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INFLUENCE PRESSURE AND SIZE PARTICLE TO EXTRACTION BY CO_2

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ABSTRACT

Supercritical fluid extraction (SFE) is an efficient extraction technique for the separation of various organic compounds from herbs, or more generally, from plant materials. These proporties of SFE make the products more advantageous in the field of foods, pharmaceuticals, and cosmetics. The aim of this study was to investigate the effect of pressure and particle size on the extraction yield and the quality of the extracts.

KEYWORDS: supercritical extraction, carbon-dioxide, sage, solvent, size particle, extracts

1. Introduction

With increasing public interest in herbal medicine and natural products, the conventional methods such as hydro-distillation and solvent extraction were found unsatisfactory. To improve efficiency and selectivity of the extraction, alternative extraction techniques such as supercritical extraction started to be developed.

Supercritical extraction is not widely used yet, but as new technologies are coming there are more and more viewpoints that could justify it, as high purity, residual solvent content and environment protection [1, 2, 3]. Some of the advantages and disadvantages of extraction by supercritical fluids compared to extraction by conventional liquid solvents for separations are:

Advantages

- Dissolving power of the SCF (supercritical fluid) is controlled by pressure and/or temperature
- SCF is easily recoverable from the extract due to its volatility:
- Non-toxic solvents leave no harmful residue
- High boiling components are extracted at relatively low temperatures
- Separations not possible by more traditional processes can sometimes be effected
- Thermally labile compounds can be extracted with minimal damage as low temperatures can be employed during the extraction

Disadvantages

- Elevated pressure required
- Compression of solvent requires elaborate recycling measures to reduce energy costs
- High capital investment for equipment

The choice of the SFE (supercritical fluid extraction) solvent is similar to the regular extraction.

Principle considerations are the followings:

- Good solving property
- Inert to the product
- Easy separation from the product
- Cheap

Carbon dioxide is the most commonly used SCF, due primarily to its low critical parameters (31.1°C, 73.8 bar), low cost and non-toxicity.

Dependence pressure and density by temperature are shown in Fig. 1 and Fig. 2 [2].

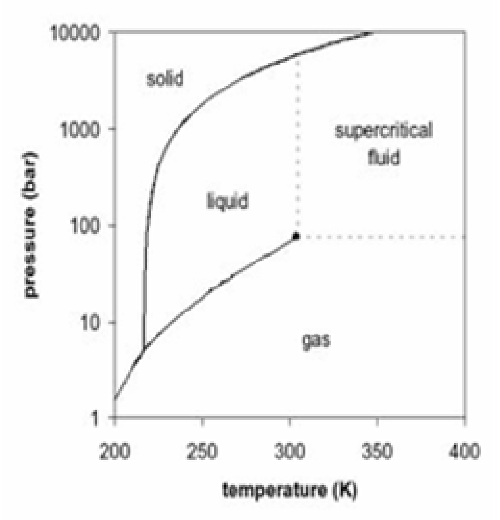

Fig. 1. *Carbon -dioxide pressure - temperature phase diagram*

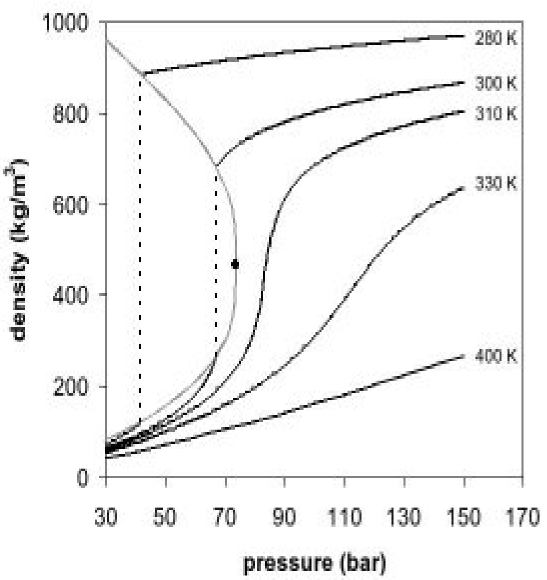

Fig. 2. *Carbon dioxide density-pressure phase diagram*

The special properties of supercritical fluids bring certain advantages to chemical separation processes. Several applications have been fully developed and commercialized.

