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ESSENTIAL OILS

Distillation

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Introduction

Essential oils are generally understood to be volatile compounds which are freely soluble in alcohol, ether and vegetable and mineral oils and are usually assumed to be the result of distillation or a steam-stripping process. The use and processing of essential oils began in the East more than 2500 years ago. The process of distillation, which is the technical basis of the essential oil industry, was also conceived and first employed in the Orient, especially in Egypt, Persia and India. Turpentine and camphor appear to be the first documented essential oils prepared by distillation in Greece by Herodotus (484–425 BC).

The use of essential oils in ancient times consisted of preparing ointments by mixing oils from flowers with fatty oils; this was done by placing flowers and roots with the oil in glass bottles which were then allowed to sit for periods of time. Sometimes the flowers or roots were macerated with wine before the fatty oil was added, and the product obtained by digestion filtered and boiled down to a thicker consistency.

Medieval alchemists laboured for many years to extract from materials found in nature what they called the *quinta essentia* or the fifth essence. They believed that a combination of earth, air, fire and water existed in some form or other from which quintessential materials could be extracted from some plants. These quintessential extracts derived from plants were believed to be remedies for a wide variety of diseases.

The production and use of essential oils did not become widespread until the second half of the 16th century. In 1507, Hieronymus Brunschwig's book on distillation, *Liber De Arte Distillandi*, described distillation techniques for four essential oils, namely, turpentine (known since antiquity), juniper wood, rosemary and spike.

Before the ninth century it was still widely believed that most essential oils had strong curative properties. Therefore it was chiefly pharmacists who developed and improved methods of distillation for the recovery and purification of natural essential oils.

Eventually, with the development of the fields of medicine and pharmacology and the dispelling of some medicinal myths, the use of essential oils in pharmaceutical products lost importance and their use became restricted to perfumes, beverages and foodstuffs.

Applications of Essential Oils

Attractive aromas which leave a pleasant memory association are used as marketing devices to sell edible and cosmetic products, including unlikely materials such as detergents. The producer is counting on the consumer preferring a product that left a pleasant aromatic memory.

Current specific uses of essential oils are to add flavour to foodstuffs and beverages and to scent perfumes, lotions, soaps, detergents and household cleaners. For example, *d*-limonine from citrus peel is a very strong solvent and it is used in a wide variety of cleaning products. Essential oils are a major part of carbonated beverage flavourings; the most common flavours include lemon, lime, orange, cassia, cinnamon and nutmeg. Essential oils are also used to flavour many foods such as sweets and candies, cookies, snacks and chewing gum.

The field of aromatherapy constitutes a small part of the essential oils industry but it is a fast-growing area and requires a wide variety of essences. Not much scientific work has been done in this area to support any of the medicinal and psychosomatic claims. Practitioners suggest that aromatherapy goes beyond the effect of simply imparting an agreeable sensation and psychological state of well-being. Some speculate that inhaling certain essential aromas can affect the limbic system, producing a measurable physiological response. More research is certainly needed to document the benefits of this application.

Other properties of essential oils with commercial potential include antimicrobial effects. The inhibition of 25 different bacteria using an essential oil of marjoram has been reported. Similar effects are noted for other volatiles and essences derived from plant materials. It was found that the short chain volatiles such as 5–8 carbon aldehydes and ketones resulting from the distillation of vegetable oils had antimicrobial properties against bacteria such as *Staphylococcus aureus* and *Escherichia coli*. In fact, this antimicrobial effect is believed to be a defence mechanism in plants against microbial pathogens. Another function of essential oils in plants is reported to be as an attractant of insects, enabling plants to use the insects as pollen carriers for plant reproduction.

The production of essential oils on a larger scale was started in the USA in the earlier 19th century. Three indigenous plants, sassafras, American wormseed, and wintergreen, as well as turpentine, were the first oils to be produced in the USA in large amounts for export worldwide.

