Supercritical fluid extraction and fractionation of essential oils and related products

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Abstract

Supercritical CO_2 extraction of essential oils is one of the most widely discussed applications in the supercritical fluid literature. Nevertheless, a comprehensive overview of the analytical, processing and modeling aspects has never been attempted. This is partly due to the difficulties involved in isolating essential oils from the other products which supercritical CO_2 can dissolve. Moreover, only a limited number of studies provide quantitative data on the parameters governing this process.

In this review, solubility data on pure compounds belonging to essential oils are analyzed. Processes proposed to isolate and fractionate essential oils by supercritical CO_2 and the corresponding modelling aspects are discussed critically. © 1997 Elsevier Science B.V.

Keywords: Essential oils; Fractionation; Solubility; Supercritical extraction

1. Introduction

The supercritical extraction (SFE) of the compounds responsible for the fragrances contained in vegetable matter is a promising field for the industrial application of supercritical fluid processing. Indeed, there is considerable interest in replacing the steam distillation and solvent extraction processes traditionally used to obtain these products.

The characteristic smell of plant materials is usually the result of the complex interactions occurring among hundreds of compounds. Correct reproduction of the natural fragrance in a concen-trated extract is therefore a complex task. The presence of thermolabile compounds, the possibility of hydrolysis and of hydrosolubilization are serious obstacles in the reproduction of natural fragrances. Moreover, severe legislative restrictions are currently being proposed to eliminate solvent residues in these products when used in the food, pharmaceutical and cosmetic industries.

By using different extraction techniques, a variety of products can be obtained. 'Concretes' and 'oleoresins' are extracts obtained using organic solvents on fresh or dried vegetable matter. These products become quasi-solid at room temperature after the removal of the solvent. A typical concrete extracted by hexane contains all the lipophilic compounds which constitute the vegetable matter.

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An 'absolute' is a liquid product obtained by post-processing a concrete with ethanol and subsequently removing the solvent. A 'volatile oil' is a liquid product obtained by post-processing a concrete by steam distillation. An 'essential oil' can be defined as the volatile material present in plants [1]. As a rule, it consists of a complex mixture of terpenes, oxygenated terpenes, sesquiterpenes and oxygenated sesquiterpenes. Essential oils can also contain diterpenes and some specific compounds which cannot be classified as belonging to any of the above-mentioned compound families. Other compounds which can be extracted from vegetable matter and can be found in concretes, absolutes and oleoresins are fatty acids and fatty acid methyl esters (FAMEs), coloring matters (β-carotene), coumarins, psoralens, sterols and flavones.

CO_2 is the supercritical solvent of choice in the extraction of fragrance compounds, since it is non-toxic and allows supercritical operation at relatively low pressures and near room temperature. Generally speaking, supercritical CO_2 behaves like a lipophilic solvent but, compared to liquid solvents, it has the advantage that its selectivity or solvent power is adjustable and can be set to values ranging from gas-like to liquid-like.

SFE of flavors and fragrances has been reviewed previously by Stahl et al. [2], by Moyler [3], and by Kerrola [4]. These authors provide overviews with the emphasis only on the analytical aspects of the problem. A comprehensive study of the influence of the process parameters and the mathematical models proposed in SFE of fragrance compounds is lacking.

This review is aimed at providing a critical analysis of the works published recently on SFE of essential oils and other related products. It is organized as follows: Section 2 deals with experimental methods, while Section 3 deals with equilibrium data in supercritical CO_2. Solid feed processing and mathematical modeling are dealt with in Section 4, while Section 5 looks at liquid feed processing. Conclusions and perspevtives are presented in Section 6.

2. Experimental methods

The vegetable material used for the extraction of volatile compounds is normally solid, but in some cases, like the post-processing of citrus essential oils, liquid feeds are used. The treatment of liquid feeds requires different experimental systems as compared to solid feeds. Another classification of SFE systems with respect to their use is the batch, semi-continuous or continuous processing of the raw material.

2.1. Processing of solid matrices

In batch processing, the solid is placed in the extraction vessel and then the supercritical solvent is fed in until the target extraction conditions are reached. Contact between the solvent and the matrix is maintained for a considerable time (up to several hours), since this kind of operation is aimed at reaching the equilibrium composition. Care should be taken to avoid pressure and temperature variations during the contacting time, and also the precipitation of the solute phase outside the sampling device.

This approach is similar to that used for solubility measurements (analytical method), but it is of limited value if the extractable material shows an affinity with the insoluble matrix. The driving force for the process will be the equilibrium concentration of solutes between the solid and the fluid phases rather than the solubility of the pure compounds in the fluid phase. Moreover, many solutes are extracted simultaneously, and one has to hypothesize that they do not influence each other. Lastly, since not all the solute can be extracted, sampling from the fluid phase does not provide a measure of the true composition of the soluble matter contained in the matrix.

In semi-batch processing, which is widely employed, raw materials are charged into the extraction vessel to obtain a fixed bed of particles. The supercritical solvent is fed continuously by a high-pressure pump at a fixed flow rate. One or more separation stages are used to precipitate the solute from the supercritical solution. These systems typically use extractors from 0.1 to 2 dm^3 on the laboratory scale and from 2 to 50 dm^3 on the pilot scale. In larger systems the solvent is recycled, as in the pilot plant shown schematically in Fig. 1. In this case, the last separation stage has to be maintained at suitable pressure and temperature
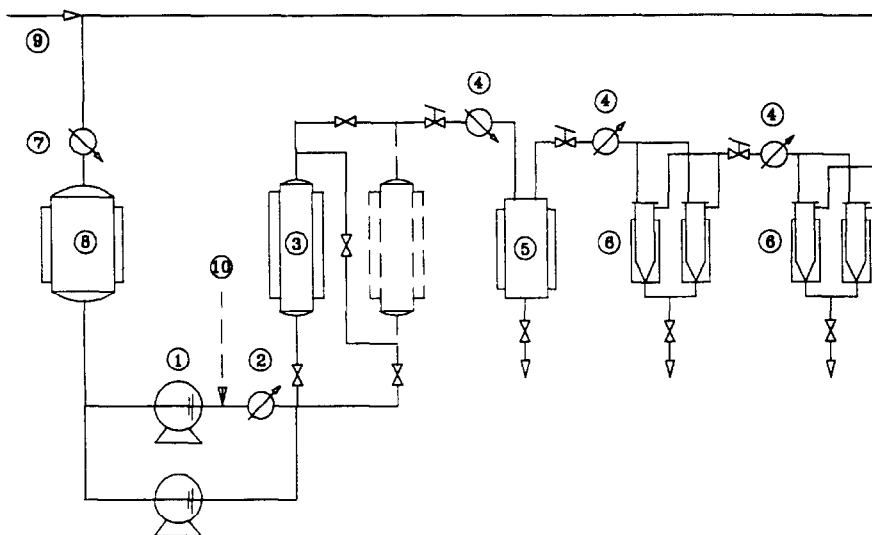
Fig. 1. Schematic representation of a pilot plant (extractor 20 dm^3) used for SFE plus fractional separation of essential oils. 1, high-pressure pump; 2, heater; 3, extractor; 4, heater; 5, separator; 6, cyclonic separators; 7, cooler; 8, CO_2 condenser; 9, CO_2 make-up.

conditions to condense the solvent to the liquid state to facilitate subsequent recompression.

Different process implementations have been attempted starting from the case of single-stage extraction and separation. Multi-stage extraction can be carried out by operating at increasing solvent densities. Moreover, it is possible to precipitate part of the solute by varying the temperature instead of using a decompression stage [2,5]. Fig. 2 shows some of the process schemes which can be applied during separation. However, only a few authors have provided some insight into the problems associated with the separation stages in supercritical fluid processing [6,7], even though the arrangement of the separation stages can be the key step towards successful SFE process implementation.

Fractional separation capabilities are particularly useful in laboratory systems where maximum processing flexibility is required. Nevertheless, industrial plants can also benefit from multi-stage operation. Fig. 3 shows a photograph of a 4×300 dm^3 industrial plant used to isolate essential oils by SFE and the fractional separation of the extracts (Essences, Salerno, Italy). In this plant, four separation stages are used in series. The last three separators are patented cyclonic separation vessels [6].

Micro SFE devices, which are commercially available, are also used. These are primarily designed for analytical purposes and are frequently connected to analytical devices like gas chromatographs (GC), gas chromatograph–mass spectrometers (GC–MS), or supercritical fluid chromatographs (SFC). These instruments use extraction vessels which can range from 0.1 cm^3 to several hundred cm^3. As a rule, they can operate in both batch and semi-batch modes, and are equipped with one separation/decompression stage. Very small quantities of raw material can be used, but this can be both and advantage and a disadvantage. Indeed, small quantities of the starting material imply low operation costs, but also very small quantities of extract. For example, a 100 mg sample containing only 1% of essential oils by weight yields a maximum extract of only 1 mg. Therefore, particular caution is required in avoiding product losses, and care is required in choosing the extraction time and the organic solvents for product collection.
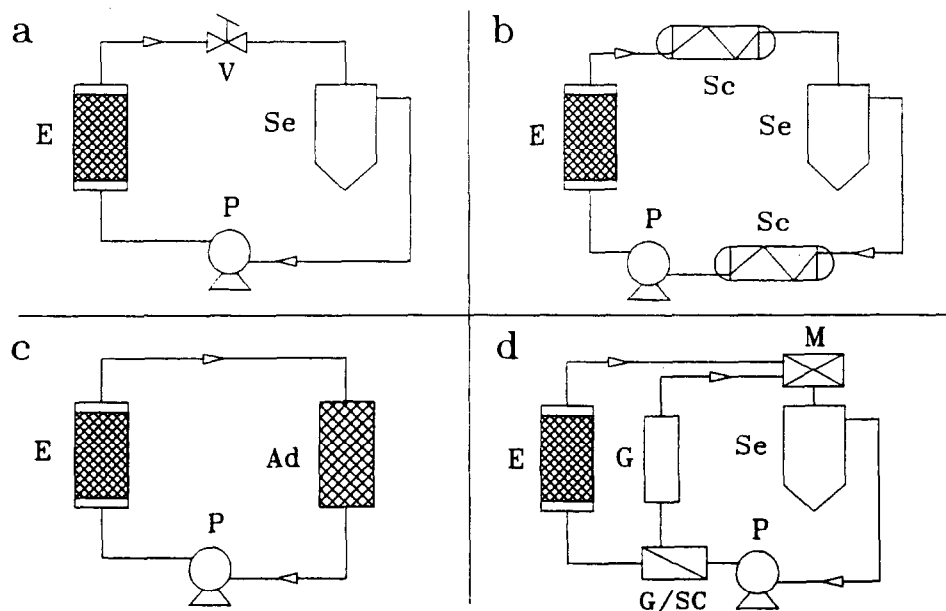
Fig. 2. Different separation processes which can be implemented after the extraction stage. (a) Decompression, (b) temperature variation, (c) adsorption, (d) antisolvent addition.
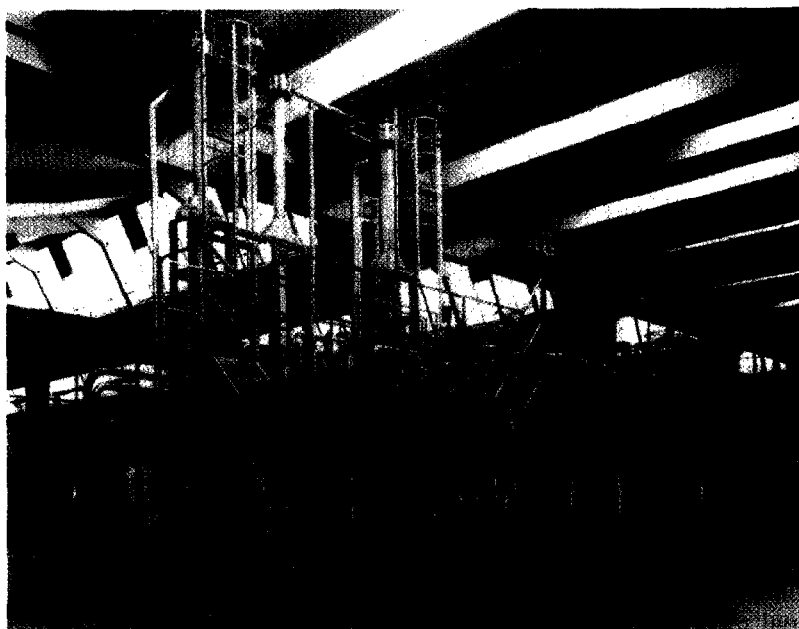

Fig. 3. Industrial plant for the SFE of essential oils by extraction and fractional separation. The plant consists of 4×300 dm^3 extractors and several separation stages in series (Essences, Salerno, Italy).

2.2. Processing of the liquid feed

Fractionation of liquid feeds can be carried out in the semi-batch mode by adsorbing the liquid to be treated on a suitable material that selectively retains the different compound families. The multiple extraction and separation procedures used for solid feed processing discussed above can be used to achieve fractional desorption of the liquid.

Continuous processing of liquid feed can also be carried out using a continuous, counter-current high-pressure tower. A schematic representation of a continuous counter-current tower used for essential oil fractonation is shown in Fig. 4. In this process, the liquid is fed continuously along the column. The supercritical solvent is fed at the bottom of the column and a recycle can be fixed at the top of the column. Two liquid fractions are collected: the light compounds are collected at the top, and the heavy compounds at the bottom. Pressure, temperature or temperature profile,

tower packing, length-to-diameter ratio, recycle ratio and feed-to-solvent ratio have to be selected correctly to obtain the required fractionation.

2.3. Experimental methods for chemical and organoleptic analysis

Complex mixtures such as volatile oils, waxes, coloring matter, etc. are commonly analyzed by GC, GC–MS and liquid chromatography (HPLC). Also, supercritical fluid chromatography (SFC) can be used for the separation, identification and quantitation of the compounds extracted. The use of one or more of these techniques is indispensable in the SFE of fragrance compounds, since it is necessary to provide precise composition information on both fragrance characteristics and undesired compounds. These techniques can also be used to monitor the evolution of composition with extraction time. Thus, they can be used to support the search for optimum extraction and fractionation conditions by iterative extraction and product analysis.

Organoleptic analysis is also useful to obtain an overall characterization of the extracts and their comparison with traditional steam-distilled and solvent extracted products. It is usually performed by 'panel testing' [8], in which experts evaluate the color, odor and taste of the extracts.

Fig. 4. Continuous counter-current high-pressure tower for the fractionation of liquid feeds by supercritical CO_2.

3. Equilibrium data in supercritical CO_2

Knowledge of the solubility of the compounds to be extracted and of the undesired compounds which must be avoided in coextraction is a fundamental information in SFE processes. This information is particularly relevant in the case of the extraction of flavors and fragrances from vegetable matter. Indeed, these matrices contain many lipophilic compounds which can be extracted by supercritical CO_2. Thus, knowledge of solubilities allows a selection of the range of the extraction pressure and temperature. It also gives some indication of the separation conditions, particularly when multistage separation procedures are used.