SFE is applied in food and flavoring industry as the residual solvent could be easily removed from the product no matter whether it is the extract or the extracted matrix. The biggest application is the decoffeinization of tea and coffee. A process for removal of caffeine from coffee using supercritical carbon dioxide was patented in the United States in 1974, and a commercial plant went on stream in the FRG in 1978. Other important areas are the extraction of essential oils and aroma materials from spices. Brewery industry uses SFE for the extraction of hop. The method is used in extracting some edible oils and producing cholesterine-free egg powder. Consequence, supercritical CO2 extraction as an environmentally friendly and efficient extraction technique was studied and numerous research paper concerning extraction of different natural products have been published [4-9]. In this papers, the influence of particular size and pressure to SFE of Salvia officinalis L. was investigated.

2. Experiment

Plant Material

For this experiments *Salvia officinalis L.* from Berkovici, near Trebinje gathered in 2006 was used.

Chemicals

Commercial carbon dioxide (99% purity, Tehno–gas, Novi Sad, Serbia) as the extracting agent was used. All other chemicals were of analytical reagent grade.

Chromatographic procedures:

MS, Finnigan – MAT 8230 BE geometry, resolution 1000, EI – CIU source at 200º. EI 70 eV, 0.5 mA; CI, 1 mtorr of isobutane 150 eV 0.2 mA.

GC/MS, Varian 3400 GC equipped with Split/Splitless injector (1:99) operated at 244°. Column J&W Scientific DB-5ms-ITD 30m, 0.25mm id, *0.25μ*m film. Carrier gas hydrogen, 1 ml/min measured at 210°. Column temperature was linearly programmed from 40° to 285° at 4.3°/min. Transfer line at 270°, coupled to Finnigan-MAT 8230 BE mass spectrometer. Ion source temperature 170^O, EI, 70eV 0.1 mA. Scan range 33-333 / 1 sec.

GC, HP5890 series II 3400 GC equipped with Split/Splitless injector (1:99) operated at 244°. Column J&W Scientific DB-5ms-ITD 30m, 0.25mm id, *0.25μ*m film. Carrier gas hydrogen, 1 ml/min measured at 210°. Column temperature was linearly programmed from 40° to 285° at 4.3°/min.

Supercritical Fluid Extraction

SFE by CO_2 was carried out with a laboratory – scale high – pressure extraction plant (NOVA – Swiss, Effretikon, Switzerland). The main parts and characteristics (manufacturer specification) of the plant were as follows: a diaphragm – type compressor (up to 1000 bar), extractor with an internal volume of 200 mL (P_{max} = 250bar), and maximum CO_2 mass flow rate of approximately 5.7 kg/h.

The mass of Salvia sample in extractor was 60g at the investigated value of pressure and at 40ºC, and the CO_2 flow rate was 97.72 dm^3/h. Separator conditions were 15 bar and 25ºC.

