Supercritical Fluid Extraction of Natural Raw Materials for the Flavor and Perfume Industry

By Patrick Pellerin, CAL/Pfizer, Grasse, France

Techniques for the extraction of active components from natural substrates have evolved significantly from early days.

The earliest extraction process was the digestion of flowers or spices in oil. This was followed by the extraction technique called enfleurage, the cold absorption of volatiles on fats. Essential oils were obtained by cold expression, and later, also by distillation. In later years, the process of extracting raw materials by various solvents, such as hexane, benzene, alcohol, etc. became widely used. After extraction, the solvent is removed by distillation, leaving a resinoid or concrete. Alcoholic extraction of the concrete produces an absolute, which is the typical commercial form.

Each of these processes can produce very high quality fragrance and flavor ingredients. However, elevated temperature (from distillation) and solvent usage can detract from total quality.

There are two problems associated with elevated temperature. First, potential damage to highly sensitive flavor or fragrance components. Second, the potential loss of highly volatile components, all of which may not be subsequently trapped.

The problem with solvents is that it is virtually impossible to remove all residual solvent. In some situations, for either esthetic or for regulatory purposes, residual solvent may be undesirable in a flavor or fragrance ingredient.

Extraction of natural raw materials with supercritical carbon dioxide effectively addresses questions associated with elevated temperature and solvent usage. Temperatures employed are fairly low, and the only solvent used, carbon dioxide, completely dissipates after the extraction.

The critical temperature of carbon dioxide is the temperature above which it cannot be liquefied, no matter how high the pressure is raised. The critical pressure is the pressure below which it cannot be liquefied, no matter how low the temperature is dropped. The supercritical state is achieved when both temperature and pressure are above their critical points.

Supercritical carbon dioxide has the density of a liquid, low viscosity, and diffuses like a gas. Supercritical carbon dioxide is an excellent solvent for a wide range of natural substrates. The selectivity of the extraction of a given substrate can be varied by varying temperature and pressure within the supercritical region.[1]

Important Dates

1822: Cagniard de la Tour[2] discovered the supercritical state of carbon dioxide
1861: G. Gore[3] rendered napthalene soluble in CO_2
1869: T. H. Andrews[4] determined the supercritical point of CO_2
1939: Horwath was issued the first patent on this technology for concentrating fruit juice
1954: A. W. Francis[5] described the solubility of 261 organic compounds soluble in CO_2
1963: K. Zosel[6] patented the extraction of 68 different raw materials by CO_2
1963-1972: The Research Institute of Krasnodar (USSR) extracted eighty different plants[7]

In recent years, research and commercial development activities with CO_2 extraction have continued to increase. Commercial examples now include hop flavor extraction, coffee and tea decaffeination and nicotine removal from tobacco. Commercial operations include: SKW and HAG in Germany, Carlton United in Australia, CAL/Pfizer and CEA-RP in France and Pfizer, General Foods and Philip Morris in the United States.

Why Supercritical CO_2

Following are several reasons why supercritical CO_2 should be used:

- Critical temperature: 31°C. Extractions can be conducted at a temperature low enough not to harm the organoleptic properties of the extract.
- Critical pressure: 73.8 bars. Easy to attain in a production operation.

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- Inert: No risk of secondary reactions, such as oxidation.
- Safe: Carbon dioxide is a harmless material with significant usage in beverages.

The polarity of carbon dioxide is close to that of pentane and hexane, solvents commonly used in traditional extractions.

The extraction parameters of supercritical carbon dioxide can be modified by the addition of small quantities of other polar products, such as water or ethanol. Extraction parameters can also be modified by the selection of specific temperature and pressure conditions. These options add flexibility, and allow the tailoring of extraction conditions to the specific requirements of the product being extracted and the end product desired.

There are other gases that also have interesting solvent properties in their supercritical state. However, for reasons of cost, explosion hazard or toxicity, they are not commonly used commercially.

