

The Poroplast Extraction Technique in the Flavor and Fragrance Industry

By Alexander Fleisher, Florasynth Inc., Teterboro, New Jersey

A complete reconstruction of the organoleptic effect of natural products was always considered the ideal objective in the creation of aroma compositions. The successful naturally scented goods must satisfy consumers for whom fresh fruits, vegetables, herbs, and flowers are always available as unquestionable points of reference for the taste and smell of the "real thing."

The growing trend of "back to nature," combined with sophistication of public taste, challenges our industry to offer highest quality, yet reasonably priced natural ingredients which will provide the full spectrum of aroma nuances.

Distillation, being a major recovery and separation technique in the production of the aroma constituents, cannot alone fulfill this objective due to the following general drawbacks:

1. Commonly practiced distillation techniques are applicable to a rather limited group of chemicals having boiling points within a relatively narrow range. Distillation of natural aroma material results in unavoidable losses of both very light and heavy fractions, whose organoleptic value is often irreplaceable.
2. The distillation process necessarily causes thermal degradation of labile important aroma bearing ingredients which, even when occurring on a small scale, deeply upsets the delicate sensory balances of the recovered material.
3. Distillation is an impractical means of separation of any closely boiling substances, regardless of differences in their chemical nature.
4. Distillation is inappropriate, even when the boiling points are markedly different if the recovery of trace amounts from a bulk mixture is desired.
5. Distillation is inefficient in recovering aroma materials from dilute aqueous media—the perpetual challenge when working with natural sources of flavor and fragrance ingredients.

An attractive alternative is provided by liquid-liquid extraction. It can be defined as a process where the constituents of the solution are separated due to their unequal distributions (different partition coefficients) between two immiscible liquids.

The rate of extraction is proportional to the interfacial contact area and the deviation of component concentrations in the liquid phases from the equilibrium position. Phase separation at the end of the process results in the desirable separation of the components of the mixture.

Although liquid-liquid extraction is a relatively simple process, its industrial application is considerably more complex than would appear at the first glance. In all industrially used liquid-liquid contactors, one phase is dispersed in the other in the form of droplets. Spherically shaped, these droplets expose a minimum surface area for a given volume. An attempt to increase the interfacial area by excessive agitation, among other problems, leads to the formation of stable emulsions which obstruct phase separation.

A more serious problem associated with mechanical dispersion of liquid phases in counter-current extraction devices is the phenomenon known as axial mixing. It results in the broad variation of material residence times in the two phases, which substantially reduces the rate of extraction and has a very negative effect on equipment performance.¹

A number of technological solutions effectively dealing with the above mentioned difficulties were proposed and applied, resulting in sophisticated and expensive devices.² In most cases, their applications are justifiable in industries where the numbers of separations are small, but large volumes are used, as in metallurgy, or applications where money is really not the object, like the nuclear industry.

In the flavor and fragrance industry, where natural products are extremely diversified, while the volumes are relatively small, the wide use of conventional effi-

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cient liquid-liquid extraction becomes cost-prohibitive.

A number of years ago an alternative approach for conducting liquid-liquid extraction was developed in the University of Leningrad.³ This approach, eventually called "the poroplast extraction technique," overcomes most of the above mentioned difficulties.

Based on the concept of liquid-liquid distribution, it principally differs 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.

Both versions of the process are being presently used in the recovery of aroma chemicals from aqueous dispersions, and in the preparation of hydrocarbon-free essential oils.

Method

A schematic representation of the recovery of aroma constituents from an aqueous dispersion is presented in Figure 1. It can be seen that the poroplast column, which serves as the liquid phase contactor, can be fed by either organic solvent or aqueous phase.

First, a predetermined volume of selected organic solvent is introduced into the poroplast column. After that, the three-way valve switches, and the aqueous dispersion is pumped into the column, so that it comes in contact with the solvent, held on the large surface of the porous support, but does not displace it from the column. During that time, aroma chemicals are transferred from the aqueous phase in the organic phase.

