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SUPERCRITICAL FLUID EXTRACTION OF ESSENTIAL OILS – RESULTS OF JOINT RESEARCH

Peppermint, creeping thyme, and sage herbs, as well as yarrow flowers were extracted with supercritical and liquid carbon dioxide at 9–13 MPa and 25–60°C. Two extraction periods were distinguished except in the case of thyme extraction. Almost pure essential oil was extracted in the first, fast period. The extraction was retarded in the second period controlled by essential oil–matrix interaction, and waxes and water prevailed over the essential oil in the extract. To estimate the effect of essential oil–vegetable oil interaction during the extraction of essential oils from seeds, the limonene + vegetable oil + CO₂ equilibrium was investigated using thermodynamic modelling. Changes in the composition of the essential oil in the extracts are demonstrated on the example of sage oil. Compared to hydrodistillation, the extracts contained less monoterpenes, the most volatile components, because the separation of the extract from gaseous CO₂ in the cold trap was incomplete. The yield of sesqui- and di-terpenes in the extracts, however, was higher than their yield by hydrodistillation. The extraction of sage essential oil was most efficient at 13 MPa and 50°C, when the yield of diterpene manool was more than two times higher than its yield by hydrodistillation.

Key words: Essential oil, Extraction, Supercritical, Carbon dioxide, Solute–matrix interaction.

Many plants that grow in the Balkan Peninsula are rich in essential oils of high quality due to the beneficial climate of the region. Therefore, the teams in Prague, Skopje, and Sofia chose the extraction of essential oils as the topic of their joint research in the field of supercritical fluids.

The supercritical fluid extraction of essential oils is one of the most widely discussed topics in the literature on supercritical fluid applications. A comprehensive overview of the analytical, processing and modelling aspects of the process was published by Reverchon [1]. Extraction with supercritical carbon dioxide (SC–CO₂) can produce superior quality products characterized by the absence of artefacts and by a better reproduction of the original flavour and fragrance. In order to suppress the co-extraction of undesired higher molecular-weight compounds, Reverchon [1] recommends the extraction of essential oils at low CO₂ densities, 0.25–0.50 g cm⁻³, which corresponds to pressures of 7.8–9 MPa at 40°C and to pressures 8.5–11 MPa at 50°C. The SC–CO₂ extracts from plants contain cuticular waxes and, therefore, they should be separated from the solvent in several vessels in series so that the less soluble waxes precipitate mainly in the first vessel and the essential oil collected in the last separator is practically free of them. According to Reverchon [1], new reliable data was needed on the solubility of essential oil components in

SC–CO₂ and, particularly, on their partition coefficients between the fluid phase and the solid phase. Further, information on the parameters that affect the process was found to be insufficient and mathematical modelling of the supercritical extraction of essential oils was only in the initial stages.

The necessity of knowledge of partition coefficients is related to the fact that the essential oils extracted from plants with SC–CO₂ are usually bound to a matrix. In the case of extraction from leaves, flowers and stems, the solute–matrix interaction may have the form of solute adsorption on active sites (Hawthorne [2], Hawthorne et al. [3]), possibly on solid lipids in plant tissue (Goto et al. [4]). When, however, the essential oil is extracted from seeds, which are always rich in fatty (vegetable) oil, the essential oil is then distributed between the phase rich in SC–CO₂ and the phase rich in fatty oil (Sovova et al. [5]).

We have studied the extraction of essential oils from caraway seeds [5], peppermint, creeping thyme, sage herbs [6–8] and yarrow flowers [9] in laboratory extraction equipment, examining simultaneously several aspects of the process. The same equipment was also used to obtain data for the thermodynamic modelling of high-pressure phase equilibrium in the system limonene + vegetable oil + CO₂, where limonene represents the essential oil extracted from seeds [10].

The aim of this study was to establish what the experiments with individual plants have in common, in order to obtain more general information on the extraction of essential oils, and also to demonstrate the importance of solute–matrix interaction in the SC–CO₂ extraction of essential oils.

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EXPERIMENTAL

Materials

Air dried peppermint (*Mentha x piperita* L.), creeping thyme (*Thymus serpyllum* L.) and sage (*Salvia officinalis* L.) herbs, yarrow (*Achillea millefolium* L.) flowers, and caraway (*Carum carvi* L.) seeds were used in the extraction experiments. The plant materials were ground or cut immediately before the extraction. The size of the particles obtained was determined using sieve analysis of the exhausted material after extraction. The purity of carbon dioxide purchased from Linde Technoplyn was higher than 99.9%.