Extraction Principles

The material to be extracted is put into a cylindrical container with porous ends, which is then placed into the extraction chamber. Temperature and pressure are selected for the specific material to be extracted, and for the end product desired. Supercritical carbon dioxide is circulated through the material in the extraction chamber, dissolving the desired fractions. Solvent and solute then circulate into a separator, where pressure is maintained below the supercritical point. The carbon dioxide becomes gaseous, losing its solvating properties. The solute thus precipitates, and is collected. The gaseous carbon dioxide circulates into a heat exchanger, where it is cooled and liquefied. The liquid carbon dioxide then recirculates back into the extraction unit under the temperature and pressure conditions that place it again in the supercritical region.

Extraction Process

Extraction of Solids—Solid raw material may be macerated or ground into smaller pieces to facilitate extraction. This material is then placed into an extraction cylinder. At each end of the cylinder is a porous metal frit cap designed to allow free circulation of the supercritical carbon dioxide and dissolved materials, while holding the solid material in place.

Supercritical carbon dioxide is then circulated through the extraction cylinder. The extent of recirculation, temperature and pressure are selected to optimize the extraction.

A wide variety of solid raw materials can be effectively extracted with this process.

Extraction of Liquids—The extractor is a classic liquid-liquid extraction column specifically designed for use under high pressure. The liquid raw material is injected into the column facing a counter-current flow of supercritical carbon dioxide. As with solids extraction, the extent of recirculation, temperature and pressure are selected to optimize the extraction.

Liquid-liquid is a continuous process, and has certain inherent operating advantages over liquid-solid batch processes. A wide variety of pumpable raw materials can be effectively extracted with this process. A few examples are essential oils, fruit juices, vegetable juices and fermentation broths.

Advantages and Disadvantages

Advantages: First of all, extracts do not undergo hydrolysis, oxidation, esterification or thermal changes, and thus quite faithfully represent the original material. Secondly, there is no residual CO_2 solvent in the extract. The third advantage is that CO_2 is an inert material.

Disadvantage: The process of equipment and extraction operation is relatively expensive. Thus, low value or low yield products might not be profitably extracted.

Characteristics of Extracts

An excellent description of the possibilities of this, technology is given by H. Brogle.[8] Steam distillation gives an extract of the most volatile fractions (essential oils). A more complete extract minus some volatile "top notes" is obtained by solvent extraction. Extracts obtained by supercritical CO_2 are similar in many respects to traditional essential oils or concretes.

Illustrations of Supercritical CO_2

Following products prepared by CAL/Pfizer, illustrate the supercritical CO_2 process in comparison with traditional extraction processes.

Extraction of Lavandin Grosso Flowers[9]—A batch of flowers was divided into three groups. One was extracted by steam distillation to yield the essential oil, another by hexane and made into an absolute, and the third by supercritical CO_2, yields were as follows:

Essential Oil	3.0%
Absolute	1.2%
CO_2 Extract	3.5%

Analytical results are summarized in Table I. The effects of hydrolysis on components of the distilled essential oil include the presence of myrcene, trans-ocimen and geranyl acetate which are not found in the extracts. A high level of linalool, which results from the hydrolysis of linalyl acetate, is also seen in the distilled essential oil. Compared with the absolute, the CO_2 extract contains lower levels of coumarin.

Extraction of Ginger Rhizomes (India)—A batch of roots was divided into three groups. One was extracted by steam distillation, another by ethanol, and the third by supercritical CO_2. Organoleptic and analytical data were collected.

Olfactory characteristics are illustrated by DICT Curves shown in Figure 1. The curve for the CO_2 extract shows it to be more complete than the other two, and also closer in shape to the roots curve.