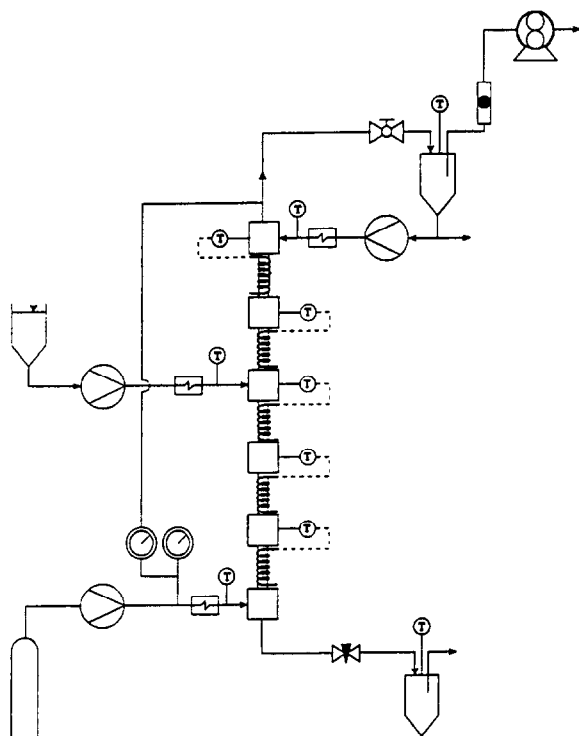Solubility data must be obtained experimentally. At present, reliable predictive calculations are not

available. Solubility data are obtained by adopting different experimental methods. The most widely used methods are the so-called static–analytic, static–synthetic and dynamic methods. In the static methods, the compounds are placed within a closed volume, and equilibrium conditions are obtained by waiting for a suitable time. In the dynamic method, the supercritical solvent flows through the solute and very long contacting times are established in the system, so that near-equilibrium conditions can be obtained. The difference between the analytic method and the synthetic method is that in the former, at equilibrium, a small sample of the two phases is drawn and then the condensed part is determined by weighing the sample flasks. When using the synthetic method, no samples are removed and the detection of a phase transition is obtained by observing the inner part of the equilibrium cell. A detailed discussion of these methods, their merits and their defects has been published recently [9].

Solubility data are reported in the form of tables or diagrams. As a rule, interpolation of this data is performed using cubic equations of state (EOS). The most widely used are the Peng and Robinson (PR) [10], Redlich and Kwong (RK) [11] and Soave (SRK) [12] EOS. More complex non-cubic EOS are also available and are sometimes used (such as those proposed by Bender [13] and Carnahan and Starling [14]). Care should be taken when extrapolating this data, since extrapolation yields only qualitative results.

A selection of solubility data on the pure compounds frequently found in essential oils is given in Table 1. The same table also reports the solubilities of some undesired compounds and of particular compounds found in vegetable matter. Table 1 does not provide an exhaustive list of all the data available in the literature. Moreover, since the data in the literature cover different pressure and temperature ranges, direct comparisons are not easy. Therefore, to compare the data at pre-set values of temperature and pressure, it is necessary to carry out graphical interpolations or calculations by interpolating equations.

Further information is available in the literature on the solubilities in supercritical CO_2 of terpenes and related compounds [2,17–19,26–29], of paraffins [21,30–32], of fatty acids [22,23,33–38], of

the methyl and ethyl esters of fatty acids [24,39,40], and of tryglycerides [22,23,35,36,41]. Other compounds of interest, such as long-chain alcohols, were studied by Yau and Tsai [20]; the solubilities of α-tocopherol, β-carotene and capsaicin were studied by Ohgaki et al. [35], Sakaki [25] and Knez and Steiner [42], respectively. The solubility of water in supercritical CO_2 was studied by Chrastil [23].

Solubility data of some compounds have been reported by more than one author. For example, limonene solubilities have been reported by four different groups [2,17–19], but the results are not always consistent. Particularly interesting is the representation given by Matos et al. [19] reported in Fig. 5, where the phase equilibria of binary systems consisting of supercritical CO_2 and limonene and supercritical CO_2 and 1-8 cineole are shown. It appears that these terpenes are completely miscible in supercritical CO_2 at 50°C for pressures above 98 bar.

Data on other compounds of interest, like some coumarins and psoralens, are not included in Table 1 since only the apparent solubility threshold in supercritical CO_2 is available in the literature [43].

Some authors studied phase equilibria, extraction selectivities and solubilities of citrus essential oils or of key compound mixtures in supercritical CO_2. Robey and Sunder [44] separated a cold-pressed lemon oil into its terpene and flavor fractions and described the results through a density-dependent local-composition equation of state. Kalra et al. [45] produced phase equilibrium data for the system lemon oil–CO_2 and a model mixture (75% limonene and 25% citral)–CO_2 system in the temperature range 49.8–81°C and at pressures ranging between 95 and 106 bar. They used a static method to obtain the data. Coppella and Barton [46] studied the vapor–liquid equilibrium of lemon-peel oil at 30–40°C and 40–90 bar. They described the phase equilibria by treating the system as a CO_2–limonene binary mixture and by using the Peng–Robinson equation of state [10]. Temelli et al. [47] extracted hydrocarbon terpenes by supercritical CO_2 from cold-pressed orange oil using a dynamic flow system. At the experimental conditions studied, hydrocarbon terpenes were solubilized to a greater extent than oxygenated com-

Table 1
Solubility data in supercritical CO_2 of some pure compounds contained in essential oils. Solubilities are expressed as mg g^{-1}

	Pressure (bar)/temperature (°C)							
	80/40	90/40	100/40	200/40	80/50	90/50	100/50	200/50
α-Pinene						28.5ª [16]		
Limonene	5.6ª [15]	CM^b [15]				17.1^c [17]	CM^b [19]	
	6.2^b [2]	65^b [2]	140^b [2]		4.9^b [2]	12.7^c [18]	141.8^b [18]	
Cineole		CM^b [15]			17.6^c [19]		CM^b [19]	
cis-Verbenol	4.8ª [16]	78.2^c [16]	120.4ª [16]		2.4ª [16]	5.8ª [16]		
1-Menthol		20^b [2]				5.7^b [2]	21.8^b [2]	
Carvone	2.2^b [2]	44^b [2]	110^b [2]		1.6^b [2]			
Anethole	2.8^b [2]	60^b [2]						
Citral						1.0^c [18]	1.9^c [18]	
Eugenol		29^b [2]				6.7^b [2]		
Caryophyllene	1.6ª [2]	38^b [2]	85^b [2]			10^b [2]		
1-Hexadecanol					2.2ª [20]	2.5ª [20]	3.6ª [20]	48.5^c [20]
Octacosane		0.2^c [21]	0.4^c [21]	1.4ª [21]				
Lauric acid			6.8^b [22]	115^c [22]				
Myristic acid		2.49^c [22]		40.0^c [22]				
Palmitic acid	3 × 10^{-3} c [22]		0.8^c [22]	4.4^c [22]				
Oleic acid			0.7ª [23]	6.3ª [23]				
Stearic acid			1.6^c [23]					
Trilaurin			1.1ª [22]	26.6^c [22]				
Trimyristin			0.5^c [22]	5.6^c [22]				
Tripalmitin				0.3^c [22]				
Ethyl palmitate		42.9^d [24]					7.9^d [24]	
Ethyl oleate		41.5^d [24]					21.7^d [24]	
β-Carotene				2.1 × 10^{-3} b [25]				2.8 × 10^{-3} b [25]
Water					1.6^b [2]		1.9^c [23]	2.8^b [2]

CM = Complete miscibility, ª = graphical interpolation, ^b = diagram, ^c = table, ^d = equation.
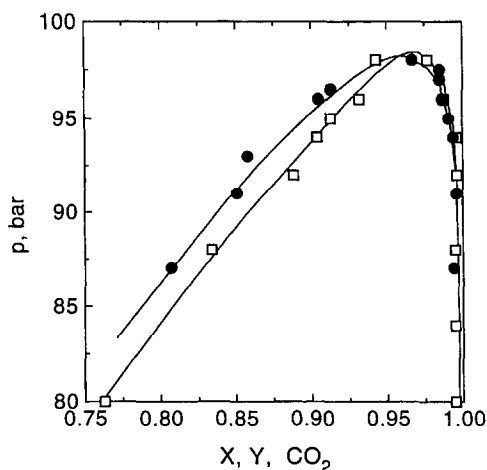
Fig. 5. Vapor–liquid equilibria for CO_2–limonene (●) and CO_2–1-8 cineole (□) at 50°C (adapted from Ref. [19]).

pounds. Phase equilibrium data ranging from 40 to 70°C and from 83 to 124 bar were presented. The authors chose limonene and linalool as the key compounds, and described the system as a ternary CO_2–limonene–linalool mixture. The data were correlated by a simple model using fugacity and activity coefficients.

The influence of temperature and pressure on the relative distribution coefficients of 12 hydrocarbons and oxygenated terpenes was studied by Platin et al. [48]. These authors observed that vapor-pressure effects, coupled with a decrease in solvating power, dominate the effects of polarity and molecular weight of the key compounds. Recently, Büdich et al. [49] measured the phase equilibria in supercritical CO_2 of an orange-peel oil, a peel-oil concentrate and a terpenic fraction. They found that the biphasic limit increased with

decreasing terpene content in the mixture. They also evaluated the selectivity of the fractionation process between terpenes and oxygenated compounds. Furthermore, selectivity increased when the terpene content was lower.

Some general considerations can be drawn from the solubility data of the typical compounds extractable from vegetable matter. At low CO_2 densities ($T=40$–$50°C$, $p=80$–90 bar), terpenes are one or more orders of magnitude more soluble than paraffins and fatty acids. The other families of compounds show negligible solubilities. At high CO_2 densities ($T=40$–$50°C$, $p=100$–200 bar), terpenes and oxygenated terpenes are completely miscible in supercritical CO_2, and the solubilities of many other compound families pass from appreciable to very high. Water deserves a particular mention. It is always present when natural matter is processed (even when previously dried). Therefore its solubility in supercritical CO_2 is particularly important in determining the possibility of water cosolvent effects during SFE. All in all, the solubility data suggest that selective SFE processing of essential oils has to be performed at 40–$50°C$ and at pressures below 100 bar. Indeed, the selectivity of the process should be very high only in this range of operating conditions.

Solubility data can be used directly to evaluate the possibility of extracting compounds only in the case in which the solutes to be extracted have no affinity with the insoluble matrix. If the compounds to be extracted are adsorbed on the solid matrix or contained inside a complex solid structure, different equilibrium relationships have to be applied. In the case of desorption from a solid matrix, desorption isotherms are required to evaluate the relative concentration in the solid and fluid phases. When solutes are located inside a complex vegetable structure, phase equilibrium can be established between the two phases. At the solid–fluid interface, the solid phase and the fluid phase solute concentrations are related through an equilibrium isotherm. Some information is available in the literature for the extraction of [6]-gingerol from ginger rhizomes from Spiro and Kandiah [50], which produced the partition factor for this system in supercritical CO_2. An example of the difference between the solubility data of the pure compound and extraction from a natural structure is given by

Goto et al. [51] in the case of 1-menthol as a pure compound to be solubilized in supercritical CO_2 and as one of the compounds extracted from peppermint leaves by supercritical CO_2 at 40, 60 and 80°C and at pressures between about 80 and 250 bar. Krishna Sastri [52] showed that during the SFE of jasmine flowers, the solubility of the pure key compounds was more than one order of magnitude greater than the extract loading of the supercritical CO_2 during the processing of the vegetable matter. This data confirms the existence of a partition factor between two phases in contact.

Solubility information is useful to establish whether or not a compound can be solubilized by supercritical CO_2 at a given condition. Indeed, the larger the compound solubility at a given extraction condition, the more favorable the corresponding desorption isotherm or phase equilibrium curve will be.

In conclusion, the analysis of solubility data indicates that low CO_2 densities should be a good choice to extract volatile compounds selectively as compared to higher molecular-weight compounds. However, knowledge of the relative solubilities of all extractable compounds does not provide all the information necessary to perform the SFE process. Mass transfer mechanisms and their possible different effects on various compound families also have to be taken into account if the process is governed by internal mass transfer resistance. Therefore, the selection of process conditions is more complex than the mere determination of the solubility data.

4. Solid-feed processing and mathematical modelling

The study of the SFE of flavors and fragrances can be broadly divided into three steps, i.e.: (1) chemical and organoleptic characterization of the extracts, (2) evaluation of the influence of process parameters, and (3) mathematical modelling.

An accurate chemical characterization is required, since essential oils are as a rule made up of tens or hundreds of compounds. Their analysis cannot be reduced to the identification of some key compounds since the presence and the concentration of several specific compounds can signifi-

cantly affect the quality of the extract. Moreover, the presence of non-volatile compounds, even in trace amounts, can greatly reduce the quality of the product. For example, the presence of bergapten in citrus-peel oils places severe restrictions on their use [53]. Product characterization is also aimed at answering another question, i.e. are the extracts obtained by SFE comparable to, different from or better than those produced by steam distillation or solvent extraction? For these reasons, a detailed analysis of fragrance compounds obtained by SFE has been proposed by many authors. The literature on this subject, starting from 1991, is summarized in Table 2. As a rule, the works aimed at product characterization give some information on the process pressure, temperature, extraction time and solvent flow rate, but a search for the optimum extraction conditions has been performed only in a few cases. Since the supercritical CO_2 extraction of vegetable matter can produce the coextraction of many undesired compounds, the analysis of volatile compounds in the extracts is insufficient. A complete characterization of the extracts should be performed to ascertain the presence and quantity of undesired compounds.

The particle size, extraction time and solvent flow rate should also be taken into account to acquire a complete knowledge of the SFE process. These parameters influence the extraction rate and the yield of the process. Moreover, when different compound families show different diffusion times, the extraction time can also affect the composition of the extracted material.

Mathematical modelling of the relevant features of the SFE process is required to interpolate or extrapolate experimental conditions and to extend the experimental information to different matters. It is useful in deciding upon a plan for experimental studies. Furthermore, it proves useful in scaling-up the process starting from laboratory results.

4.1. Chemical and organoleptic characterization of extracts

4.1.1. Characterization of the products at different extraction conditions

A number of previous reviews on the characterization of essential oils and oleoresins by supercriti-

Table 2
Supercritical fluid extraction of flavor and fragrance compounds (analytical results)

Angelica (root)	Nykanen et al. [54]
Anise (seed)	Ondarza and Sanchez [55]
Basil (leaf)	Reverchon et al. [56]
Cardamom (seed)	Gopalakrishnan and Narayanan [57]
Chamomile (flower)	Reverchon and Senatore [58]
Cinnamon (leaf)	Sanders [59]
Citron (peel)	Poiana et al. [60]
Coriander (fruit)	Cieslinski et al. [61], Kallio and Kerrola [62], Kerrola and Kallio [63]
Dragonhead (leaf)	Hawthorne et al. [64]
Evodia Rutaecarpa (herb)	Ma et al. [65]
Franchincense (herb)	Ma et al. [65]
Geranium (leaf)	Machado et al. [66]
Ginger (rhizome)	Sankar [67], Bartley and Foley [68]
Hops (fruit)	Verschuere et al. [69], Langenzaal et al. [70]
Iris (rhizome)	Bicchi et al. [71]
Jasmine (flower)	Gopalakrishnan and Narayanan [72], Rao et al. [73], Sankar [67], Reverchon et al. [74]
Lavander (flower)	Adasoglu et al. [75], Reverchon et al. [76]
Lavandula (flower)	Oszagyan et al. [77]
Kumquat (peel)	Poiana et al. [60]
Marjoram (leaf)	Reverchon et al. [78], Reverchon [79], Hawthorne et al. [64]
Massoi (bark)	Dick et al. [80]
Mirrh (herb)	Ma et al. [65]
Onion (bulb)	Sinha et al. [81]
Oregano (leaf)	Ondarza and Sanchez [55]
Pampelmousse (peel)	Poiana et al. [60]
Paprika (fruit)	Knez et al. [82]
Pepper (fruit)	Sankar [67]
Peppermint (leaf)	Reverchon et al. [83], Hawthorne et al. [64]
Rose (flower)	Reverchon et al. [84]
Rosemary (leaf)	Reverchon and De Camillis [85], Reverchon and Senatore [86], Mendes et al. [87], Oszagyan et al. [77]
Sage (leaf)	Reverchon et al. [88]
Savory (leaf)	Hawthorne et al. [64]
Spearmint (leaf)	Barton et al. [89]
Strawberry (berry)	Polesello et al. [90]
Thyme (leaf)	Oszagyan et al. [77]
Tsuga Canadiensis (leaf)	Guinamant [91]
Vanilla (pod)	Nguyen et al. [92]

cal CO_2 have been published. Particularly useful are the reviews by Stahl et al. [2] and Moyler [3]. They provide comprehensive lists of the vegetable matter treated by SFE. Table 2 can be regarded as an updated list covering the literature up to the beginning of 1995.