Many aromatic plants for essential oils grow wild or are cultivated in small scale family-oriented businesses. Today only a few essential oils are produced by modern or centralized methods. An example of these is the cultivation and harvesting of aromatic flowers in the Grasse region of southern France, where essential oil distillation units are placed near the fields to extract and recover the essential oils on site. In the case of citrus oils, for example, much larger scale distillation systems are set in place at juice-processing plants. These aroma distillation units are set up next to the evaporators where the concentration of juices is taking place. These systems are common in the USA as well as in other large citrus-producing countries such as Brazil and China. It should be noted that these aroma distillation units are used not only in citrus-processing plants but in any plant that concentrates fruit juices by evaporation.

In addition to improving production and purification processes for the recovery of essential oils, the essential oil industry has been active in developing synthetic aromas. Essential oils are some of the most studied chemical compounds as regards their composition and physical and chemical properties. Advances in organic chemistry have allowed for the establishment of techniques to define the component profiles of many aromas and fragrances which permit the establishment of composition standards for trade regulations and for the synthesis of aromas using less costly starting raw materials.

Table 1 Classification of components in essential oils

Component	*Examples*
Hydrocarbons	*d*-Limonene in lemon oil
Alcohols	Borneol in camphor
Esters	Methyl salicylate in oil of wintergreen
Aldehydes	Benzaldehyde, decanals
Ketones	Menthone in oil of peppermint
Lactones	Coumarin from Tonka beans

Essential oils are commonly grouped into six classes according to their chemical nature. **Tables 1** and **2** list some of the most commonly utilized essential oils worldwide.

The most common essential oil used as a food aroma and flavour is orange essence (Table 2). Over 50% of the commercial essential oils and natural extracts are obtained from cultivated plants. Examples of these include mint aroma and flower essences such as rose, geranium, mints, coriander, lavender and jasmine.

Citrus oils such as orange, lemon and grapefruit aromas are considered by-products of juice extraction and concentration. Orange oil, for example, is marketed both as a flavour and as a material for use in cleaning products. In this case the distinction has to be made that orange oil and citrus oils in general are recovered in two ways; one way is as *d*-limonine, in which the oil resulting from the peel of the fruit as the

Table 2 Main essential oils produced in the world

Essential oil	*Main components*
Orange	Limonene, terpeniols
Mint	Linalool, linalil acetate
Eucalyptus	Cineole, pinene, limonene
Citronella	Geraniol, citronellal, citronelol
Clove	Eugenol, caryophylene
Lime	Limonene, terpeniols
Spearmint	Mentheol, menthone, pulegone
Lavander	Pinene, lemonene, caphene, octanone
Marjoram	Tojuene, pinene, sabinene
Camphor	Bisabolol, cadinol cubenol
Coriander	Terpinene, *p*-cymen, pinene
Patchouli	Patchoulool, sesquiterpenes
Rose	Citronellol, geraniol, linalool
Cinnamon	Fenchene, cinnamaldehyde, pinene
Sandalwood	Santalene, curcumene
Lemongrass	Citral, linaloo, geraniol
Jasmin	Benzyl acetate, linalool, benzyl benzoate
Ginger	Terpenio, neral, geraneal
Anis	*Trans* anethol, chavicol

juice is extracted. This has a lower value and is sold as flavouring and also as a cleaning agent. The true volatiles from citrus are what results from volatilization during the evaporation of the juice and this is a product that commands a higher value and has a wider range of aroma components such as aldehydes, ketones and terpenes. Other oils such as clove or pepper oil may come from spices, or as oils, oleoresins, extracts or flavours.

Other raw materials for essential oil production are harvested in the wild. Wild thyme and rosemary, for example, are common in Spain and grow back abundantly following harvest. Sumatran cinnamon trees are similarly self-rejuvenating. However, due to high demand, some countries have resorted to overharvesting plants for essential oil production from the wild. This has created local problems of forest destruction and the sustainability of the industry has become a serious concern for some underdeveloped countries. As a result, some countries, such as Brazil, have implemented harvest moratoriums or banned the harvesting of some species in order to avoid wiping out some species of aromatic plants. These conservation efforts and replanting programmes have meant that some oils are now available again commercially.

