Available online at www.pharmacie-globale.info ISSN 0976-8157

Review Article

PHARMACIE GLOBALE

INTERNATIONAL JOURNAL OF COMPREHENSIVE PHARMACY

EXTRACTION OF HERBAL AROMA OILS FROM SOLID SURFACE

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Received: 12 April 2011; Revised: 20 August 2011; Accepted: 25 August 2011; Available online: 5 September 2011

ABSTRACT

Fragrance extraction refers to the extraction of aromatic compounds from raw materials, using methods such as distillation, solvent extraction, expression or enfleurage. The results of the extracts are either essential oils, absolutes, concretes or butters, depending on the amount of waxes in the extracted product. To a certain extent, all of these techniques tend to distort the odour of the aromatic compounds obtained from the raw materials. Heat, chemical solvents or exposure to oxygen in the extraction process denature the aromatic compounds, either changing their odour character or rendering them odourless. This technique is very costly and is rarely used today. It reached its peak in 1860 and made the reputation of Grasse. It is a labour-intensive process that yields the highest quality of absolutes because it does not involve heat. Heat always alters the fragrance. It is used on delicate flowers that cannot stand up to the high heat and that continue to release essential oils after they have been picked. Examples of these flowers are Jasmine, Violet, Tuberose and Rose. Enfleurage goes back thousands of years to the ancient Egyptians. It works on the principle that fats absorb smells. Petals or other fragrant parts of a plant are steeped in fat or non-evaporating oil which will absorb their fragrance. A mixture of pork, lard and beef suet is smeared on to a glass plate in a wooden frame called a chassis. The flowers are placed on the fat and left to release their oils for several days. This process was repeated several times with fresh flower heads until the fat was totally absorbed with essential oil, the resultant substance being known as 'pomade', the oil was then retrieved from the fat by dissolving in an alcoholic solvent. This is mechanically mixed with alcohol for up to one week, and is chilled to 68°F. The essential oils dissolve in the alcohol and the fat does not. The mixture is chilled and filtered several times to remove all the fat. The alcohol is then evaporated to leave the pure absolute. Sometimes enfleurage is now carried out with cloth soaked in olive oil or liquid paraffin, which is laid over the frames instead of fat, the resultant perfumed oil being then known as 'huile antique'.

Keywords: Essential oil, enfleurage, pomade, supercritical fluid extraction, cohobation, sponge expression, cold pressed method, machine abrasion, maceration, hypercritical carbon dioxide, Florasols/Phytols Method.

INTRODUCTION

Essential oils are volatile and liquid aroma compounds from natural sources, usually plants. Essential oils are not oils in a strict sense, but often share with oils a poor solubility in water. Essential oils often have an odor and are therefore used in food flavoring and perfumery. Essential oils are usually prepared by fragrance extraction techniques such as distillation including steam distillation), cold pressing, or extraction (maceration). Essential oils are distinguished from aroma oils (essential oils and aroma compounds in an oily solvent), infusions in a vegetable oil, absolutes and concretes. Typically, essential oils are highly complex mixtures of often hundreds of individual aroma compounds.[1] (Figure **1**)

An **essential oil** is a concentrated hydrophobic liquid containing volatile aroma compounds from plants. Essential oils are also known as **volatile oils**, **ethereal oils** or **aetherolea**, or simply as the "oil" of the plant from which they were extracted, such as *oil of clove*. An oil is "essential" in the sense that it carries a distinctive scent, or essence, of the plant. Essential oils do not form a distinctive category for any medical, pharmacological, or culinary purpose. Essential oils are generally extracted by distillation. Other processes include expression, or solvent extraction. They are used in perfumes, cosmetics, soaps and other products, for flavoring food and drink, and for adding scents to incense and household cleaning products. Various essential oils have been used medicinally at different periods in history. Medical application proposed by those who sell medicinal oils range from skin treatments to remedies for cancer, and often are based on nothing better than historical accounts of use of essential oils for these purposes. Claims for the efficacy of medical

Figure 1. Essences from floral unit

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treatments and treatment of cancers in particular, are now subject to regulation in most countries. (Table **1**)