Nykanen et al. [54] performed a detailed analysis of angelica root compounds extracted by supercritical CO_2. They analyzed the extracts obtained at 40°C and under increasing pressure. A summary of their results is given in Table 3, where the percentages of the various compound families are reported. Terpenes and sesquiterpenes constituted the major constituents of angelica root oil. Some coumarins and psoralens were also found. The miscellaneous compounds in Table 3 were mainly paraffins. From this data it is evident that the content of non-volatile compounds in supercritical CO_2 extracts of angelica root increases significantly with extraction pressure. Particularly, coumarins and psoralens contents are 7% at 80 bar and 50% at 200 bar. At this latter pressure, the overall content of undesired compounds is 66%. Moreover, it is very interesting to note the comparison made by these authors with the product obtained by steam distillation of angelica root. The percentage of the various compound families in the steam-distilled product was similar to the extracts obtained by SFE at 80 and 90 bar.

The problem of essential oil contamination by undesired high molecular-weight compounds was also noted by Sankar [93] during the SFE of black pepper. He tested various extraction pressures (from 80 to 100 bar) and temperatures (from 40 to 60°C), and found that at 100 bar and 60°C the pungent principal (piperine) was not recovered. Operating at 100 bar and 40°C the oil also contained some monoglycerides. Evaporation residues ranged from

19 to 24% by weight. In a later work, the same author optimized the SFE of black pepper oleoresin [67]. The best composition was obtained at 280 bar and 55°C, with a piperine content of over 50%. In that case, essential oil was coextracted together with piperine and fixed oil. Thus, Sankar concluded that the best selectivity (i.e. the selective extraction of essential oil versus undesired compounds) was obtained when supercritical CO_2 was used at conditions near the critical point.

Verschuere et al. [69] fractionated supercritical CO_2 extracts obtained from hops by performing successive extractions at increasing CO_2 densities. They started at 0.2 g cm^{-3} and performed several extraction tests on the same sample up to 0.9 g cm^{-3}. In this manner, they were able to separate the essential oil from the bitter principals of hops (e.g. humulones and lupulones).

Another (albeit qualitative) indication that the composition of supercritical CO_2 extracts changes with extraction pressure was given by Guinamant [91], who extracted essential oil from *Tsuga Canadiensis* leaves. He analyzed materials extracted at CO_2 densities of 0.25, 0.40, 0.60 and 0.80 g cm^{-3}, and noted the progressive appearance of high molecular-weight compounds (mainly diterpenes) in the extract at increasing CO_2 density.

Gopalakrishnan and Narayanan [57] tested the extraction of cardamom-seed essential oil in the temperature range 40–60°C and at pressures ranging from 100 to 600 bar. They found an increase in non-volatile compounds with pressure, from a minimum of 4.5% at 100 bar to a maximum of 9.5% at 500 bar. Their conclusion was that the best operating conditions were at the lowest pressure (i.e. 100 bar).

Reverchon et al. [83] conducted a comparison of the SFE of peppermint leaves at two different

Table 3
Composition of angelica root extracts obtained by SFE at 40°C and at various pressure conditions and by steam distillation (SD) (adapted from Ref. [54])

	SFE					SD
Pressure (bar)	80	90	100	150	200	
Terpenes and sesquiterpenes (%)	78	80	68	41	34	81
Benzopiranoids (%)	7	8	22	3	50	8
Miscellaneous compounds (%)	15	12	10	15	16	11

extraction conditions: 90 bar and 50°C, and 120 bar and 40°C. On increasing the CO_2 density, oxygenated monoterpenes in the extracts decreased from 84.4% to 72.7%, whereas sesquiterpenes increased from 4.6% to 13.2%. Moreover, the coextraction of waxes increased from about 10% to 30% by weight compared to the yield of peppermint essential oil.

The coextraction of undesired compounds during SFE of essential oil was also noted by Kerrola and Kallio [63] during supercritical and liquid CO_2 extraction of coriander fruit. In the products extracted at 90 bar and 40°C, these authors identified some fatty acids, FAMEs and high molecular-weight hydrocarbons. Oszagyan et al. [77] also observed the presence of waxes and resins in SFE of various herbs.

Globally, experimental results show that at extraction temperatures between 40 and 50°C and at extraction pressures lower than 100 bar, higher molecular-weight compounds are not coextracted with essential oil. Indeed, at these operating conditions their solubilities are negligible, as shown in Table 1.

Paraffinic compounds were found in the extracts at all process conditions, even when the pure compound solubility data indicated that their solubilities in supercritical CO_2 were very low. This result can be explained by observing the schematic representation of the leaf structure shown in Fig. 6 [79]. Waxes are located on the leaf's surface, where they exert a controlling role on its perspiration. Essential oil compounds are preferably located inside the cellular structure in vacuoles [94].
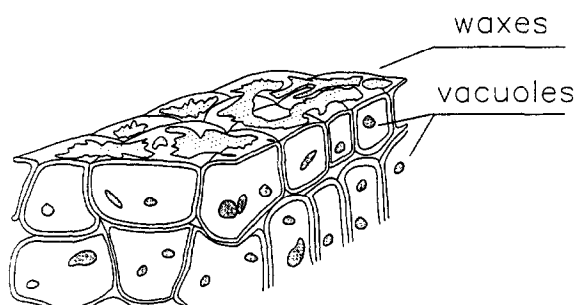

Fig. 6. A schematic representation of the leaf structure. The locations of cuticular waxes and vacuoles are shown (adapted from Ref. [79]).

Similar structures can also be proposed for other vegetable matters. Therefore, allowances should also be made for the different mass transfer mechanisms which operate during wax and essential oil extraction. Waxes have no affinity with the other parts of the leaf surface, and thus they are extracted with very limited mass transfer resistances in the solid phase. Therefore, if the residence time of the supercritical solvent is sufficiently long, their concentration in the supercritical solution at the exit of the extractor could be near the thermodynamic value. Therefore, even when higher molecular-weight compounds are not coextracted, SFE products are more similar to a concrete than to an essential oil. In contrast, essential oil compounds show very large solubilities or complete miscibility in supercritical CO_2, but larger mass transfer resistances in the solid phase characterize their extraction process. As a result, essential oil extraction can be controlled by mass transfer mechanisms.

The problem of the coextraction of waxes can be solved by introducing fractional separation of the extracts. This technique consists of a separation of the compounds contained in the supercritical solution by operating two or more separators in series. The separators are set at different pressure and temperature conditions to precipitate the extracted compounds selectively. Indeed, when both the essential oil and the waxes are in the supercritical solution, no mass transfer resistance is present and only solubility conditions apply. Therefore, it is possible to use the solubility data to choose the appropriate separation conditions. This process arrangement was first proposed by Stahl and co-workers [2,95] for various vegetable matters. It takes advantage of the different solubilities exhibited by paraffins and terpenes at temperatures of around 0°C in liquid CO_2. At these conditions, the solubility of paraffins is near to zero. In contrast, terpenes are completely miscible at these conditions. Therefore, paraffins larger than C_{25}, solubilized during supercritical extraction, can be precipitated in the first separator set at about 0°C, whereas essential oil compounds will be collected in the second separator, where a large pressure reduction induces the passage of CO_2 to the gaseous state.

The efficiency of the fractional separation

process was demonstrated by Reverchon and Senatore [86] when they isolated rosemary essential oil. They operated SFE at 100 bar and 40°C and used a single-stage and a two-stage separation procedure. Tests performed using single-stage separation produced a concrete-like extract (see Fig. 7 for the GC trace of this extract). Fractionation was performed by setting the first separator at 80 bar and 10°C and the second separator at 25 bar and 0°C. The separation procedure allowed the isolation of the pure rosemary oil, while in the first separator a nearly odorless white mass consisting of waxes was collected. Another example of fractional separation is shown in Fig. 8, where GC traces of basil essential oil and waxes are reported [56]. The same procedure was used successfully in SFE of marjoram leaves [79]. In this case, the efficiency of the fractionation at various operating conditions was also reported. The range of separation conditions explored was from 80 to 90 bar and from 0 to −30°C. Fractional separation was also adopted for the isolation of essential oils from SFE products for peppermint [83], chamomile [58] and lavender [76]. An example of the detailed identification of waxes is given in Table 4 for chamomile. In this case, paraffins and small quantities of olefins were found. More generally, the waxes coextracted consist of odd carbon-atom paraffins ranging between C_{25} and C_{35}. SFE plus fractional separation was replicated in a pilot-scale apparatus designed on the basis of the laboratory results. It was operated at the same extraction conditions as in the laboratory unit, and could use up to three separation stages. Separation condi-
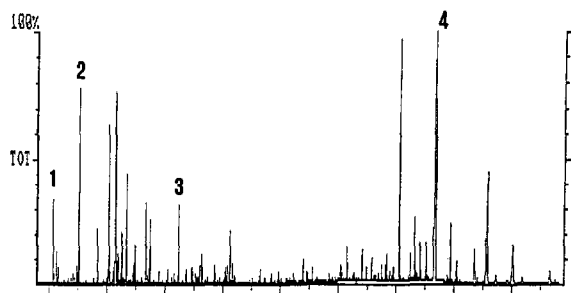

Fig. 7. GC trace of rosemary concrete-like extract obtained by SFE at 100 bar and 40°C. No fractional separation was performed (adapted from Ref. [85]).

tions in the last stage were modified to allow for CO_2 recirculation. Based on the laboratory and pilot-plant studies, an industrial-scale plant with 4×300 dm^3 extractors has been built, and has been in operation since the beginning of 1996. It was constructed by Fedegari (Pavia, Italy) and is being used by Essences (Salerno, Italy). Fig. 3 is a photograph of this industrial system.

A fractional separation technique was also used by Yonei et al. [96] to divide supercritical fluid extracts of ginger into pungent principles (mainly represented by [6]-gingerol) and essential oil. They operated extraction at 246 bar and 40°C. The first separation stage was tested at various pressures ranging from 79 to 109 bar, and at 60°C. The second separation stage was kept constant at 45 bar and 30°C. According to these authors, the quantity of pungent principles recovered in the first separator increased with pressure, whereas the separation selectivity decreased.

4.1.2. Comparison between liquid and supercritical CO_2 extracts

Taking as a starting point the discussion on the fractional separation of the supercritical extract, one can deduce that if extraction is performed by liquid CO_2, the problem of the coextraction of waxes will be alleviated or resolved. It is true that liquid CO_2 extracts very low quantities of paraffins, particularly when the extraction temperature is near 0°C. This temperature coincides with that suggested for fractional separation. However, the density of liquid CO_2 ranges between 0.8 and 1.1 $g\,cm^{-3}$ under commonly used extraction conditions, and it exhibits a very high solvent power towards all lipophilic compounds contained in vegetable matter. Its selectivity is low. Indeed, liquid CO_2 coextracts large percentages of high molecular weight compounds, as shown by the experimental data. For example, Bestmann et al. [97] used liquid CO_2 in a Soxhlet-like apparatus to extract essential oil from thyme leaves. The authors carried out a detailed analysis of the extracts, which contained about 28% paraffins and fatty acids. Chen and Ho [98], during liquid CO_2 extraction of ginger, found up to 67% of non-volatile matter constituted by pungent principles and unidentified components. Kallio and Kerrola
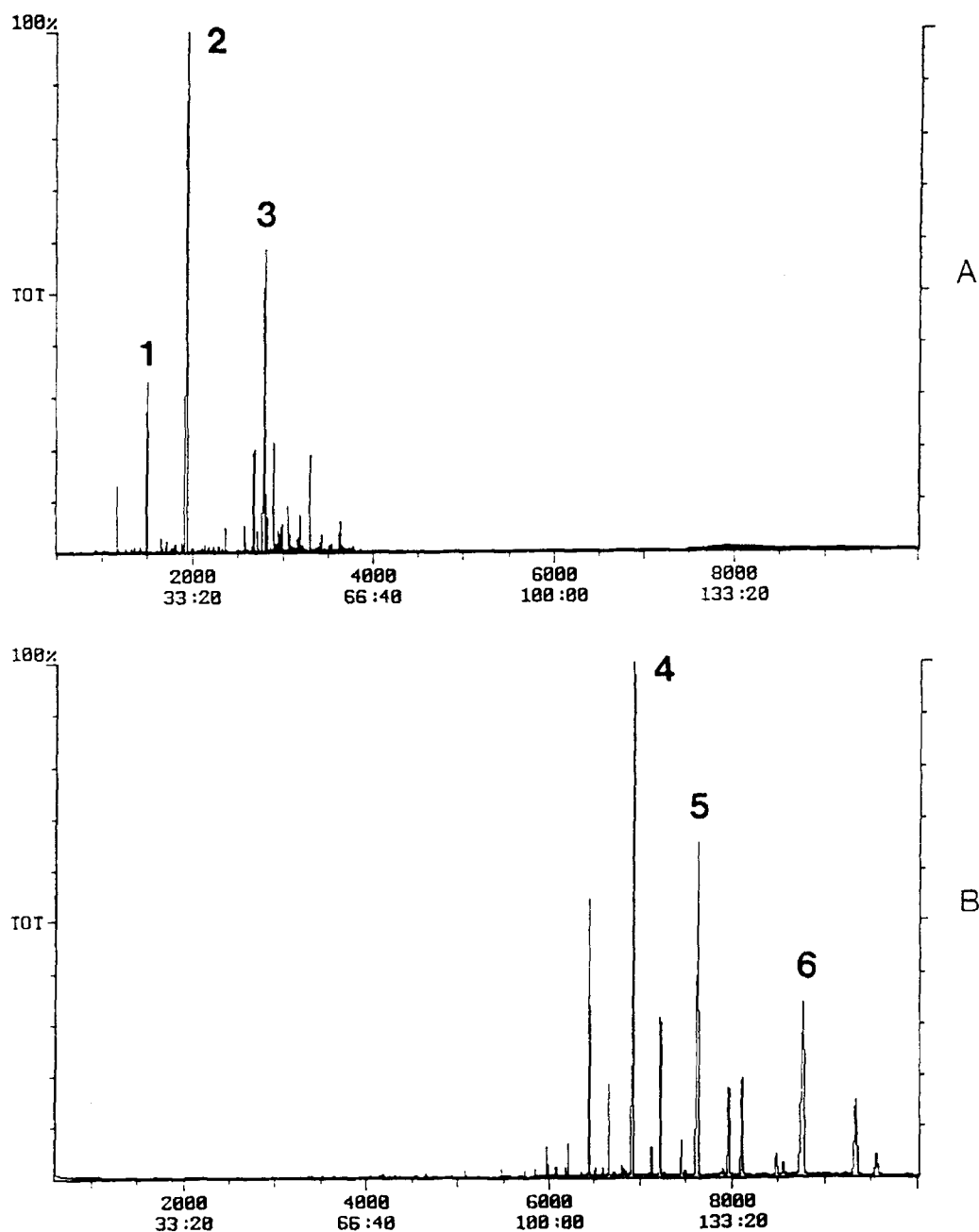
Fig. 8. GC traces of basil essential oil (A) and basil waxes (B) obtained by SFE at 100 bar and 40°C plus fractional separation of the extracts. 1, linalool; 2, estragol; 3, methyl eugenol; 4, nonacosane; 5, entriacontane; 6, tritriacontane (adapted from Ref. [56]).

