Obtention of a Brewed Coffee Aroma Extract by an Optimized Supercritical CO₂-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_2 is the most used in the preparation of ingredients for flavorings and perfumes because it is a safe, noncombustible, odorless, tasteless, inexpensive, and readily available solvent. Also, most of the organoleptic volatile compounds have proven to be soluble in supercritical CO_2 (SC- CO_2) 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, andMinimal and Maximal Values Included in the SimplexOptimization

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

 CO_2 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 $SC-CO_2$ 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; Berridge, 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_2 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_2 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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Table 2. Experimental Runs and Results of the Simplex Optimization

vertex	simplex	retained	ope	rating variabl	es								re	spon	se						
no.	no.	vertexes	D (g/mL)	F (mL/min)	$T(\min)$	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}
1			0.50	1.0	2.00	0	0	5													
2 3			0.78	1.1	2.20	10															
3			0.55	1.5	2.24	0	0	3	6												
4	1		0.55	1.1	2.94	0	10														
5	2	1, 3, 4	0.30	1.3	2.55		0	2	2		3	9									
6	3	1, 3, 5	0.35	1.4	1.58			0	2		1	2	4	0	4	3					
7	4	3, 5, 6	0.30	1.7	2.24				0		5										
8 ^a	5	5, 6, 7	0.08	1.4	2.01					BV											
9^b	6	5, 6, 7	0.45	1.5	2.18						6	0	0	4	0	0	6	1	1	3	5
10	7	5, 6, 9	0.40	1.0	1.96							4	5								
11	8	6, 9, 10	0.50	1.3	1.27								6	6							
12	9	6, 9, 11	0.45	1.8	1.39									5	9						
13	10	6, 9, 12	0.35	1.8	2.17										2	3	1	8			
14	11	6, 9, 13	0.30	1.3	2.56											9	7				
15	12	9, 13, 14	0.35	1.7	3.02												1	4	7		
16	13	9, 13, 15	0.45	1.9	2.35													2	3	4	4
17	14	9, 15, 16	0.50	1.6	2.87														4	8	
18	15	9, 16, 17	0.60	1.7	1.91															Õ	3
19	16	9, 16, 18	0.50	1.8	1.42															2	3

^{*a*} Boundary violation. ^{*b*} Negative contraction coefficient = -0.5.

constituents were tentatively identified by GC-MS and the extract composition compared to those obtained by other procedures such as solid-phase microextraction (HS-SPME) or solvent extraction.

EXPERIMENTAL PROCEDURES

Coffee. A commercial sample (100% Arabica coffee, roasted) was used to optimize the supercritical fluid extraction. Hot (92 \pm 2 °C) drinking water (1 L) was poured on the coffee powder (80 g) in a filter paper (Melitta, Lisbon, Portugal) yielding 0.9 L of the coffee brew (temperature 55 \pm 5 °C).

Supercritical Fluid Extraction. A Hewlett-Packard model 7680A supercritical fluid extractor equipped with a variable restrictor was used in the present study. The extraction cell utilized was a self-sealing 7 mL stainless steel thimble. Three milliliters of coffee, brewed as previously described, were the sample volume used throughout the study. To retain the brewed coffee, a supercritical CO_2 -washed cotton wool was used as a support and placed inside the extraction cell. Carbon dioxide (SFC grade, Liquid Carbonic, Madrid, Spain) was used as a superritical fluid. In all the experiments, extraction temperature was 60 °C, i.e., approximately the temperature at which the brewed coffee was obtained.

The aroma components of the brewed coffee extracted by the SC- CO_2 were collected at -25 °C in a piece of filter paper (approximately 0.06 g) placed in the chamber of a previously described assembly (Ibañez et al., 1997). The filter paper containing the brewed coffee aroma extract was sensorially evaluated by a panel of experts.

Liquid–**Liquid Extraction.** In a separation funnel, the brewed coffee (75 mL) was extracted either with methylene chloride or with pentane (75 mL) for 8 h at room temperature. The organic layer was separated and then concentrated to a volume of 1 mL by distilling off the solvent on a Vigreux column (2.5 cm i.d. \times 50 cm length) at 40 °C.

Headspace-Solid-Phase Microextraction. A solid-phase microextraction syringe (Supelco, Bellefonte, PA) was used to extract the headspace of a coffee brew. The procedure used had been previously described (Ibañez and Bernhard, 1995) for pyrazine extraction. Three milliliters of coffee brew was placed in a vial (20 mL) closed with Parafilm, the fiber (poly-(dimethylsiloxane), 100 μ m) was introduced, and the headspace was sampled for 10 min at 60 °C, the temperature at which the brewed coffee was obtained.