Upon solvent saturation (after pumping a definite volume of aqueous dispersion) the three-way valve is switched back to the organic solvent and a new portion is pumped into the column. The added portion of fresh solvent displaces the saturated one out of the column, and replaces it on the support surface.

The process continues in this cyclical manner until a desirable amount of aqueous dispersion is treated. The eluted liquids (the solutions of aroma constituents in organic solvent and the exhausted aqueous phase) form two layers in the separator. The exhausted aqueous phase is dumped, while the solution of aroma constituents in organic solvent is continuously discharged into the product recovery unit where the pure aroma constituents are collected, and the stripped solvent is returned immediately to the extraction base.

Principles and Calculations

In order to conduct an efficient extraction process, it is necessary to maximize the contact surface of the liquid phases and insure their perfect counter-current plug-

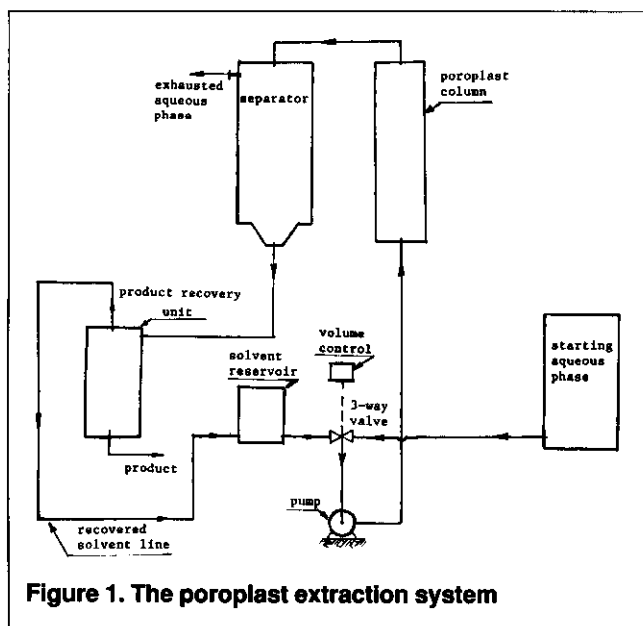


Figure 1. The poroplast extraction system

flow.¹ The distribution of the organic phase as a thin (approx. $1\mu\text{m}$) and uniform layer on the porous support allows a very close approximation of these requirements.

As described above, it can be seen that in each particular cycle the process closely resembles frontal chromatography, and consequently can be described using well known calculations applied in the theory of column partition chromatography.

Let us consider the case of aroma recovery from an aqueous dispersion.

The curve showing the concentration of components in the aqueous phase eluting from the column is presented in Figure 2A, where:

C_0 = total concentration of aroma substances in the aqueous phase.

C_1, C_2, \dots = concentrations of particular components.

$V_{R1}, V_{R2}, \dots, V_{Rn}$ = retention volumes of particular components.

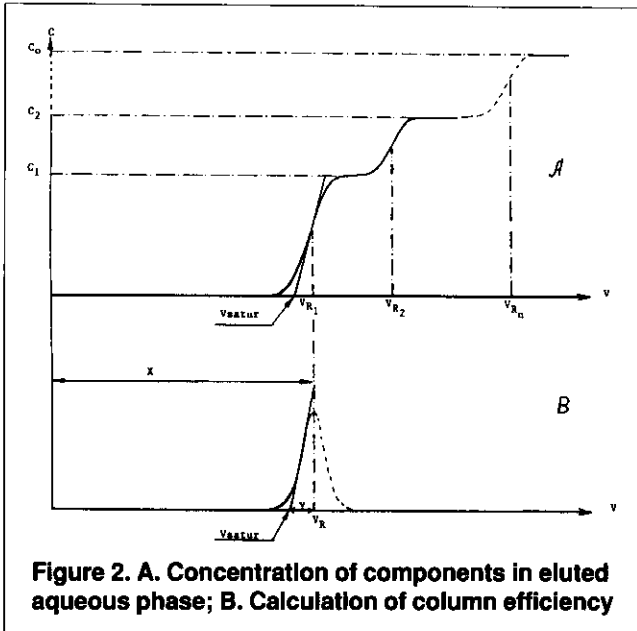
V_{sat} = the volume of aqueous phase passed through the column before a noticeable concentration of the least retainable (most polar) component appears in the effluent liquid.