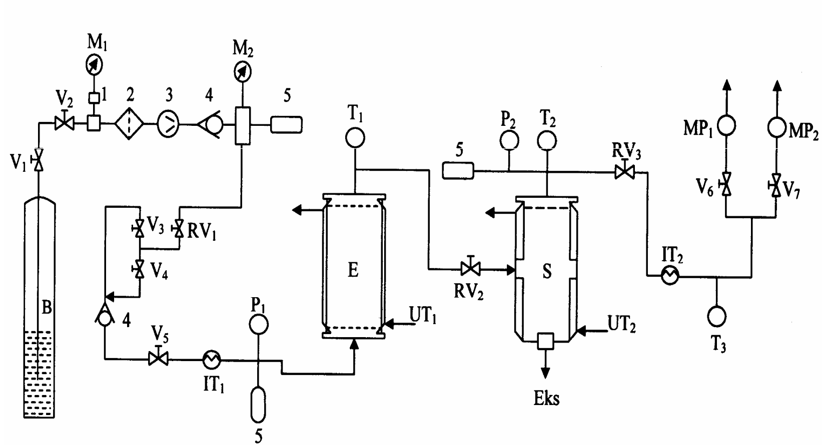

Fig. 3. *Laboratory scale high pressure SFE plant*

3. Results and Discussion

The supercritical fluid extraction (SFE) of *Salvia officinalis* L. by carbon dioxide (CO_2) was investigated. Firstly, supercritical extraction of *Salvia officinalis* L was performed at different particles size, all other extraction conditions were the same (Table 1).

Table 1. *Conditions for supercritical extraction by different particles size*

Sample	Particle diameter size (mm)	Extraction time (h)	Flow rate of carbon dioxide (kg/min)	Temperature (°C)	Pressure (bar)
F_1	0.21	4	$3.225 \cdot 10^{-3}$	40	100
F_2	0.43	4	$3.225 \cdot 10^{-3}$	40	100
F_3	1.13	4	$3.225 \cdot 10^{-3}$	40	100

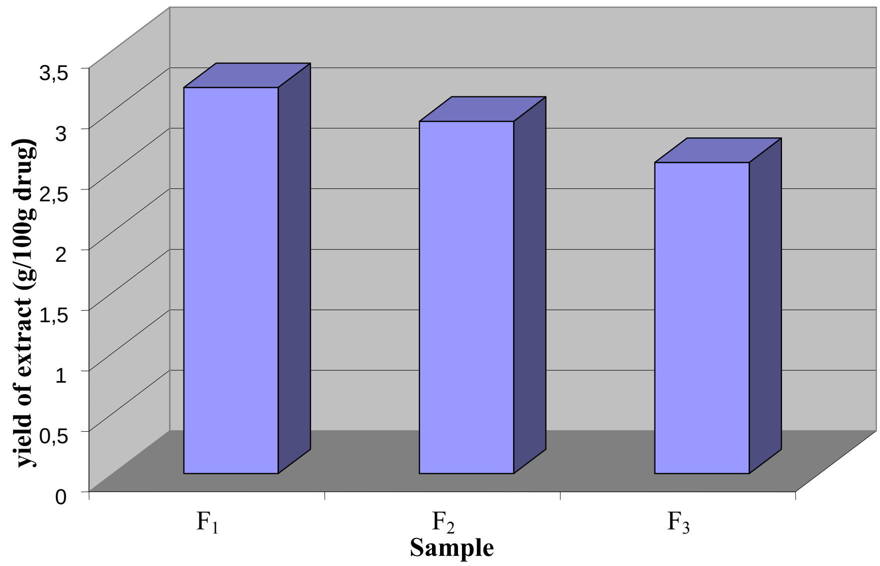

Fig. 4. *Yield of extract for different particles diameter size*

It was found that yield of extracts increases as particle diameter size decreases.

The relative contents identified compounds of SC-CO_2 extracts are given in table 2.

***Table 2**. Composition of Salvia extract for different particle size*

Number	R_t (min)	Compound	Sample			I_k
			F_1	F_2	F_3	
1	10.902	α – thujone (cis)	2.7013	0.5419	0.2741	1102.7
2	12.188	camphor	10.7024	-	-	1138.4
3	12.998	Isoborneol	9.6996	9.1258	6.2918	1162.8
4	13.274	Terpineol L-4	1.7389	1.2051	0.6254	1169.7
5	16.771	Bornyl acetate	4.3975	4.9818	2.0299	1268.1
6	16.828	Sabinyl acetate	2.7628	0.5966	-	1274.4
7	20.983	Isocaryophyllene	1.5904	1.7771	1.0393	1389.1
8	21.554	α - gurjunene	0.5673	0.5612	0.4568	1406.8
9	22.088	γ - elemene	11.3822	15.6045	9.8248	1424.9
10	26.156	Selina–3,7(11) diene	13.6412	20.4167	18.9666	1559.9
11	26.575	1,11-epoxyhumulene	3.9439	6.2998	5.7718	1573.1
12	27.221	Caryophyllene oxide	2.3676	3.2769	2.9539	1595.4
13	37.777	phyllocladene	21.6559	28.5225	38.8671	1995.1
total			87.2	92.9	87.1	

R_t = chromatographic retention time

In supercritical extract obtained for different particle size, 13 compounds were identified, with major compounds being: isoborneol, γ – elemene, Selina–3,7(11) diene and phyllocladene.