[62] used liquid CO_2 to extract volatile oil from coriander fruits. They operated at 47 and 54 bar and at 25°C and at 69 bar and 45°C in a Soxhlet-like apparatus, and found a lower monoterpene hydrocarbon content (13.5%) than in steam-distilled oil (20%). FAMEs and fatty acids were 1.1% in steam-distilled oil, and ranged from 5.4 to 17.5% at the different liquid CO_2 conditions used. These

Table 4
Identification and percentages of chamomile waxes collected in the first separator during SFE at 90 bar and 40°C plus fractional separation of the extracts (adapted from Ref. [58])

	Area (%)
Hexadecene	0.44
Octadecene	2.17
Docosene	0.83
Tricosane	1.64
Tetracosane	0.31
Pentacosane	10.50
Hexacosane	1.52
Methylhexacosane	0.26
Heptacosane	17.56
Octacosane	2.74
Methylheptacosane	0.85
Nonacosane	24.12
Triacontane	2.86
Entriacontane	19.71
Methyltriacontane	1.26
Dotriacontane	1.54
Methylentriacontane	1.16
Tritriacontane	9.46
Methyldotriacontane	1.13

results were confirmed by the recent work of Moyler [99], who made a comparative study of liquid CO_2 and steam-distilled extracts of celery seed, hops, clove bud, juniper berry, mace and ginger using extraction conditions between 50 and 80 bar and 0 and 10°C. Among the others, celery seed and mace extracts showed a lipidic content of 60 and 50%, respectively.

During SFE of sage leaves, Reverchon et al. [88] performed some experiments on a sage charge which had been treated previously in long-duration experiments at low CO_2 density (90 bar and 50°C) and therefore did not contain essential oil. Using this procedure, all the material extracted was representative of the fraction of high molecular-weight compounds which can be extracted by high-density CO_2. They tested supercritical CO_2 at 200 bar and 40°C and liquid CO_2 at 100 bar and 18°C for 150 min. Fractional separation was also used to avoid the coprecipitation of cuticular waxes. Both tests yielded about 0.6% by weight of the charge (1.35% was the asymptotic yield of sage essential oil) and showed a similar qualitative composition. These extracts consisted of traces of essential oil

compounds. Diterpenes (manool and sclareol) were the main compounds, and large percentages of flavones, phenantrenones and triterpenic compounds were also identified.

In conclusion, when comparing liquid CO_2 extracts and supercritical CO_2 products, the former show a lower content of paraffins balanced by lower extraction selectivities, which yield a larger content of high molecular-weight compounds which cannot be considered among the constituents of essential oils. The selective elimination of the high molecular-weight fraction is more difficult than the elimination of paraffins.

4.1.3. Comparison between SFE and steam-distilled products

Several authors have compared the volatile compounds extracted by supercritical CO_2 with the corresponding essential oil produced by steam distillation, the latter being the reference product. Sankar [93] studied SFE of black pepper and compared the volatile oil contained in the supercritical extracts with the steam-distilled oil. CO_2 extracts contained larger amounts of high boiling-point fraction. In pepper oil the terpenes provide the body of the flavour and the sesquiterpenes provide the spicy note. Therefore, the ratio of terpenes to sesquiterpenes describes the quality of the product. In SFE performed at 100 bar and 60°C, this ratio was 0.97, as compared to 2.73 in steam-distilled oil. Similar conclusions were also obtained by Vidal and Richard [100] in previous work on black pepper.

A comparison between the essential oil obtained by steam distillaton and the product obtained by SFE plus fractional separation was performed by Reverchon and Senatore [86] in SFE of rosemary oil. They found that steam-distilled oil contained higher percentages of terpene hydrocarbons (see Table 5). In contrast, the SFE oil contained a higher percentage of oxygenated compounds. Organoleptic tests confirmed that steam-distilled oil possesses a less intense rosemary aroma. A comparison between marjoram essential oil [78] obtained by SFE and steam distillation showed that supercritical CO_2 extraction did not produce thermal degradation of cis-sabinene hydrate and cis-sabinene hydrate acetate that are among the

Table 5
Comparison between rosemary oil isolated by SFE at 40°C and
100 bar with fractional separation, and steam-distilled oil (SD)
(adapted from Ref. [86])

Area (%)	SFE	SD
Monoterpene hydrocarbons	15.5	36.5
Monoterpenes oxygenated	73.7	59.4
Sesquiterpene hydrocarbons	6.6	2.2
Sesquiterpenes oxygenated	0.8	0.9
Other compounds	1.3	0.7

most characteristic compounds of marjoram fragrance. Also, thermal degradation of the characteristic compounds of essential oils did not occur during SFE of chamomile [58]. In this case, steam distillation converted matricine into chamazulene, which is responsible for the characteristic blue colour of chamomile oil obtained by steam distillation. In lavender oil extraction [76], supercritical CO_2 extraction avoided the partial hydrolysis of linalyl acetate, which occurs when vapor is used as a distillation medium (see Fig. 9). The SFE lavender oil contained 34.7% linalyl acetate, whereas the steam-distilled oil contained only 12.1% of this compound.

On the whole, experimental evidence confirms that SFE avoids degradation of thermosensible compounds and the hydrosolubilization or hydrolysis of water-soluble or -sensible compounds.

4.1.4. The consequences of using cosolvents

The solvent power or the selectivity of CO_2 can be modified by adding small amounts of liquid solvents. These cosolvents are chosen to enhance the affinity of the solvent mixture towards polar compounds which, as a rule, have a very low solubility in supercritical CO_2. Some recent examples of cosolvent addition in the extraction of flavor and fragrance compounds are given in the literature [71,73,90].

Rao et al. [73] used methanol, acetone and DMSO to modify CO_2 solvent selectivity versus fragrance compounds contained in jasmine flowers. They used an equilibrium extraction apparatus at 120 bar and 40°C, and found that acetone (3.5 mol%) enhanced the solubility of cis-jasmone by 266% and produced the highest dissolution

enhancement of n-anthranilate and benzylacetate, all characteristic compounds of jasmine fragrance. However, these compounds are also soluble in supercritical CO_2 alone. The authors did not assess the effect of this modified selectivity on the overall jasmine fragrance.

Bicchi et al. [71] used methanol (3%) as a cosolvent to extract irones and iridals from iris rhizomes, since pure supercritical CO_2 proved to be ineffective in extracting these compounds. Methanol was added directly to the material to be extracted, and SFE tests were conducted at 60°C and 218 bar. A higher iridal recovery was obtained compared with that obtained using liquid organic solvent extraction.

Polesello et al. [90] added 100 ml of acetone to a mixture of strawberries and silica (about 3 g) to recover furaneol (i.e. the water-soluble character impact of strawberries). They operated SFE in successive steps at 77 and 91 bar and at 40°C over total time of 57 min. High percentages of furaneal were extracted effectively.

Cosolvents are a useful resource when the target of the process is to extract particular compounds such as furaneol and iridals. Their use is far less jusitified when the target is to obtain a faster extraction, or when the compounds to be extracted constitute a complex mixture (as in essential oils). In this case the natural fragrance will also be modified. Moreover, since cosolvents are liquids, they will be recovered together with the extracts, and a further process step will be required for their elimination.

4.1.5. Post-processing of intermediate products

In some cases, the raw materials containing essential oil are treated at an early stage to avoid the degradation of their fragrance. In particular, this happens for scent extracts from flowers and other vegetable materials which are difficult to store. Steam distillation is unsuitable to process such materials since it induces the thermal degradation of several compounds. Therefore, solvent extraction is used. When the solvent is removed, a concrete extract is obtained. This procedure is widely used, and concretes of many vegetables are commercially available. As discussed above, a concrete can also be obtained by processing the vegeta-
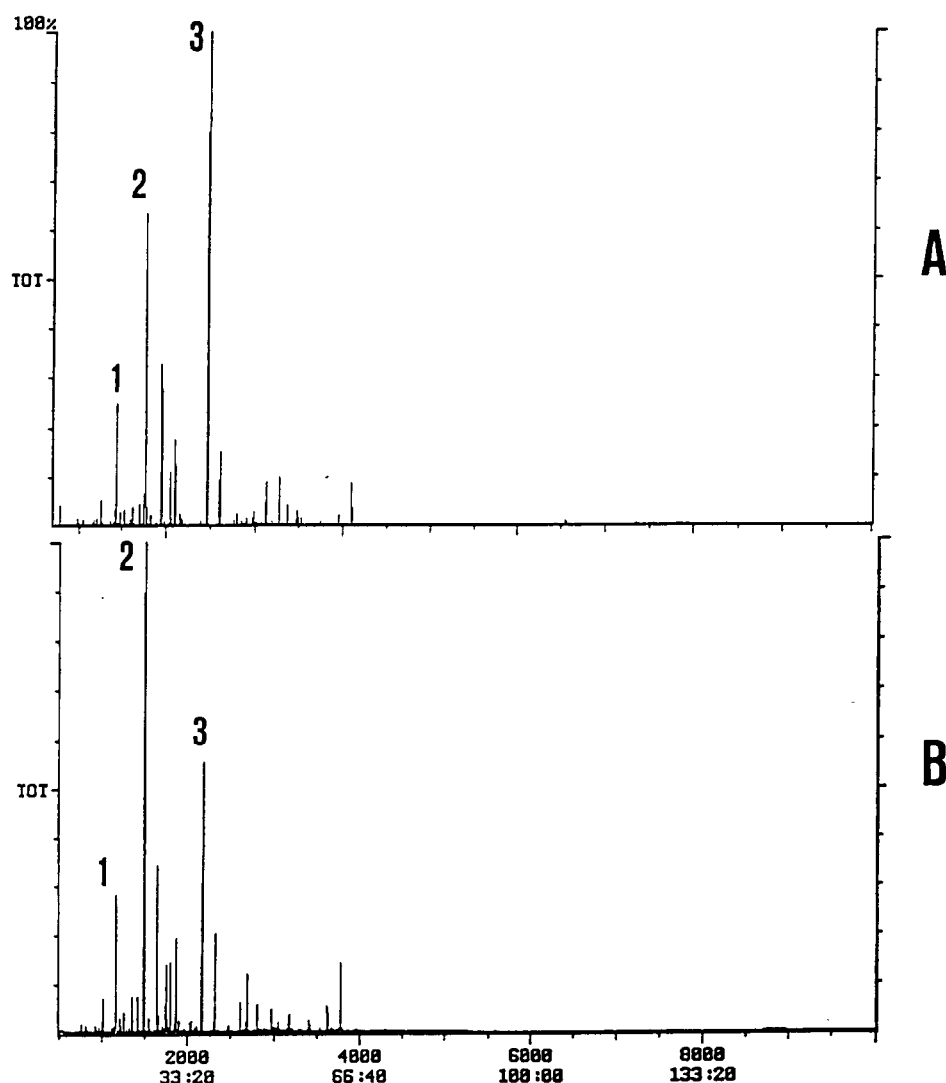
Fig. 9. Comparison of GC traces of lavender essential oil obtained by SFE at 90 bar and 50°C with fractional separation (A) and steam distillation (B). 1, 1-8 cineole; 2, linalool; 3, linalyl acetate (adapted from Ref. [76]).

ble matter with supercritical CO_2 at densities greater than 0.6 g cm^{-3} if only a single separation stage is used to recover the extracted fractions. A concrete contains fragrance-related compounds, but also undesired compounds like fatty acids and their methyl esters, diterpenes and other high molecular-weight lipophilic compounds. Moreover, high quantities of paraffins (50–70% by weight) are present in the concretes. A concrete can be post-processed by steam distillation or ethyl alcohol solubilization to obtain a volatile oil or an

absolute, respectively. Obviously, these techniques induce thermal degradation and solvent contaminaton of the products. Therefore, some authors attempted the fractionation of concretes by liquid or supercritical CO_2 extraction.

Gopalakrishnan and Narayanan [57] proposed post-processing of jasmine concrete by liquid CO_2. They mixed clean white sand with jasmine concrete at 55–60°C and treated this mixture at 100 bar and 20°C with 30 min of contacting time before releasing the supercritical solution into a

single-stage separator. The product was highly viscous due to the coextraction of volatile compounds and high quantities of waxes. The wax content in the extract increased with the number of extractions performed on the same charge of concrete. Moreover, their extracts contained from about 13 to 20% of FAMEs.

Sankar [67] attempted jasmine concrete fractionation using supercritical CO_2 at 100 bar and 50°C. He did not report the percentage of waxes and FAMEs in the extracts, but the lower density adopted in the SFE process, if compared to the liquid CO_2 process used by Gopalakrishnan and Narayanan [57], should assure lower paraffin and FAME contents. The yield of jasmine absolute was also reported as a function of the mass of CO_2 used (see Fig. 10).

Reverchon et al. [74] developed a concrete fractionation process in which SFE was coupled with fractional separation of the extracts. They processed a jasmine concrete mixed with 2 mm glass beads in three successive steps at 40°C and at pressures of 80, 85 and 200 bar. The two separation stages were set at 80 bar and 0°C and 25 bar and −10°C, respectively. The extraction step performed at 80 bar produced a volatile fraction mainly formed by benzyl acetate (62.4%), benzyl benzoate (12.6%) and linalool (12.3%). Only small amounts of FAMEs were detected (overall percentage 2.7%). No other high molecular-weight compounds were extracted. No paraffins polluted the volatile oil because they were completely precipitated in the first separator. The oil yield relative to this step of the process was 17.3% by weight of the charge. Organoleptic analysis classified the product as top-notes jasmine. The second extraction step, performed at 85 bar, produced a liquid extract with a high content of benzyl benzoate (28.3%) and phytol (28.6%). Large quantities of various FAMEs were also extracted (38.0% overall). The yield of this part of the process was 13.1% by weight, and sensory analysis classified this product as middle- and bottom-notes jasmine. The last extraction step at 200 bar produced an odorless liquid fraction; a very small percentage of fragrance compounds were found, whereas FAMEs were at 83.1%. The yield of this step was 18% by weight. The authors concluded that mixing the fractions obtained during the first two steps of the process showed the best overall reproduction of the jasmine fragrance. Thus, the yield of jasmine fragrance was 30.3% globally. Throughout the extraction process, the waxes collected in the first separator were 14% by weight of the jasmine concrete.

