

# Obtention of a Brewed Coffee Aroma Extract by an Optimized Supercritical CO<sub>2</sub>-Based Process

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Supercritical fluid extraction (SFE) was used to obtain brewed coffee extracts with an aroma as similar as possible to the original brewed coffee. The optimization of the process operating variables was performed by means of a sequential simplex method whose response was based on the sensorial evaluation of the aroma extracts. Subsequently, the composition of the extracts obtained at the optimal SFE conditions was determined by using a purge-and-trap device coupled to a GC-MS. For comparison, extracts obtained by using liquid–liquid extraction and headspace-solid-phase microextraction were also obtained and analyzed by GC-MS.

**Keywords:** *Supercritical fluid extraction; brewed coffee; aroma; simplex method*

## INTRODUCTION

Since aroma is one of the most appreciated attributes of coffee, the composition of the volatile fraction of roasted coffee has been intensively studied for years. Several hundreds of compounds have been reported since the late 1960s as constituents of coffee aroma (Stoll et al., 1967; Tressl and Silwar, 1981; Illy and Viani, 1995; Holscher and Steinhart, 1992). Recently, the character impact odorants of coffee brews have been studied (Semmelroch and Grosch, 1995; Semmelroch et al., 1995; Semmelroch and Grosch, 1996). Before these studies, few data had been published on aroma components of coffee brews.

Coffee aromas are products of high value for the present confectionery, bakery, alcoholic drinks, and soft drinks industries. Many procedures have been applied to obtain coffee aroma extracts. In all cases, the quality of the extracts is strongly dependent on the operating conditions. In general, the most natural and true tasting extracts from foods are obtained in conditions in which undesirable oxidative reactions or degradative heat processes have been avoided.

Supercritical fluid extraction (SFE) has been described as a technique that provides aroma extracts with a closer resemblance to the original material (King and Bott, 1993). Among the different supercritical fluids, CO<sub>2</sub> is the most used in the preparation of ingredients for flavorings and perfumes because it is a safe, non-combustible, odorless, tasteless, inexpensive, and readily available solvent. Also, most of the organoleptic volatile compounds have proven to be soluble in supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) at relatively low temperatures and without the need of temperature increase for solvent evaporation. This provides some advantages specifically related to the obtention of extracts free of off-notes, with more top notes and with a higher concentration of aromatics. Therefore, supercritical fluid extraction with

**Table 1. Operating Variables, Origin, Step Sizes, and Minimal and Maximal Values Included in the Simplex Optimization**

operating variables	origin	step size	minimal value	maximal value
density, <i>D</i> (g/mL)	0.5	0.3	0.25	0.85
flow rate, <i>F</i> (mL/min)	1	0.5	0.5	2
extraction time, <i>T</i> (min)	2	1	1	

CO<sub>2</sub> has been used for aroma extraction of different food products such as strawberries (Polesello et al., 1993), soy sauce (Shimoda et al., 1994), and spices (King and Bott, 1993; Bartley and Foley, 1994; Reverchon et al., 1992; Udaya Sankar, 1994), but only a few reports have been presented for coffee extraction (Brimmer, 1995) and none, to our knowledge, has been published about SC-CO<sub>2</sub> extraction applied to the recovery of aroma compounds from brewed coffee.

Supercritical fluid extraction processes involve an appreciable number of variables that should be handled simultaneously for the design of the operating conditions. Experimental designs have proven to be a useful tool for SFE process design and optimization (Lopez-Sebastian et al., 1997) with a moderate number of experimental runs. Among the different experimental design methods available, the sequential simplex method (Spendley et al., 1962) has been widely recognized as a very efficient empirical optimization procedure (Morgan and Deming, 1973; Åberg and Gustavsson, 1982; Beridge, 1986; Blanch et al., 1993).

The aim of the present investigation was to design at laboratory scale the SFE process conditions to obtain a natural brewed coffee aroma extract with sensorial attributes as similar as possible to those of the original brew. The main operating variables relative to CO<sub>2</sub> solvent strength and mass transfer were optimized by using a sequential simplex method. Since the simplex method can be applied by ranking the results obtained in the experimentation, a sensory evaluation of the supercritical CO<sub>2</sub> extracts of the brewed coffee was used as a response for the optimization procedure.