Supercritical fluid extraction

The scheme of the extraction apparatus is shown in Figure 1. Carbon dioxide from a pressure bottle was pumped by a compressor (1) to the pressure regulator (2) controlling the outlet pressure to the value required for the extraction. The regulator was connected to an extractor (3) immersed in a water bath (4) maintained at constant temperature. The extractor was a cylindrical vessel of volume either 150 or 12 cm³ filled with the extracted plant material. The solution flowing out of the extractor was depressurised in a heated expansion valve (5). The extract was precipitated and collected in a glass trap (6) that was cooled in a bath (7) containing dry ice and ethanol. Gaseous carbon dioxide flowing through the trap was vented after passing a gas meter (8).

After filling the extractor with plant material and pressurising it with CO₂, the extractor was equilibrated for several minutes before the expansion valve was opened and the solution started flowing out of the extractor. The extraction conditions are listed in Table 1. Beside supercritical fluid, we also applied liquid CO₂ below 31.1°C. Three additional experiments with sage

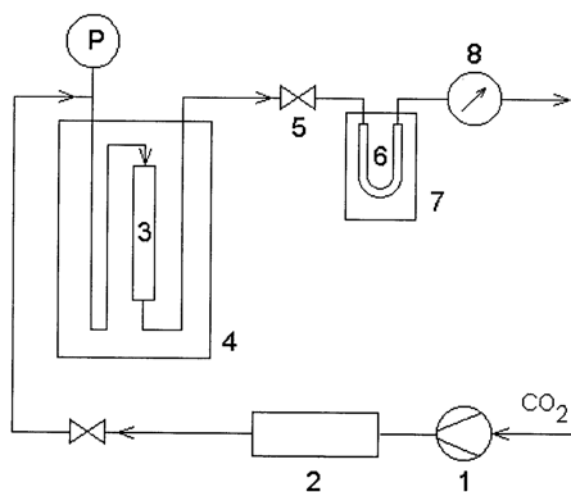


Figure 1. Scheme of the equipment for supercritical fluid extraction. (1) compressor of the high-pressure pump; (2) pressure regulator; (3) extractor; (4) water bath connected with a thermostat; (5) heated micrometer valve; (6) trap; (7) cooling bath; (8) gas meter

Table 1. Extraction conditions

Plant	Feed, g	Pressure, MPa	Temperature, °C	Flow rate, g/min
Peppermint herb	10–44	9–12	25–50	0.4–1.8
Creeping thyme herb	10–40	9–11	40–50	0.4–1.8
Sage herb	1–4	9–13	25–50	0.05–0.4
Yarrow flowers	25	10	40–60	0.6
Caraway seeds	25–75	9–10	23–40	1.8

oil extraction from 1 g of dry herb at 40°C and 10 MPa were performed with a different cold trap, a test tube filled with *n*-hexane. Two extract samples were collected in these experiments; the first sampling was finished after 2.1–3.6 g CO₂ had passed through the extractor and the second sampling at the end of the extraction run when a total of 18 g CO₂ had passed. The first sample was collected at a CO₂ flow rate as low as 0.05 g/min; then the flow rate was increased two or three times. Defined amounts of hexane had to be added to the trap during the extraction run as the level of solution in the trap decreased due to evaporation.

Measurement of the upper phase equilibrium concentration [10]

The dynamic solubility measurement was carried out at 40°C and 8–12 MPa using the equipment for supercritical fluid extraction. The extractor was filled with gravimetrically determined amounts of fatty oil (refined black currant oil) and limonene, which was chosen as a model compound for the essential oil that is extracted from seeds with supercritical CO₂. After pressurisation with CO₂, two equilibrium phases were formed; a lower phase containing the fatty oil, limonene and CO₂, and an upper phase rich in CO₂, also containing limonene and a negligible amount of the fatty oil. A very low SC-CO₂ flow rate from the bottom to the top of the extractor was applied, so the upper phase was slowly withdrawn and the phase equilibrium in the extractor was permanently renewed. The instantaneous limonene-to-CO₂ ratio in the upper phase was determined after the separation of limonene from CO₂ in the cold trap, and the limonene-to-fatty oil ratio in the extractor was calculated from the mass balance. The measurement was repeated as long as the limonene increase in the trap was measurable.