Since the usual purpose is the recovery of a full complex of substances dispensed in the aqueous phase, the value V_{sat} can be considered a measure of the column saturation.

For further consideration, two appropriate simplifications should be accepted:

1. In frontal chromatography, the starting part of the compound concentration curve at the column exit may be approximated to a Gaussian curve.
2. Since the total concentration of aroma components in the aqueous dispersion is usually low, it can be viewed as a polycomponent ideal solution. In this case, the equilibrium of each particular component between the liquid phases is independent of the

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partitioning of the others and is determined only by the distribution coefficient of the pure substance. This means that the V_{satur} value is determined only by the V_{R1} value and the column parameters which influence the shape of the Gaussian curve.

When the substance passes through the chromatographic column, its retention volume can be found as:

$$V_R = V_a + Kd V_{Org} \quad (I)^4$$

where V_a = volume of the aqueous (moving) phase in the column.

V_{org} = volume of the organic (stationary) phase in the column.

Kd = the distribution coefficient of the substance in the aqueous-solvent system.

It is also known that column efficiency, measured by the number of theoretical plates N , may be found as:

$$N = 4 (x/y)^2 \quad (II)^5$$

Figure 2B

$$\text{but } x = V_R \text{ and } V_{satur} = x - y$$

From the combination of equations (I) and (II), it can be found:

$$V_{satur} = (V_a + Kd V_{Org}) \left(1 - \frac{2}{\sqrt{n}}\right) \quad (III)$$

All parameters of equation (III) can be determined experimentally.⁶ It is clear that for any given column, V_w , V_{org} , and N are practically constant values. The only parameter that must be determined is Kd , which depends on the particular aroma material and the selected solvent.

Organic solvent—The criteria for choosing the organic

solvent used in the described method are not different from those used for usual solvent extraction. The solvent should be water-insoluble, preferably low boiling, and evaporate completely without leaving any odorless residue. The utilization of liquified gases, such as Freons or CO₂ is particularly attractive.

The important criteria is a reasonable value of distribution coefficients of the aroma constituents into the aqueous-solvent system. As can be seen from equation (III), the K_d value is the major factor which determines the V_{sat} value. (In practice, it is convenient to use solvents in which K_d value of the most polar component is about 250-400.)

Porous support—Selecting the material and the method of preparation of the column packing are important points in the development of the presented method. Porous polytetrafluorethylene (PTFE) prepared in blocks⁷ was found to be an ideal material. This material is outstanding in its chemical inertness, so any changes in the oil chemical composition are excluded. PTFE does not swell in any known solvent, and thus provides the possibility to work with any chosen solvent system.

The ability to hold the organic phase is based on the fact that PTFE is well wetted by organic solvents with a

surface tension coefficient less than 23 but not wetted by water or water solutions.

The preparation of the solid support in blocks is of special importance for large diameter columns. The following advantages, compared to powder packed columns are:

1. Uniformity of support particle size distribution which substantially increases column efficiency.
2. Elimination of gradual thickening of the solid support which results in decreasing the organic solvent volume held by the column and increasing the column resistance to aqueous phase flow.
3. Good contact between the support and the column body and elimination of channel formation inside the solid support.

In dynamic conditions, e.g., when the aqueous phase passes through the column at a rate of ca. 15ml/cm²/min, the volume of the solvent, held by the solid support, is about 20% of the column volume.

Column efficiency—The column efficiency is measured by the number of theoretical plates (N), or by the height equal to the theoretical plate (HETP).

HETP is a complicated function of the moving phase velocity, the support uniformity, the selected stationary phase, and the quantity of stationary phase on the support.⁸ For a column of about 300 mm diameter at an aqueous phase flow rate of 15 ml/cm²/min, HETP values of 20-50 mm were achieved. This rather high efficiency for an industrial-scale liquid-liquid extractor is due mainly to the column design.