Table 1. Essential oils from plants

Agar oil distilled from Agarwood (*Aquilaria malaccensis*). Highly prized for its fragrance.	Ajwain oil, distilled from the leaves of Bishop's weed (*Carum copticum*). Oil contains 35-65% thymol.	Angelica root oil, distilled from the *Angelica archangelica*.	Anise oil, from the *Pimpinella anisum*, rich odor of licorice, used medicinally.
Asafoetida, used medicinally and to flavor food.	Balsam oil, from the *Myroxylon pereirae*.	Basil oil is used in making perfumes, as well as in aromatherapy.	Bay is used in perfumery; Aromatherapeutic for sprains, colds, flu, insomnia, rheumatism.
Bergamot oil, used in aromatherapy and in perfumes.	Black Pepper essential oil is distilled from the berries of *Piper nigrum*. The warm, soothing effect makes it ideal for treating muscle aches, pains and strains.	Buchu oil, made from the buchu shrub. Considered toxic and no longer widely used. Formerly used medicinally.	Birch is aromatheapeutic for gout, Rheumatism, Eczema, Ulcers.
Camphor is used for cold, cough, fever, rheumatism, arthritis.	Cannabis flower essential oil, used as a flavoring in foods, primarily candy and beverages. Also used as a scent in perfumes, cosmetics, soaps, and candles.	Caraway oil, used a flavoring in foods. Also used in mouthwashes, toothpastes, etc. as a flavoring agent.	Cardamom seed oil, used in aromatherapy and other medicinal applications. Extracted from seeds of subspecies of Zingiberaceae (ginger). Also used as a fragrance in soaps, perfumes, etc.
Carrot seed oil (essential oil), used in aromatherapy.	Cedarwood oil, primarily used in perfumes and fragrances.	Chamomile oil, There are many varieties of chamomile but only two are used in aromatherapy- Roman and German. Both have similar healing properties but German chamomile contains a higher level of azulin (an anti-inflammatory agent).	Calamus Root, used medicinally.
Cinnamon oil, used for flavoring and medicinally.	Citronella oil, from a plant related to lemon grass is used as an insect repellent, as well as medicinally.	Clove leaf oil, used as a topical anesthetic to relieve dental pain.	Coffee, used to flavor food.
Coriander	Costmary oil (bible leaf oil), from the *Tanacetum balsamita.*	Costus Root, used medicinally.	Cranberry seed oil, equally high in omega-3 omega-6 fatty acids, primarily used in the cosmetic industry.
Cubeb, used medicinally and to flavor foods.	Cumin oil/Black seed oil, used as a flavor, particularly in meat products. Also used in veterinary medicine.	Curry leaf, used medicinally and to flavor food.	Davana oil, from the *Artemisia pallens*, used as a perfume ingredient and as a germicide.
Dill oil, chemically almost identical to caraway seed oil. High carvone content.	Eucalyptus oil, historically used as a germicide. Commonly used in cough medicine, among other medicinal uses.	Fennel seed oil, used medicinally, particularly for treating colic in infants.	Fenugreek oil, used medicinally and for cosmetics from ancient times.
Frankincense oil, used for aromatherapy and in perfumes.	Galangal, used medicinally and to flavor food.	Geranium oil, used in aroma therapy, used for hormonal-imbalance. Geranium oil is often known as "female" oil.	Ginger oil, used medicinally in many cultures.
Grapefruit oil, extracted from the peel of the fruit. Used in aromatherapy. Contains 90% limonene.	Henna oil, used medicinally.	Jasmine oil, used for its flowery fragrance.	Juniper berry oil, used as a flavor. Also included in traditional medicine.
Lavender oil, used primarily as a fragrance. Also used medicinally.	Lemon oil, similar in fragrance to the fruit. Unlike other essential oils, lemon oil is usually cold pressed. Used medicinally, as an antiseptic, and in cosmetics.	Lemongrass. Lemongrass is a highly fragrant grass from India. In India, it is used to help treat fevers and infections. The oil is very useful for insect repellent.	Lime, antiseptic, antiviral, astringent, aperitif, bactericidal, disinfectant, febrifuge, haemostatic, restorative and tonic.
Litsea cubeba oil, lemon-like scent, often used in perfumes and aromatherapy.	Melissa oil (Lemon balm), sweet smelling oil used primarily medicinally, particularly in aromatherapy.	*Mentha arvensis* oil/Mint oil, used in flavoring toothpastes, mouthwashes and pharmaceuticals, as well as in aromatherapy and other medicinal applications.	Mugwort oil, used in ancient times for medicinal and magical purposes. Currently considered to be a neurotoxin.
Mustard oil (essential oil), containing a high percentage of allyl isothiocyanate or other isothiocyanate, depending on the species of mustard.	Myrrh oil, warm, slightly musty smell. Used medicinally.	Neem oil or Neem Tree Oil. Used medicinally.	Neroli is produced from the blossom of the bitter orange tree.
Nutmeg	Orange oil, like lemon oil, cold pressed rather than distilled. Consists of 90% d-Limonene. Used as a fragrance, in cleaning products and in flavoring foods.	Oregano oil, contains thymol and carvacrol, making it a useful fungicide. Also used to treat digestive problems.	Orris oil is extracted from the roots of the Florentine iris (*Iris florentina*) and used as a flavouring agent, in perfume and medicinally.
Parsley oil, used in soaps, detergents, colognes, cosmetics and perfumes, especially men's fragrances.	Patchouli oil, very common ingredient in perfumes.	Perilla essential oil, extracted from the leaves of the perilla plant. Contains about 50-60% perillaldehyde.	Pennyroyal oil, highly toxic. It is abortifacient and can even in small quantities cause acute liver and lung damage.
Peppermint oil, used in a wide variety of medicinal applications.	Pine oil, used as a disinfectant, and in aromatherapy.	Rose oil, distilled from rose petals, Used primarily as a fragrance.	Rosehip oil, distilled from the seeds of the *Rosa rubiginosa* or *Rosa mosqueta*. Used medicinally.

Rosemary oil, distilled from the flowers of *Rosmarinus officinalis*. Used in aromatherapy, topically to sooth muscles, and medicinal for its antibacterial and antifungal properties.	Rosewood oil, used primarily for skin care applications. Also used medicinally.	Sage oil, used medicinally.	Sandalwood oil, used primarily as a fragrance, for its pleasant, woody fragrance.
Sassafras oil, from sassafras root bark. Used in aromatherapy, soap-making, perfumes, and the like. Formerly used as a spice, and as the primary flavoring of root beer, *inter alia*.	Savory oil, from Satureja species. Used in aromatherapy, cosmetic and soap-making applications.	Schisandra oil, from *Schisandra chinensis*, used medicinally.	Spearmint oil, often used in flavoring mouthwash and chewing gum, among other applications.
Spikenard, used medicinally.	Star anise oil, highly fragrant oil using in cooking. Also used in perfumery and soaps, has been used in toothpastes, mouthwashes, and skin creams. 90% of the world's star anise crop is used in the manufacture of Tami_flu, a drug used to treat influenza, and is hoped to be useful for avian_flu.	Tarragon oil, distilled from *Artemisia dracunculus*, used medicinally.	Tea tree oil, distilled from *Melaleuca alternifolia*, used medicinally. Being a powerful antiseptic, antibacterial and antiviral agent, tea tree's ability to fight infection is second to none.
Thyme oil, used medicinally.	Turmeric, used medicinally and to flavor food.	Valerian, used medicinally.	Vetiver oil (khus oil) a thick, amber oil, primarily from India. Used as a fixative in perfumery, and in aromatherapy.
Wintergreen and Yarrow oil is used medicinally, to relieve joint pain	Ylang-ylang from *Cananga odorata* used in aromatherapy.	Zedoary, used medicinally and to flavor food.	