Other techniques

Hydrodistillation in an Unger type apparatus was applied to quantitatively extract pure essential oil from the plant. Gas chromatography was used to determine the composition of the essential obtained by SC-CO₂

extraction and hydrodistillation. Hexadecane was added to the samples as an internal standard. Four to five standards were available for each essential oil; the other components were identified tentatively according to their retention times. Each sample was dissolved in n-hexane to several concentrations and its analysis was repeated to check that the peak areas were directly proportional to the concentration. More details on the applied techniques are given elsewhere [5–7,9].

Thermodynamic modelling [10]

The measurement of the upper phase equilibrium composition, even though complemented with the calculated mean essential oil-to-fatty oil ratio in the extractor, did not yield enough information to understand the examined limonene + fatty oil + CO₂ equilibrium, as the data on the lower phase composition was missing. To obtain a complete picture of the system behaviour, we had to combine the experimental results with thermodynamic modelling of the phase equilibrium. The model was based on the Soave-Redlich-Kwong equation of state with the one fluid van der Waals mixing rule and, alternatively, with the MHV2 mixing rule. The fatty oil was modelled as triolein. In contrast to CO₂ and limonene, the critical parameters and acentric factor for a compound of such high molecular weight factor of triolein had to be theoretically estimated because this information is experimentally unattainable. The best prediction of the examined three-component equilibrium was obtained with the MHV2 mixing rule, revised to account for the large molecule of triolein, compared to the molecules of the other two components.

RESULTS AND DISCUSSION

Total extract

Figure 2 shows the extraction yield as a function of $q = Q/N$ for four herbs or flowers, where Q is the mass

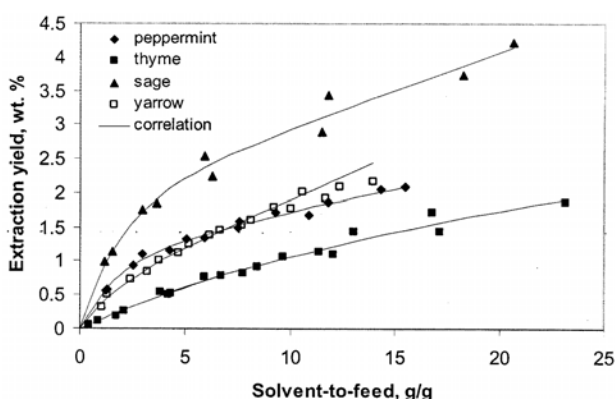


Figure 2. Total extract from peppermint, thyme and sage herbs and yarrow flowers. Extraction conditions: 10 MPa (9.5 MPa for thyme), 40 °C. Correlation: $e = e_1 [1 - \exp(-k_1q)] + k_2q$ where e is the extraction yield, g/g feed, and q is the solvent-to-feed ratio, g/g feed

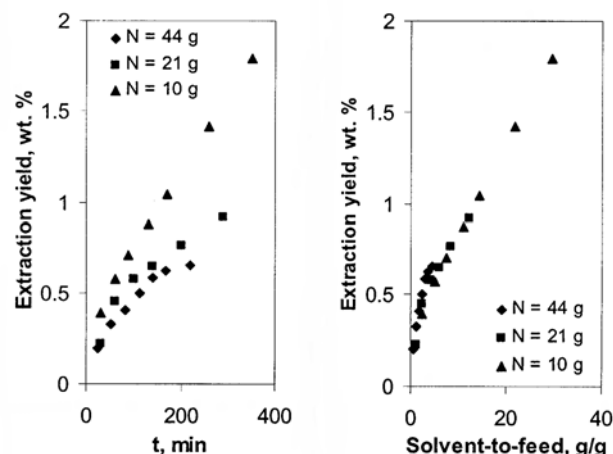


Figure 3. Extraction yield (extraction pressure 9 MPa, temperature 40 °C, CO₂ flow rate 0.9 g/min) for different feeds of peppermint herb, N , plotted against the extraction time and against the passed carbon dioxide-to-feed ratio. The overlapping curves in the second graph indicate the equilibrium-controlled regime in both extraction periods

of SC-CO₂ passed through the extractor and N is the mass of plant feed. Except for creeping thyme herb, two extraction periods were observed. Initially, the extract collected in the trap was similar to the essential oil obtained using hydrodistillation, with a negligible amount of co-extracted cuticular waxes and water. During the second extraction period, the rate of extraction decreased and the co-extracted substances dominated in the extract. The extracts from creeping thyme contained a large portion of cuticular waxes from the very beginning.

