

# Citrus Hydrocarbon-Free Essential Oils

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Citrus flavors are among the most popular in the food market and take the largest share of flavor in the soft beverage industry.

## Cold Pressed Natural Citrus Oils

Citrus oils are usually produced by cold pressing of fresh citrus fruits. This process is very gentle with regard to chemical composition and the resulting freshly produced citrus oils possess aromatic qualities which are very true to nature in providing a complete olfactory impression of the citrus fruits.

Unfortunately, the exquisite aroma of cold pressed fresh citrus oils does last very long. All citrus oils contain large quantities (90-98%) of unsaturated hydrocarbons—predominately limonene, with small amounts of other monoterpenes and sesquiterpenes. The organoleptic impact of hydrocarbons is negligible. Their solubility in water is insignificant and they, in fact, represent an undesirable ballast in citrus oils.

Hydrocarbons undergo a rapid oxidation in the presence of air. The odor of the reaction products is a strong one and totally foreign to citrus. Even a low degree of oxidation radically changes the flavor characteristics of citrus oils. It is not surprising that over the years numerous techniques were proposed and implemented in order to reduce the hydrocarbon content of citrus oils.

## Distillation

The bulk of deterpenated citrus oils marketed today are still prepared by the oldest of techniques—fractional distillation. This technique, rather simple and convenient, produces citrus oils with a substantially reduced content of hydrocarbons.

This process, however, is harmful to the organoleptic

qualities of the product. Low-boiling flavor components are usually lost. Although the content of monoterpenes in citrus oils can be substantially decreased by distillation, the sesquiterpenes remain in the oil in their entirety since their boiling range is similar to those of the oxygenated aroma constituents. High temperature causes some of the constituents to undergo thermal degradation disturbing the delicate flavor balance.

However, distillation remains the most common method of deterpenating citrus oils because of its low cost, and because the process has been in use for so long, the odor profile of distilled citrus oils has long been accepted for use in flavors and fragrances.

## Counter-Current Extraction

More than 100 years ago it was noted that oxygenated constituents of citrus oils are soluble in aqueous alcohol while the respective solubility of monoterpenes and especially sesquiterpenes is very low. Dispersion of citrus oils in aqueous alcohol and subsequent separation produces an almost entirely hydrocarbon fraction called “washed citrus oils” and an aqueous alcohol solution called “washed extracts,” in which the proportion of oxygenated constituents is much larger than in the starting (pressed) citrus oils.

The flavor qualities of the washed extracts are high and despite numerous technical inconveniences caused by low concentration of the flavor ingredients and the necessity to mix, chill, filter and transport huge quantities of alcohol, they are widely used by the soft drink industry.

The washed extracts are usually prepared in batches. This single-stage extraction results in rather poor utilization of citrus oils since only 50-60% of the flavor carriers are transferred to the alcohol phase. In order to increase the oil content in the washed extracts and to maximize the utiliza-

tion of essential oils, they must be sequentially extracted with small portions of aqueous alcohol. This well-known principle of liquid-liquid extraction was implemented in the late 1930s in the development of a counter-current extraction process for the deterpenation of essential oils.<sup>1</sup>

Numerous devices are known in today's chemical technology for conducting this process. All are based on the same common idea of mechanical dispersion of one liquid phase in another. For the commercial deterpenation of essential oils, aqueous alcohol and light petroleum hydrocarbons are usually used. The components of citrus oils preferentially migrate to one of the liquid phases. As a result, the oxygenated fraction is concentrated in the alcohol phase while the monoterpenes and sesquiterpenes end up in the hydrocarbon phase.

Despite its apparent simplicity, the practical application of counter-current extraction is very complex. The rate of migration of constituents from one liquid phase to another is determined by the interfacial contact area. In order to maximize the rate of extraction, it is necessary to disperse the phases as fine as possible. Fine dispersion results in the formation of stable emulsions which interfere with the second essential stage of the process—the separation of the phases.