As the use of essential oils has declined in evidence-based medicine, one must consult older textbooks for much information on their use. Modern works are less inclined to generalize; rather than refer to "essential oils" as a class at all, they prefer to discuss specific compounds, such as methyl salicylate, rather than "oil of wintergreen". Interest in essential oils has revived in recent decades with the popularity of aromatherapy, a branch of alternative medicine that claims that essential oils and other aromatic compounds have curative effects. Oils are volatilized or diluted in carrier oil and used in massage, diffused in the air by a nebulizer, heated over a candle flame, or burned as incense.[2] The techniques and methods first used to produce essential oils was first mentioned by Ibn al-Baitar (1188–1248), an Andalusian physician, pharmacist and chemist. (Table **2**).

Table 2. Various types of essential oils

Aromatherapy Essential Oils		
Chamomile Essential Oil	Bergamot Essential Oil	Ylang-ylang Essential Oil
Eucalyptus Essential Oil	Dill Essential Oil	Frankincense Essential Oil
Geranium Essential Oil	Fennel Essential Oil	Tea-tree Essential Oil
Lavender Essential Oil	Jasmine Essential Oil	Sandalwood Essential Oil
Lemon Essential Oil	Angelica Essential Oil	Basil Essential Oil
Peppermint Essential Oil	Aniseed Essential Oil	Rosemary Essential Oil

ISOLATION METHODS

Enfleurage

Enfleurage is a process that uses odorless fats that are semisolid at room temperature to capture the fragrant compounds exuded by plants. It is also known as Cold Fat Extraction. The process can be "cold" enfleurage or "hot" enfleurage.

Cold enfleurage: A large framed plate of glass, called a chassis, is smeared with a layer of animal fat, usually 2 part of lard & 1 part of tallow (from pork or beef, respectively) and allowed to set. Botanical matter, usually petals or whole flowers, is then placed on the fat and its scent is allowed to diffuse into the fat over the course of 1-3 days. The process is then repeated by replacing the spent botanicals with fresh ones until the fat has reached a desired degree of fragrance saturation. This procedure was developed in southern France in the 18th century for the production of high-grade concentrates. The technique is yet extensively used in France for the bulk production of absolute of specific flowers.

Hot enfleurage: Solid fats are heated and botanical matter is stirred into the fat. Spent botanicals are repeatedly strained from the fat and replaced with fresh material until the fat is saturated with fragrance. This method is considered the oldest known procedure for preserving plant fragrance substances.

In both instances, once the fat is saturated with fragrance, which is known as "Enfleurage Pomade" is then taken separately (Defleuraged). The enfleurage pomade was either sold as it was, or it could be further washed or soaked in ethyl alcohol to draw the fragrant molecules into the alcohol. The alcohol is then separated from the fat and allowed to evaporate in an instrument called as "Batteuses" which uses vacuum for evaporation purpose & leaves behind the absolute of the botanical matter. The spent fat is usually used to make soaps since it is still relatively fragrant. (Figure **2**)

Figure 2. Process of enfleurage

Significance: The enfleurage fragrance extraction method is by far one of the oldest. It is also costly but is the sole method of extracting the fragrant oil in delicate floral botanical such as Jasmine, Lily, Rose, Tuberose, which would be destroyed or denatured by the high temperatures required by methods of fragrance extraction such as steam distillation. The method can't supersede by more efficient techniques such as solvent extraction or supercritical fluid extraction using liquid carbon dioxide (CO_2) or similar compressed gases because they interfere with the genuine fragrance of the essential oils.[3]

Advantages: Heat sensitive essential oils can be separated in pure & unaltered form; Heating/Electricity is not required; Eco-friendly technique; No Waste products while used wax is used in soap production.

Pomade

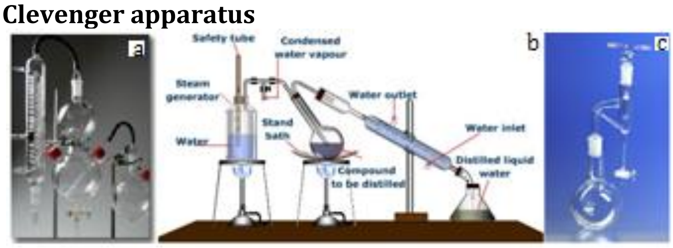
Pomade is a greasy or waxy substance that is used to style hair. Pomade makes hair look slick and shiny. Unlike hair spray and hair gel, pomade does not dry and often takes several washes to remove. It can be easily removed using a high-detergent shampoo or other de-greasers such as olive oil, dish washing liquid and lemon juice. Most pomades contain petroleum jelly (in fact, petroleum jelly can be used alone as a pomade) and mineral oil and many also contain some sort of wax. They may be anhydrous or emulsified with an aqueous carrier, which makes them easier to remove. They may also contain perfume and coloring agents. A wide range of pomades are in production today and vary in factors such as weight, shine and scent. The stiffest will have a higher proportion of waxes such as beeswax while the lightest may have a higher proportion of oils. (Figure **3**)