The higest persentage phyllocladene is in sample F_3 (38.87%), Selina–3,7(11) diene and β - elemene in sample F_2 (20.42%; 15.60%).

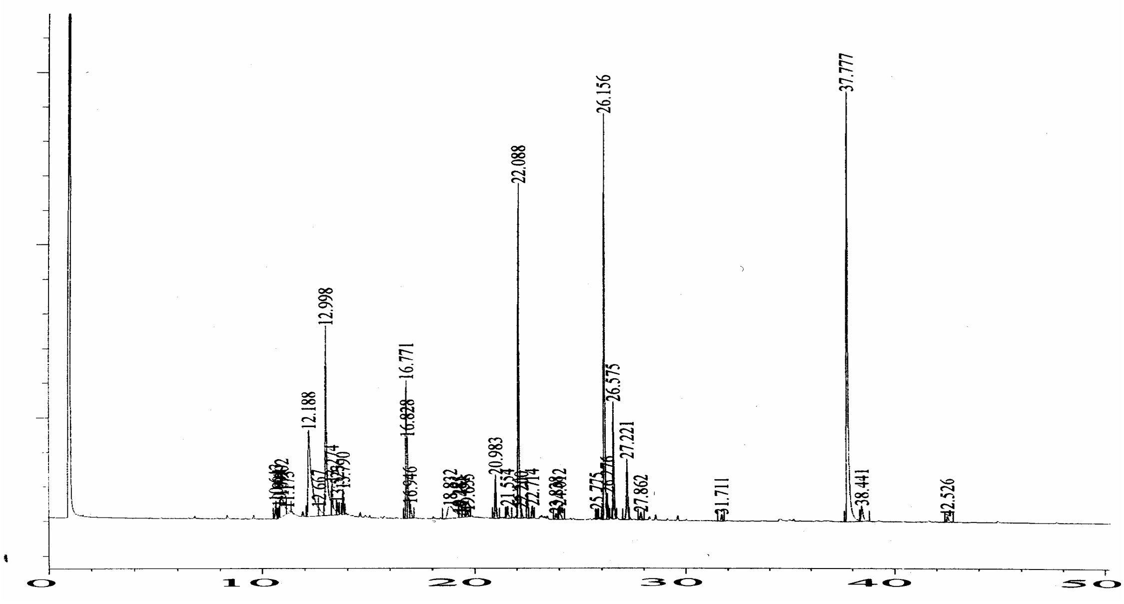

***Fig. 5.** GC chromatogram of Salvia extract (sample F_1)*

Figure 6 ilustrates the effects extraction time to yield of Salvia extract for different particle size.

Extraction rate rapidly increased in first 90 minute, and for farther extraction slowly increased.

Effect particle size to yield of extract is small. Now, SFE was performed at different pressure (80, 100, 150, 200 and 300 bar), all other extraction conditions were the same(Tabele 3).