Mechanical dispersion results in the formation of spheric droplets which expose a minimum surface area for a given volume which, in turn, significantly reduces the rate of extraction. The rate of phase separation is a function of the difference in their specific gravity. This requires the utilization of dilute alcohol with high specific gravity and dramatically increases the amount of alcohol needed for the quantitative recovery of the oxygenated fraction. Other ways of dealing with this problem include further dilution of citrus oil (which does not contain too much of the oxygenated constituents in the first place) with light solvent, or the addition of various chemicals to the alcohol phase to increase its specific gravity. Consequent recovery of deterpenated oil becomes quite a difficult task.<sup>2</sup>

The factors mentioned above make extracted oils rather expensive and cost restrictive for most flavor applications.

### Poroplast Extraction

The most recent technological breakthrough in conducting the liquid-liquid extraction process is the development of the so-called "poroplast extraction technique."<sup>3</sup>

Based on the concept of liquid-liquid distribution, it differs principally from conventional methods in its mode of inducing phase contact. The solute transfer takes place when an aqueous (moving) phase passes through a column

with a low polar organic (stationary) phase nonspecifically held on a hydrophobic surface of a porous inert support. Depending on the particular purpose and the selected system of liquid phases, desirable components can be transferred from the aqueous phase into the organic one, or vice versa, providing an efficient recovery and/or separation of natural materials.

Figure 1 illustrates the process as it occurs in a single capillary. First [1], a certain amount of neat citrus oil is introduced. In stage 2 [2A and 2B] the system is being charged with aqueous alcohol which pushes the oil through the capillary and distributes it over the internal hydrophobic surface resulting in the formation of an oil layer approximately one micron thick. At the same time it extracts the oxygenated compounds from the oil, leaving the hydrocarbon fraction sorbed on the inner surface of the capillary [3].

When the oil stationed on the surface is sufficiently exhausted a new portion of fresh oil is introduced into the system [4], washing away the exhausted portion and taking its place [5] on the surface of the capillary. Immediately following the fresh oil is a charge of aqueous alcohol which continues the cycle of spreading the fresh oil and simultaneously extracting the oxygenated compounds.

This approach overcomes most of the difficulties associated with conducting a liquid-liquid extraction process. This method has been commercialized for the production of a variety of natural products and, in particular, for the preparation of many hydrocarbon-free essential oils.\*

\* These hydrocarbon-free essential oils are known under the trade name "Super-X" essential oils, which are products of Florasynth, Inc.