Figure-3: Pomade containing Fragrance

Steam distillation

Steam distillation is a special type of distillation (a separation process) for *temperature sensitive* materials like natural aromatic compounds. Many organic compounds tend to decompose at high sustained temperatures. Separation by normal distillation would then not be an option, so water or steam is introduced into the distillation apparatus. By adding water or steam, the boiling points of the compounds are depressed, allowing them to evaporate at lower temperatures, preferably below the temperatures at which the deterioration of the material becomes appreciable. If the substances to be distilled are very sensitive to heat, steam distillation can also be combined with vacuum distillation. After distillation the vapors are condensed as usual, usually yielding a two-phase system of water and the organic compounds, allowing for simple separation. (Figure **4**)

Figure 4. Steam distillation (a) unit & (b) Process (c) Clevenger apparatus



Principle: When a mixture of two practically immiscible liquids is heated while being agitated to expose the surfaces of both the liquids to the vapor phase, each constituent independently exerts its own vapor pressure as a function of temperature as if the other constituent were not present. Consequently, the vapor pressure of the whole system increases. Boiling begins when the sum of the partial pressures of the two immiscible liquids just exceeds the atmospheric pressure (approximately 101 kPa at sea level). In this way, many organic compounds insoluble in water can be purified at a temperature well below the point at which decomposition occurs. For example, the boiling point of bromobenzene is 156°C and the boiling point of water is 100°C, but a mixture of the two boils at 95°C. Thus, bromobenzene can be easily distilled at a temperature 61°C below its normal boiling point.

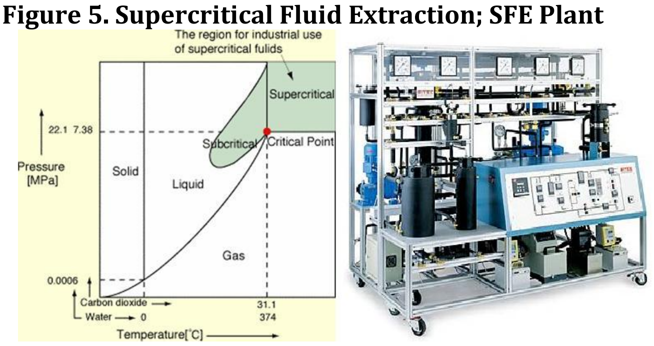
Applications: Steam distillation is employed in the manufacture of essential oils, for instance, perfumes. In this method, steam is passed through the plant material containing the desired oils. Eucalyptus oil and orange oil are obtained by this method on the industrial scale. Steam distillation is also sometimes used to separate intermediate or final products during the synthesis of complex organic compounds. Steam distillation is also widely used in petroleum refineries and petrochemical plants where it is commonly referred to as "steam stripping".

Equipment: On a lab-scale steam distillations are carried out using steam generated outside the system and piped through macerated biomass or steam generation *in-situ* using a Clevenger-type apparatus.[4] (Figure **4c**)

Supercritical Fluid Extraction (SFE)

SFE is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids as the extracting solvent. Extraction is usually from a solid matrix, but can also be from liquids. SFE can be used as a sample preparation step for analytical purposes, or on a larger scale to either strip unwanted material from a product (e.g. decaffeination) or collect a desired product (e.g. essential oils). Carbon dioxide (CO_2) is the most used supercritical fluid, sometimes modified by co-solvents such as ethanol or methanol. Extraction conditions for supercritical CO_2 are above the critical temperature of 31°C and critical pressure of 74 bar. Addition of modifiers may slightly alter this. The discussion below will mainly refer to extraction with CO_2, except where specified. (Figure **5**)

Figure 5. Supercritical Fluid Extraction; SFE Plant



Procedure: The system must contain a pump for the CO_2, a pressure cell to contain the sample, a means of maintaining pressure in the system and a collecting vessel. The liquid is pumped to a heating zone, where it is heated to supercritical conditions. It then passes into the extraction vessel, where it rapidly diffuses into the solid matrix and dissolves the material to be extracted. The dissolved material is swept from the extraction cell into a separator at lower pressure and the extracted material settles out. The CO_2 can then be cooled, re-compressed and recycled, or discharged to atmosphere.

Pumps: Carbon dioxide (CO_2) is usually pumped as a liquid, usually below 5°C and a pressure of about 50 bars. The solvent is pumped as a liquid as it is then almost incompressible; if it was pumped as a supercritical fluid, much of the pump stroke would be "used up" in compressing the fluid, rather than pumping it. For small scale extractions (up to a few grams/minute), reciprocating CO_2 pumps or syringe pumps are often used. For larger scale extractions, diaphragm pumps are most common. The pump heads will usually require cooling and the CO_2 will also be cooled before entering the pump.

Pressure vessels: It can range from simple tubing to more sophisticated purpose built vessels with quick release fittings. The pressure requirement is at least 74 bars and most extractions are conducted at less than 350 bars. However, sometimes higher pressures will be needed, such as extraction of vegetable oils, where pressures of 800 bars are sometimes required for complete miscibility of the two phases. The vessel must be equipped with a means of heating. It can be placed inside an oven for small vessels or an oil or electrically heated jacket for larger vessels. Care must be taken if rubber seals are used on the vessel, as the CO_2 may dissolve in the rubber, causing swelling and the rubber will rupture on depressurization.