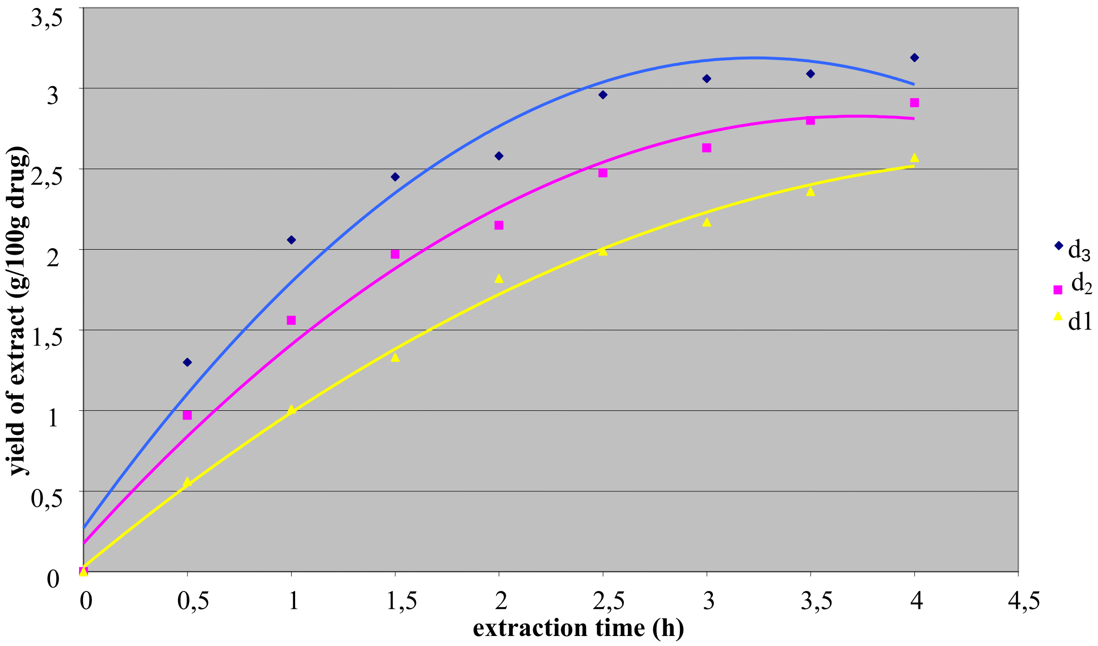

Fig. 6. *Yield of extract vs. extraction time for different particle size*

Table 3. *Conditions for supercritical extraction by different pressure*

Sample	Mean particle diameter (mm)	Extraction time (h)	CO_2 flow rate (kg/min)	Temperature (°C)	Pressure (bar)
F_4	0.3157	4	$3.225\cdot10^{-3}$	40	80
F_5	0.3157	4	$3.225\cdot10^{-3}$	40	100
F_6	0.3157	4	$3.225\cdot10^{-3}$	40	150
F_7	0.3157	4	$3.225\cdot10^{-3}$	40	200
F_8	0.3157	4	$3.225\cdot10^{-3}$	40	300