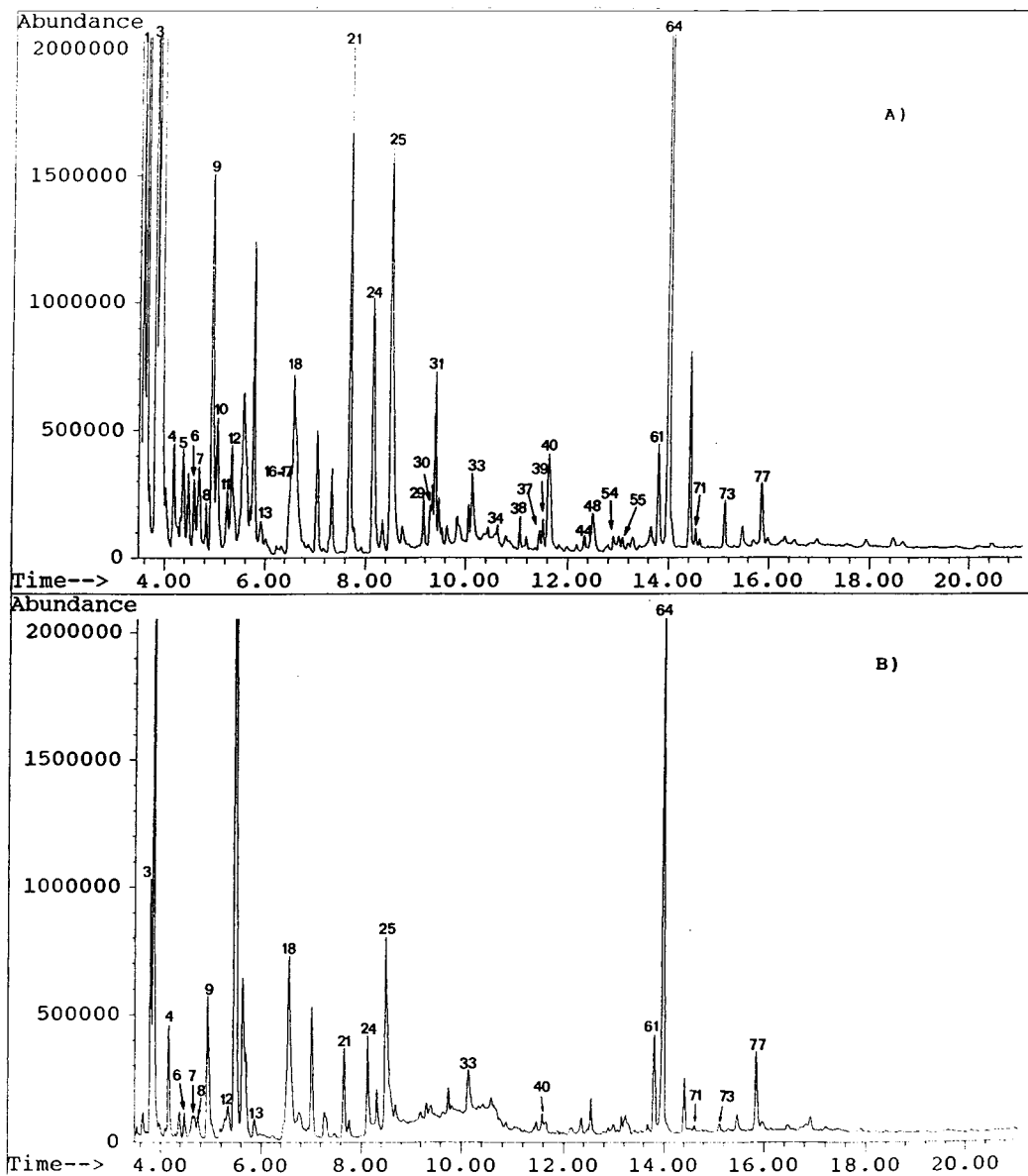
The composition of an extract of arabica brewed coffee obtained in the optimal conditions was studied. The

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**Figure 1.** Chromatograms obtained by analyzing extracts from supercritical fluid extraction at two different extracting conditions: (A) optimum ( $\text{CO}_2$  density, 0.5 g/mL;  $\text{CO}_2$  flow rate, 1.8 mL/min; extraction time, 1.4 min); (B) vertex 2 ( $\text{CO}_2$  density, 0.78 g/mL;  $\text{CO}_2$  flow rate, 1.1 mL/min; extraction time, 2.2 min). Identification: peak numbers as in Table 3.

temperature) to 180 °C at 15 °C min<sup>-1</sup>. The final temperature was maintained for 15 min.