From equation (III), it can be seen that the V_{sat} value depends not on N but \sqrt{N} . Thus, for the recovery of the aroma constituents from aqueous dispersion, it is not reasonable to work with two efficient columns, and for practical purposes N = 20-25 (column length 600-800 mm) is satisfactory enough.

Applications

The poroplast extraction technique was found to be effective in the recovery of the aroma materials from a variety of water dispersions, such as fermentation broth, aqueous reaction products, etc. Due to the efficiency of the extraction process, the aroma constituents can be quantitatively and economically recovered even from dilute sources (100-500ppm). The amounts of the solvents used in the processing are small, rarely exceeding 0.1-1% relative to the amount of treated aqueous phase.

The poroplast extraction technique is used successfully in the recovery of the essential oil constituents from the aqueous condensate formed during oil distillation. The detailed chemical study of the water soluble fractions produced during essential oil preparation will be reported in a separate publication.

The technique described above will be illustrated by the following examples:

Natural benzaldehyde—In recent years, the source and methods of preparation of natural benzaldehyde

have become a matter of extreme concern to the flavor industry. Although occurring in a large number of the botanicals,⁹ benzaldehyde is found in commercially viable quantities only in the kernels of *Prunus* spp., such as apricots, peaches, plums and cherries.¹⁰ Recently, the presence of substantial levels of benzaldehyde was found in genera *Eucalyptus* (fam. Myrtaceae) and *Zieria* (fam. Rutaceae), as cited by Lawrence.¹¹

One of the classic sources of benzaldehyde is cherry laurel (*Prunus laurocerasus* L.).¹⁰ This has long been known as a medicinal plant,¹² and is officially recognized as such, in a number of countries. It is mostly used for the preparation of cherry laurel water which is the condensate obtained after hydrodistillation of macerated fresh leaves.¹³ Attempts to recover cherry laurel oil by redistillation (cohobation), lead to average yields of 0.05%.¹⁰ According to Arctander, the oil of cherry laurel can be viewed mostly as a curiosity item.¹⁴

P. laurocerasus is not native to the New World where several other members of genus *Prunus* such as choke cherry (*P. virginiana*), black cherry (*P. serotina*), and pin cherry (*P. pensylvanica*) are found. The bark of *P. serotina*, which is found to contain 0.15% of HCN,¹³ is extracted and the cherry bark extract is approved for use

in alcoholic and nonalcoholic beverages, baked goods, frozen desserts, etc. (FEMA 2276, FDA 182.10).

In plant materials, benzaldehyde is not usually found as such, but in the form of the cyanogenic glucosides of which the most commonly encountered are amygdalin (also known as laetrile), and mandelonitrile glucoside.¹⁵ Enzymatic breakdown of the above-mentioned glucosides, leads to the formation of hydrogen cyanide, benzaldehyde and glucose. This is usually accomplished by maceration of the crushed plant material in warm water, followed by steam distillation in order to recover benzaldehyde.

Considerable discrepancies exist between the reported levels of HCN and the yields of oil from the leaves of *Prunus* spp. As mentioned before, the yield of the cherry laurel oil averages 0.05% by weight, from the fresh leaves which are found to contain 0.12% of HCN.¹⁶

The enzymatic splitting of cyanogenic glucosides produces a molecule of benzaldehyde for each molecule of HCN.¹⁷ Considering the molecular weights of both substances, 0.12% of HCN corresponds to 0.52% of benzaldehyde, i.e., ten times higher than the reported yields.

The explanation can be found in the relatively high solubility of benzaldehyde in water. As a result, the redistil-

lation of the aqueous solution of benzaldehyde (cohobation), is not an effective method of recovery with most of it remaining in the discarded aqueous phase.

The application of the poroplast extraction technique to remove the volatiles from the aqueous distillate of macerated *P. serotina* leaves, results in the recovery of the cherry oil, the partial composition of which is presented in Table I.

The relatively high yields of the oil (1-1.5%), the wide distribution of *Prunus* spp., and the simplicity of the extraction procedure, suggests an economical and convenient way to prepare truly natural benzaldehyde.