Recovery of Essential Oils

The aroma and fragrance industry has been estimated at approximately $2 billion per year, with a growth rate of 3.5% per year. Orange oil is both the largest volume oil and, as a by-product of the orange juice industry, relatively inexpensive, ranging from $0.75 to $1.40 a pound. Although the US production of citrus oil is declining, with South America and China growing in importance as a major producer, the USA continues to be a major producer of mint and cedar oils. The mint oils as a group – peppermint, spearmint (both grown in the USA) and cornmint (produced in India and China and as a by-product of menthol production) – are the highest value oils, with peppermint selling for about $12–15 a pound.

Distilled essential oils are generally recovered by three methods, classified according to the way heat is applied to materials: boiling water, steam distillation or a combination of both. Conditions of temperature, pressure or vacuum, and processing time will depend on the characteristics of the essential oil, particularly as regards susceptibility to oxidation and heat decomposition.

The basic process consists of macerating or comminuting the plant materials to rupture the oil sacs. This allows the essential oil to be exposed and carried by the steam or water used. Common materials used in the recovery of essential oils are flowers, roots, seeds, leaves and twigs of aromatic plants.

Once the plant materials have been prepared, the method for removing the essential oil depends on the type of product being handled. For example, a combination of boiling water and steam injection is used with flower petals in order to avoid agglutination of the materials in the distillation unit. **Figure 1** illustrates this simple method of distilling essential oils. This type of distillation is commonly set up in the fields where the raw materials are being harvested in order to prevent spoilage and deterioration of aromas during transportation or storage.

A simple distillation apparatus consists of a retort or still, a condenser and a receiver. This system is commonly used in the fields for processing lavender. Typical conditions for this method are to heat a mixture of raw material with water to boiling point (100°C) while injecting steam. The resulting vapours are then condensed and recovered. This usually results in two phases: a heavy phase, mostly composed of water, and a light phase, which contains the essential oil.

A variation of this method is to apply vacuum (10–25 in Hg) to the system to allow boiling to take place at a lower temperature and thus prevent the thermal decomposition of the essential oil.

Some aroma systems involve the use of only steam in order to obtain a more concentrated essential oil in the condenser. This system is applicable where there is no agglomeration or agglutination of raw materials. When the raw material is liquid, such as fruit juice or macerated materials in water, the fresh liquid flows in countercurrent with vapour. Vapour–liquid-contacting devices such as a sieve plate column or a packed column are sometimes used. Under ideal conditions, it is advisable to have a rectification column next to the distillation unit in order to obtain a more concentrated and pure essential oil. This is the most efficient way from the standpoint of steam consumption as well. Such a scheme is illustrated in **Figure 2**, with distillation/rectification as the concentration step.

As mentioned above, essential aromas from citrus are recovered as a by-product from the production of citrus juice concentrates. These juices are usually concentrated by multiple effect evaporation. There are four or more effects where the first effect is usually heated by live steam and then subsequent effects are heated by the steam generated in the preceding effect. The vapours generated in the first effect are the richest in the essential oils and the essence is condensed and recovered in a distillation column. This is the most important source of essential oils with regard to volume, estimated worldwide at 25 000 metric tons and more than 60 million US dollars.

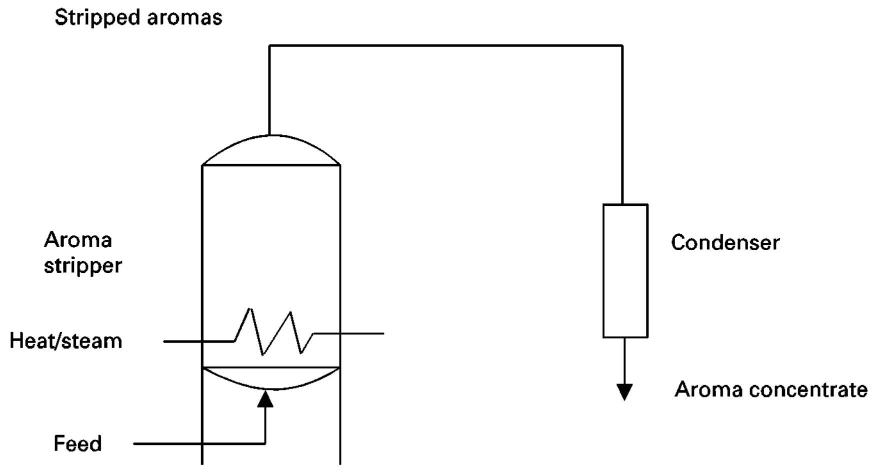

Figure 1 Aroma recovery unit by hydrodistillation.

