ESSENTIAL OILS

What is an essential oil?

- **Essential oils are the concentrated extracts (liquid from) of volatile and non-water-soluble 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 (distilled).

An oil is "essential" in the sense that it carries a distinctive scent, or essence, of the plants.
So, we can cay essence or essential oils from native plants, we can call oil.

The history of essential oils

The benefits of essential oils have been recognised for thousands of years.

Their use is described in the New Testament of the Bible.

They were used in rituals and in healing the sick.

The ancient Egyptians used essential oils for embalming, religious rites and medicinal purposes.

King Tut's tomb was found to contain 50 jars of essential oil when it was opened in 1922.

Distribution

The main essential oil plants have been found in some families such as Umbelliferae, Lamiaceae, Rutaceae, Myrtaceae, Compositae, Rosaceae, Iridaceae, Zingiberaceae, Lauraceae, Pinaceae etc…

In general Mediterranean region,

Found in some parts of the plants,

Such as;

Flos-Lavandula

Petal-Rose

Folia-Menthae

Fructus-Coriandri, Anisi, Oranges

Herba-Thymus

Cotex-Cinnamomi

Radix -Valerianae

Turkey is very rich in terms of essential oil bearing plants
Especially Isparta, Burdur, Alanya, Manisa..

The Most Important Products in Turkey Exports

• Rose oil	7.6 milyon $
• Stearopten oil	2.9 milyon $
• Itır oil	1.4 milyon $
• Thyme oil	1.1 milyon $

It is among the most consumed essential oil in the world annually.

2300 tons of lemon essential oil
1400 tons of eucalyptus essential oil
70 tons of clove essential oil is used.

Properties of essential oils

- **Almost entirely VOLATILE…**
- **Density: the density of most essential oils are less than 1g/ml.**
  - **2 are heavier from water – Cinnamon and Clove oil.**
- **Soluble in ether, chloroform and alcohol.**
- **Slightly soluble in water: give it a characteristic odour & taste.**
- **Leaves a temporary stain on paper which disappears as the oil volatilizes.**
- **Most are colourless. Oxidize on exposure to air and resinify; colour becomes darker (odour changes slightly).**
- **All are characteristic odours.**
- **Most are optically active.**

FUNCTION: In most cases, the biological function of the terpenoids of essential oils remains obscure – it is thought that they play an ecological role – protection from predators and attraction of pollinators.

Physical Properties

Although volatile oils differ greatly in their chemical constitution, they have a number of physical properties in common:

1. **They possess characteristic odors.**

2. **They are characterized by high refractive indices.**

3. **Most of them are optically active.**

4. **Their density is generally lower than that of water (the essential oils of sassafras, clove, or cinnamon are the exceptions).**

5. **As a rule, volatile oils are immiscible with water, but they are sufficiently soluble to impart their odor to water. The aromatic waters are dependent on this slight solubility.**

Localization of the essential oils

Synthesis and accumulation of essential oils are generally associated with the presence of specialized histological structures (normally pre-exist in the plant – stored in a special secretory tissue), often located on or near the surface of the plant:

- Oil cells: Zingiberaceae
- Glandular trichomes: Lamiaceae
- Secretory cavities: Myrtaceae or Rutaceae
- Secretory canals: Apiaceae or Astereraceae (Compositeae)

Variability factors of essential oils

1. **Occurrence of chemotypes**
2. **Influence of the vegetative cycle**
3. **Influence of environmental factors**
4. **Influence of preparation method of the essential oil**

1. Chemotypes

Chemical diversity commonly occur in plants containing volatile oils, e.g. Thyme (*Thymus vulgaris*) – has 7 different chemotypes, each with slightly different types & amounts of volatile oils and components.

2. The vegetative cycle

Proportions of the different constituents of a volatile oil may vary greatly throughout its development.

Wide ranges are commonly found in fennel, carrot and coriander (linalool is higher in ripe fruit than unripe fruit). *Mentha* (peppermint) is also greatly affected by the vegetative cycle.

3. Environmental Factors

Temperature, humidity, duration of daylight (radiation), and wind patterns all have a direct influence on volatile oil content, especially in those herbs that have superficial histological storage structures (e.g. glandular trichomes). When the localization is deeper, the oil quality is more constant.

Example: Peppermint: long days & temperate nights, higher yields of oil & menthofuran. Cold nights lead to an increase in menthol.

The volatile oil of *Laurus nobilis* (Bay) is greater in the southern hemisphere than the northern.