Recently, Reverchon and Della Porta [101] adopted a different approach during rose concrete fractionation. In this case, they first ascertained by GC–MS analysis that rose concrete did not contain FAMEs. Then, they used a one-step SFE process (80 bar and 40°C) while maintaining the fractional separation of the products. Separation in this case was the most difficult step of the process owing to the presence of low molecular-weight paraffins and long-chain paraffinic alcohols (steroptens). These compounds worsen the quality of rose volatile oil and are very difficult to precipitate in the first separator. Very low temperatures were required in the first separator to obtain their supersaturation and precipitation. Indeed, temperatures down to −16°C were used to precipitate paraffins and steroptens selectively. The rose oil yield was 49% by weight of the charged material. A comparison of the SFE volatile oil of rose and the products obtained by steam distillation and by solubilization of the rose concrete in ethyl alcohol was performed [84]. The major differences appeared in the phenyl
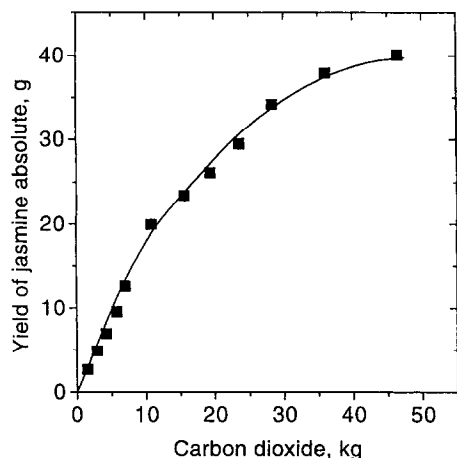

Fig. 10. Yield of jasmine absolute obtained by supercritical extraction as a function of the total amount of CO_2 used (adapted from Ref. [67]).

ethyl alcohol (PEA) content and in the percentages of paraffins and steroptens. PEA is a characteristic compound of the rose fragrance; it was present at 50.0% in the SFE volatile oil, at 10.4% in the steam-distilled oil, and at 28.3% in the alcoholic solution. Most of the PEA was lost during steam distillation since this product is water-soluble. A qualitative comparison is also possible from Fig. 11, which reports the GC traces of SFE and steam-distilled rose oil obtained from concrete. The steam-distilled and solvent-extracted products also contained 22.7 and 46.4% of paraffins, respectively, whereas the SFE oil contained only 15.1% of the lighter paraffins. Steroptens were present at 3.7% in steam-distilled oil, at 3.5% in solvent-extracted oil, and at 2.8% in SFE oil.

Large modifications of the rose volatile oil com-

position were also found for extraction times greater than 240 min due to the progressive exhaustion of the lighter compounds and to the consequent progressive enrichment of the heavier compounds in SFE extracts. Some tests were performed on a semi-industral scale using a 20 dm^3 internal volume extractor. It was charged with about 2 kg of rose concrete, and produced about 1 kg of rose volatile oil.

An extension of the fractionation processes can be proposed for other intermediate products to take advantage of the selectivity of the process and its operation on smaller extraction volumes.

4.1.6. Further comments

The extraction of essential oils by supercritical CO_2 is sometimes carried out under drastic condi-
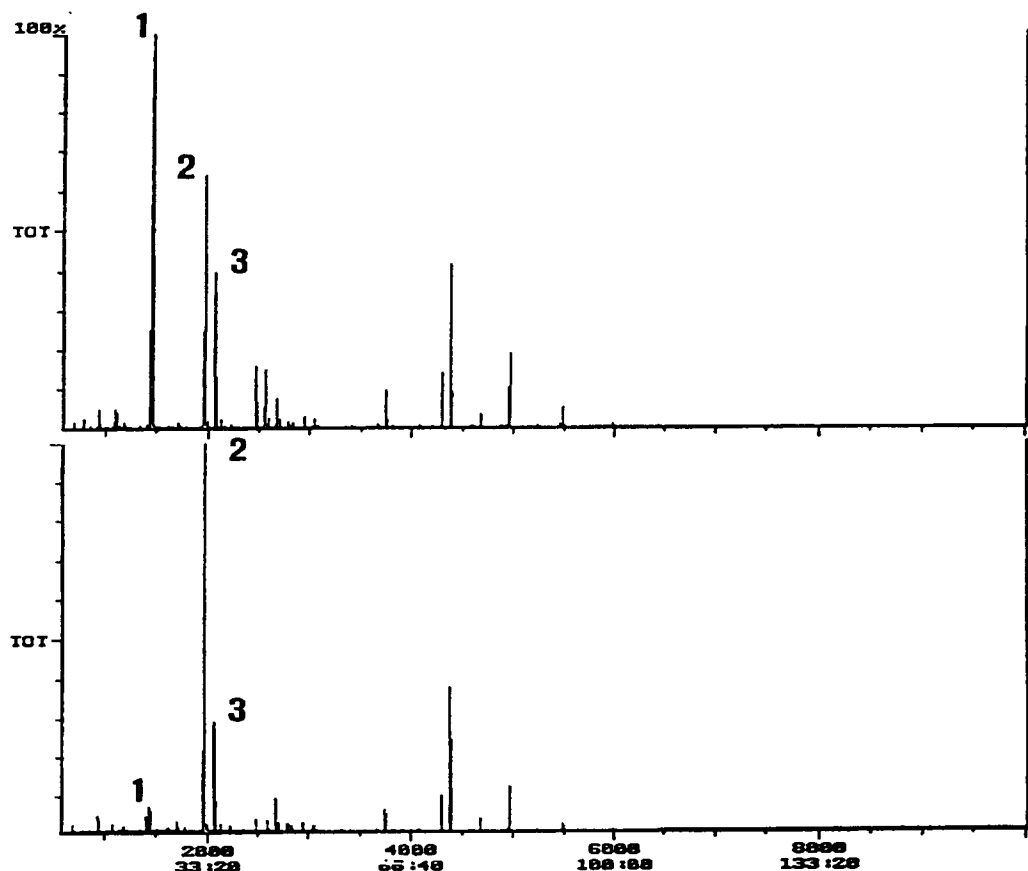

Fig. 11. Comparison of GC traces of rose oils obtained from concrete by SFE at 80 bar and 40°C with fractional separation (A) and by steam distillation (B). 1, phenyl ethyl alcohol; 2, citronellol; 3, phenyl ethyl acetate (from Ref. [84]).

tions (i.e. at 200–300 bar and 40–60°C). However, relatively low pressures are sufficient to extract these compounds selectively. This conclusion is supported by solubility data, and is confirmed by experimental data on many vegetable matters.

The use of a high extraction pressure favors the coextraction of undesired high-molecular-weight compounds. Furthermore, liquid CO_2 extraction produces the coextraction of many undesired compounds since it operates at very similar densities to those of high-pressure supercritical CO_2.

The specific problem of essential oil isolation which arises from the coextraction of waxes can be resolved by introducing extract fractionation during multiple-stage separation.

4.2. Influence of the process parameters

An analysis of the SFE products and an assessment of their optimum composition as a function of the extraction pressure and temperature has been performed for several vegetable matters, as described above. However, these research activities do not cover all the problems related to the SFE of essential oils. Process parameters like the extraction time, the solvent flow rate (or residence time for a given bed geometry), the particle size and particle size distribution (PSD) have to be considered. Indeed, some or all of these parameters can affect the extraction rate of the process. The extraction time can also influence the composition of the extracts. Study of these parameters is also required to postulate reliable models of the extraction process and to perform scale-up procedures.

Information on the extraction rate is generally given as an integral measure such as the yield curve against the extraction time (see, for example, Fig. 12, where the normalized yield in the simultaneous extraction of vegetable oil, essential oil and water is reported for the SFE of coriander seeds at 200 bar and 40°C for a particle size of 0.90 mm) [102]. The normalized yield (yield %) is obtained by assuming the asymptotic yield of the most abundant among the compound families extracted to be equal to 100.

Sometimes the results are expressed as a function of the specific mass of the solvent utilized, which is m_s/m_0 (where m_s is the amount of solvent used
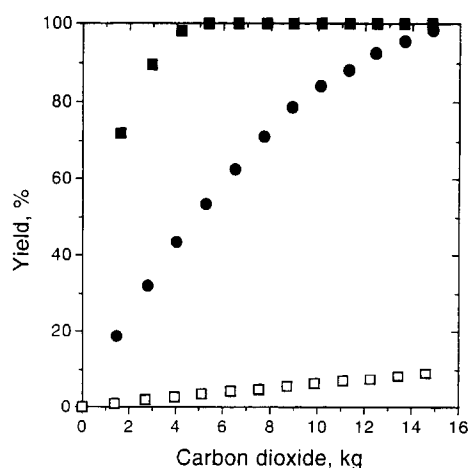

Fig. 12. Yield of simultaneous extraction of oil, essential oil and water from coriander seeds at 200 bar and 40°C as a function of the total amount of CO_2 used. ■, Essential oil; ●, vegetable oil; □, water (adapted from Ref. [102]).

and m_0 is the quantity of vegetable matter loaded into the extractor).

In principle, the yield curve for the SFE of essential oils can evolve according to the following steps. The first part of the graph can be representative of the equilibrium conditions. If this is the case, this first part of the curve will be a straight line. The slope of the curve can be used to calculate the equilibrium data at given pressure and temperature conditions. However, the linear variation in the yield curve does not necessarily prove that equilibrium conditions have been reached. If none of these conditions apply to the process studied, the yield curve displays curvature. The second part of the yield curve describes the approach to an asymptotic value which represents the total amount of extractable material for the given extraction conditions.

Some authors (for example Goto et al. [51] during the SFE of spearmint) assumed that all essential oil compounds are extracted simultaneously and studied the SFE by monitoring the concentration of a single key component which was chosen among the more characteristic compounds of the essential oil studied. The yield of the key compound will thus be representative of the essential oil yield. However, by studying the composition of SFE extracts obtained from spear-

mint leaves, Ozer et al. [103] found that monoter-penes were preferably extracted at the beginning of the process, whereas higher molecular-weight compounds were preferably extracted later. Kerrola et al. [104] performed supercritical CO_2 extraction of angelica root at 120 bar and 50°C. They considered three extract fractions (F1, F2 and F3) collected at increasing extraction times. Monoterpene hydrocarbons were present at 83% and 55% in fractions F1 and F2, respectively, and at about only 14% in the F3 fraction. Oxygenated monoterpenes and sesquiterpenes were mainly collected in the F2 fraction. The highest molecular-weight compounds dominated the third fraction, which contained about 34% coumarins and pso-ralens and 43% fatty acids and other less volatile compounds. In this case, many undesired compounds were coextracted. Their presence in the extracts can be explained by the authors' choice of too severe extraction conditions. In the SFE of essential oil from sage leaves, Reverchon et al. [88] monitored the composition of sage essential oil extracted by supercritical CO_2 at 90 bar and 50°C against the extraction time. Their results are shown in Fig. 13, in which a large variation of composition with extraction time is noted among the different families of componds which constitute sage oil. This behavior can be explained by the different diffusion times of the different families of

compounds inside the vegetable matter. According to these results, the monitoring of a single key compound concentration in the extracts cannot be representative of the behavior of all the compounds extracted.

Yield curves for the same vegetable matter, although obtained at different extraction pressures and temperatures, have also been proposed by some authors. For example, Sankar and Manohar [105] and Sankar [93] extracted pepper oleoresin at 80 bar and 40 and 60°C, and at 100 bar and 40 and 60°C. This kind of yield curve is of very limited significance. Indeed, the volatile oil content in a given batch of vegetable matter is fixed. Thus, if all volatile material is accessible, different extraction conditions can only yield different extraction rates. The different yields obtained by varying the extraction conditions therefore depend on the relative quantities of the undesired compounds which are coextracted.

If the internal mass transfer mechanisms constitute the controlling step of the extraction process, the particle size of the vegetable matter and its distribution can significantly influence the extraction time required to obtain a given yield of essential oil. In this case, extraction at different particle sizes will largely depend on the length of the diffusion path. For example, Reverchon and Sesti Ossèo [106] reported the influence of particle size in the case of SFE of basil essential oil. Moreover, different PSDs produced different shapes of the yield curve at lower extraction times and during the approach to the asymptotic yield. If external mass transfer or equilibrium are the controlling steps of the process, the particle size cannot affect the extraction rate by very much.

The solvent flow rate can control extraction if equilibrium conditions apply or if the external mass transfer mechanism is the prevailing resistance factor during the extraction process. In contrast, if the internal mass transfer resistance controls the process, there will be a negligible influence of the solvent flow rate on the kinetics of the extraction process (i.e. different CO_2 flow rates do not modify the extraction rate; see, for example, Fig. 14, where two different CO_2 flow rates produce practically the same extraction rate of sage essential oil [107]).
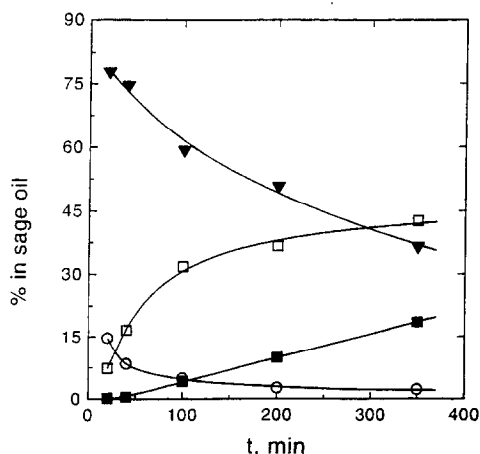

Fig. 13. Variation of sage oil composition with extraction time. ○, Terpenes; ▼, oxygenated terpenes; □, sesquiterpenes; ■, oxygenated sesquiterpenes (adapted from Ref. [88]).
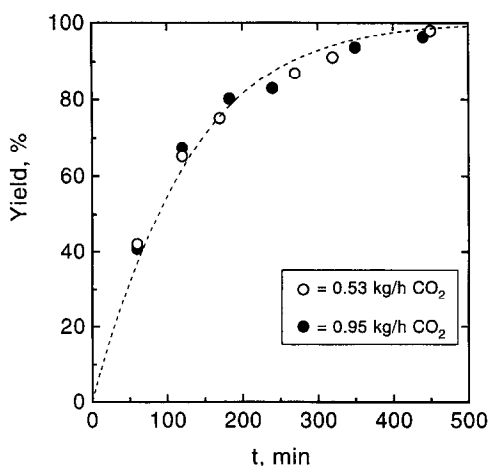
Fig. 14. Influence of CO_2 flow rate on the yield of sage essential oil extraction (adapted from Ref. [107]).

It is also possible that different mass transfer mechanisms can exert a controlling role at different stages of the SFE process. Frequently, mass transfer can be controlled by a combination of different mechanisms, and the switch from one to another has to be allowed for.

4.3. Mathematical modelling

The initial distribution of the solute within the solid substrate affects the selection of the possible models. The extractable substances may be free on the surface of the solid material, adsorbed on the outer surface, located within pores or evenly distributed within plant cells. Each different description corresponds to a different model. Experimental results also contribute towards selecting a model. Experimental evidence can highlight the influence of different mass transfer resistances or the existence of equilibrium conditions. Also, the transition between different mass transfer mechanisms can be seen.

Essential oils can have different localizations in different vegetable structures. For example, leaves can contain essential oil in two distinct structures: epidermal hairs and vacuoles. Epidermal hairs are characteristic structures located near the surface of many kinds of leaves. Vacuoles are cell organules characteristic of vegetable cells, and are located inside the leaf structure (see Fig. 6).