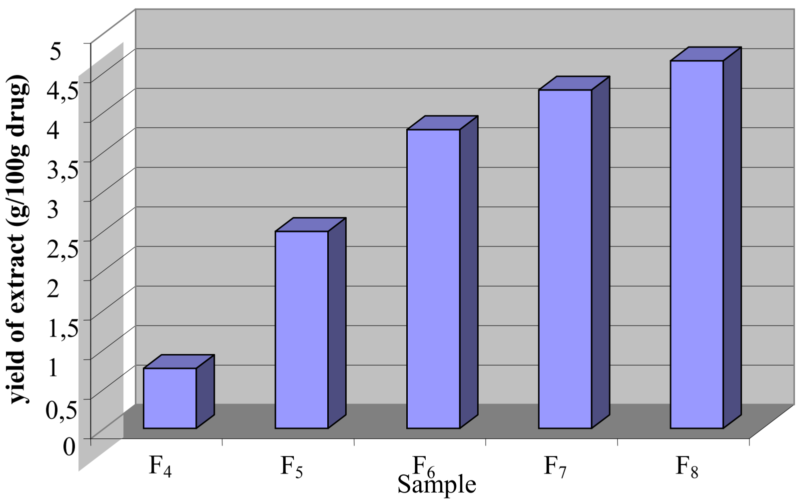

Fig. 7. *Yield of extract for different pressure values*

Table 4. *Composition of Salvia extract for different pressure*

Num.	R_t (min)	Compound	Sample				
			F_4	F_5	F_6	F_7	F_8
1	10.870	α – thujone	0.663	4.445	4.183	3.769	5.153
2	11.901	ß – thujone	-	-	0.1952	0.7016	-
3	12.175	Camphor	1.433	11.929	11.372	14.877	15.239
4	13.001	Isoborneol	11.287	7.389	6.804	9.523	8.167
5	13.214	Terpineol L-4	2.081	0.321	0.248	0.332	0.298
6	16.769	Bornyl acetate	5.905	3.586	2.015	4.621	3.959
7	16.946	Sabinyl acetate	1.053	0.534	0.406	0.643	0.421
8	20.979	Isocaryophyllene	2.745	1.179	0.839	1.300	1.168
9	21.549	α – gurjunene	1.448	0.544	0.439	0.621	0.549
10	22.085	γ – elemene	24.982	9.309	7.018	9.731	9.001
11	26.155	Selina-3,7 (11) diene	11.253	12.168	13.827	12.507	12.141
12	26.574	1,11-epoxyhumulene	8.989	4.557	5.869	4.958	4.921
13	27.220	caryophyllene oxide	2.755	2.662	2.640	2.390	2.456
14	37.783	Phyllocladene	10.420	26.056	30.645	21.990	24.603
Total			85.0	84.7	86.5	88.0	88.1

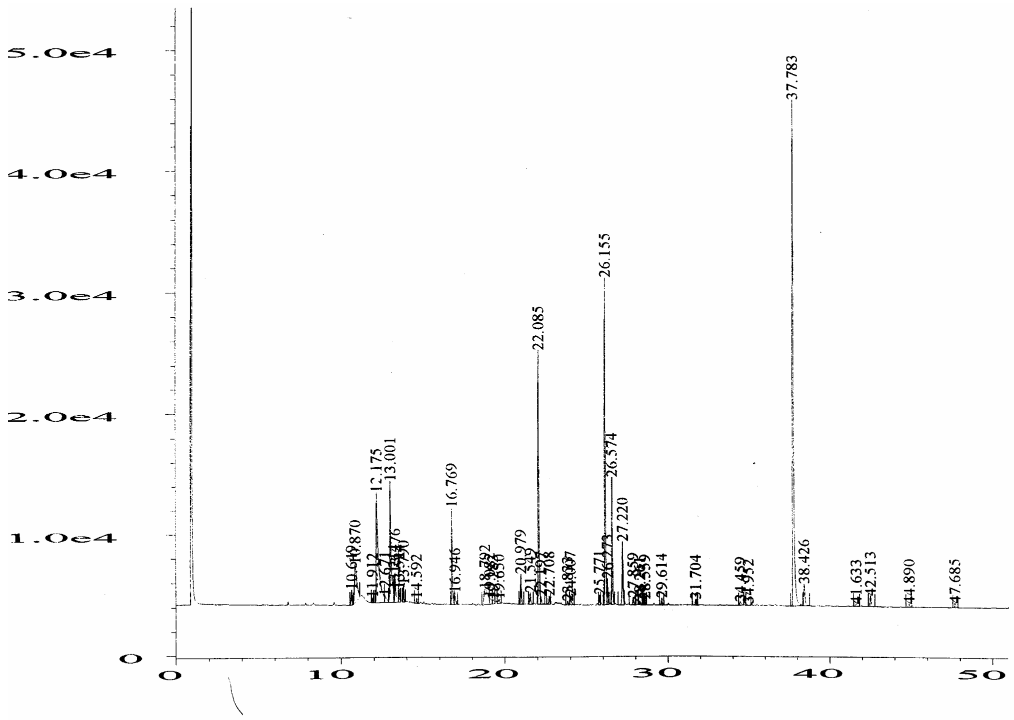

Fig. 8. GC chromatogram of Salvia extract (sample F_5)

Fig. 9 ilustrates the effects extraction time to yield of Salvia extract for different pressure. Extraction rate rapidly increased in the first 90 minutes, and for farther extraction slowly increased. Effect to yield of extract is more different for pressure p = 80bar from other pressure. In supercritical extract obtained for different pressure, 14 compounds were identified, with major compounds being: isoborneol, γ–elemene, Selina–3,7(11) diene and phyllocladene.The higest persentage phyllocladene (30.6%), and Selina–3,7(11) diene (13.8%) is in sample F_6 and γ - elemene in sample F_4 (24.98%).