The two graphs in Figure 3 indicate whether the extraction of peppermint essential oil was controlled by equilibrium or mass transfer. Three extraction runs were carried out under the same extraction pressure, temperature and solvent flow rate, but for different plant feeds, which means for different solvent residence times in the extraction bed. The measured extraction yields are plotted first against the extraction time and then against the solvent-to-feed ratio q . If the extraction is controlled solely by mass transfer, the extraction curves would overlap in the first graph. If phase equilibrium is achieved at the extractor outlet, the curves would overlap in the second graph, as in this case. In this way we proved that the extraction was equilibrium-controlled for the four extracted herbs and flowers, which was enabled by the relatively high feed-to-solvent flow ratio, the excellent transport properties of the supercritical fluid, and the fact that almost all the essential oil in these plants is deposited on the surface of the leaves and petals, in the fragile glandular hairs. Another evidence of the negligible effect of mass transfer resistance was that the extraction curves for the finely ground yarrow flower and for the intact flowers were identical almost up to the end of the experimental runs.

When the data from the extraction of essential oil from ground caraway seeds [5] were plotted into such a pair of graphs, the extraction curves did not overlap in any of them. This implies that both phase equilibrium and mass transfer control the extraction; a large part of the essential oil is deposited inside the seed particles and oil diffusion to the particle surface is slow. To simulate the extraction curves for caraway essential oil we had to apply a complex mathematical model with a numerical solution, as described elsewhere [5].

In this paper we only discuss the extraction of solutes deposited mainly on the particle surface. Taking into account that the extraction yields were determined only by the phase equilibrium and solvent flow pattern in the extractor, we propose a semi-empirical model:

$$e = e_1 [1 - \exp(-k_1 q)] + k_2 q \quad (1)$$

where e is the extraction yield, q the solvent-to-feed ratio, and e_1 , k_1 and k_2 are the model parameters. If the condition $k_1 = N/M$ is fulfilled (M is the mass of solvent in the void space between the plant particles), the model simulates the extraction of two solutes deposited in a continuous-flow ideal mixer where mass transfer resistance in the solvent is negligible. The first solute of the yield e_1 is completely miscible with the solvent and the solubility of the second solute in the solvent is k_2 .

Tables 2 and 3 list the model parameters evaluated from the experiments with different plants and under different extraction conditions. The k_1 values do not show any trend and, except for thyme, fluctuate in the

Table 2. Parameters of Eq. (1) for the extraction yield from four plants extracted with CO₂ at 10 MPa (9.5 MPa for thyme) and 40 °C

Plant	Oil content ^a , g/g	e_1 , g/g	k_1 , g/g	k_2 , g/g
Peppermint herb	0.019	0.010	0.55	0.0007
Sage herb	0.027	0.018	0.51	0.0011
Yarrow flowers	0.0065	0.0053	0.56	0.0014
Creeping thyme herb	0.010	0.010	0.10	0.0004

^aThe initial essential oil content in the plants results from hydrodistillation

Table 3. Parameters of Eq. (1) for the extraction yield from peppermint herb: effect of extraction pressure and temperature

P , MPa	T , °C	d^a , g/cm ³	e_1 , g/g	k_1 , g/g	k_2 , g/g
9	25	0.800	0.0194	0.44	0.00043
9	40	0.487	0.0036	0.65	0.00048
9.5	40	0.581	0.0066	1.00	0.00058
10	40	0.630	0.0102	0.55	0.00070
11.9	50	0.580	0.0157	0.59	0.00054

^aCarbon dioxide density

range 0.44–1.0 g/g, not far from the expected values of N/M . Thus, interpretation of the data with the model mentioned above is possible. The first solute represents the more soluble essential oil components that are really completely miscible with CO₂ under the extraction conditions applied in this work (see e.g. limonene [10]), and possibly some other compounds completely miscible with CO₂ that are co-extracted with the essential oil. A part of the essential oil, however, is not dissolved immediately and forms the second solute together with cuticular wax and water.