Apple essence—One of the promising fields of application is in the recovery of valuable natural flavor materials from the aqueous streams of the fruit and vegetable processing, such as fruit essences.

Table II shows the chemical composition of the oil phase recovered from the commercial 150-fold aqueous apple essence. A product, organoleptically close to natural apple aroma, was recovered with a yield of 0.053%, leaving an exhausted aqueous phase nearly odor free.

Preparation of Hydrocarbon-free Essential Oils

The fact that essential oils contain hydrocarbons, and that the elimination of the hydrocarbons from the oils is a desirable act, is of importance to the flavor and fragrance industry.

Ruys, one of the inventors of the counter-current extraction process for deterpenation of the essential oils,¹⁸ wrote: "The hydrocarbons, present in all natural essential oils, exercise an extremely adverse effect on the solubility of the oil in dilute alcohol. If this is further complicated by the presence of unsaturated hydrocarbons, there is also a danger of terpene-oxides forming, which either oxidize the alcohol to acetaldehyde or are else broken down and transformed into carvone. Both these processes result in the complete deterioration of the oil's odoriferous properties..."

"It will be obvious, therefore, that the hydrocarbons present in essential oils, and in particular terpenes and

Table I. Partial chemical composition of cherry (*Prunus serotina*) oil

<u>Compound</u>	<u>Percentage</u>
n-hexanal	0.13
limonine	0.11
trans-2-hexenal	4.72
cis-2-pentenol	0.24
cis-3-hexenol	1.05
trans-2-hexenol	0.22
benzaldehyde	90.15
benzyl alcohol	0.44
phenylethyl alcohol	0.21
cis-3-hexenyl benzoate	0.02
eugenol	0.81
4-ethylbenzaldehyde	tr
α-hydroxy acetophenone	tr

Table II. Chemical composition of apple essence oil phase

Alcohols	
n-butanol	3.12
iso-butanol	0.15
n-heptanol	0.10
n-hexanol	40.58
trans-2-hexenol	2.68
cis-3-hexenol	0.14
methanol	0.06
2-methyl-1-butanol	5.50
3-methyl-1-butanol	1.83
6-methyl-5-hepten-2-ol	0.15
n-octanol	0.25
n-pentanol	0.18
Esters	
amyl acetate	0.08
isoamyl acetate	1.98
butyl acetate	4.59
isobutyl acetate	0.06
butyl propionate	0.02
ethyl acetate	0.07
ethyl butyrate	0.69
ethyl 2-methylbutyrate	0.48
ethyl propionate	0.20
hexyl acetate	0.88
hexyl butyrate	0.29
propyl acetate	0.21
propyl propionate	0.03
Aldehydes	
benzaldehyde	0.07
decanal	0.01
n-hexanal	8.45
trans-2-hexenal	19.38
Acids	
hexanoic	0.06
octanoic	0.18
Miscellaneous	
methyl chavicol	0.01
methyl eugenol	0.03