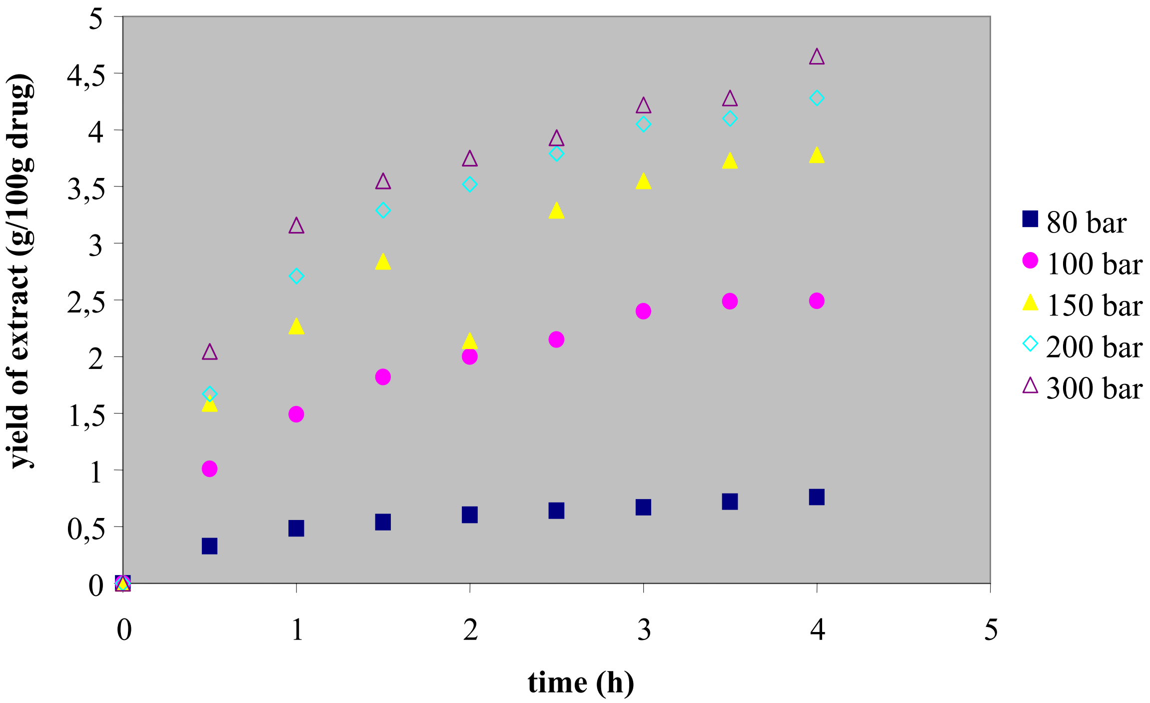

Fig. 9. *Yield of extract vs. extraction time for different pressure*

4. Conclusions

As expected from the studies on Salvia officinalis, the main compounds in extract are camphor, isoborneol, γ – elemene, selina – 3,7 (11) – diene and phyllocladene.The composition of main compounds in supercritical extract is not largely influenced by extraction pressure, exception pressure p=80bar. Indeed, chemical analysis of sage extract at different pressures evidenced composition variations along the extraction process but it they are not too large. The composition of main compounds in extract at pressure p=80 bar is largely different from composition at other pressures.

In the first 90 minutes of extraction, yield of extract rapidly increased, and for father extraction yield of extract slowly increased.

The five most abundant compounds (camphor, isoborneol, γ – elemene, selina – 3,7 (11) – diene, phyllocladene) represent 66.851 % of the extract (sample F_5).

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