distillation prior to a potentiometric or spectrometric method.

The determination of distillation range is a method of establishing the purity of materials. Specific standard methods are available, for example, for methanol, ethylene glycol and propylene glycol. Many unpublished in company methods are used for products and intermediates to validate purity standards and to establish the suitability of materials for subsequent use.

As trace analysis of residual compounds in consumables has become more important, methods of extracting these compounds have been developed. A method known as simultaneous distillation extraction developed from the original work of Likens and Nickerson has been particularly popular and effective for extracting the volatiles from foods and plant materials, and the herbicide and pesticide residues in agricultural products. The method involves steam distilling the compound of interest from an aqueous suspension of the crude sample while the condensed steam is continuously extracted with an immiscible organic solvent refluxing within the apparatus. The design of the apparatus allows the volatiles that are extracted from the condensed water to be flushed into the flask containing the organic solvent. After a previously determined time of extraction, the apparatus may be disassembled and the organic solvent removed by evaporation from the now concentrated extract. Further analytical techniques can be used to identify and quantify the components of the residue according to the particular requirements.

A common application of distillation in the separation sciences is the purification and recovery of solvents especially from HPLC and GPC usage. There is a range of equipment supplied for recycling of solvents and useful sources of information can be found on the internet, for example the web pages for B/R Instruments and Recycling Sciences are included in the Further Reading.

The applications of distillation in analysis are widespread, with the technique being used to characterize materials and as a means of preparing samples prior to analysis. Standard apparatus and methods are described for many specific applications. Reference to the general texts and the standards detailed in the Further Reading will provide a source of information for future applications.

See also: **II/Distillation:** Energy Management; Historical Development; Laboratory Scale Distillation; Multicomponent Distillation; Vapour-Liquid Equilibrium: Theory.

Further Reading

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ANION EXCHANGERS FOR WATER TREATMENT: ION EXCHANGE

See **III / WATER TREATMENT / Anion Exchangers: Ion Exchange**

ANTIBIOTICS

High-Speed Countercurrent Chromatography

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Introduction

Development of antibiotics requires considerable research effort in isolation and purification of the desired compound from a complex matrix such as fermentation broth and crude extract. The purification of antibiotics by liquid–liquid partition dates back to the 1950s when the countercurrent distribution method (CCD) was used for separation of various natural products such as peptide antibiotics, aminoglycoside antibiotics and penicillin. However, CCD had serious drawbacks such as bulky fragile apparatus, long separation times and excessive dilution of samples. In the early 1970s an efficient continuous countercurrent separation method called countercurrent chromatography was introduced followed by the advent of high speed countercurrent chromatography (HSCCC) a decade later. Because of its high partition efficiency and speedy separation,