Epidermal hairs decompose during the drying process. Therefore, when treating dried leaves, it is reasonable to suppose that essential oil is mainly contained in vacuoles. Small quantities of essential oil can also be near the surface of the leaf particles due to cell breaking during grinding.

Mathematical models enable us to generalize the experimental results, which can be applied to new process conditions and to materials other than those studied. Moreover, they are useful in the development of scaling-up procedures from laboratory to pilot and industrial scale. However, a model should not be a mere mathematical instrument, but should reflect the physical insight arising from the knowledge of the structure of the vegetable matter and from experimental observations. Mathematical models which have no physical correspondence to the materials and the process studied are of limited validity, although they can be used to fit some experimental data.

Three different approaches have been proposed for the mathematical modelling of the SFE of essential oils: (1) empirical, (2) models based on heat transfer analogy, and (3) differential mass balance integration.

4.3.1. Empirical models

Naik et al. [108] extracted several vegetable materials including clove, cardamom, sandalwood, ginger and vetiver by liquid CO_2. They represented the extraction yield (Y) against the extraction time (t) in terms of a Langmuir-like empirical equation:

$$Y = \frac{Y_\infty t}{B + t} \tag{1}$$

where Y_∞ is the yield after an infinite extraction. The extraction rate of most of the vegetable matter conformed well to this equation, as shown by Fig. 15. In this case, the yield is expressed as the ratio of the percentage extracted to the weight of the vegetable charge (yield %, w/w).

Barton et al. [89] treated the SFE of vanilla oleoresin as a chemical reaction. A kinetic constant was used instead of the mass transfer and equilibrium relationships. The authors assumed that the rate of extraction was proportional to the concentration of oleoresin left in the vegetable particle
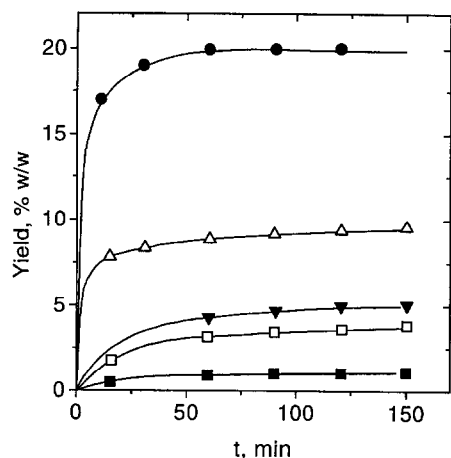
Fig. 15. Empirical modelling of the extraction rate by liquid CO_2 for various vegetable matters. ●, clove; △, cardamom; ▼, sandalwood; □, ginger; ■, vetiver. The curves are from the model of Eq. (1) (adapted from Ref. [108]).

(q_{rs}), and proposed the following differential equation:

$$\frac{dq_{rs}}{dt} = -kq_{rs} \qquad (2)$$

where k is the kinetic constant. This equation can be readily integrated with the initial condition that at $t = 0$, $q_{rs} = q_{rs0}$, obtaining:

$$q_{rs} = q_{rs0} \exp(-kt) \qquad (3)$$

According to these authors, if internal diffusion is the controlling step, it is possible to set $k = DA/Vz$, where A/V is the particle surface-to-volume ratio and z is the diffusion distance. They found a best-fit value of the internal diffusivity D of 3×10^{-13} m^2 s^{-1} by applying this model to experimental data on vanilla oleoresin.

Kandiah and Spiro [109] used a similar approach in the representation of ginger SFE. They also found a strong dependence of the extraction rate on the ginger particle size, which confirmed the controlling role exerted by internal diffusion.

The empirical approach can be useful when information on the mass transfer mechanisms and on the equilibrium relationships is missing; however, these models are little more than an interpolation of the experimental results.

4.3.2. Models based on heat transfer analogy

In this case, the SFE is treated as a heat transfer phenomenon. Each single vegetable particle is considered as a hot ball cooling in a uniform medium.

Assuming that the components to be extracted are uniformly distributed inside the particle, and by applying Fick's second law of diffusion, the heat transfer analogy and the Fourier transforms, the material balance across an internal surface of the particle can be solved analytically [110], giving:

$$\frac{q}{q_0} = \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2\pi^2 Dt}{r^2}\right) \qquad (4)$$

where n is an integer, r is the radius of the sphere (m), D is the diffusion coefficient of the solute in the sphere (m^2 s^{-1}), t is the extraction time (s), q is the concentration of the solute remaining in the sphere (kg m^3), and q_0 is the initial concentration of the extractable material. The extension of the results to the whole bed of particles is immediate, since all the particles are assumed to be at the same extraction conditions.

Bartle et al. [111] applied this model to the SFE of various physical systems. For example, they monitored the SFE of rosemary leaves by analyzing the content of 1-8 cineole in the extracts. They concentrated their attention on the asymptotic trend of the yield curves to obtain an extrapolation method to evaluate the extraction time necessary for matrix exhaustion.

Reverchon et al. [112] applied this model to describe the yield curves of essential oils isolated by SFE plus fractional separation of various vegetable matrices (basil, rosemary and marjoram). Experimental results were described fairly well by this model, as shown in Fig. 16 for rosemary essential oil. Three different particle sizes in the SFE of the basil essential oil were also tested [56]. Once again, a fairly good agreement between the model and the yield data was obtained. The particle size distribution of the various basil charges was also considered. With the addition of this information, the model tended to overestimate the extraction yield. This behavior was somewhat expected, since this model considers the ideal extraction behavior for each single particle, neglecting their interactions.
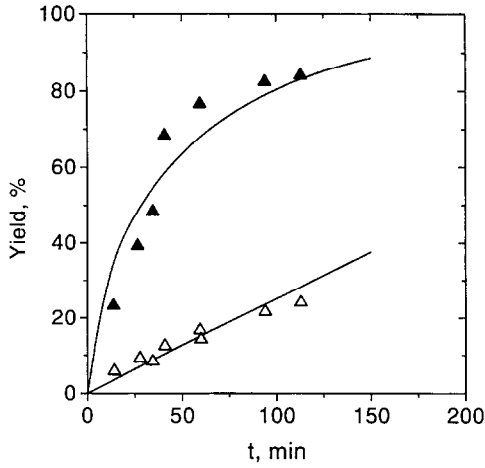
Fig. 16. Heat transfer analogy in modelling the SFE and fractional separation of rosemary essential oil and waxes at 100 bar and 40°C. ▲, Essential oil; △, waxes. The curves represent the model of Eq. (4) (adapted from Ref. [112]).

4.3.3. Models based on differential mass balance

Material balances along a section of the extractor have been widely used to describe the behavior of fixed beds during solid–liquid operations like adsorption/desorption, chemical reaction and extraction. Material balances also constitute a flexible mathematical tool.

All the mass balance models proposed up to now have been developed with the assumption of negigible axial dispersion, constant solvent density and flow rate along the bed, and that the essential oil can be modelled as a single compound. On the basis of these hypotheses, two independent mass balances can be written over an element of the extractor of a height dh. For example, the mass balances can be written as:

$$uV\frac{\partial c}{\partial h} + \epsilon V\frac{\partial c}{\partial t} + (1-\epsilon)V\frac{\partial q}{\partial t} = 0 \qquad (5)$$

$$(1-\epsilon)V\frac{\partial q}{\partial t} = -A_p K(q-q^*) \qquad (6)$$

where ϵ is the bed porosity, V is the extractor volume (m^3), c is the extract concentration in the fluid phase ($kg\,m^{-3}$), q is the extract concentration in the solid phase ($kg\,m^{-3}$), u is the superficial solvent velocity ($m\,s^{-1}$), A_p is the total surface of particles (m^2), q^* is the concentration at the solid–fluid interface which is assumed to be in equilibrium with the fluid phase ($kg\,m^{-3}$), h is the spatial coordinate along the bed (m), t is the extraction time (s), q_0 is the initial concentration in the solid phase ($kg\,m^{-3}$), and K ($m\,s^{-1}$) is the internal mass transfer coefficient.

The solid phase balance can also be proposed on a single spherical particle. In this case, the mass balance will be:

$$\frac{\partial q}{\partial t} = \frac{D_e}{r^2}\frac{\partial\left(r^2\frac{\partial q}{\partial r}\right)}{\partial r} \qquad (7)$$

where r (m) is the particle fractional radius, and D_e ($m^2\,s^{-1}$) is the effective intraparticle diffusion coefficient. In this case it will be possible to model the concentration profiles along the particle.

If we choose to represent the SFE process by the differential mass balances given by Eqs. (5) and (6), they can be solved with the appropriate initial and boundary conditions provided that the solid versus fluid phase equilibrium relationship $q^*(c)$ is known. A linear relationship is usually used in the modelling of SFE processes due to the lack of experimental data on the phase equilibrium:

$$c = k_p q^* \qquad (8)$$

where k_p is the volumetric partition coefficient of the extract between the solid phase and the fluid phase at equilibrium.

The system of partial differential equations (Eqs. (5) and (6)) with the equilibrium relationship (Eq. (8)) and the initial condition at $t=0$, $c=0$ and $q=q_0$ and the boundary condition at $h=0$, $c(0,t)=0$ can be solved numerically applying, for example, the method of characteristics.

In Eq. (6), the group $A_p K/(1-\epsilon)V$ depends on the geometry of the particles through $A_p K$. This group is dimensionally equal to 1/s. Therefore, it is possible to define the internal diffusion time as $t_i = (1-\epsilon)V/A_p K$, where t_i is a characteristic time of the extraction process. Thus, Eq. (6) can be rewritten as:

$$\frac{\partial q}{\partial t} = -\frac{1}{t_i}(q-q^*) \qquad (9)$$

Moreover, if the extraction is assumed to be uniform along the bed (i.e. $\partial c/\partial h = $ constant), Eqs. (5) and (9) can be rewritten as a system of ordinary differential equations:

$$\left(\frac{W}{\rho}\right)c + \epsilon V \frac{dc}{dt} + (1-\epsilon)V\frac{dq}{dt} = 0 \qquad (10)$$

$$\frac{dq}{dt} = -\frac{1}{t_i}(q - q^*) \qquad (11)$$

where W is the solvent mass flow rate (kg s^{-1}) and ρ is the solvent density (kg m^{-3}). In this case, a solution can be obtained numerically using the fourth order Runge–Kutta method. Starting with Eqs. (10) and (11), if the accumulation of the extract in the fluid phase can be neglected ($\partial c/\partial t = 0$), a simple analytical solution can be obtained.

Reverchon [107] proposed the extraction of sage oil as a model case for SFE from leaves. SFE was performed at 90 bar and 50°C and fractional separation was performed to isolate a sage essential oil that did not contain coextracts [88]. Experiments were repeated at four different particle sizes and at two different CO_2 flow rates. The SFE rate largely depended on the particle size; therefore, according to the schematic representation of the leaf structure proposed in Fig. 6, a model with a controlling internal mass transfer resistance was adopted. The mathematical model was based on Eqs. (5) and (9) with the equilibrium relationship as given in Eq. (8). The Villermaux [113] relation was used to introduce the internal diffusivity D_i:

$$t_i = \mu \frac{l^2}{D_i} \qquad (12)$$

where μ is a coefficient depending on particle geometry. In the case of spherical particles μ is equal to 3/5, whereas for cylinders and slabs it is equal to 1/2 and to 1/3, respectively. l is the ratio between particle volume and particle surface.

Reverchon [107] first assumed that sage particles were spherical. The deviation of the model curves from the experimental points increased with particle size. A possible explanation could be that the description of the particle geometry is not correct. Slab geometry was therefore introduced in the

calculation by assuming the mean thickness of sage leaves (0.29 mm) as the height of the slab particles. The other two dimensions of the slab were determined from the mean particle size of the charge as measured by sieving. A fairly good fit was obtained for the whole range of particle sizes studied. The best fit among the yield curves and the experimental data was obtained for $D_i = 6.0 \times 10^{-13}$ m^2 s^{-1} (see Fig. 17). The fit was particularly good, even when considering the largest sage particles (3.1 mm). The hypothesis that internal diffusion is the limiting stage of the mass transfer mechanism was verified by performing SFE of sage oil at different CO_2 flow rates: yield curves substantially overlapped when expressed against the extraction time (see Fig. 14).

To obtain a simpler representation of the SFE of essential oils, simplified models were also tested. Reverchon and Sesti Ossèo [106] in the SFE of basil oil neglected the accumulation of solute in the fluid phase and assumed that extraction was uniform along the extraction bed. With these assumptions, an analytical solution was obtained from which D_i could be determined from a fit of the experimental data. The limits of the applicability of the simplified mass balances when applied to SFE of leaves can be explained by comparing two characteristic process times, namely the
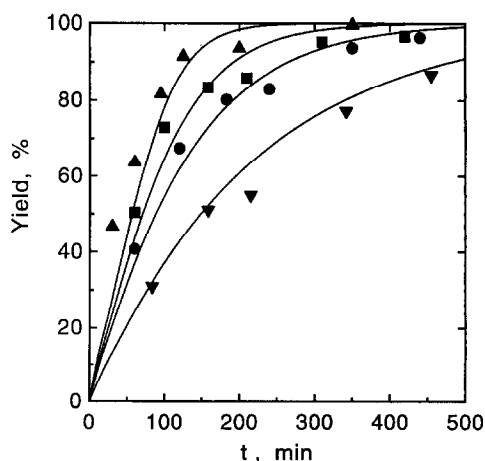

Fig. 17. Best fit of data for SFE of sage oil from Eq. (10) and Eq. (11) at different particle sizes. ▲, 0.25 mm; ■, 0.50 mm; ●, 0.75 mm; ▼, 3.1 mm. $D_i = 6.0 \times 10^{-13}$ m^2 s^{-1} (adapted from Ref. [107]).

internal diffusion time and the residence time. During the SFE of basil essential oil [56] and of sage essential oil [88], the internal diffusion times were generally very large as compared to the residence time, especially when particles larger than 0.3 mm were considered. Fluid phase concentration profiles were smooth, partly justifying the assumptions made in developing the simplified models.

Sovovà et al. [114] proposed a more articulated approach when modelling the SFE of essential oil from caraway seed, further developing a model previously presented by the same research group for the SFE of seed oils [115,116]. These authors proposed a physical representation of the seed particles as being composed of cells broken up during grinding and of cells which are still intact. They hypothesized the existence of two mass transfer resistances during SFE. The first is located in the supercritical mixture and controls the extraction process until all the essential oil in the broken cells is exhausted. The second is in the walls of the undestroyed cells and controls the remaining part of the process. These hypotheses were transferred to the mathematical model by introducing two mass balances for the solid phase (similar to those in Eq. (6)). One was written for the easily accessible essential oil, and the other was written for the essential oil protected by the walls of the closed cells. The relative proportions of these contributions were determined by the grinding efficiency. A third diffreential mass balance was proposed for the fluid phase. The system of three PDEs constituted by the mass balance equations was solved by numerical integration. Five adjustable parameters were determined using the least-squares method. Experimental results were proposed at different extraction conditions, and experiments were performed in upflow and downflow conditions. The effect of channelling was observed in the upflow operation. However, to validate models with a large number of adjustable parameters, an adequate number of experimental data sets has to be used.