Citrus: higher temperatures = higher oil content.

4. Preparation and cultivation

Cultivation practices also play an important factor to the yield and quality of the final product.

Fertilization and the amounts of N, P and K have been studied for various species.

The irrigation also plays an important role.

Essential oil drugs in European Pharmacopeia

- Anise Oil
- Bitter orange Flower Oil
- Cassia Oil
- Cinnamon bark Oil
- Cinnamon Leaf Oil
- Citronella Oil
- Clove Oil
- Eucalyptus Oil
- Lavander Oil
- Lemon Oil
- Thyme Oil
- Nutmeg Oil
- Peppermint Oil

Composition of the essential oils

- Essential oils are mixtures of organic compounds.
- Terpenes are the key components of all essential oils, its mean that the essential oils are composed of mainly terpenes and some aromatic compounds

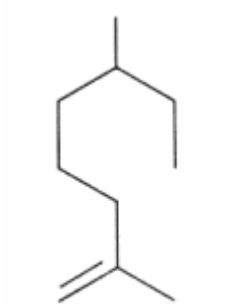
- The distinctive character of an essential oil can be attributed to the *functional group* present in its key molecule.
- Esters, aldehydes, ketones and alcohols are all found in essential oils.

1.Terpenoids
2.Aromatic compounds
3. Hydrocarbon type compound
4. Nitrogen (azote) and sulphur containing compounds

Composition of Volatile Oils

- **Volatile oils are generally mixtures of hydrocarbons and oxygenated compounds derived from these hydrocarbons.**

- **The odour and taste of volatile oils is mainly determined by these oxygenated constituents, which are to some extent soluble in water but more soluble in alcohol.**



2,6-dimethyloctane

2,6 dimetilokten

- **Practically all volatile oils consist of chemical mixtures that are often quite complex; they vary widely in chemical composition.**

- **Almost any type of organic compound may be found in volatile oils (hydrocarbons, alcohols, ketones, aldehydes, ethers, oxides, esters, and others).**

- **It is not uncommon for a volatile oil to contain over 200 components, and often the trace constituents are essential to the odor and flavor. The absence of even one component may change the aroma.**

Determination of the structure of terpenes

Chemical constituents of volatile oils may be divided into 2 broad classes based on their biosynthetic origin:

1- Aromatic compounds formed via **shikimic acid**. These contain C6 phenyl ring with an attached C3 propane side chain.

2- Terpene derivatives formed via acetate **mevalonic pathway**.

Terpenes, or terpenoids, are the largest group of secondary products (metabolites).

They are all formed from acetyl CoA or glycolytic intermediates.

All terpenes are formed from 5-C element

Isoprene is the basic structural element.

Classification of terpenes

Terpenes are classified by the number of 5-C atoms they contain

10-Carbon terpenes (contain 2 C-5 units) – monoterpenes

15- Carbon terpenes (3 C-5 units) are called sesquiterpenes.

20-carbon terpenes (4 C-5 units) are diterpenes.

Larger terpenes (30 Carbons) are called triterpenes (triterpenoids),

40 Carbons – called tetraterpenes and if more polyterpenoids.

Essential oils contain only the most volatile terpenes (i.e. molecular weight is not too high) → mono and sesquiterpenes

May occur as oxygenated derivatives, e.g. alcohols, aldehydes, ketones, phenols, oxides & esters.

OXYGENATED COMPOUNDS – responsible for the odour/smell of the oil. They are slightly water soluble – Rose water & Orange Water; more alcohol soluble.

Most volatile oils are terpenoid. Some are aromatic (benzene) derivatives mixed with terpenes.

Some compounds are aromatic, but terpenoid in origin (e.g. Thymol)

Biosynthetic Pathways

Volatile oils are divided into 2 main classes based on their biosynthetic origin

a. Terpene derivatives (formed via the acetate- mevalonic acid pathway)

b. Aromatic compounds (formed via the shikimic acid-phenylpropanoid route)

c. Miscellaneous Origin

Prodcution of the essential oils

Essential oils are generally obtained by distillation

Only 4 procedures may be used to prepare official oils

i. Distillation
ii. Expression
iii. Anfloraj
iv. Extraction-Maceration

Main types of volatile oil **products**

i. Concretes
ii. Resinoids
iii. Absolutes

CONCRETES

Prepared from raw-fresh materials of vegetable origin (bark, flowers, leafs, roots etc.)

Extracted by an organic-nonpolar solvents, rather than distillation or expression – Becomes **necessary when the essential oil is adversely affected by hot water or steam** (e.g. jasmine).