Pressure maintenance: The pressure in the system must be maintained from the pump right through the pressure vessel. In smaller systems (up to about 10 mL/min) a simple restrictor can be used. This can be either a capillary tube cut to length or a needle valve which can be adjusted to maintain pressure at different flow rates. In larger systems a back pressure regulator will be used, which maintains pressure upstream of the regulator by means of a spring, compressed air or electronically driven valve. Whichever is used, heating must be supplied, as the adiabatic expansion of the CO_2 results in significant cooling. This is problematic if water or other extracted material is present in the sample, as this may freeze in the restrictor or valve and cause blockages.

Collection: The supercritical solvent is passed into a vessel at lower pressure than the extraction vessel. The density and hence dissolving power, of supercritical fluids varies sharply with pressure and hence the solubility in the lower density CO_2 is much lower, and the material precipitates for collection. It is possible to fractionate the dissolved material using a series of vessels at reducing pressure. The CO_2 can be recycled or depressurized to atmospheric pressure and vented. For analytical SFE, the pressure is usually dropped to atmospheric and the now gaseous carbon dioxide bubbled through a solvent to trap the precipitated components.[5]

Heating and cooling: This is an important aspect. The fluid is cooled before pumping to maintain liquid conditions and then heated after pressurization. As the fluid is expanded into the separator, heat must be provided to prevent excessive cooling. For small scale extractions, such as for analytical purposes, it is usually sufficient to pre-heat the fluid in a length of tubing inside the oven containing the extraction cell. The restrictor can be electrically heated, or even heated with a hairdryer. For larger systems, the energy required during each stage of the process can be calculated using the thermodynamic properties of the supercritical fluid. There are two essential steps to SFE, transport (by diffusion or otherwise) from with the solid particles to the surface, and dissolution in the supercritical fluid. Other factors, such as diffusion into the particle by the SF and reversible release such as desorption from an active site are sometimes significant, but not dealt with in detail here. Figure **5** shows the stages during extraction from a spherical particle where at the start of the extraction the level of extractant is equal across the whole sphere. As extraction commences, material is initially extracted from the edge of the sphere, and the concentration in the center is unchanged. As the extraction progresses, the concentration in the center of the sphere drops as the extractant diffuses towards the edge of the sphere.

The relative rates of diffusion and dissolution are illustrated by two extreme cases in Figure **5** which shows a case where dissolution is fast relative to diffusion. The material is carried away from the edge faster than it can diffuse from the center, so the concentration at the edge drops to zero. The material is carried away as fast as it arrives at the surface and the extraction is completely diffusion limited. Here the rate of extraction can be increased by increasing diffusion rate, for example raising the temperature, but not by increasing the flow rate of the solvent. Figure **5** shows a case where solubility is low relative to diffusion. The extractant is able to diffuse to the edge faster than it can be carried away by the solvent, and the concentration profile is flat. In this case, the extraction rate can be increased by increasing the rate of dissolution, for example by increasing flow rate of the solvent. The extraction curve of % recovery against time can be used to elucidate the type of extraction occurring. Figure-5 shows a typical diffusion controlled curve. The extraction is initially rapid, until the concentration at the surface drops to zero and the rate then becomes much slower. The % extracted eventually approaches 100%. Figure **5** shows a curve for a solubility limited extraction. The extraction rate is almost constant, and only flattens off towards the end of the extraction. Figure-5 shows a curve where there are significant matrix effects, where there is reversible interaction with the matrix, such as desorption from an active site. The recovery flattens off, and if the 100% value is not known, then it is hard to tell that extraction is less than complete.

Optimization: The optimum will depend on the purpose of the extraction. For an analytical extraction to determine, say, antioxidant content of a polymer, then the essential factor is complete extraction in the shortest time. However, for production of an essential oil extract from a plant, then quantity of CO_2 used will be a significant cost, and "complete" extraction not required, a yield of 70-80% perhaps being sufficient to provide economic returns. In another case, the selectivity may be more important, and a reduced rate of extraction will be preferable if it provides greater discrimination. Therefore few comments can be made which are universally applicable.

Maximizing diffusion: This can be achieved by increasing the temperature, swelling the matrix, or reducing the particle size. Matrix swelling can sometimes be increased by increasing the pressure of the solvent, and by adding modifiers to the solvent. Some polymers and elastomers in particular are swelled dramatically by CO_2, with diffusion being increased by several orders of magnitude in some cases.

Maximizing solubility: Generally, higher pressure will increase solubility. The effect of temperature is less certain, as close to the critical point, increasing the temperature causes decreases in density, and hence dissolving power. At pressures well above the critical pressure, solubility is likely to increase with temperature. Addition of low levels of modifiers (sometimes called entrainers), such as methanol and ethanol, can also significantly increase solubility, particularly of more polar compounds.

Optimizing flow rate: The flow rate of CO_2 should be measured in terms of mass flow rather than by volume because the density of the CO_2 changes according to the temperature both before entering the pump heads and during compression. Coriolis flow meters are best used to achieve such flow confirmation. To maximize the rate of extraction, the flow rate should be high enough for the extraction to be completely diffusion limited (but this will be very wasteful of solvent). However, to minimize the amount of solvent used, the extraction should be completely solubility limited (which will take a very long time). Flow rate must therefore be determined depending on the competing factors of time and solvent costs and also capital costs of pumps, heaters and heat exchangers. The optimum flow rate will probably be somewhere in the region where both solubility and diffusion are significant factors.[6]

Advantages:

Environmental improvement and reduced product contamination: SFE is an alternative to liquid extraction using solvents such as hexane or dichloromethane. There will always be some residual solvent left in the extract and matrix and there is always some level of environmental contamination from their use. In contrast, carbon dioxide is easy to remove simply by reducing the pressure, leaving almost no trace, purchased CO_2 has almost always been reclaimed, which reduces the total carbon foot-print. The use of SFE with CO_2 is approved by the Soil Association for organic products. The CO_2 used is largely a byproduct of industrial processes or brewing and its use in SFE does not cause any extra emissions.