The existence of two forms of essential oil in the plant, one completely miscible with CO₂ and the other only partially miscible, is explained by the essential oil-matrix interaction. According to the equilibrium relationship published by Perrut et al. [12,13], the solubility or more precisely the equilibrium fluid phase concentration, y^+ , depends on the solid phase concentration, x . At lower solid phase concentrations all of the solute interacts with the matrix and $y^+ = Kx$, where K is the partition coefficient. Above a certain solid phase concentration x_t corresponding to the matrix capacity for interaction, part of the solute remains free. Its equilibrium fluid phase concentration, equal to the solute solubility in the solvent, is not affected by the matrix, and is higher than that of the solute interacting with the matrix. Thus, the free essential oil represents the first solute that completely dissolves in CO₂ at the beginning of extraction and the essential oil interacting with the matrix is part of the second solute. If no fast extraction period is observed, as in our experiments with creeping thyme and in many essential oil extractions described in the literature, all of the essential oil is bound to the matrix from the very beginning. Then, the term containing e_1 and k_1 in Eq. (1) may be related to the essential oil interacting with the matrix and the second solute, characterised by k_2 , includes only cuticular wax and water.

According to Table 3, the dependence of parameters e_1 and k_2 in Eq. (1) on the extraction conditions is the same as the common dependence of solubility in supercritical and near-critical fluids, namely the values of both parameters increase with increasing solvent density and temperature. According to the model discussed above, the extraction pressure and temperature affect not only the equilibrium fluid phase concentration of the mixture extracted in the second extraction period, but also the matrix capacity for interaction with the essential oil to a large extent.

Solute-matrix interaction in seeds

Figure 4 shows part of the experimental data for the high pressure equilibrium of the limonene + fatty oil + CO₂ system and the thermodynamic modelling predictions. The measured limonene-to-fatty oil ratio in the upper phase is plotted against the mean limonene-to-fatty oil ratio in the extractor. The higher the

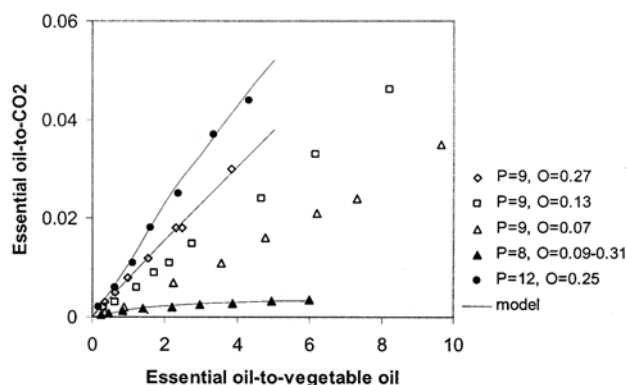


Figure 4. The equilibrium limonene-to- CO_2 mole ratio in the solvent phase as a function of the total limonene-to-vegetable oil mole ratio in the extractor at 40 °C. P is the pressure given in MPa and O is the amount of vegetable oil in the extractor, g. The limonene solubility in CO_2 at 8 MPa is 0.0032 (mole fraction); at 9 MPa and higher pressures limonene is fully miscible with CO_2 . The curve calculated using the thermodynamic model is shown for the experiments at 8 MPa, for the experiment at 10 MPa with 0.27 g of vegetable oil in the extractor and for the experiment at 12 MPa with 0.25 g of vegetable oil in the extractor

oil content in the extractor, the larger was the lower phase volume and the closer was the quantity plotted on the horizontal axis to the limonene-to-fatty oil ratio in the lower phase, which was information required to determine the limonene partition coefficient.

Table 4. Composition of the sage oil samples extracted with SC-CO_2 at different extraction conditions and the sage oil obtained using hydrodistillation (peak area, %)

Pressure, MPa	9	9–9.5	10–11	12–12.8	Hydro-distillate
Temperature, °C	25	40	40	50	
Compound					
α -Pinene	1.60	2.05	1.35	2.05	4.33
Camphene	2.80	3.41	2.48	3.59	7.57
β -Pinene	–	0.24	0.27	0.46	0.91
1-Octen-3-ol	–	0.30	0.42	0.56	0.85
γ -Terpinene	0.42	0.27	0.42	0.50	0.76
p-Cymene	1.34	1.81	1.48	1.68	2.69
1,8-Cineole	3.80	4.82	4.82	5.15	7.84
α -Thujone	19.28	23.26	19.26	19.92	25.00
β -Thujone	2.80	3.30	3.22	3.09	4.00
Camphor	21.03	24.26	21.82	22.50	23.99
Borneol	2.58	2.90	2.99	2.76	2.67
Terpinen-4-ol	–	0.27	0.41	0.44	0.38
Bornyl acetate	2.21	2.69	2.35	2.50	2.67
β -Caryophyllene	4.47	4.43	4.02	4.56	2.22
α -Humulene	5.21	4.76	4.79	4.99	2.79
Viridiflorol	7.33	5.05	6.31	5.79	6.29
Citronallyl propionate	1.05	0.52	0.80	0.77	0.81
Manool	16.85	11.97	15.09	12.11	4.03