Produces a more **true-to-nature fragrance.**

Concretes contain about **50 % wax and 50 % essential oil** (jasmine).

Advantages of concretes:

They are **more stable and concentrated** than pure essential oils.

RESINOIDS

Prepared from natural resinous material **(dried material)** by extraction with a nonpolar solvent, e.g. Petroleum ether or hexane.

Can be viscous liquids, semi-solid or solid.

Usually homogeneous mass of non-crystalline character.

Uses: in perfumery as fixatives to prolong the effect of a fragrance.

ABSOLUTES

Obtained from a concrete, pomade, or a resinoid by **alcoholic extraction**.

The extraction process may be repeated.

The ethanol solution is cooled & filtered to eliminate waxes.

The ethanol is then removed by distillation.

They are usually highly concentrated viscous liquids.

DISTILLATION METHODS FOR ESSENTIAL OILS

Distillation is method for separation of components from a liquid mixture which depends on the differences in boiling points of the individual components and the distributions of the components between a liquid and gas phase in the mixture (un-isotermic)

1. Hydrodistillation

- In this type distillation, the plant material can be set the system with water and boling together.
- The heating system produces the steam.
- The steam blow away the essential oil through the condenser then graditional burette. Finally, The essential oil collected and obtained.

I- Distillation Methods:

- **There are two types of traps:**

  One for oils ***lighter than water*** and the other for ***oils heavier than water.***

- These two types differ only in the ***mechanism of the return of the aqueous layer to the distillation flask***, keeping the volatile oil layer in its position.

Types of distillation used:

1-Water and steam distillation

2-Direct steam distillation

2. Steam distillation

- Steam distillation is one of the methods used to extract essential oils from plants. Steam passes over the plant and extracts the essential oil. The mixture evaporates and passes into the condenser. The essential oil vapour is cooled and collected.

During steam distillation, the water, acidity and tempereature may induce hydrolysis of the esters. Rearrangements, isomerizations, racemiazations, oxidations and other reactions are also occur, all of which change the composition.

2. Water-Steam distillation

- In this case, the plant material can be set the system together with water. Same as the steam distillation, the steam passes over the plants. The mixture evaporates and passes into the condenser. The essential oil vapour is chilled and collected.

EXPRESSION

Most facilities allow for the simultaneous or sequential recovery of the fruit juice and of the essential oil, by collecting the oil with a spray of water after the abrasion (scarification – puncture by pins) before or during the expression of the fruit juice.

Especially it is used **for Citrus oils** as a mechanical action, or mechanic method.

In the past sponge method….

Some volatile oil can´t be distilled without decomposition and are usually obtained by:

II- Expression method

Expression can be carried out by means of any of the following three processes:

a) Sponge method:

- The citrus fruit (orange, lemon) is washed, cut into halve and the juicy part removed.
- The rind is squeezed, when secretion glands rupture and the oil collected by mean of the sponge, until the sponge becomes saturated with water and oil.
- The sponge is then periodically squeezed in a vessel.
- The upper oily layer in the vessel is separated.

b) Scarification method:

- Citrus oil involve puncturing the oil glands by rolling the fruit over a trough lined with sharp projection that are long enough to penetrate the epidermis.
- By repeatedly rotating the instrument after placing lemons in the bowel the oil glands are punctured (scarified) and discharge their contents which collect in the handle.
- The liquid is poured off at interval into a large vessel, where it is allowed to stand until the oil can be decanted and filtered.

c) Machine processes:

- These machine methods have now almost completely replaced the old hand methods. A centrifuge may be used to separate the emulsion of oil and water.

SOLVENT EXTRACTION

PRODUCTION OF CONCRETES & RESINOIDS

Extraction is generally preceded by a process of: bruising the fresh, wilted or semi-desiccated organs, chopping herbaceous drugs, pounding roots & rhizomes or turning wood into chips or shavings.

The procedure is conducted in specialized facilities

Soxhlet-type extractor.

The **solvent selection** is influenced by technical & economical factors

Selectivity (being a good solvent for the specific constituents).

Stability (chemical inertness)

Boiling point should not be so high that the solvent can be completely eliminated; nor too low, to limit losses & control cost

Handling **safety**

Solvents most used are aliphatic HC's – **petroleum ether, hexane, propane** & **liquid butane**.