Selectivity: The properties of a supercritical fluid can be altered by varying the pressure and temperature, allowing selective extraction. For example, volatile oils can be extracted from a plant with low pressures (100 bar), whereas liquid extraction would also remove lipids. Lipids can be removed using pure CO2 at higher pressures and then phospholipids can be removed by adding ethanol to the solvent.

Speed: Extraction is a diffusion-based process, with the solvent required to diffuse into the matrix and the extracted material to diffuse out of the matrix into the solvent. Diffusivities are much faster in supercritical fluids than in liquids and therefore extraction can occur faster. Also, there is no surface tension and viscosities are much lower than in liquids, so the solvent can penetrate into small pores within the matrix inaccessible to liquids. Both the higher diffusivity and lower viscosity significantly increase the speed of the extraction: An extraction using an organic liquid may take several hours, whereas supercritical fluid extraction can be completed in 10-60 minutes.

Limitations: The requirement for high pressures increases the cost compared to conventional liquid extraction, so SFE will only be used where there are significant advantages. Carbon dioxide itself is non-polar, and has somewhat limited dissolving power, so cannot always be used as a solvent on its own, particularly for polar solutes. The use of modifiers increases the range of materials which can be extracted. Food grade modifiers such as ethanol can often be used, and can also help in the collection of the extracted material, but reduces some of the benefits of using a solvent which is gaseous at room temperature.7

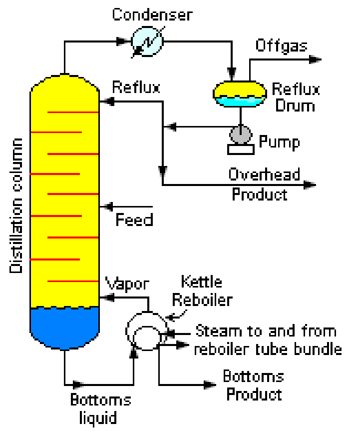
Water Distillation Method

In water distillation, the botanical material is completely immersed in water and then is boiled. This method protects the oil to be extracted till a certain degree since surrounding water prevents it from overheating. Then it is condensed and cooled down. The oil is then separated out, as it layers on the top of the water. The water separated out in this process is termed as floral waters (also called hydrosol or sweet water) such as rose water, orange water and lavender water. Water distillation can be operated at low pressures to reduce boiling temperature. This helps in protecting the botanical material and essential oil as well. This method is used for extraction of oils that are sensitive to heat. If a lot of exposure to hot water is not mentioned for a particular plant such as lavender, it is best to find an extraction method better suited. Any botanical material that contains high amounts of esters does not take well to this extraction method, since the exposure to hot water will break down the esters into alcohols and carboxylic acids.

Steam Distillation Method

Steam distillation is the most common method of extracting essential oils. Steam distillation is done in a still (The still is all with a head and a well-insulated swan's neck proceeded by a mechanism to prevent fumes and impurities passing through). Fresh, or sometimes dried, botanical material is placed in a closed container of the still, and pressurized steam is generated which enters the container and circulates through the plant material. The heat of the steam forces the intercellular pockets that hold the essential oils to open and release them. The temperature of the steam should not be very high as it can damage the botanical material but should be high enough to open the pockets which hold the essential oil. Tiny droplets of essential oil evaporate and attach to the steam. The steam which then contains the essential oil, is passed through a cooling system to condense the steam, which forms a liquid from which the essential oil and water is then separated by decantation. The oil forms a layer on the water surface as it does not dissolves in water and hence is separated easily. This method is not used for extraction of oils that are sensitive to heat. (Figure **6**)

Figure 6. Steam distillation unit



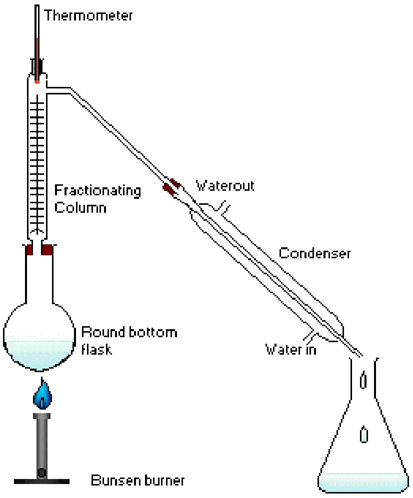
Hydro Diffusion Method

Hydro Diffusion method for extraction of oils is a type of steam distillation and is only different in the way in which steam is enters the container of the still. In hydro diffusion, steam is fed in from the top onto the botanical material while in the case of steam distillation; steam is fed from the bottom. In this way the steam can saturate the plants more evenly and in less time than with steam distillation. The condensation of the oil containing steam mixture occurs below the area in which the botanical material is held. The main advantage of this method over steam distillation is that less steam is used hence shorter processing time and therefore a higher oil yield. This method is also less harsh on the botanical material.