Coelho et al. [117] adopted the model proposed by Sovovà [115] for seed oils to model the liquid CO_2 extraction of basil essential oil. This model neglects the term related to solute accumulation in

the fluid phase ($\partial c/\partial t = 0$), and presents an analytical solution. Experiments were performed at two different process conditions (69.8 bar and 29°C, and 79.8 bar and 32°C). However, the low content of essential oil in basil leaves (around 1% as a rule) and the different structure of leaves as compared to seeds should give very small or zero fractions of readily extractable material. The limited number of experiments presented by the authors can also be explained using a model containing only the internal diffusion resistance. Mira et al. [118] proposed the use of this same model in studying SFE of dried orange peel at 150 bar and 50°C. They studied the influence of particle size and CO_2 flow rate on the extraction rate. Observations similar to those put forward in the work of Coelho et al. [117] could be made for the application of this model to orange-peel oil extraction. A model with internal diffusion as the limiting stage seems applicable in this case for all particle sizes explored except for the experiments performed at the smallest particle size.

Goto et al. [51] performed SFE of peppermint oil from leaf pieces of about 3 mm in size. They performed SFE at 88 bar and 60°C and measured the extraction yield by monitoring the concentration of the extracts in 1-menthol. Experiments at three different CO_2 flow rates were performed. They hypothesized that the peppermint essential oil was adsorbed in waxes located on the leaf surface, i.e. they considered only the fraction of essential oil originally located in the epidermal hairs. These authors modeled peppermint particles as slabs of infinite length and considered as a uniform extraction in the fluid-phase mass balance ($\partial c/\partial h = $ constant). The solid-phase mass balance for a single slab-like porous particle was written as:

$$\beta \frac{\partial q_i}{\partial t} = D_e \frac{\partial^2 q_i}{\partial y^2} - (1-\beta)\frac{\partial q}{\partial t} \tag{13}$$

where β is the porosity of the leaf, q_i is the concentration of solute in leaf pores, and y is the leaf coordinate. They also assumed that the combined external and internal mass transfer processes can be described by the linear driving-force approximation [119]. Moreover, it was supposed

that equilibrium in the pores was established instantaneously. An analytical solution was thus obtained. The only parameter in the model was the adsorption equilibrium constant, which was best fitted to the experimental results. The experimental data and the model curves are reported in Fig. 18. They concluded that mass transfer in both the particle and the external film was so fast that adsorption equilibrium alone controlled the overall extraction rate.

When porous, spherical particles are considered, in which the solute exists in pores as a trapped liquid and the solid has no affinity for the liquid, the driving force for the extraction process is represented by the solubility of the solute in the fluid phase. Such a situation can be described by the shrinking-core model. As solute is extracted, the front between the solute and the solvent phase recedes towards the centre of the particle. Therefore, the solute contained within the particle is concentrated in a core of diminishing radius. In this case, the solid-phase mass balance, written for a single spherical particle, can be represented by Eq. (7). This model was first proposed by King and Catchpole [120] to describe the SFE of vegetable oil from seeds (peanuts). The hypothesis of a linear equilibrium condition at the particle surface and the linear driving force approximation were
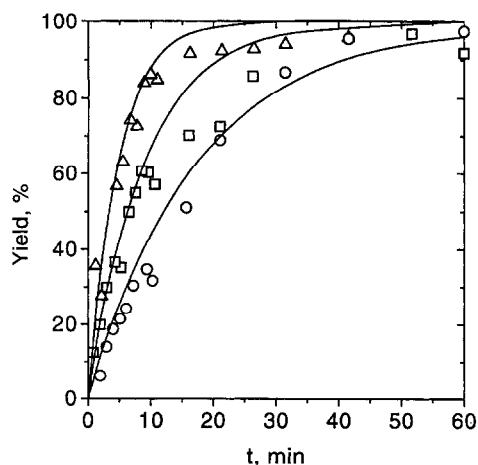

Fig. 18. Modelling of the SFE of peppermint oil as a desorption process. Effect of CO_2 flow rate on the extraction of 1-menthol. $\bigcirc$, 3.3×10^{-5} kg s^{-1}; $\square$, 6.5×10^{-5} kg s^{-1}; $\triangle$, 13×10^{-5} kg s^{-1} (adapted from Ref. [51]).

proposed. An analytical solution was obtained assuming a parabolic concentration profile inside the particles. Then, Catchpole et al. [102] used this model to fit the experimental data for the simultaneous SFE of vegetable oil, essential oil and water from coriander seeds at 200 bar and 40°C (see Fig. 12 for a graphical representation of the data). Goto et al. [121] and Roy et al. [122] used the shrinking-core model to fit the experimental data on the SFE of ginger rhizomes performed at three different CO_2 flow rates. Two adjustable parameters were used in the model: solubility and effective intraparticle diffusivity. Yield curves plotted against the extraction time were coincident, indicating that the extraction process was controlled by the mass transfer mechanism. However, only one of the yield curves produced at different particle sizes was fitted by the model.

The shrinking-core model seems more applicable to the seed structure than to other vegetable matter. Seed structure can be described by porous particles, and the content of vegetable oil is very high (frequently over 50% by weight). It is far less justifiable to use the shrinking core model to describe, for example, the structure of ginger rhizomes. Indeed, the maximum ginger oil yield, as measured by Roy et al. [122], is lower than 4% by weight. Moreover, Spiro and Kandiah [50] demonstrated for SFE of ginger rhizomes that a partition factor applies between the solid and fluid phase solute concentration, i.e. the driving force for the process is not the solubility in supercritical CO_2, since the solute is not freely available in the solid phase.

Hortacsu et al. [123] proposed two mathematical models representing the plant matter as arrays of cellular, permeable tubes or as serially interconnected, perfectly mixed tanks. These representations were suggested by an analysis of the physical structure of the vegetable matrix. However, these models were not tested on experimental data.

Reverchon and Poletto [124] recently proposed the modeling of rose and tuberose concrete extraction. They observed by optical microscopy that concretes consist of an oily phase mainly formed by compounds which are easily soluble in supercritical CO_2 and a waxy phase where insoluble waxes are predominant, and in which small quanti-

ties of liquids are trapped. On the basis of the experimental results obtained at different CO_2 flow rates, they formulated a model in which extraction from the oily phase was controlled by equilibrium, and a variable mass transfer resistance controlled the extraction of solute from the waxy phase. The mathematical representation by differential mass balances produced a fairly good fit of the experimental data.

4.3.4. Further comments

Different models have been proposed to describe the major features of the SFE of essential oils. However, their general validity is not the same. Since the composition of the SFE extracts varies with the extraction pressure and temperature, a preliminary optimization of the extraction conditions is required. Moreover, accurate experimental data on the essential oil yield cannot be obtained without the adoption of the fractional separation technique. More information is still required on the influence of the various process parameters like the extraction time, particle size, etc. The extraction mechanisms postulated in the models must correspond to the real structure of the vegetable matter.

5. Liquid feed processing

Citrus-peel oils and many other essential oils consist of large quantities of hydrocarbon terpenes and sesquiterpenes, and of small percentages of oxygenated terpenes. Terpenes are unsaturated compounds which can undergo structural rearrangements and hydration reactions; they are also oxidized rapidly by air. As a rule, citrus-peel oils are produced by cold pressing. This process also releases non-negligible quantities of non-volatile compounds like coumarins and psoralens into the oil. Some of them, like bergapten, have a well-ascertained phototoxic activity [125,126]. For this reason, strong limitations have been imposed on the use of citrus-peel oils. IFRA (the International Fragrance Association) recommended a maximum content of 0.4% of cold-pressed bergamot oil and a maximum content of 2% of the other citrus-peel oils in products which are applied to skin areas

exposed to sunshine [53]. Oxygenated compounds are highly odoriferous and are the principal odor carriers, although hydrocarbon terpenes and sesquiterpenes can also contribute to their flavor [127].

There is considerable interest in developing techniques which can produce concentrated peel oils with a low hydrocarbon content. At present, the most commonly used procedures to concentrate peel oils are vacuum distillation, extraction with alcohol, partition between two solvents with different polarities, and preparative adsorption chromatography. These processes suffer some disadvantages: specifically, organic solvents have to be removed, and distillation may induce thermal degradation of the product. No specific procedures have yet been proposed to eliminate allergenic compounds.

Supercritical CO_2 may be used as a very selective solvent, and does not produce thermal degradation or solvent contamination of products. Therefore, it should be possible to set up new processes to deterpenate essential oils and to eliminate allergenic compounds. To date, two different approaches have been proposed in the supercritical fractionaton of essential oils. These are (1) supercritical desorption and (2) continuous countercurrent tower processing.

5.1. Supercritical desorption

Yamauchi and Saito [128] used a semi-preparative supercritical chromatographic system to fractionate a cold-pressed lemon-peel oil. It was injected directly into a 50 mm × 7.3 mm ID column packed with silica gel. The column temperature was held constant at 40°C while the outlet pressure was increased from 100 to 200 bar. Ethanol was also added in the last part of the experiments. Four fractions were obtained, and were mainly composed of terpenes, oxygenated terpenes, oxygenated terpenes removed by ethanol addition, and high molecular-weight compounds.

Cully et al. [129] proposed citrus-peel oil desorption from several adsorbents (silica gel, aluminium oxide, Kieselgur, cellulose, bentonite and magnesium silicate) using supercritical CO_2. They used temperatures ranging from 50 to 70°C and

pressures of 70–90 bar, and claimed a maximum reduction of the terpene content of 95%.

Knez et al. [82] gave some descriptive indications on the supercritical deterpenation of lemon-peel oil operating at increasing pressures.

Barth et al. [130] used supercritical desorption to deterpenate lemon-peel oil and to eliminate coumarins and psoralens. They operated the desorption by increasing the CO_2 density in successive steps. GC–MS was used to analyze systematically the desorbed fractions and the undesorbed residue and to establish the duration of the various steps of the process. Desorbed fractions were precipitated in two high-performance thermostated cyclonic separators operated in series. These separators allowed the analysis of the precipitates during the desorption process, since it was possible to discharge the product at fixed time intervals from the bottom of the separators. The experimental procedure began by charging the peel oil into the desorber and waiting for 12 h for its adsorption on 100 g of silica gel in a 180 cm³ high-pressure column. A terpenic fraction was desorbed at 75 bar and 40°C (CO_2 density of 0.22 g cm^{-3}); a deterpenated and psoralen-free fraction was obtained at 85 bar (CO_2 density of 0.40 g cm^{-3}). Desorption of waxes was obtained at about 120 bar (CO_2 density of 0.70 g cm^{-3}), whereas coumarins and psoralens were removed from the adsorbent by washing the column with warm ethanol. GC traces of the products obtained are reported in Fig. 19. Fig. 19(a) shows the terpenic fraction and Fig. 19(b) shows the deterpenated fraction, while waxes are reported in Fig. 19(c). The enrichment of oxygenated compounds in the deterpenated fraction was about 20-fold. The presence of some steroids was also seen in the residues. Another possible use of this tecnique could be to analyze high moleclar-weight trace compounds which are strongly concentrated during successive stages of desorption.

The same process was extended to other citrus-peel oils. Bergamot oil [131], mandarin and lime oil [132] and bitter orange oil (bigarade) [133] were fractionated using similar processing conditions. Tables 6 and 7 summarise the composition of the various desorbed fractions for bigarade and bergamot peel oils, respectively. Compounds are
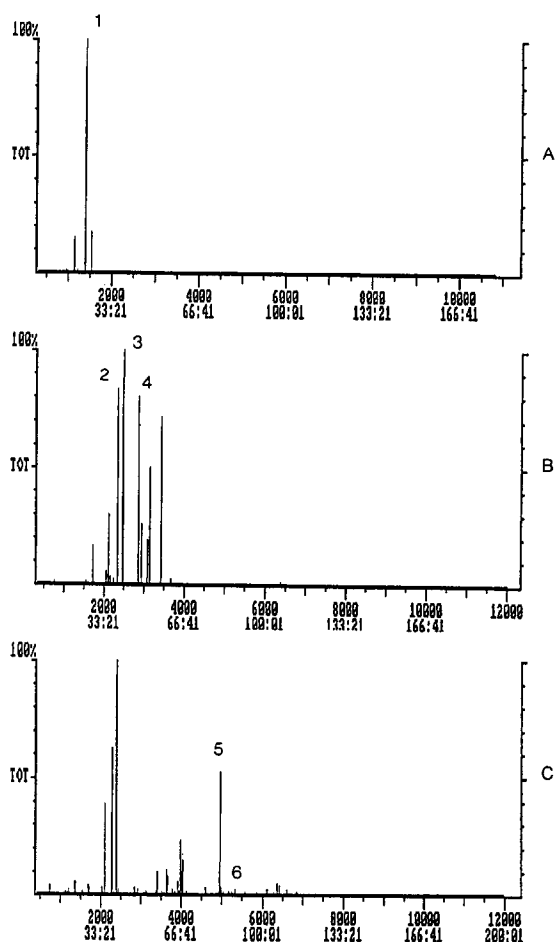

Fig. 19. GC traces illustrating lemon-peel oil fractionation by supercritical CO_2 desorption. (A) Crude oil, (B) deterpenated fraction, (C) residue. 1, limonene; 2, neral; 3, geranial; 4, neryl acetate; 5, citropten; 6, bergapten (from Ref. [130]).

arranged according to families in order to provide a synthetic representation of their distribution among the desorbed fractions. In the case of bergamot oil desorption, selectivity at various silica-gel loadings was also studied.

Dugo et al. [134] proposed the supercritical deterpenation of sweet orange and lemon peel oils. They tested various adsorbents, and found that sand and magnesium sulphate produced no fractionation. Celite was very selective for aldehydes, but linalool was almost completely extracted with hydrocarbon terpenes. Calcium sulphate gave a good deterpenation, but the results depended

Table 6
Bigarade peel oil fractionation by supercritical CO_2 desorption. (Terpenic fraction desorbed at 77 bar and 40°C. Deterpenated fraction desorbed at pressures up to 120 bar. Residue collected from the desorption column by washing with warm ethanol. Adapted from Ref. [133].)

Compound family	Crude oil (%)	Terpenic fraction (%)	Deterpenated fraction (%)	Residue (%)
Hydrocarbon terpenes	92.41	99.41	45.84	5.00
Oxygenated terpenes	7.59	0.59	49.87	23.77
Sesquiterpenes			1.82	
Oxygenated sesquiterpenes			2.47	6.17
Waxes/FAMEs				1.18
Coumarins and psoralens				59.56
Polymethoxyflavones				1.18
High molecular weight compounds				3.24

Table 7
Bergamot peel oil fractionation by supercritical CO_2 desorption (Terpenic fraction desorbed at 75 bar and 40°C. Deterpenated fraction desorbed at pressures up to 100 bar. Residue collected from the desorption column by washing with warm ethanol. Adapted from Ref. [131].)

Compound families	Crude oil (%)	Terpenic fraction (%)	Deterpenated fraction (%)	Residue A (%)	Residue B (%)
Hydrocarbon terpenes	53.76	88.96	10.91	14.74	6.90
Oxygenated terpenes	44.32	10.95	86.03	54.88	31.09
Sesquiterpenes	1.55	0.09	2.63	3.39	8.81
Oxygenated sesquiterpes	0.02			4.61	20.44
Waxes	0.21			0.36	8.35
Coumarins, psoralens	0.17			19.67	2.19
FAMEs			0.47	0.19	5.85
High molecular-weight compounds				2.15	16.1

strongly on the water content of the adsorbent, thus showing a low reproducibility of desorption. Silica gel was confirmed as the best adsorbent for this task. The work was carried out in two steps: 122 bar and 40°C for 20 min and 405 bar and 60°C for 100 min, and a micro SFE apparatus was used. Most hydrocarbons were desorbed during the first step. The fraction desorbed at higher CO_2 density still contained 20–30% of hydrocarbon terpenes. The product obtained by supercritical desorption was compared to the deterpenated oils produced by vacuum distillation. The traditional deterpenation technique produced a loss of the more volatile aliphatic aldehydes.