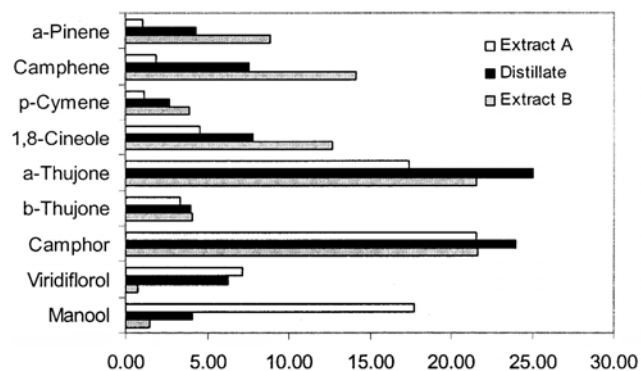


Figure 5. Composition of sage oil obtained using hydrodistillation (distillate) and sage oil extracted with SC-CO_2 at 10 MPa and 40 °C (extracts A, B). Extract A is the total extract collected in the cold trap, extract B is the extract collected into hexane in the cold trap during the first extraction period $q = 2.1\text{--}3.6$ g/g. The results are based on triplicate experiments

Thermodynamic modelling revealed a very close relationship between the three-component phase equilibrium and the phase behaviour of limonene + CO_2 . The critical pressure in the binary system at 40 °C is $P_c = 8.3$ MPa. When the limonene-to-fatty oil ratio increases in the ternary system at a pressure lower than the critical pressure, the equilibrium limonene-to- CO_2 ratio in the upper phase follows a bowed curve asymptotically approaching the limonene solubility in CO_2 measured in a binary system (see Figure 4, data for 8 MPa, limonene solubility in CO_2 equal to 0.0032 mole fraction). When the pressure is, however, higher than P_c , the partition coefficient for limonene between the upper and lower phase is almost constant for a wide range of limonene-to-fatty oil ratios. Though the partition coefficient monotonously increases with pressure, the largest increase is achieved near P_c . Therefore we recommend extracting essential oils from seeds at pressures close to $1.2P_c$, where P_c is the critical pressure of the oil in equilibrium with CO_2 , as any further increase in pressure would only slightly increase the essential oil partition coefficient, but would enhance the co-extraction of undesired compounds much more.

Essential oil composition and yield

The percentage of monoterpenes in essential oils extracted with CO_2 was lower than their percentage in hydrodistillates, and the percentage of less volatile sesqui- and diterpenes was higher, as indicated by gas chromatography. The results are illustrated on the example of sage oil. Table 4 shows the oil composition; the components are listed in order of increasing retention times, which is also the order of decreasing volatility. To check whether the lower content of highly volatile compounds in the CO_2 extracts is not caused by their incomplete collection in the cold trap, in additional experiments a cold trap filled with n-hexane was used similarly as in the supercritical extraction for analytical

Table 5. Recovery of the major sage oil components extracted with SC-CO₂ at different pressures and temperatures (% of the hydrodistillation yield)

Component	9 MPa	9–9.5 MPa	10–11 MPa	12–12.8 MPa	10 MPa
	25°C	40°C	40°C	50°C	40°C ^a
α-Pinene	15.75	28.79	18.48	37.94	88.05
Camphene	15.72	27.00	19.21	37.99	80.72
β-Pinene	–	12.69	16.95	39.69	54.68
1-Octen-3-ol	–	16.70	28.21	51.33	63.99
γ-Terpinene	23.15	16.90	32.33	51.32	65.49
p-Cymene	20.69	38.41	31.90	48.52	63.76
1,8-Cineole	20.42	36.95	36.11	51.71	76.54
α-Thujone	33.90	56.39	45.93	65.54	48.65
β-Thujone	29.74	49.21	47.09	61.30	59.99
Camphor	37.84	60.21	53.50	75.84	58.09
Borneol	49.97	76.25	71.70	97.62	64.79
Terpinen-4-ol	–	32.68	62.42	90.36	46.59
Bornyl acetate	34.53	56.19	51.41	72.67	35.11
β-Caryophyllene	84.94	115.05	105.40	158.90	70.37
α-Humulene	78.87	98.39	99.71	137.52	59.80
Viridiflorol	48.84	45.63	57.68	69.87	29.06
Citronallyl propionate	53.02	30.56	55.39	69.80	30.64
Manool	177.12	172.42	216.07	224.08	107.39

^aExtract collected in the cold trap with hexane

purposes. The first extract sample was collected to $q = 2.1\text{--}3.6$ g/g, which is after the first extraction period, and the second sample during the second extraction period to $q=18$ g/g. The percentage of highly volatile components in the samples collected in hexane in the first extraction period was much higher compared not only to the total extracts collected in the empty trap, but also to the hydrodistillate (see Figure 5), which indicates strong essential oil fractionation during the extraction process.