Simplex Optimization. The sequential simplex method (Spendley et al., 1962) is based on an initial set of k + 1 trials for k variables. These k + 1 trials are the vertexes of a geometric figure, called simplex, in a k-dimensional space.

Once all the experimental runs in a simplex have been performed, the obtained results (responses) are compared. The vertex corresponding to the worst response is rejected and replaced by its symmetric with respect to either the line (two variables), face (three variables), or hyperplane (more than three variables) formed by the retained vertexes. The new simplex is then formed by the retained vertexes plus the new vertex. By using this optimization procedure, the system moves toward the most favorable conditions and empirically searches for the best levels of the control variables. The optimization process ends when the response cannot be improved further or when the researcher decides that enough improvement has been achieved.

Nelder and Mead (1965) proposed a modification of the above-described basic simplex method. The modified simplex method can adjust its shape and size to provide for accelerated or decelerated progress depending of the response in each step.

Table 1 shows the experimental variables included in the optimization search, their origins (i.e., the values corresponding to the first experimental run; CO_2 density, 0.5 g/mL; CO_2 flow rate, 1 mL/min; and extraction time, 2 min), and their step sizes (i.e., a measure of the extent of change of each variable). Also, in Table 1, the minimal and maximal values of each variable are shown. These values are boundaries beyond which the experimental domain must not be extended.

The response used to evaluate the quality of the SF extracts was the resemblance of their aroma with that of a freshly brewed coffee cup based on a human olfaction test. Five expert panelists judged the similarity of the aromas. To reject the aroma extracts which were most different in comparison to the freshly brewed coffee extract, each panelist assigned 2 points to the worst extract and 1 point to the second worse extract; therefore, the optimization procedure was to minimize the score of the panelists.

Purge-and-Trap-Gas Chromatography–Mass Spectrometry Analysis. The piece of filter paper containing the optimized aroma coffee extract was analyzed in a Hewlett-Packard HP purge-and-trap concentrator model 7695. Compounds purged from the sample (helium flow rate through the sample = 35 mL/min; purge time = 15 min; sample preheat temperature = 100 °C) were retained in a trap packed with Carbopack B/Carbosieve S-III (Supelco, Bellefonte, PA) at room temperature. After purging, desorption was carried out by heating the trap at 220 °C for 5 min and the compounds were cryofocused at -100 °C at the beginning of the chromatographic column.

To perform the analysis of the extracts, a Hewlett-Packard model HP-5890 gas chromatograph with a mass spectrometer detector model 5971A (EI 70 eV) and a 50 m \times 220 μ m i.d. BP-20 [poly(ethylene glycol), MW = 20 000] ($d_{\rm f}$ = 0.20 μ M) fused silica capillary column (SGE, Victoria, Australia) was used. Injection was carried out by thermal desorption at 200 °C for 2 min. Helium was the carrier gas (10 psi). The oven temperature was programmed from 40 °C (5 min constant

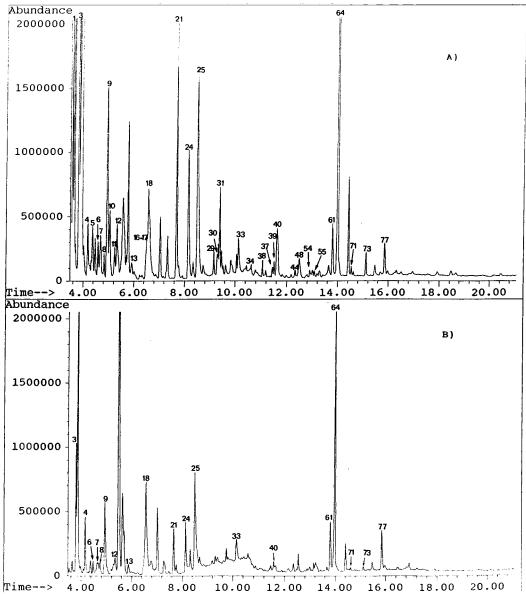


Figure 1. Chromatograms obtained by analyzing extracts from supercritical fluid extraction at two different extracting conditions: (A) optimum (CO₂ density, 0.5 g/mL; CO₂ flow rate, 1.8 mL/min; extraction time, 1.4 min); (B) vertex 2 (CO₂ density, 0.78 g/mL; CO₂ flow rate, 1.1 mL/min; extraction time, 2.2 min). Identification: peak numbers as in Table 3.