Compounds were tentatively identified by mass spectrometry in SCAN mode by using a mass interval ranging 40–400. Their spectra were compared with those in a general-purpose library.

**Gas Chromatography–Mass Spectrometry Analysis of Extracts Obtained by Liquid–Liquid Extraction and HS–SPME.** One microliter of the extract obtained by liquid–liquid extraction with either pentane or methylene chloride was injected into a Hewlett-Packard model HP-5890 gas chromatograph equipped with a mass spectrometer detector model 5971A (EI, 70 eV). The column and chromatographic conditions used were as described previously. Injection was performed at 250 °C and with a split ratio of 1:20.

The poly(dimethylsiloxane) fiber used to perform the HS-SPME was thermally desorbed by heating the injector to 200 °C for 10 min (splitless). Chromatographic conditions used were as described.

## RESULTS AND DISCUSSION

**Optimization of the Supercritical Fluid Extraction Process.** The experiments were started by using

the modified simplex procedure proposed by Nelder and Mead (1965), but due to the expansions or contractions determined by this method, frequent comparisons had to be done among vertexes of different simplexes. This implied the test, and therefore new preparation, of old extracts. Furthermore, and since the needed extracts could not be known in advance, a second working session of the panelists was always required. All these practical drawbacks recommended changing from the modified simplex procedure to the basic simplex method, which only requires comparisons among vertexes of the same simplex. The change was carried out after vertex 11.

Experimental data set of simplex optimization is collected in Table 2. The first three columns show the experimental points (vertexes) included in each simplex. For instance, simplex 9 is composed by retained vertexes 6, 9, and 11 plus the new vertex 12. Columns 4, 5, and 6 give the experimental conditions of each vertex. The response columns contain the scores assigned by the sensory panel to the SFE extract corresponding to each

**Table 3. Compounds Identified in the Arabica Coffee Extracts Obtained by Using the Different Extraction Methods Described under Experimental Procedures [Normalized Areas (%)]**