Finally, the extraction yields of the essential oil components were compared to their yields by hydrodistillation. In the first step, the areas of the chromatographic peaks of the essential oil components in each chromatogram were related to the peak area of the fixed amount of internal standard added to the sample and divided by the mass of sage herb from which the sample was extracted. The ratio of these quantities determined for a component in any two samples is equal to the ratio of the extraction yields of the component in these samples.

The calculated extract-to-hydrodistillate ratios for the individual components, expressed as the percentage of the hydrodistillation yield, are listed in Table 5. The cause of the low extraction yields of the highly volatile components is their inefficient collection in the trap, not the extraction itself. Even their collection

into hexane was not 100% efficient, as shown by the last column of the table. The collection efficiency was the better, the earlier the sample was taken. The larger the amount of gas that had passed through the trap, the more vapours of the volatile components escaped and, therefore, particularly their loss from the extracts collected in the second extraction period was large. Moreover, part of the extract was lost with hexane evaporating from the trap. Therefore, the recovery of α-pinene and camphene, which were extracted preferably in the first extraction period (the ratio of the amounts collected into hexane in the first and second sample was 80:20 for both of them), was close to 100 %, but the recoveries of the less soluble volatile compounds, which were extracted mostly in the second extraction period, in Table 5 decrease gradually even below their recovery in an empty trap.

The extraction conditions were most favourable at 12.8 MPa and 50 °C when the recovery of less volatile oxygenated monoterpenes, borneol and terpinen-4-ol, was almost 100 %, the recovery of sesquiterpenes was approximately 140–160%, and the recovery of diterpene manool was even more than 200%. The recovery of oxygenated low volatile terpenes viridiflorol and citronallyl propionate in the CO₂ extracts is, on the other hand, low. It is possible that their amount in hydrodistillate was increased by the hydrolysis of some terpenic hydrocarbons.

CONCLUSION

The extraction was controlled by phase equilibrium and the effect of mass transfer resistance on the extraction yield was negligible in the experiments performed with herbs and flowers. Two extraction periods were observed except for the extraction of creeping thyme herb. Eq. (1) was proposed to correlate the extraction yield with the solvent passed through the extractor. The extract collected in the first extraction period was almost pure essential oil, the extract collected in the second period contained waxes and water and a small amount of essential oil. The essential oil extraction in the second period was governed by the solute–matrix interaction and was, therefore, retarded.

The solute–matrix interaction during essential oil extraction from seeds has the form of essential oil partition between CO₂ and the vegetable oil that is present in all seeds. Based on the experimental data combined with thermodynamic modelling for the system limonene (representative of the essential oil) + black currant oil + CO₂, the optimum pressure for the extraction of essential oil from seed was found to be close to 1.2P_c, where P_c is the minimum pressure under which the essential oil and carbon dioxide oil are completely miscible at the given temperature.

GC analysis demonstrated large differences in the composition of the essential oil extracted from sage herb using hydrodistillation and supercritical extraction with

the extract collected in either an empty cold trap or a cold trap filled with hexane. Hexane substantially increased the collection efficiency for the more volatile monoterpenes, but it was less efficient for the higher terpenes. Essential oil fractionation was observed: all its components were extracted in both extraction periods, but the ratio of their recovery in the first extraction period to that in the second extraction period was the higher the more volatile the compound. Compared to hydrodistillation, the recovery of sesquiterpenes with SC-CO₂ was similar at optimum extraction conditions (12.8 MPa and 50°C) and the recovery of oxygenated diterpene manool was more than twofold.