There is another method of distillation used by very specialized flavour companies called molecular distillation. In this evaporation system the liquid introduced is spread on the walls of a heated vertical cylinder under high vacuum (less than 50 mmHg) by wiper blades forming a thin layer. This produces highly efficient mixing and heat transfer of the fluid, reducing the residence time to a minimum. Variable temperature allows for the fractionation of aroma components according to their molecular weight. Heat-sensitive aromas and specialized aromas such as dairy flavours are manufactured by the industry using this type of distillation system.

Other methods for recovering aromas and fragrances are solvent extraction (hexane, alcohols) and supercritical CO_2 extraction. Strictly speaking, the resulting oils from these extraction methods are not essential oils since no evaporation or distillation takes place. However, recovery of high priced aromas and fragrances by supercritical extraction is growing worldwide and extraction of some low price essential oils is also done using hexane or alcohol. Supercritical extraction has the advantage that it does not involve the application of high heat and addition of steam or water. Also, the extractability properties of CO_2, namely affinity for hydrophobic or hydrophilic com-

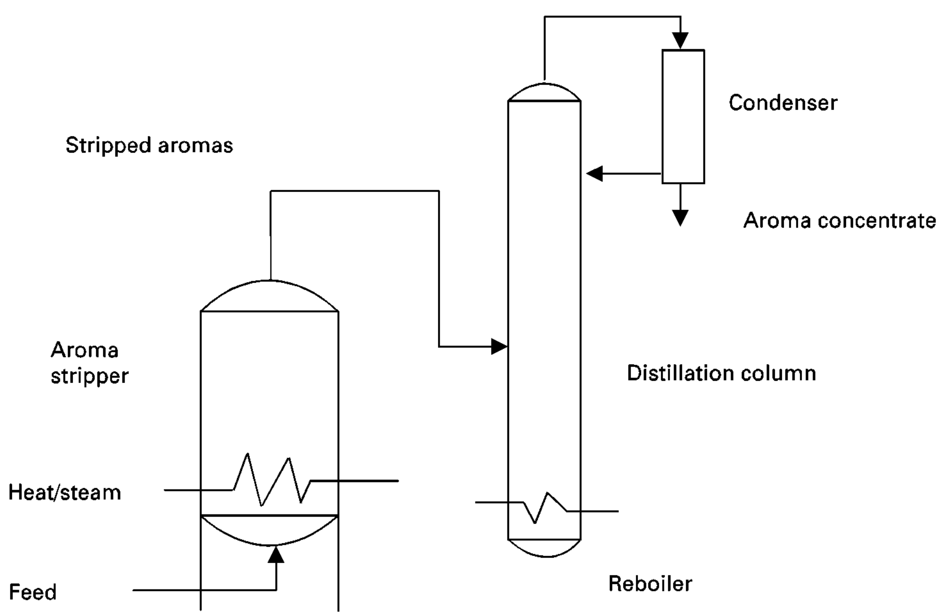

Figure 2 Aroma recovery unit with distillation column.

pounds, can be manipulated with pressure and temperature. Extraction methods by steam distillation, solvent extraction and supercritical CO_2 usually produce different results with regards to yield and composition profiles of the extracted materials. Steam distillation usually gives the lowest yield of recovered aroma but produces a concentrate that is a true essential oil. Solvent extraction with hexane or alcohols produces the highest yield but there is always the possibility that unwanted involatile materials might end up in the final product. Also, solvent extraction uses high temperatures. Supercritical CO_2 extraction produces a lower yield than conventional solvent extraction but higher than steam distillation and it also has the advantage of using little or no heat and no steam or moisture in the process. However, this method has the disadvantage of being expensive since it involves high pressure and sophisticated equipment and controls. In some cases the quality of the aroma extracts from CO_2 extraction is superior to aromas recovered by steam distillation.

