

# Distillation<sup>☆</sup>

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## Introduction

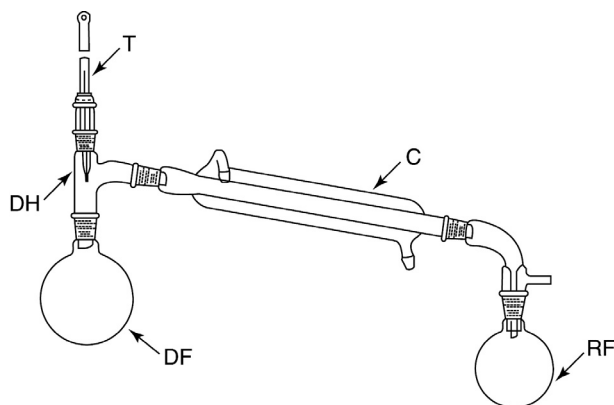
Distillation is a widely used technique in chemical analysis for characterizing materials by establishing an index of purity and for separating selected components from a complete matrix. The technique is even more widely used in preparative chemistry and throughout manufacturing industry as a means of purifying products and chemical intermediates. Distillation operations differ enormously in size and complexity from the semimicro scale to the “thousands of tons 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 vapor 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 (**Fig. 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 (**Fig. 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

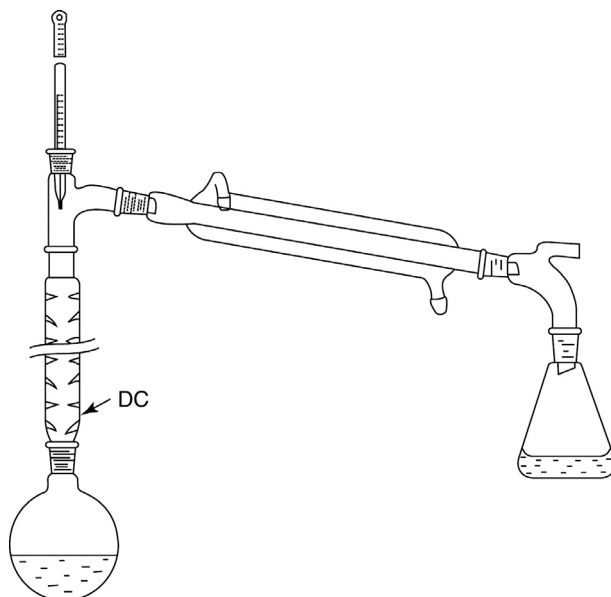
The underlying principles are conveniently illustrated by reference to a vapor–liquid equilibrium diagram (**Fig. 3**). The diagram relates to a binary mixture containing components P and Q. The lower curve gives the composition of the liquid boiling at various temperatures whilst the upper curve gives the composition of the vapor 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 vapor 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



**Fig. 1** Simple distillation apparatus comprising distillation flask (DF), distillation head (DH), thermometer (T), condenser (C), and receiver (or collection) flask (RF). Reproduced from Furniss, B.S., Hannaford, A.J., Smith, P.W.G., and Tatchell, A.R. (1989). *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., pp. 168–197. Harlow: Longman Scientific and Technical.

<sup>☆</sup> *Change History:* September 2018. F. Regan updated the Further Reading section.

This is an update of J.D. Green, DISTILLATION, Editor(s): Paul Worsfold, Alan Townshend, Colin Poole, *Encyclopedia of Analytical Science* (Second Edition), Elsevier, 2005, Pages 281–285.