Fractional Distillation Method

When we say fractional distillation, it only refers to normal distillation process. In this only difference is that the oil is not collected continuously, but is collected in parts i.e. fractions and oil normally so extracted is "Ylang-Ylang oil". (Figure **7**)

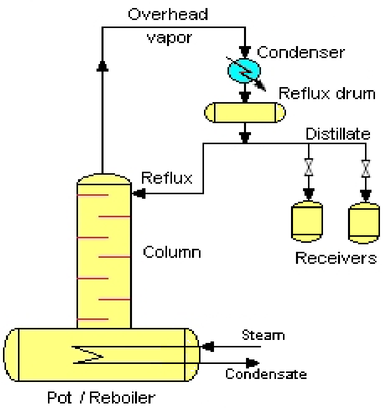
Figure 7. Fractional distillation unit



Rectification Method

When an essential oil contains any impurities, it can be purified by re-distillation; either in steam or in vacuum and this purification of oil by re-distillation is referred to as rectification. This process is used to make oils of standard quality. An example of rectification is eucalyptus oil. (Figure **8**)

Figure 8. Rectification unit



Cohobation Method

In some essential oil extractions, some chemical or part of the essential oil gets dissolved in water and therefore gets removed from the oil. So to get the whole oil, we add the deficient chemical to the deficient oil and re-distillation is done until we get the complete oil. An example of this is rose oil.[8]

Sponge Expression Method

Most citrus essences are extracted by means of expression, and in the past were done by hand where the fruit pulp was removed, with the rind and pith then soaked in warm water to make the rind more pliable, since the pith of the fruit absorbed the water. After the fruit has absorbed the water and become more elastic, it was inverted which helped to rupture the oil cells and a sponge placed next to the rind. It was then squeezed to release the volatile oil, which was then collected directly into the sponge. As soon as the sponge became saturated with oil, it was squeezed and the essential oil collected in a vessel and then decanted.[9] (Figure **9**)

Figure 9. Sponge expression method

Cold Pressed Method

Another expression method of extracting essential oils is coldpressed expression, or scarification method. It is used to obtain citrus fruit oils such as bergamot, grapefruit, lemon, lime, mandarin, orange, and tangerine oils. In this process, fruit rolls over a trough with sharp projections that penetrate the peel. This pierces the tiny pouches containing the essential oil. Then the whole fruit is pressed to squeeze the juice from the pulp and to release the essential oil from the pouches. The essential oil rises to the surface of the juice and is separated from the juice by centrifugation. It is important to note that oils extracted using this method have a relatively short shelf life, so make or purchase only what you will be using within the next six months.[10] (Figure **10**)

Figure 10. Cold pressed method

Machine Abrasion Method

Machine Abrasion is very much same as cold pressed expression method and is mainly used in extraction of citrus essential oils. In machine abrasion, a machine strips off the outer peel of the botanical material, which is then removed by running water and left over is then fed into a centrifugal separator. The centrifugal separation is done extremely fast. But, it should be noted that due to the fact that the essential oil is combined with other cell content for some time, some alteration could occur in the oil due to enzymatic action.[11] (Figure **11**)

Figure 11. Machine abrasion method

Solvent Extraction Method

Very delicate aromatics, Jasmine, Linden Blossom, etc.

cannot survive the process of distillation. To capture their magical aromas, a process of solvent extraction is used. A hydrocarbon solvent (usually hexane) is added to the botanical material to help dissolve the extractable matter from the botanical material which includes non-aromatic waxes, pigments and highly volatile aromatic molecules. When this solution is filtered and then the filtrate is subjected to distillation at low pressure, a substance containing resin (resinoid), or a combination of wax and essential oil (known as concrete) is left. The concrete is further processed to remove the waxy materials which dilute the pure essential oil. To prepare the absolute from the concrete, the waxy concrete is warmed and stirred with alcohol (usually ethanol). When we heat and stir the concrete, it breaks up into minute globules, and separation takes place as aromatic oil is more soluble in alcohol than that in wax. But along with the aromatic molecules a certain amount of wax is also dissolved and this can be removed only by agitating and freezing the solution at very low temperatures (around minus -35°C). In this way most of the wax precipitates out. As a final precaution the purified solution is cold filtered leaving only the wax-free material (the absolute) i.e. the essential oil. This solvent extraction actually yields three usable products; first the concrete (as in rose concrete, my favorite solid perfume), the precious absolutes i.e. the oils, and the floral waxes, for addition to candles, thickening creams and lotions as a softly floral scented alternative to beeswax. Although more cost-efficient than enfleurage, solvent extraction is more expensive than steam distillation so it is reserved for costly oils which cannot be distilled. This is not considered the best method for extraction of essential oils, as the solvents can leave a residue behind which could cause allergies and effect the immune system, but it's great for making resins for this very reason.[12]

Maceration Method

Maceration actually creates more of *infused oil* rather than an *essential oil* and is most often used for creating extracts and resins. The botanical material is soaked in vegetable oil, water, or another solvent. If it's soaked in vegetable oil, and then heated and strained, it can be used for massage and if soaked in water or another solvent such as alcohol, will create a much thicker extract or resin.[13] **(Figure-12)**

Figure 12. Maceration method

Hypercritical Carbon dioxide (CO_2) Method

The use of hypercritical carbon dioxide extraction is a fairly new way to extract essential oils from botanical material and although a bit on the expensive side, does yield good quality oils. Carbon dioxide becomes hypercritical at 33 degrees celsius, which is a state in which it is not really gas or liquid, but has qualities of both, and is an excellent solvent to use in the extraction of essential oils since low temperature is required and the fact that the process is near to instantaneous.