Main disadvantages of solvent extraction
- Lack of selectivity
- Toxicity of solvents
-Residues
-Expensive

Main Advantages
-Temperature stable
-Odour natural
-No decomposed compounds because of the heating

ENFLEURAGE

Some kind of distillation but ISOTERMIC.

A glass plate is covered with a thin coating of especially prepared and odourless fat (called a chassis).

The freshly cut flowers are individually laid on to the fat which in time becomes saturated with their essential oils. The flowers are renewed with fresh material.

Eventually the fragrance-saturated fat, known as pomade, may be treated with alcohol to extract the oil from the fat.

Extraction method

- This method is used for the preparation of those oils which ***decompose by the action of steam or are present in extremely small quantities in plant organs containing them.***
- The minute quantities of oil actually distilling over, are lost in the large volume of distillation water from which the oil cannot be recovered.
- This is applied to flowers such as jasmine, gardenia, violet, and few others.
- The method of extraction is carried out using:

  a) Volatile solvents of low boiling point such as hexane.

  b) Non-volatile solvents such as fat (lard).

Extraction with volatile solvents

- The material containing the volatile oil is extracted with the volatile solvent with low boiling point by percolation.

- The volatile oil solution obtained is evaporated under reduced pressure, where the volatile solvent will evaporate, leaving the volatile oil behind although some of the volatile oil will be lost.

Advantage of extraction over distillation:

- Uniform temperatures (usually 50°C) can be maintained during most of the process.

But the distillation method is a low-cost operation compared to the extraction process.

Extraction with volatile solvents:

Floral concrete:

- In preparing volatile oil with volatile solvents e.g. hexane, petroleum ether the completely concentrated and purified products represent the so called ***floral concretes.***

- These floral concretes contain the odoriferous principles of the natural flower perfume plus a considerable amount of plant waxes and color pigments.

- The concretes are solid and only partly soluble in alcohol 95%.

Absolute:

- First precipitaion and eliminating the insoluble waxes from the floral concretes with strong alcohol and concentrating the filtered alcoholic solutions.

EXTRACTION BY SUPERCRITICAL GASES
Supercritical fluid extraction

Beyond its critical point, a fluid can have the density of a liquid & the viscosity of a gas → therefore diffuses well through solids, resulting in a good solvent.

CO2 is the main gas used

Advantages of CO2

- chemically inert, non-flammable
- non-toxic
- easy to completely eliminate
- selective
- readily available
- Inexpensive

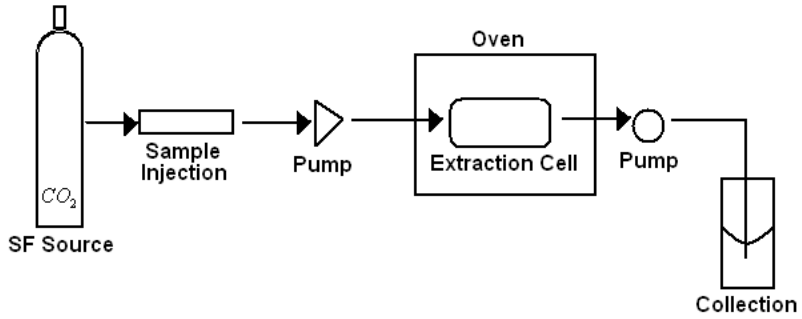
Disadvantages of the method high cost of initial investment

ADVANTAGES:

****obtain extracts which are very close in composition to the natural product.**
****It is possible to adjust the selectivity & viscosity, etc by fine tuning the temperature & pressure**
****All result in the increase of popularity of this type of method**

USES

Initially developed to decaffeinate coffees, prepare hops extracts or to remove nicotine from tobacco, the method is now used to
- Prepare spice extracts (ginger, paprika, celery)
-Specific flavours (black tea, oak wood smoke)
- Plant oils
-To produce specified types of some products



Headspace & solid phase extraction (Trapping)

Measuring Headspace Volatiles Emitted by Arabidopsis
modified version of solid-phase microextraction (S-PME),

This method has the advantage of having a shorter running time when compared to S-PME. It utilizes a silica fiber or “needle” that is coated with the solid phase, which can be solid or liquid.
Typically, it is a polymeric organic liquid.
This fiber is then placed into the “headspace” above the liquid sample.