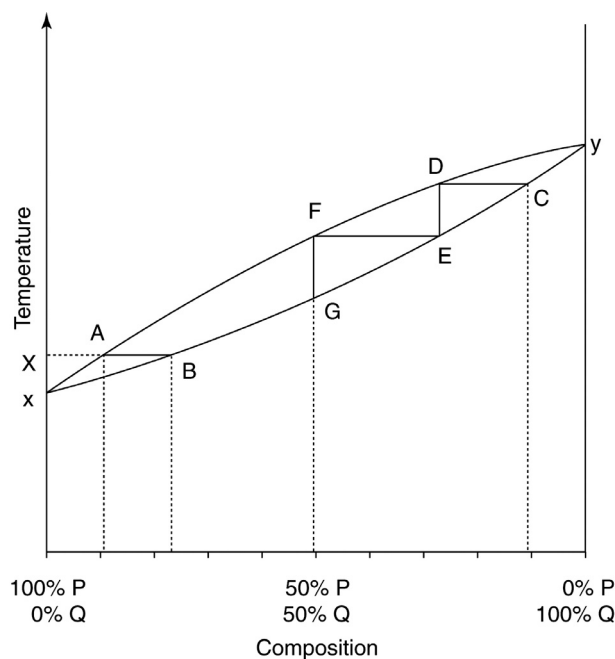


**Fig. 2** Distillation apparatus including distillation column (DC). Reproduced from Furniss, B.S., Hannaford, A.J., Smith, P.W.G., and Tatchell, A.R. (1989). *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., pp. 168–197. Harlow: Longman Scientific and Technical.

composition C (90% Q, 10% P) vaporizes to vapor of composition D, which condenses to liquid of composition E. Subsequently, liquid E becomes vapor 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



**Fig. 3** Vapor-liquid diagram for a binary mixture of components “P” and “Q”, illustrating the principles of distillation (see text for details).

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.

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.

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 Applications section)
- Dean and Stark distillation (see Applications 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. Alternatively, 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 Further Reading). Standards referring to the design and use of distillation apparatus have been published by the British Standards Institute (BSI) and the American Society for Testing and Materials (ASTM). 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 packing 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

## Applications

Documentation of analytical applications of distillation is widely dispersed. Distillation is used not only for the assessment of purity and characterization of volatile materials but also as a means of removing volatile compounds from an involatile matrix as part of an analytical procedure. Thus, distillation will be found in analytical procedures relating to volatile hydrocarbons, to

**Table 1** Types of distillation column

<i>Column type</i>	<i>Description/comments</i>
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 vapor 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 600–3000 rpm as the vapor–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–vapor equilibrium

**Table 2** Distillation column packings

<i>Packing</i>	<i>Description</i>
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, aluminum, 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

polymers, and to environmental samples. Standards including distillation are concerned with specifying products, characterizing materials, preparing samples for analysis, and defining methods in terms of sampling, equipment, and procedures. Most advanced industrial countries have their own Standards Institutes with connections to International Organizations that promote harmonization of measurement and analysis. **Table 3** gives examples of the organizations whose standards are most frequently quoted in measurement science.

A search of the BSI and ASTM sites reveals several hundred standards involving distillation, including current and withdrawn versions, for material specifications and characterizations or for descriptions of sampling, equipment, and procedures of analytical methods involving distillation. As requirements change and analytical capabilities improve, new standards are introduced and old standards are modified or withdrawn. It is therefore advisable to consult the latest documentation prior to considering new testing methods.

Hydrocarbons derived from crude oil and other fossil deposits are separated into their various fractions by using distillation and so it is not surprising that distillation is used as an analytical tool to characterize them. **Table 4** list examples of applications of distillation to hydrocarbon characterization including bituminous materials, tars, fuels, and derived organic materials.

In a similar way to hydrocarbons the purity of organic chemicals is defined by the distillation range over which they distil under carefully controlled conditions. A range of organic compounds including alcohols, esters, and chlorinated compounds are specified in this way. Examples of the associated specification standards are listed in **Table 4**. Moisture and water content are important parameters in the processing and sale of materials from foodstuffs to petroleum based fuels. Azeotropic distillation is commonly used to determine water content using apparatus developed by Dean and Stark and an immiscible liquid such as toluene as the codistillate.

Some aspects of water quality can also be determined by methods involving distillation; these include determination of “phenol index,” nitrate content, and ammonium content.