Vega-Bancel and Subra [135] conducted supercritical desorption experiments on a model mixture of citrus-peel oils consisting of six hydrocarbon terpenes and six oxygenated terpenes. They first adsorbed and then desorbed this mixture at CO_2

densities of 0.50 and 0.75 g cm^{-3} (corresponding to temperatures of between 37 and 57°C and pressures from 109 to 170 bar), obtaining breakthrough curves for each compound of the mixture. At the highest CO_2 density studied, practically no selectivity was observed (i.e. all the breakthrough curves almost overlapped). At 0.50 g cm^{-3}, two distinct families of breakthrough curves were found, one for the hydrocarbon terpenes and one for the oxygenated terpenes. At the same CO_2 density, selectivity decreased slightly with increasing temperature. It is reasonable to suppose that if lower CO_2 densities are employed (for example, 0.25 g cm^{-3}, as used by Barth et al. [130]) an even better separation can be obtained.

Chouchi et al. [131] also reported a first attempt to model the supercritical desorption of bergamot oil. They considered the oil as consisting of two key compound families, and measured the yield

according to this subdivision against the desorption time. The yield curves for desorption were obtained (see Fig. 20). The data was fitted by developing a simplified model of the process. The overall mass balance on the desorption bed was written as in Eq. (5). To define the mass balance in the solid medium (silica gel), information about the mass transfer coefficient is needed. Moreover, an equilibrium relationship is required to connect the oil concentration between the fluid phase and the solid phase. For a complex system such as bergamot oil, this information is missing. Therefore, the simplified approach suggested by Tan and Liou [136,137] was followed. These authors described the desorption of ethyl acetate (EA) from activated carbon by means of supercritical CO_2, obtaining a fairly good fit between supercritical desorption data and the model. Tan and Liou [136,137] suggested a mass balance in the solid phase written in terms of a linear desorption kinetics model:

$$\frac{\partial q}{\partial t} = -kq \tag{14}$$

with the initial condition at $t=0$, $q=q_0$, where k is the desorption constant (1/m). Chouchi et al. [131] chose $q_0 = q_1 + q_2$, where q_1 and q_2 are the concentrations of the hydrocarbon terpenes and the oxygenated terpenes, respectively, at the beginning of the desorpton process.

Eqs. (5) and (14) were solved analytically, giving:

$$c_{ex} = \frac{1-\epsilon}{\epsilon} q_0 \left\{ \exp\left[-k\left(t - \frac{\epsilon H}{u} \right) \right] - \exp\left(-kt \right) \right\} \tag{15}$$

where c_{ex} is the concentration in the fluid phase at the exit of the desorber, and H is the bed height (cm).

The desorbed amount (Y) was then calculated by integrating c_{ex} over time, i.e.:

$$Y = \int c_{ex} Q \, dt \tag{16}$$

where Q is the volumetric flow rate ($cm^3 \, min^{-1}$) of CO_2. Two different values of k are obtained from the model (one for each key compound) by fitting Eq. (16) to the experimental data. A fairly good agreement between the model curves and the experimental results was obtained, as shown in Fig. 20.

5.2. Fractionation in a continuous counter-current tower

Several investigators attempted the deterpenation of citrus-peel oils using a continuous method. Stahl et al. [2] proposed the supercritical fractionation of peel oils using a continuous, counter-current, high-pressure column. They treated bitter and sweet orange-peel oil at a pressure of 80 bar. The axial temperature profile aong the column displayed the highest temperature in the middle of the column (85°C), whereas the temperature at the head of the column was fixed at 75°C, and at the bottom at 60°C. The starting composition of the orange-peel oil was 90% hydrocarbon terpenes. They obtained less than 1% oxygen-containing compounds at the top of the column and a hydrocarbon content of 42% at the bottom. According to these authors, for given conditions of temperature and pressure, the degree of enrichment can be regulated via the relative solvent throughput.

Perre et al. [138] described a pilot-scale apparatus for continuous counter-current operation capable of treating 250 dm^3 of citrus-peel oil per
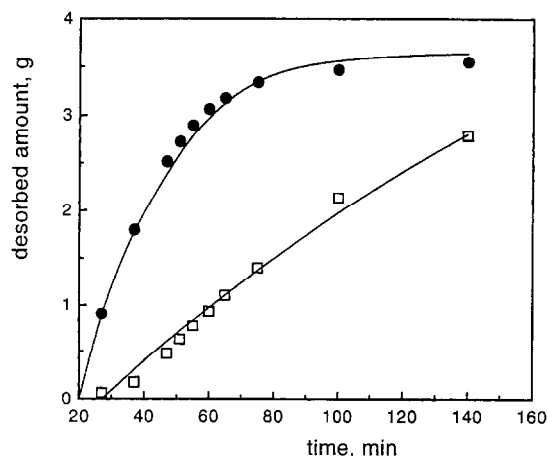

Fig. 20. Desorption of bergamot peel oil. The curves are according to the model of Eq. (16). ●, hydrocarbon terpenes; □, oxygenated terpenes (adapted from Ref. [131]).

day. According to these authors, the main parameter of the process was the flow ratio of CO_2 to peel oil.

Sato et al. [139] used a model mixture composed of limonene–linalool and citral in a 20 mm ID, 1800 mm long column packed with 3 mm Dixon packings. They used both semi-batch and continuous modes of operation. The semi-batch procedure consisted of charging the liquid feed at the bottom of the column, charging the column with supercritical CO_2 from the top, and then starting the fractionation by feeding CO_2 from the bottom of the column. They operated both with and without an axial temperature gradient along the column, and found that at pressures greater 110 bar and temperatures of 60°C one phase solution of oil and supercritical CO_2 was formed. Therefore, no separation was possible at these operating conditions. The actual operating conditions selected were 88 bar and an axial temperature of 40–60°C, or 60°C without temperature gradient. The temperature profile affected fractional extraction due to the internal reflux and counter-current contact between the liquid solute and the supercritical CO_2. They operated in the continuous mode at 88 and 98 bar, and confirmed that selectivity increases with the solvent-to-feed ratio for fixed temperature and pressure conditions.

The same authors [140] successively employed a different semi-batch procedure. They used a fractionation column (9 mm ID, 1000 mm long) connected at the bottom to a 70 cm^3 extractor. The extractor was charged with a 33 wt.% mixture of limonene, linalool and citral. Supercritical CO_2 flowed into the extractor, solubilized part of the charge and then passed through the fractionation column. The pressure and temperature ranges were as in the previous work [139]. The best operating conditions were found to be 88 bar and a temperature profile from 40 to 60°C. At these operating conditions, limonene, linalool, neral and geraniol (the components of citral) were extracted sequentially and with a good selectivity. Changes in the composition of the extracts at the optimum fractionaton conditions are reported in Fig. 21 for a CO_2 flow rate of 0.302 g s^{-1}. In the same paper, they also reported the fractionation of orange-peel oil.
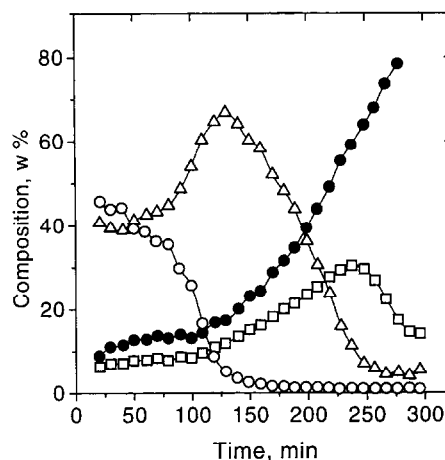

Fig. 21. Changes in composition of extracts for supercritical CO_2 fractionation of a model citrus oil mixture. ○, Limonene; △, linalool; □, neral; ●, geranial (adapted from Ref. [140]).

Simoes et al. [141] chose the model system limonene–1-8 cineole to model eucalyptus essential oil fractionation (78.8% 1-8 cineole, 21.2% limonene). They used a continuous counter-current tower (2.4 mm ID, 1 m long) packed with CY laboratory Sulzer gauze packings. Liquid feed was charged at the top of the column. They operated at temperatures of 40 and 45°C and at pressures up to 90 bar, and discussed their results in terms of the selectivity at a given operating condition. The highest selectivity was obtained at around 78 bar, but the selectivity was around 1.10–1.15 (i.e. a very low value). Separation was thus not economically feasible at these conditions.

Reverchon [142] used the continuous counter-current tower process to ascertain whether it could produce a fractionation between hydrocarbon and oxygenated terpenes which was comparable to that obtained by supercritical desorption. The continuous counter-current high-presure tower used for this study is illustrated schematically in Fig. 4. It consists mainly of five sections with an intenal diameter of 1.75 mm and a height of 30.5 mm. It also operates with a recycle of the flow exiting at the top of the column. Bergamot oil deterpenation is currently in progress. Qualitative information on the efficiency of the fractionation process is given in Fig. 22, where GC traces of crude bergamot oil and of the fraction collected at the top of
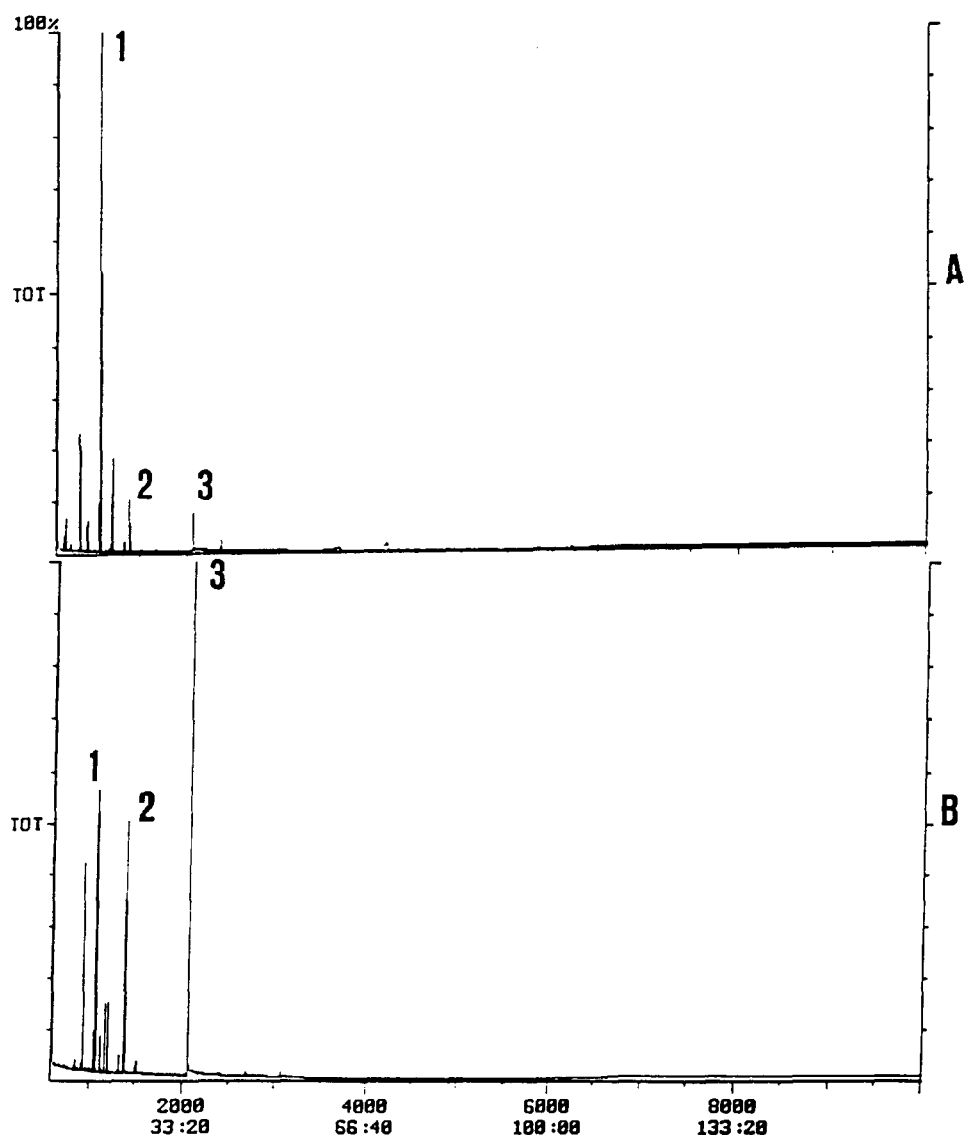
Fig. 22. GC traces of bergamot oil continuous fractionation. (A) Top fraction, (B) bottom fraction. 1, limonene; 2, linalool; 3, linalyl acetate (from Ref. [142]).

the column are reported. Small percentages of linalool and linalyl acetate are still present in the top fraction.

5.3. Further comments

Silical gel proved to be the best adsorbent for the supercritical desorption of citrus-peel oils. Process conditions at very low CO_2 densities

$(0.25–0.30 \text{ g cm}^{-3})$ should be preferred to eliminate the hydrocarbon terpene fraction, since the selectivity of the process decreases at higher densities.

Some further considerations are possible when comparing supercritical desorption to the continuous counter-current tower process. Supercritical deterpenation allows hydrocarbon terpene reduction as well as the elimination of

coumarins and psoralens, but large plant volumes will be required for industrial-scale operation. For example, a 200 dm^3 volume for a charge of 20 kg of crude essential oil can be required. The continuous counter-current tower allows hydrocarbon terpene elimination but oxygenated compounds and non-volatile compounds will be collected together at the bottom of the column. This process allows the treatment of high volumes of crude essential oils in the continuous mode. Therefore, the best process arrangement appears to be a continuous counter-current tower and a supercritical deterpenation column operated in series. In this manner, the advantages of both techniques can be exploited. The continuous counter-current tower should be used for the deterpenation of high quantities of crude essential oil, whereas supercritical desorption should be used for coumarin and psoralen elimination from the concentrated products obtained in the previous stage of the process.

6. Conclusions and perspectives

It has been demonstrated that SFE can produce superior quality products characterized by the absence of artefacts and by a better reproduction of the original flavour or fragrance. The suggested recipe to extract essential oils by SFE is to operate at low CO_2 densities (0.25–0.50 g cm^{-3}) and to add fractional separation of the extracts. Higher CO_2 densities can be useful only if non-essential oil compounds are required in the extract.

From an industrial point of view, SFE oleoresins are commercially available and essential oils produced by SFE are now being put on the market.

However, much research is still needed in all aspects related to the supercritical fluid extraction of essential oils. More extended and reliable solutility data is required for essential oil components. Data on the partition factor between the fluid phase and the solid phase is very much needed. Information on the process parameters which affect the SFE process is still scattered, and mathematical modelling of the major features of the process is still in its initial stages.

To date, post-fractionation of essential oils is by far the least studied aspect. However, the improve-

ment in essential oils achieved by eliminating terpenes and other undesired compounds is highly attractive, since fractionated essential oils can have a longer shelf life and a very high added value.

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