peak	$t_r$	compd	pentane	CH <sub>2</sub> Cl <sub>2</sub>	HS-SPME	SFE
1	3.43	heptane, 2-methyl-	6.3			2.4
2	3.60	propanal				0.5
3	3.71	octane	13.3			9.5
4	4.13	3-octene				2.0
5	4.33	octane, 2-methyl-	1.6			1.8
6	4.59	furan, 2-methyl-				0.8
7	4.70	butanal				0.5
8	4.83	acetic acid, ethylester				0.6
9	4.95	nonane	5.2			5.9
10	5.10	2-butanone	0.6			1.6
11	5.24	butanal, 2-methyl-				0.6
12	5.33	butanal, 3-methyl-				1.9
13	5.91	3-buten-2-one				0.4
14	6.11	nonane, 2-methyl-	0.7			
15	6.32	nonane, 3-methyl-	0.1			
16	6.48	2-pentanone				0.2
17	6.52	pentanal				0.3
18	6.76	2,3-butanedione		0.9		5.7
19	7.00	decane	2.1			
20	7.78	2-butenal				0.2
21	7.96	benzene, methyl-	9.6	1.0		7.8
22	8.10	furan, 2,5-dihydro-				<0.1
23	8.33	disulfide, dimethyl-				0.5
24	8.44	2,3-pentanedione	0.7	0.9	0.7	5.7
25	8.49	hexanal				10.7
26	9.08	undecane	0.7			
27	9.33	2,3-pentanedione, 4-methyl-				0.3
28	9.52	1 <i>H</i> -pyrrole, 1-methyl-				0.2
29	9.68	benzene, ethyl-	0.9			0.8
30	9.83	benzene, 1,3-dimethyl-	1.0			0.3
31	9.95	benzene, 1,4-dimethyl-	4.0			1.8
32	10.00	1-butanol				<0.1
33	10.13	heptanal				1.2
34	10.62	furan, 2,3-dihydro,4-methyl-				0.2
35	10.73	benzene, 1,2-dimethyl-	1.2			0.3
36	11.22	pyrazine		0.4		
37	11.44	1-pentanol				0.2
38	11.58	furan, 2-(methoxymethyl)-		0.0		0.4
39	11.60	3-buten-1-ol, 3-methyl-		0.1		0.4
40	11.63	3(2 <i>H</i> )-furanone, dihydro-2-methyl-				2.6
41	11.80	octanal				1.0
42	12.04	pyrazine, methyl-	2.6	6.0	4.4	
43	12.31	2-butanone, 3-hydroxy-		1.4		
44	12.33	3-penten-2-ol				0.2
45	12.57	1-propanol, 2-methyl-		4.3		
46	12.68	2-propanone, 1-hydroxy			0.5	
47	12.70	5-hepten-2-one, 6-methyl-				<0.1
48	12.79	pyrazine, 2,5-dimethyl-	1.6	1.2	1.1	1.1
49	12.87	pyrazine, 2,6-dimethyl-	1.6	1.4	0.9	
50	12.95	pyrazine, ethyl-	0.9	0.5	0.4	
51	13.01	2-cyclopenten-1-one, 2-methyl-				0.2
52	13.11	pyrazine, 2,3-dimethyl-	0.4	0.7		
53	13.19	dodecane				0.1
54	13.43	nonanal			0.1	0.2
55	13.55	pyrazine, 2-ethyl-6-methyl-	1.0	0.2	1.9	0.2
56	13.63	pyrazine, 2-ethyl-5-methyl-	0.6	0.3	0.9	
57	13.78	pyrazine, trimethyl-	1.2	0.6	1.3	
58	13.87	2,5-furandione		0.3		
59	14.08	pyrazine, 2,6-diethyl-			0.1	
60	14.21	pyrazine, 2-ethyl-3,5-dimethyl-	0.5		0.2	
61	14.22	acetic acid		1.6	2.6	1.7
62	14.42	2-propanone, 1-(acetyloxy)-	0.9	7.3		
63	14.43	5,5-dimethyl-2-cyclopenten-1-one				3.1
64	14.55	furfural	2.9	5.7	2.1	23.4
65	14.62	benzaldehyde				0.1
66	14.69	3,5-diethyl-2-methylpyrazine			0.8	
67	14.80	furfuryl formate	0.4	0.2		
68	15.01	ethanone, 1-(2-furanyl)-	1.4	1.5	0.5	
69	15.06	2-butanone, 3,3-dimethyl-		0.3		
70	15.11	2-butanone, 1-(acetyloxy)-		0.1		
71	15.19	furfuryl alcohol, acetate	5.2	1.6	8.3	0.2
72	15.48	butanoic acid				0.5
73	15.78	furfural, 5-methyl-	8.8	5.7	5.2	0.8
74	15.98	ethanone, 1-phenyl				0.2
75	16.31	1 <i>H</i> -pyrrole-2-carboxaldehyde, 5-methyl-			0.2	

**Table 3 (Continued)**

peak	$t_r$	compd	pentane	CH <sub>2</sub> Cl <sub>2</sub>	HS-SPME	SFE
76	16.40	2-formyl-1-methylpyrrole	1.2	0.6		
77	16.52	furfuryl alcohol	3.8	41.1	6.9	1.2
78	16.61	2(3 <i>H</i> )-furanone, dihydro-		4.9		
79	16.72	ethanone, 1-(1-methyl-1 <i>H</i> -pyrrol-2-yl)-	0.4			
80	17.18	2-acetyl-3-methylpyrazine	0.4			
81	17.38	1-acetyl-3-methylpyrrole		0.6		
82	18.41	furfural,5-(hydroxymethyl)-	1.9			
83	18.71	hexanoic acid			6.0	
84	18.83	1 <i>H</i> -pyrrole, 1-(2-furanylmethyl)-			1.7	
85	18.84	2-cyclopenten-1-one, 2-hydroxy-3-methyl-		1.4		
86	18.87	<i>N</i> -furfuryl pyrrole	0.5			
87	19.36	benzoic acid, butyl ester			1.8	
88	19.41	phenol, 2-methoxy	1.2	0.7		
89	19.86	ethylcyclopentenolone(ethylcyclotene)		0.6		
90	20.52	heptanoic acid			1.5	
91	20.61	1-dodecanol			6.9	
92	21.57	ethanone, 1-(1 <i>H</i> -pyrrole-2-yl)-	1.5			
93	22.06	isopropyl myristate			4.3	
94	22.92	octanoic acid			17.9	
95	26.23	decanoic acid			13.8	
96	26.88	docosane	4.4			
97	28.30	ethanone, 1-(2-hydroxy-5-methylphenyl)-	6.5		7.2	
98	31.83	1,2-benzenedicarboxylic acid, bis(methylpropyl)ester		6.2		
99	37.53	1,2-benzenedicarboxylic acid, diethylester	0.8			

vertex. For instance, at simplex 9, vertexes 6, 9, 11, and 12 received the scores 0, 4, 6, and 5 respectively; therefore, vertex 11 must be rejected. These scores only are meaningful for comparisons between vertexes of the same simplex (i.e., in the same response subcolumn). So, the same vertex can have a different score in different simplexes.