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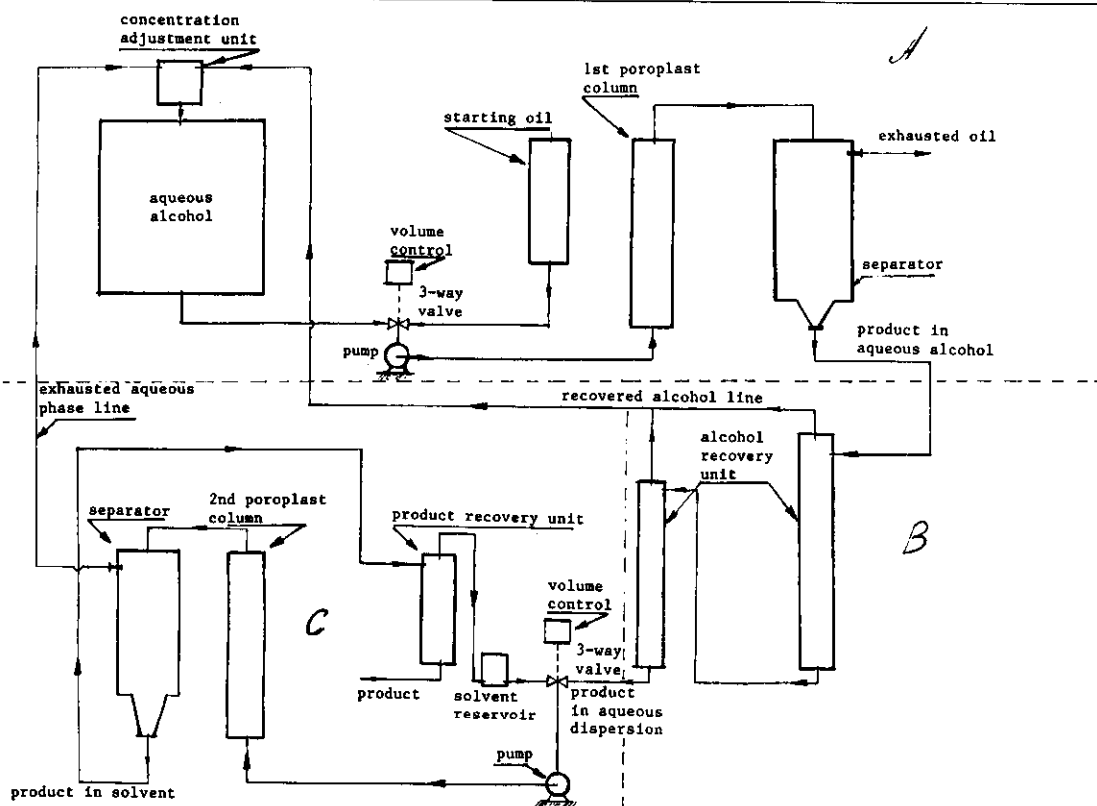


Figure 3. System for the preparation of hydrocarbon-free essential oils

sesquiterpenes, have been regarded as Public Enemy No. 1 by perfumers for many years now and that research has been directed for several decades to finding ways and means of eliminating them as far as possible.¹⁹

The utilization of aqueous alcohol to produce the deterpenated citrus oils has been known for a very long time. In 1899, Mitchell described some methods for the determination of lemon oil in the flavoring alcohol extracts.²⁰ It is obvious that the alcohol extracts of citrus oils were used before that. They are widely used by the industry to this date.

The solubility of hydrocarbons, especially sesquiterpenes, in aqueous alcohol is low, while oxygenated components of essential oils are completely soluble. Decrease of the alcohol concentration leads to a sharp decrease in the solubility of hydrocarbons. The alcohol extract, therefore, corresponds to deterpenated essential oil.

Many articles have been written on the alcohol deterpenation of essential oils. While referring the reader to the most important original publications on the subject,^{18,19,21-24} I would like to point out the critical difficulties associated with this method:

1. *Long-equilibration time.* In a recent publication, on the alcohol deterpenation of citrus oils, a 24-hour agitation was conducted to achieve equilibration.²⁵
2. *The formation of stable emulsions leads to a long-separation time.* Mechanical dispersion of

essential oils, especially citrus oils, in aqueous alcohol, usually results in the formation of stable emulsions. A period of several days is required to accomplish separation.²⁵

3. *A necessity of multi-stage contact.* Ruys shows that five sequential equilibrations of lemon oil and 70% alcohol are required to recover 95% of citral.²¹ Obviously, more stages are necessary to recover less polar ingredients of lemon oil, such as esters.

4. *Recovery of the oxygenated constituents from the alcohol solution is difficult.* The problems associated with this rather important and probably most delicate and expensive step in the preparation of deterpenated oils have been discussed in detail elsewhere.²²

The important contribution to the process which takes place when the essential oil comes in contact with the aqueous alcohol, is not a question of solubility, but relates to the partitioning of the oxygenated components between the aqueous alcohol and the hydrocarbons of the essential oil. The process of the alcohol deterpenation, therefore, is just a particular case of liquid-liquid extraction, and can be easily accomplished using poroplast extraction technique.

A schematic presentation of the system used for the preparation of hydrocarbon-free essential oils can be seen in Figure 3. It consists of the oil extraction section A, alcohol recovery section B, and product recovery section C.