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REFERENCES

- [1] E. Reverchon, Supercritical fluid extraction and fractionation of essential oils and related products, *J. Supercrit. Fluids* **10** (1997) 1–37
- [2] S.B. Hawthorne, Analytical-scale supercritical fluid extraction, *Anal. Chem.* **62** (1990) 633–642
- [3] S.B. Hawthorne, M.L. Riekolla, K. Serenius, Y. Holm, R. Hiltunen, K. Hartonen, Comparison of hydrodistillation and supercritical fluid extraction for the determination of essential oils in aromatic plants, *J. Chromatography* **634** (1993) 297–308
- [4] M. Goto, M. Sato, T. Hirose, Extraction of peppermint oil by supercritical carbon dioxide, *J. Chem. Eng. Japan* **26** (1993) 401–407
- [5] H. Sovová, R. Komers, J. Kuřera, J. Jeřábek, Supercritical carbon dioxide extraction of caraway essential oil, *Chem. Eng. Sci.* **49** (1994) 2499–2505
- [6] S. Aleksovski, H. Sovová, F.A. Poposka, S. Kulevanova, M. Ristic, Comparison of essential oils obtained from *Mentha piperita* L. using supercritical carbon dioxide extraction and hydrodistillation, *Acta Pharm.* **49** (1999) 51–57
- [7] S. Aleksovski, H. Sovová, F.A. Poposka, Extraction of thyme oil: comparison between hydrodistillation and supercritical CO₂ extraction, *Acta Pharm.* **51** (2001) 305–310
- [8] S. Aleksovski, H. Sovová, Supercritical CO₂ extraction of *Salvia officinalis* L. (to be published)
- [9] M. Bocevska, H. Sovová, Supercritical CO₂ extraction of essential oil from yarrow, *J. Supercrit. Fluids* (submitted)
- [10] H. Sovová, R.P. Stateva, A.A. Galushko, Essential oils from seeds: solubility of limonene in supercritical CO₂ and how it is affected by fatty oil, *J. Supercrit. Fluids* **20** (2001) 113–129
- [11] M. Perrut, J.Y. Clavier, M. Poletto, R. Reverchon, Mathematical modeling of sunflower seed extraction by supercritical CO₂, *Ind. Eng. Chem. Res.* **36** (1997) 430–435
- [12] H. Sovová, Mathematical model for supercritical fluid extraction of natural products and extraction curve evaluation, *J. Supercrit. Fluids* **33** (2005) 35–52

IZVOD

DOBIJANJE ETERIČNIH ULJA PRIMENOM NATKRITIČNIH FLUIDA – REZULTATI ZAJEDNIČKIH ISPITIVANJA

(Naučni rad)

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Ekstrakcija eteričnih ulja iz mente, majčine dušice (timija), žalfije kao i cveta hajdučke trave realizovana je primenom ugušćenog (natkritičnog) ugljen dioksida na 9–13 MPa i 25–60°C. U svim slučajevima primećeno je da postoje dve karakteristične faze tokom ekstrakcije: brza i spora ekstrakcija (izuzev kod majčine dušice). U prvoj brznoj fazi ekstrakcije ekstrahuju se praktično čista eterična ulja. U drugoj fazi pretežno se izdvajaju voskovi, a manje eterična ulja. Brzina spore faze ekstrakcije zavisi od jačine veze između matriksa i eteričnog ulja tj. mesta gde je ono locirano. U cilju definisanja interakcije između eteričnog ulja i biljnog materijala analizirana je ravnoteža između limonena, eteričnog ulja i ugljen dioksida korišćenjem odgovarajućih termodinamičkih modela. Promena sastava eteričnog ulja prikazana je na primeru ekstrakcije iz žalfije. U odnosu na sastave eteričnog ulja koje se dobija klasičnim postupkom hidrodestilacije, ekstrakt dobijen primenom ugušćenog ugljen dioksida sadrži manje monoterpena koje su najlakše isparljive komponente ulja. Ovo je najverovatnije posledica, pre svega, nepotpune separacije lakih frakcija ekstrakta i gasovitog ugljendioksida na niskoj temperaturi do koje dolazi nakon izvršene dekompresije smeše ugljovodonika i ugljen dioksida. Prinos seskviterpena i diterpena je veći kod eteričnih ulja dobijenih sa natkritičnim ugljen dioksidom u odnosu na ulja dobijena hidrodestilacijom. Ekstrakcija eteričnog ulja iz žalfije je najefikasnija na 13 MPa i 50°C, kada je utvrđena najveća koncentracija manol diterpena koja je više od dva puta veća nego u slučaju ulja dobijenog hidrodestilacijom.

Ključne reči: Eterična ulja, Natkritična ekstrakcija, Hidrodestilacija, Ugljen dioksid, Interakcija matriksa i ulja.