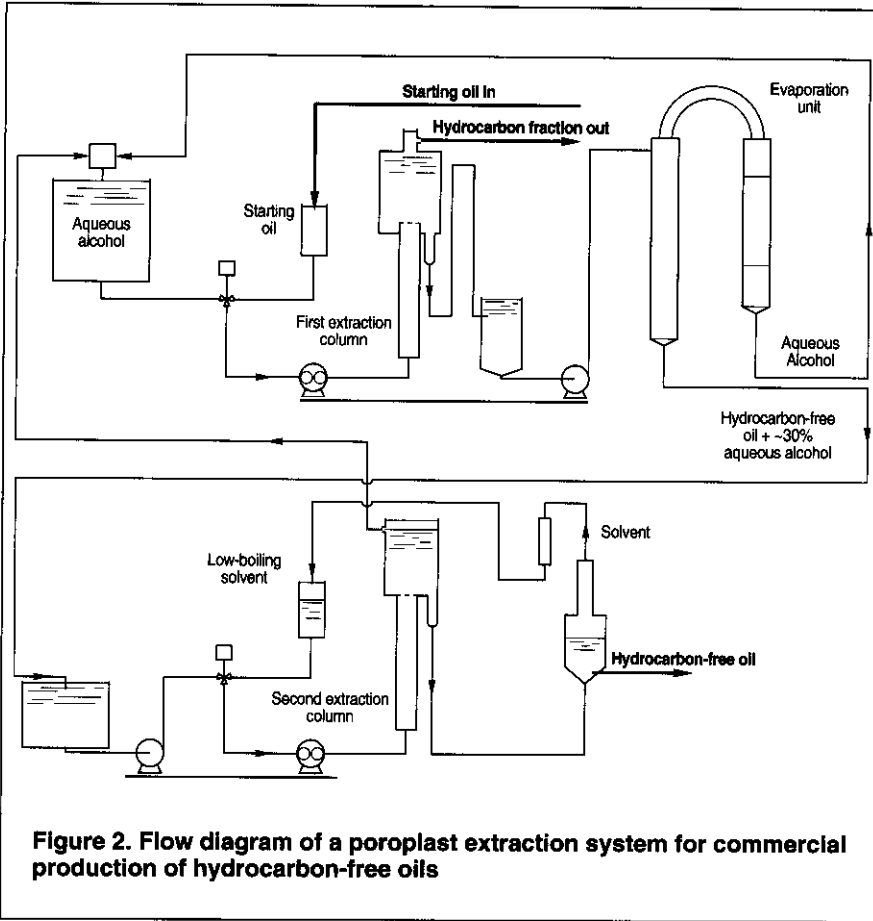


Figure 2. Flow diagram of a poroplast extraction system for commercial production of hydrocarbon-free oils

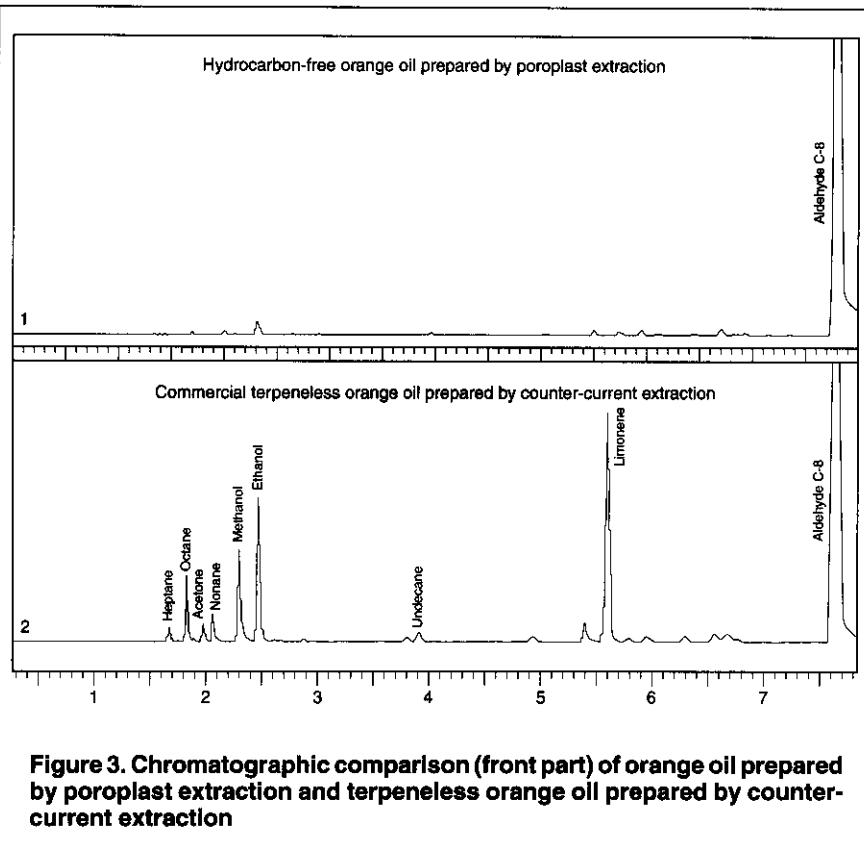


Figure 3. Chromatographic comparison (front part) of orange oil prepared by poroplast extraction and terpeneless orange oil prepared by counter-current extraction