Industry Standards and Trends

With the exception of large companies that have access to sophisticated analytical means, the assessment of quality of essential oils is difficult. However, the composition of many essential oils is well known and the industry can adopt standards that can be applied to essential oils. Oils used in medical applications, for example, camphor oil, must meet the standards set forth in the US pharmacopeia. Oils used in food products must meet the Food Chemical Codex standards and the Fragrance Manufacturers Association (formerly the Essential Oil Association, or EOA) is in the process of updating a specifications book.

It is common practice for large producers of essential oils to process their oils further following pressing or distillation, either to produce a standard product year after year, or to change the characteristics of the oil. For example, peppermint oil is commonly redistilled to remove some of the front-end components that give the oil an unwanted flavour or aroma note.

Another common practice is folding of oils, or concentrating them by removing certain components. It is common practice to redistil citrus essential oils, in some cases removing up to 90% of the original volume in order to remove most of the unwanted terpenes. This is known as terpeneless citrus oils, which carry a higher price in the essence markets. These folded oils are more stable, have a better flavour, are more water-soluble and are easier to blend in beverages and foodstuffs.

Well-known profiles of components of essential oils are instrumental in setting standards for the assessment of quality and prevention of adulteration. Knowing the chemistry of essential oils has allowed the successful manufacture of synthetic essential oils; however, some essential oils are so complex that the odour and flavour characteristics just cannot be duplicated.

See Colour Plates 81, 82.

See also: **II/Chromatography: Gas:** Headspace Gas Chromatography. **Distillation:** Extractive Distillation. **Extraction:** Solvent Based Separation. **III/Citrus Oils: Liquid Chromatography.**

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Gas Chromatography

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An essential oil is internationally defined as the product obtained by steam distillation, hydrodistillation or expression (for citrus fruits) of a plant or of a part of it. This definition is now less strictly applied, and the fractions resulting from several other techniques that sample the volatile fraction of a plant are now erroneously classified as essential oils. In general it would be more correct to call them volatile fractions of a vegetable matrix, and to use the term essential oil more specifically for samples obtained by distillation or expression. In addition to distillation or expression, the volatile fraction of a vegetable matrix can be obtained through static or dynamic headspace gas chromatography (HS-GC), solid-phase microextraction (SPME-GC), simultaneous distillation–extraction (SDE), solvent extraction or supercritical fluid extraction (SFE).

Components of an essential oil are generally medium-to-highly volatile with medium-to-low polarity, and as a consequence GC is the technique of choice for their analysis. **Figure 1** shows the structure of some typical essential oil components. These characteristics also facilitate their identification, which in general can be achieved by combining chromatographic (retention indices) data with mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (GC-FTIR).

This article aims to cover the main aspects related to the analysis of essential oils, in particular with sample preparation techniques related to GC; GC separation of enantiomers; multidimensional GC; identification of essential oil components through GC and/or combined techniques (GC-MS, GC-FTIR); GC-Isotope ratio mass spectrometry and authenticity of an essential oil; GC-sniffing for sensory evaluation; and statistical analysis applied to GC profiles.

Sample Preparation

Steam Distillation and Hydrodistillation

An essential oil is classically obtained by steam or hydrodistillation via equipment based on the circulatory distillation apparatus introduced by Clevenger in 1928. Apparatus and operation modes are now well established. Several pharmacopoeias give diagrams and instructions of how to obtain essential oils. **Figure 2** is taken from the *European Pharmacopoeia*.

On the other hand, sampling techniques for the volatile material are under constant evolution. The most used techniques are static or dynamic HS-GC, SPME/GC, SDE and SFE.

Headspace Sampling (HS-GC)

Static HS-GC, dynamic HS-GC HS is a sampling technique applied to the determination of volatiles in the gaseous phase in equilibrium with the matrix to be sampled.

HS-GC sampling is generally classified as static or dynamic HS. In static HS-GC, the analyte is sampled from a hermetically sealed vial after the matrix has reached equilibrium with its vapour at a predetermined temperature. **Figure 3**A shows the static HS-GC pattern of a sage sample. The sample was