temperature) to 180 $^\circ C$ at 15 $^\circ C$ min^-1. 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 an 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	$t_{ m r}$	compd	pentane	CH_2Cl_2	HS-SPME	SFE
1	3.43	heptane, 2-methyl-	6.3			2.4
2	3.60	propanal	10.0			0.5
3	3.71	octane	13.3			9.5
4	4.13	3-octene	1.0			2.0
5 6	4.33 4.59	octane, 2-methyl- furan, 2-methyl-	1.6			1.8 0.8
7	4.39	butanal				0.5
8	4.83	acetic acid, ethylester				0.6
9	4.05	nonane	5.2			5.9
10	5.10	2-butanone	0.6			1.0
11	5.24	butanal, 2-methyl-				0.
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.
17	6.52	pentanal				0.
18	6.76	2,3-butanedione	0.1	0.9		5.
19	7.00	decane	2.1			0
20	7.78	2-butenal	0.6	1.0		0.
21	7.96	benzene, methyl- furan 2.5 dibudra	9.6	1.0		7. <0.
22 23	8.10 8.33	furan, 2,5-dihydro- disulfide, dimethyl-				<0. 0.
23 24	8.44	2,3-pentanedione	0.7	0.9	0.7	0. 5.
24 25	8.44 8.49	hexanal	0.7	0.9	0.7	5. 10.
25 26	8.49 9.08	undecane	0.7			10.
20 27	9.08	2,3-pentanedione, 4-methyl-	0.7			0.
28	9.52	1 <i>H</i> -pyrrole, 1-methyl-				0.
29	9.68	benzene, ethyl-	0.9			0.
30	9.83	benzene, 1,3-dimethyl-	1.0			0.
31	9.95	benzene, 1,4-dimethyl-	4.0			1.
32	10.00	1-butanol				<0.
33	10.13	heptanal				1.
34	10.62	furan, 2,3-dihydro,4-methyl-				0.
35	10.73	benzene, 1,2-dimethyl-	1.2			0.
36	11.22	pyrazine		0.4		
37	11.44	1-pentanol				0.
38	11.58	furan, 2-(methoxymethyl)-		0.0		0.
39	11.60	3-buten-1-ol, 3-methyl-		0.1		0.
40	11.63	3(2 <i>H</i>)-furanone, dihydro-2-methyl-				2.
41	11.80	octanal	0.0	0.0		1.
42	12.04	pyrazine, methyl-	2.6	6.0	4.4	
43	12.31	2-butanone, 3-hydroxy-		1.4		0
44 45	12.33	3-penten-2-ol		4.3		0.
45 46	12.57 12.68	1-propanol, 2-methyl- 2-propanone, 1-hydroxy		4.3	0.5	
40 47	12.08	5-hepten-2-one, 6-methyl-			0.5	<0.
47	12.70	pyrazine, 2,5-dimethyl-	1.6	1.2	1.1	<0. 1.
49	12.75	pyrazine, 2,6-dimethyl-	1.6	1.2	0.9	1.
50	12.95	pyrazine, ethyl-	0.9	0.5	0.4	
51	13.01	2-cyclopenten-1-one, 2-methyl-	0.0	0.0	0.1	0.
52	13.11	pyrazine, 2,3-dimethyl-	0.4	0.7		0.
53	13.19	dodecane	5.1			0.
54	13.43	nonanal			0.1	0.
55	13.55	pyrazine, 2-ethyl-6-methyl-	1.0	0.2	1.9	0.
56	13.63	pyrazine, 2-ethyl-5-methyl-	0.6	0.3	0.9	51
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.
62	14.42	2-propanone, 1-(acetyloxy)-	0.9	7.3		
63	14.43	5,5-dimethyl-2-cyclopenten-1-one				3.
64	14.55	furfural	2.9	5.7	2.1	23.
65	14.62	benzaldehyde			a -	0.
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.
72	15.48	butanoic acid	<u> </u>	~ ~	F 0	0.
73	15.78	furfural, 5-methyl-	8.8	5.7	5.2	0.8
~ 4	15.98	ethanone, 1-phenyl				0.3
74 75	16.31	1 <i>H</i> -pyrrole-2-carboxaldehyde, 5-methyl-			0.2	

Table 3 (Continued)

peak	$t_{ m r}$	compd	pentane	CH_2Cl_2	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-1H-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 $\hat{8}$, 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; CO₂ flow rate = 1.8 mL/min; extraction time = 1.4 min) because of its lesser CO₂ 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 (CO₂ density, 0.78 g/mL; CO₂ flow rate, 1.1 mL/min; extraction time, 2.2 min) and to the optimum (CO₂ density, 0.5 g/mL; CO₂ 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 CO₂ 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 CO₂ 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 (Ibañez and Bernhard, 1996). Only the $SC-CO_2$ 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 $SC-CO_2$ extraction of brewed coffee in the optimized conditions provided aroma extracts with high olfactory resemblance to the original brewed coffee. The composition of the $SC-CO_2$ extract showed appreciable differences to those obtained by other techniques of isolation and concentration such as SPME and solvent extraction.