Gustative characteristics are illustrated by the Scoville index, determined by the ASTA method:

Table I. Lavandin "Grosso" GC Study

Volatile Constituents	Oil	$PFICO_2$	Absolute
α- and β-pinene	1.0	-	-
myrcene	1.1	-	-
1,8-cineole	7.2	3.2	-
cis-ocimene	1.1	0.5	-
trans-ocimene	0.6	-	-
linalool	42.5	17.5	10.1
camphor	7.8	4.5	1.7
borneol	2.7	1.6	1.5
terpinen-4-ol	2.5	1.5	1.1
α-terpineol	3.9	-	-
linalyl acetate	21.0	33.5	28.4
lavandulyl acetate	2.5	1.9	1.8
geranyl acetate	1.4	-	-
coumarin	-	5.3	7.7
α- and β-caryophyllene	1.3	3.4	2.4
"a" unknown	-	9.0	1.6
herniarin	-	1.6	2.6
"b" unknown	0.6	2.4	2.8
"c" unknown	-	-	2.3
Volatiles content	100%	81%	66%

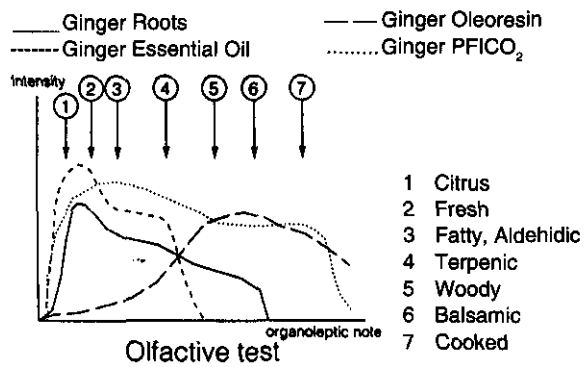
% calculated in regard of the total extract

Table II. Indian Ginger

Constituents	$PFICO_2$	Oleoresin	Oil
GC Method			
α-curcumene	3.7	2.3	10.0
α-zingiberene	19.6	12.1	44.0
β-zingiberene	3.4	2.0	8.0
β-bisabolene	3.7	2.4	8.3
β-sesquiphellandrene	7.9	4.9	17.8
zingerone	0.7	0.3	0.8
HPLC Method			
6-gingerol	16.4	0.9	0.1
8-gingerol	3.1	0.7	0.3
10-gingerol	3.8	0.8	-
6-shogaol	2.8	6.3	0.3
8-shogaol	-	1.6	-

% calculated in regard of the total extract

Figure 1. Ginger (India) Duct curves



Essential Oil	Zero
Oleoresin	480,000
CO_2 Extract	1,080,000

Several cooked dishes (soup, fish, poultry) were seasoned with ginger prepared by the three methods. Tasters commented favorably on flavor balance and fresh characteristics of foods seasoned with CO_2 extracted ginger.

HPLC and GLC chromatographic data is summarized in Table II.

Summary—The above two examples demonstrate the primary advantages of supercritical CO_2 extraction in comparison with distillation and solvent extraction.

In the case of lavandin flowers, an extract was obtained that quite faithfully reflects nature. Chemical comparisons confirmed this.

In the case of ginger, a very high gingerols/shogaols ratio was seen. In solvent extraction, an inversion due to the transformation of gingerols into shogaols is seen.

Data on the following extracts has also been reported: celery seed and galbanum gum,[10] and ginger root, rosemary and sage.[11]

CAL/Pfizer Research and Production Goals

- Preparation of extracts that organoleptically and chemically represent the original raw material faithfully.
- Isolation and/or concentration of active principles such as antioxidants, colors, organoleptically characteristic constituents, phytotherapeutic constituents, etc.
- Preparation of selective extracts free from unwanted constituents such as caffeine, nicotine, cholesterol, bergaptene, etc.
- Preparation of extracts from fermentation derived raw materials.

A Commercial Reality

CAL/Pfizer now markets several products prepared by supercritical CO_2 extraction in a new state-of-the-art plant in Grasse, France. These are in addition to hop extract, which is prepared by liquid CO_2 extraction in a plant located in Sydney, Nebraska USA. Pfizer CO_2 extracts are sold under the trademark $PFICO_2$.

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Address correspondence to Patrick Pellerin, Process Development Manager, CAL/Pfizer, 27 Av Ste Lorette, Boite Postal 94, 06333 Grasse, France.

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