Table I. Typical composition of a poroplast-extracted hydrocarbon-free orange oil

hexanal	0.04
heptanal	0.09
1,8-cineole	0.09
hexyl acetate	0.06
octanal	14.17
cis-3-hexenol	0.02
heptyl acetate	0.01
nonanal	2.57
heptanol	0.11
cis-limonene oxide	0.23
trans-limonene oxide	0.63
citronellal	2.87
decanal	12.72
linalool	29.99
octanol	2.25
undecanal	0.94
dihydrocarvone	0.10
trans-2-nonenal	0.22
nonanol	0.26
neral	2.81
$\alpha$ -terpineol	2.90
dodecanal	1.93
nonyl propionate	0.13
geranial	4.21
carvone	1.07
decanol	0.94
citronellol	0.63
perilla aldehyde	1.89
nerol	0.25
2,4-decadienal	0.29
trans-carveol	0.38
geraniol	0.43
cis-carveol	0.05
nerolidol	0.12
octanoic acid	0.12
elemol	0.48
$\beta$ -sinensal	0.31
decanoic acid	0.47
perilla alcohol	0.10
$\alpha$ -sinensal	0.24
nootkatone	0.73

Super-X hydrocarbon-free orange oil is a trademarked product of Florasynth, Inc.

**Table II. Solubility of several poroplast-extracted oils in propylene glycol at 25°C**

Hydrocarbon-free oils	Minimum solubility in propylene glycol %
Orange oil	5
Orange essence oil	10
Lime expressed oil	10
Lemon oil	5
Lime distilled oil	infinite

Super-X oils are trademarked products of Florasynth, Inc.

The principal scheme of the commercial production of hydrocarbon-free essential oils using poroplast extraction is presented in Figure 2. The first poroplast column is charged in cycles with alternate charges of essential oil and an aqueous alcohol. The first charge of essential oil coats the inside hydrophobic surface of the column. Then the alcohol phase passes through the column, extracting the oxygenated constituents from the essential oil immobilized on the porous support, and leaves the hydrocarbon fraction behind. A new charge of fresh essential oil displaces the hydrocarbon fraction which is discharged from the system, leaving a fresh coating of oil on the inner surface. No emulsion is formed during this process and the liquid phases of very close specific gravity (less than 0.005 g/cm<sup>3</sup> differential) are quickly separated after elution from the column.

The alcohol solution of oxygenated constituents enters a continuous evaporation unit which reduces the alcohol concentration to approximately 30% and the recovered alcohol is returned into the process. The aqueous dispersion of oil is then extracted with low boiling solvent in the second poroplast column. The hydrocarbon-free oil is collected while the exhausted aqueous phase and the low-boiling solvent are each returned to the process for reuse. This poroplast extraction system combines the advantages of liquid-liquid extraction with the extreme efficiency of chromatography. Thus complex separation tasks are performed in an elegant and cost-effective way.

Vis-a-vis counter-current extraction methods, the use of extraneous materials and solvents is minimized in this production process. As illustrated by Figure 3, this allows the achievement of high purity of finished materials without solvent residues.

Oils are processed gently and quickly at low temperature. The hydrocarbon content is reduced to a negligible level while the oxygenated constituents, from light to very heavy, remain largely intact providing a true organoleptic profile. This can be seen from the typical composition of a poroplast-extracted orange oil presented in Table I.

Hydrocarbon-free essential oils prepared by the poroplast

method are totally natural, with no discernable artifacts. Complete removal of hydrocarbon constituents makes these products extremely stable and ultimately soluble in aqueous alcohol. They exhibit substantial solubility even in pure propylene glycol as can be seen in Table II. It makes them suitable for application in alcohol-free products.

The poroplast extraction technology, as used in our process, is waste-free. Only pure essential oil enters the system and only two products exit it—washed citrus oil and hydrocarbon-free oil. All other materials are continuously reused and nothing is discharged, making the production environmentally friendly.

Years of experience accumulated in the commercial production of a large variety of hydrocarbon-free oils have shown that these high quality, and often unique products are particularly appropriate for flavor and fragrance applications.

#### References

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