The carbon dioxide is inert and therefore does not chemically react with the essence that is being extracted and hence, essential oils can be extracted in a similar way as other solvent extraction methods. To remove the carbon dioxide solvent, you simply need to remove the pressure applied. This process has to take place in a closed chamber since the hypercritical pressure required for carbon dioxide is 200 atmospheres. To achieve this pressure specific equipment is required which is very expensive. The advantage of this method, of course, is that no solvent residue remains, since at normal pressure and temperature, the carbon dioxide simply reverts to a gas and evaporates. Hypercritical carbon dioxide extraction has given us essences of some aromatics that don't yield essential oils, for example Rose Hip Seed and Calendula. Many carbon dioxide extractions have fresher, cleaner, and crisper aromas than steam-distilled essential oils, and they smell more similar to the living plants. Scientific studies show that carbon dioxide extraction produces essential oils that are very potent and have great therapeutic benefits.[14] (Figure **13**)

Figure 13. Hypercritical CO_2 method

Florasols/Phytols Method

This extraction method uses a new type of benign gaseous solvents. The unique properties of these solvents are used for the extraction of aromatic oils and biologically active components from botanical materials. Florasol is the solvent upon which the process is based. Extraction occurs at or below ambient temperatures; hence there is no thermal degradation of the products. The extraction process utilizes the selectivity of the solvent and produces free flowing clear oil free of waxes. (Figure **14**)

Figure 14. Florasol method

'Florasols' Are NOT 'Essential Oils'! Why? 'Essential' oils are made by steam or water distillation. The plant material is boiled for several hours in a kettle with lots of water (typically three times its weight). Some of the water turns to steam which carries the fragrant oil with it. The steam is condensed back to water by cooling it in condensers. The 'essential' oil floats on the surface of the condensed water and is skimmed off. So, 'essential oil' has all been cooked. Heat will have damaged and changed many of the fragile, naturally occurring substances. Much of the most delicate, fragrant, light, volatile components will have been lost during the condensation. Much of the fragrant is also lost – dissolved in the condensed waters (rose water is a fragrant!), this loss have been at the expense of the oil. This process uses huge amounts of fossil fuel to boil the plant/water mix, pollutes, and also produces vast quantities of boiling hot liquid waste.

'Florasols' Are NOT 'Absolutes'! Why?

'Absolutes' are made from 'concretes' by milling them with 98% alcohol. Strong alcohol dissolves the 'absolutes' out of the buttery mass of 'concretes'. This alcohol solution is frozen to – minus 10°C (14°F), which precipitates the waxes. This cold solution is filtered and the filtrate/solution concentrated by rigorously boiling off of the alcohol under vacuum. The 'absolutes' is the oil which is left after the alcohol has been boiled away. Alcohol boils at 78°C. So "absolutes' have been through TWO 'boiling-off' processes (the first from hexane, the second from alcohol), Volatile fragrant components will have been stripped out and lost and damage will have been done to the delicate heat sensitive components of the oil on both occasions.

'Florasols' Are NOT 'Concretes'! Why? 'Concretes' are made by stirring up vegetable matter with hexane (gasoline) or chlorinated solvents (such as methylene chloride). Hexane dissolves (extracts) many of the plant's components. The hexane solution is then evaporated to dryness at 75°C. The 'concrete' is what it's left, after the hexane has been driven off/boiled away. So, 'concretes' have also been heated. They also contain residual hexane. They contain about 50% of the plant's waxes, pigments, resins, fats, (triglycerides and fatty acids) and sterols and their esters. Heating will have caused damage to the fragile components and the loss of their delicate 'volatiles, particularly if the hexane has been removed under high vacuum (which is usual practice) hexane is lost into the atmosphere where it is a serious 'Volatile Organic Compound' – VOC pollutant, contributing to toxic. Needless to say, the process is also extremely hazardous as hydrocarbons are all flammable. We can however extract from Concretes using our HFC Process and, in this case, we first coat the Concrete onto a carrier medium and then extract using the normal 'FLORASOLS' process. The extraction time will be longer than a standard extraction, but the yield will of cause be proportionally higher as the concentration of the oil in the Concrete is higher also. As an example; 1kg of Rose Concrete may produce 500 gms of oil whereas 1 kg of Rose will provide 1 gm of oil.

'Florasols' Are NOT 'SCFE Oil'! Why? Warm carbon dioxide gas at exceeding high pressure can be used to dissolve fragrant/flavour oils from some plant materials. The acidic gas, carbon dioxide, is passed through the warm plant material at 300 – 500 times the pressure of the atmosphere (pressure such as those found in the nature at the bottom of the Pacific Ocean, three miles down!) - don't try this at home! This 'fluid' dissolves oil, resins and waxes out of the plant material. When the pressure is allowed to fall to only 100 'Bar' (=100 time atmospheric pressure, the oil form into a mist and can be collected. Needless to say, the equipment needed for this process is massive in the extreme and very costly and uses huge quantities of electricity to drive it. This is why products are so expensive. The effect of the high degree (all low as pH 2.0) at these temperatures on the 'naturalness' of SCFE products, will reward further study.[15]

Commonly used Techniques for Aroma Oil Extraction (Table **3**)

Table 3. Different types of extraction

Methods	
Water Distillation	Cold pressed Expression
Steam Distillation	Machine Abrasion
Hydro Diffusion	Solvent Extraction
Fractional Distillation	Maceration
Rectification	Enfleurage
Cohobation	Hypercritical Carbon Dioxide (CO_2)
Sponge Expression	Florasol

Use of essential oils with aromatherapy (Table **4**)

Table 4. Use of essential oils with aromatherapy

Use of essential oils		Aromatherapy Recipes	
Air reshening	Bathing	Emotional Balance	Physical Balance
Compresses	Foot and hand baths	Acne	Sun Screen
Hair care	Jacuzzis	Massage	Bubble Baths
Massage	Saunas	Cleansers & Toners	Moisturizers
Showers	Sitz bath	Shower gels	Shampoos
Skin care	Steam inhalations, Vaporization	Face oils	Perfumes and Colognes

CONCLUSION

Nature produces essential oils in flowers which are extracted by several processes to make perfumes or essences from ancient period. All the fragrances are well accepted for various purposes in our daily routine for making natural harmony with nature.

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