Table III. Chemical composition of hydrocarbon-free orange oil

<u>Compound</u>	<u>Percentage</u>
octanal	6.85
nonanal	1.87
trans-sabinene hydrate	0.18
cis-limonene oxide	0.25
octyl acetate	0.21
trans-limonene oxide	0.08
citronellal	3.59
decanal	15.91
linalool	34.55
octanol	2.87
terpinen-4-ol	1.02
cis-dihydrocarvone	0.07
undecanal	0.31
trans-dihydrocarvone	0.05
neral	3.92
α -terpineol	5.06
geranial	6.47
neryl acetate	1.52
geranyl acetate	1.79
carvone	0.25
citronellol	1.23
dodecanal	1.96
nerol	1.55
cis-carveol	0.09
geraniol	0.96
trans-carveol	0.08
nerolidol	0.24
β -sinensal	0.83
α -sinensal	0.56
nootkatone	0.53

The poroplast column of section A is sequentially charged with an essential oil (either neat or diluted with a suitable low polar solvent) and aqueous alcohol of an appropriate concentration.

Each cycle lasts approximately 15 minutes during which time the oxygenated components are transferred (with over 90% efficiency) into the alcohol phase. Since no emulsion is formed, the liquid phases are instantly separated after elution from the column. Exhausted essential oil (the hydrocarbon fraction) is continuously discharged, while the alcoholic solution of the oxygenated constituents, is transferred to the alcohol recovery section B.

Two continuous evaporators, connected in sequence, reduce the alcohol concentration to about 30%. The recovered alcohol is transferred through the concentration adjustment unit into an aqueous alcohol holding tank in section A for further processing.

In section C, the hydrocarbon-free essential oil is recovered from the aqueous dispersion precisely as explained in the method description. Pure product is collected, while the exhausted aqueous phase (which still contains about 30% alcohol) is returned to section A.

Table IV. Partial chemical composition of hydrocarbon-free lemon oil

<u>Compound</u>	<u>Percentage</u>
1,4 cineole	0.06
limonene	0.07
1,8 cineole	0.08
octanal	0.53
methyl heptenone	0.09
nonanal	0.94
trans-sabinene hydrate	0.07
citronellal	0.24
decanal	0.59
linalool	1.58
cis-sabinene hydrate	0.09
octanol	0.18
terpinen-4-ol	1.42
undecanal	0.15
citronellyl propionate	0.55
neral	22.16
α -terpineol	3.10
geranial	41.29
neryl acetate	9.11
geranyl acetate	8.37
nerol	0.75
geranyl butyrate	0.21
cis-carveol	0.07
geraniol	0.74
trans-carveol	0.05
α -bisabolol	0.64
nootkatone	0.15
5,7 dimethoxy coumarin	0.59

The technique described above is suitable for the deterpenation of any essential oil. If an essential oil naturally contains a high proportion of hydrocarbons (such as citrus oils, fir needle oil, etc.), it can be used undiluted. In that case, the hydrocarbons are playing a role of a low-polar organic phase. If the natural content of the hydrocarbons is low, the oil can be diluted with an appropriate low-polar solvent. The composition of hydrocarbon-free orange and lemon oils, prepared using this technique, is presented in Tables III and IV, respectively.

The choice of an aqueous phase is not limited to the alcoholic solutions. Principally, any water soluble material, the selection of which is justifiable, can be utilized.

Conclusions

The poroplast extract technique described in the present report is based on liquid-liquid chromatography modified for industrial use. Its application facilitates the achievement of following objectives:

1. Exhaustive recovery and/or separation with minimum equilibration and settling time;
2. Minimization of amounts of solvents required for efficient extraction;
3. Utilization of universal and simple equipment suitable for recovery and/or separation of a large variety of raw materials.

The poroplast extraction technique provides a convenient and cost-effective way to prepare natural aroma ingredients, which takes advantage of liquid-liquid extraction in a very practical and convenient way.

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Address correspondence to Alexander Fleisher, Florasynth Inc., 300 North Street, Teterboro, NJ 07608.

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