Uses and Importance of the essential oils

Essential oils are widely used in perfumes, cosmetic products, cleaning products, in foods and in aromathepay…

- **Therapeutically** (Oil of Eucalyptus)
- **Flavouring** (Oil of Lemon)
- **Perfumery** (Oil of Rose)
- **Starting materials** to synthesize other compounds (Oil of Turpentine)
- **Anti-septic** – due to high phenols (Oil of Thyme). Also as a preservative (oils interfere with bacterial respiration)
- **Anti-spasmodic** (Ginger, Lemon balm, Rosemary, Peppermint, Chamomile, Fennel, Caraway)
- **Aromatherapy**

ANALYSIS OF THE ESSENTIAL OILS

Gas Chromatography (GC)

*Gas chromatography is a chromatographic technique that can be used to separate volatile organic compounds.

*It consists of

- ✓a flowing mobile phase
- ✓an injection port
- ✓a separation column (the stationary phase)
- ✓an oven
- ✓a detector.

Principle: *The organic compounds are separated due to differences in their partitioning behavior between the mobile gas phase and the stationary phase in the column.*

GC Columns

Packed columns

- Typically a glass or stainless steel coil.
- 1-5 total length and 5 mm inner diameter.
- Filled with the st. ph. or a packing coated with the st.ph.

Capillary columns

- Thin fused-silica.
- Typically 10-100 m in length and 250 μm inner diameter.
- St. ph. coated on the inner surface.
- Provide much higher separation eff.
- But more easily overloaded by too much sample.

GC Detectors

After the components of a mixture are separated using gas chromatography, they must be detected as they exit the GC column.

Thermal-conduc. (TCD) and flame ionization (FID) detectors are the two most common detectors on commercial GCs.

The others are

1. Atomic-emmision detector (AED)
2. Chemiluminescence detector
3. Electron-capture detector (ECD)
4. **Flame-photometric detector (FPD)**
5. **Mass spectrometer (MS)**
6. Photoionization detector (PID)

MASS Detector

Uses the difference in mass-to-charge ratio (m/e) of ionized atoms or molecules to separate them from each other.

Molecules have distinctive fragmentation patterns that provide structural information to identify structural components.

The general operation of a mass spectrometer is:

1. Create gas-phase ions
2. Separate the ions in space or time based on their mass to charge ratio
3. Measure the quantity of ions of each mass-to-charge ratio.

Gas Chromatography

- Good for volatile samples (up to about 250 ^{o}C)
- 0.1-1.0 microliter of liquid or 1-10 ml vapor
- Can detect <1 ppm with certain detectors
- Can be easily automated for injection and data analysis

Advantages of Gas Chromatography

- Requires only very small samples with little preparation
- Good at separating complex mixtures into components
- Results are rapidly obtained (1 to 100 minutes)
- Very high precision
- Only instrument with the sensitivity to detect volatile organic mixtures of low concentrations
- Equipment is not very complex (sophisticated oven)

Qualitative Analysis

Gas chromatograms are widely used as criteria of purity for organic compounds. Contaminants, if present, are revealed by the appearance of additional peaks; the areas under these peaks provide rough estimates of the extent of contamination. The technique is also useful for evaluating the effectiveness of purification procedures. Retention times should be useful for the identification of components in mixtures. **Gas chromatography provides an excellent means of confirming the presence or absence of a suspected compound in a mixture.**

The Retention Index

The retention index (RI) was first proposed by Kovats for identifying solutes from chromatograms. The retention index for any given solute can be derived from a chromatogram of a mixture of that solute with at least two normal alkanes having retention times that bracket that of the solute. That is, normal alkanes are the standards upon which the retention index scale is based. The retention index for a normal alkane is equal to 100 times the number of carbons in the compound regardless of the column packing, the temperature, or other chromatographic conditions. Within a homologous series, a plot of the logarithm of adjusted retention time $t`_R$ ($t`_R = t_R - t`_M$) versus the number of carbon atoms is linear.

Quantitative Analysis

The detector signal from a gas-liquid chromatographic column has had wide use for quantitative and semi quantitative analyses. An accuracy of 1% relative is attainable under carefully controlled conditions. Reliability is directly related to the control of variables; the nature of the sample also plays a part in determining the potential accuracy.

Interfacing Gas Chromatography with Spectroscopic Methods

Gas chromatography is often coupled with the selective techniques of spectroscopy, thus giving so-called hyphenated methods that provide the chemist with powerful tools for identifying the components of complex mixtures.

Gas Chromatography/Mass Spectrometry (GC/MS)

The flow rate from capillary columns is generally low enough that the column output can be fed directly into the ionization chamber of the mass spectrometer. For packed columns and megabore capillary columns however, a jet separator must be employed to remove most of the carrier gas from the analyte.