At vertex 8, a boundary violation in the density is produced. According to the modified simplex rules (Nelder and Mead, 1965), the corresponding experiment was not run; instead, a new vertex was calculated by applying a negative contraction (contraction coefficient = -0.5). As previously explained, after vertex number 11, the basic simplex method was used.

At simplex 16, the panelists experienced some difficulty to distinguish among the aroma of the extracts as can be seen by the close scores obtained for vertexes 9, 16, 18, and 19. As a consequence, little or no improvement can be expected from this point and the simplex search was stopped. Vertexes 18 and 19 both attained the best qualification (3), but vertex 19 was finally selected as the optimum (density = 0.5 g/mL; CO<sub>2</sub> flow rate = 1.8 mL/min; extraction time = 1.4 min) because of its lesser CO<sub>2</sub> consumption and extraction time. At this point, 19 different extracts had been sensorially evaluated and the panelists agreed about the great similarity of the aroma of the four extracts of the last simplex with the genuine aroma of the freshly brewed coffee.

The chromatographic analysis revealed objective differences among the extracts obtained in the different conditions experimented in the optimization procedure. Figure 1 shows the chromatograms of the extracts obtained at conditions corresponding to vertex number 2 (CO<sub>2</sub> density, 0.78 g/mL; CO<sub>2</sub> flow rate, 1.1 mL/min; extraction time, 2.2 min) and to the optimum (CO<sub>2</sub> density, 0.5 g/mL; CO<sub>2</sub> flow rate, 1.8 mL/min; extraction time, 1.4 min). The differences between the two chromatographic profiles are essentially quantitative and demonstrate variations in the composition of the extracts that produce the modifications in the aroma appreciated by the panelists.

**Aroma Extracts Analysis.** Aroma extracts obtained by supercritical fluid extraction with CO<sub>2</sub> at the optimal

conditions were analyzed by using a purge-and-trap device coupled to a GC-MS. The obtained results were compared to those corresponding to liquid-liquid extraction with either pentane or methylene chloride and to headspace solid-phase microextraction procedures.

Table 3 shows the list of the compounds identified in the extract obtained by supercritical CO<sub>2</sub> extraction as well as those identified in the extracts mentioned above (L-L extraction and HS-SPME). All of them had been previously described by other authors as present in the coffee aroma. Some of the compounds identified in the present research (such as pyrazines or furan compounds and guaiacol) had been suggested by some authors as potent odorants of coffee brews (Semmelroch and Grosch, 1996). Obviously, the composition of the four extracts shown in Table 3 is different due to the different performance of the extraction methods, for example, HS-SPME with a poly(dimethylsiloxane) fiber has demonstrated a strong affinity for pyrazine compounds (Ibanez and Bernhard, 1996). Only the SC-CO<sub>2</sub> extract could be sensorially evaluated whose resemblance with the original aroma of the brewed coffee had been previously established during the optimization process. It was not possible to evaluate properly the liquid-liquid extracts since the olfactory test is interfered by the high amount of solvent in the sample; attempts to eliminate the residual solvent always produced coevaporation of the most volatile components and changes in aroma.

An appreciable content in hydrocarbons was detected in the supercritical fluid and pentane extracts. Tests were performed in order to check if their presence was due to the sample or to contamination. Blank analyses were assayed at the same conditions as described in Experimental Procedures for 75 mL of pentane concentrated to 1 mL by using a Vigreux column and for a supercritical fluid extract obtained at the same extracting conditions but with no coffee in the extraction cell. Both blank extracts, analyzed by GC-MS, showed no hydrocarbons; therefore, their presence cannot be due to contamination. These compounds do not contribute to the genuine coffee aroma, but they are present in the coffee probably due to the contact with storage or transportation materials, as it has already been suggested by some authors (Grob et al., 1991, 1992).

In conclusion, the SC-CO<sub>2</sub> extraction of brewed coffee in the optimized conditions provided aroma extracts with high olfactory resemblance to the original brewed coffee. The composition of the SC-CO<sub>2</sub> extract showed appreciable differences to those obtained by other techniques of isolation and concentration such as SPME and solvent extraction.

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