**Table 3** Organizations involved with the development and promotion of standards and test methods

<i>Organization</i>	<i>Web address</i>
British Standards Institute	<a href="http://www.bsonline.techindex.co.uk">www.bsonline.techindex.co.uk</a>
American Society for Testing and Materials	<a href="http://www.astm.org">www.astm.org</a>
American National Standards Institute	<a href="http://www.ansi.org">www.ansi.org</a>
Institute of Petroleum	<a href="http://www.intertek-cb.com">www.intertek-cb.com</a>
International Standards Organization	<a href="http://www.iso.ch">www.iso.ch</a>
US Environmental Protection Agency	<a href="http://www.epa.gov">www.epa.gov</a>

**Table 4** Examples of standards involving application of distillation in analysis

<i>Application</i>	<i>Standards</i>
<i>Hydrocarbon characteristics and purity</i>	
Tars for road purposes	BS 76
Creosote for wood preservation	BS 144
Middle distillate contamination in petroleum	BS 2000-459.1
Tar, water gas, and coke yields from brown coals and lignite	ISO 647
<i>Organic liquids</i>	
Methanol specification for industrial use	BS 506-1
Butanol specification for industrial use	BS 508-1
Acetone specification for industrial use	BS 509-1
Ethyl acetate specification for industrial use	BS 553
Diethyl ether specification (technical)	BS 579
Propan-2-ol specification for industrial use	BS 1595-1
Methylene chloride specification	BS 1994
Acetic anhydride specification	BS 2068
<i>Standard methods</i>	
Methanol test methods	BS 506-2
Propan-2-ol test methods	BS 1595-2
Specification for apparatus for determination of distillation range	BS 658
Specification for Dean and Stark apparatus	BS 756
Methods for determination of:	
Water in petroleum and bituminous products	BS 2000-74; ISO3733
Distillation characteristics of cutback bitumen	BS 2000-27
Determination of asphaltenes in crude petroleum	BS 2000-143
<i>Nitrogen content</i>	
Chemical analysis of cheese (nitrogen)	BS 770
Nitrogen content of coal and coke	BS 1016-106.2
Liquid milk and cream (nitrogen)	BS 1741-5.2
Total nitrogen in ammonium nitrate	BS 4267-2
Ammoniacal nitrogen in fertilizers	BS 5551-4.1.2
<i>Moisture/water content</i>	
Methods of analysis for coal and coke (total moisture)	BS 1016
Water in formulated detergents	BS 3762
Moisture in condiments and spices	BS 4585-2
<i>Water quality determination</i>	
Ammonium determination	BS 6068-2.7; ISO 5664
Phenol index determination	BS 6068-2.12; ISO 6439
Inorganic total fluoride determination	BS 6068-2.48
<i>Miscellaneous methods involving distillation</i>	
Residue from essential oils after distillation	BS 5991
Sulfur dioxide in fruit and vegetable juices	BS EN 13196
Determination of boron in steel	ISO 13900

This table is not intended to be comprehensive but is included to show the scope of different analyses that involve analysis.  
Compiled by selection from websites (March 2004).

The determination of nitrogen by the Kjeldhal method includes a preliminary distillation of the sample. Protein content can be estimated using these methods as can the determination of ammoniacal and total nitrogen in various samples including fertilizers.

As trace analysis of residual compounds in consumables has become more important, methods for 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.

Distillation is an accepted method of material purity specification when carried out according to standard and agreed procedures. It is also a method of sample pretreatment prior to analysis by other methods including spectroscopy, titrimetry, or potentiometry.

## Further Reading

- AnalaR Standards. *AnalaR Standards for Laboratory Chemicals*, 1984 (AnalaR is a Registered Trademark of Merck Ltd).
- American Society for Testing and Materials. ASTM International: [https://www.standardsportal.org/usa\\_en/sdo/astm.aspx](https://www.standardsportal.org/usa_en/sdo/astm.aspx) (2018).
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