LITERATURE CITED

- Åberg, E. R.; Gustavsson, A. G. T. Design and evaluation of modified simplex methods. *Anal. Chim. Acta* **1982**, *144*, 39– 53.
- Bartley, J. P.; Foley, P. Supercritical fluid extraction of australian-grown ginger (zingiber officinale). *J. Sci. Food Agric.* **1994**, *66*, 365–371.
- Berridge, J. C. Automated Optimization in High-Performance Liquid Chromatography. *Anal. Chim. Acta* **1986**, *191*, 243– 259.
- Blanch, G. P.; Herraiz, M.; Reglero, G.; Tabera, J. Preconcentration of samples by steam distillation–solvent extraction at low temperature. J. Chromatogr. 1993, 655, 141–149.
- Brimmer, J. Process for extraction of coffee oil containing aroma constituents. German Federal Republic Patent Application 1995 (DE4335321A1).
- Grob, K.; Lanfranchi, M.; Egli, J.; Artho, A. Determination of food contamination by mineral oil from jute sacks using coupled LC-GC. J. AOAC Int. **1991**, 74 (3), 506–512.
- Grob, K.; Artho, A.; Biedermann, M.; Caramaschi, A.; Mikle, H. Batching oils on sisal bags used for packaging foods: analysis by coupled LC/GC. *J. AOAC Int.* **1992**, *75* (2), 283– 287.
- Holscher, W.; Steinhart, H. Investigation of roasted coffee freshness with an improved headspace technique. *Z. Lebensm. Unters. Forsch.* **1992**, *195*, 33–38.
- Ibañez, E.; Bernhard, R. A. Solid-Phase Microextraction (SPME) of pyrazines in model reaction systems. *J. Sci. Food Agric.* **1996**, *72*, 91–96.
- Ibañez, E.; Lopez-Sebastian, S.; Ramos, E.; Tabera, J.; Reglero, G. Analysis of highly volatile components of foods by offline SFE/GC. J. Agric. Food Chem. 1997, 45, 3940–3943.
- Illy, A.; Viani, R. *Espresso Coffee. The Chemistry of Quality;* Academic Press: London, U.K., 1995.
- King, M. B.; Bott, T. R. Extraction of natural products using near-critical solvents; Blackie Academic & Professional: Glasgow, U.K., 1993.
- López-Sebastián, S.; Ramos, E. Ibañez, E.; Bueno, J. M.; Ballester, L.; Tabera, J.; Reglero, G. Dearomatization of

antioxidant rosemary extracts by treatment with supercritical carbon dioxide. *J. Agric. Food Chem.* **1998**, *46*, 13– 19.

- Morgan, S. L.; Deming, S. N. Simplex Optimization of Analytical Chemical Methods. *Anal. Chem.* **1974**, *46* (9), 1170– 1181.
- Nelder, J. A.; Mead, R. A simplex method for function minimization. *Comput. J.* **1965**, *7*, 308–313.
- Polesello, S.; Lovati, F.; Rizzolo, A.; Rovida, C. Supercritical fluid extraction as a preparative tool for strawberry aroma analysis. J. High Resolut. Chromatogr. 1993, 16, 555–559.
- Reverchon, E.; Donsi, G.; Pota, F. Extraction of essential oil uisng supercritical CO2: effect of some process and preprocess parameters. *Ital. J. Food Sci.* **1992**, *3*, 187–194.
- Semmelroch, P.; Grosch, W. Analysis of roasted coffee powders and brews by gas chromatography-olfactometry of headspace samples. *Lebensm.-Wiss. Technol.* **1995**, *28*, 310–313.
- Semmelroch, P.; Grosch, W. Studies on character impact odorants in coffee brews. J. Agric. Food Chem. 1996, 44, 537-543.
- Semmelroch, P.; Laskawy, G.; Blank, I.; Grosch, W. Determination of potent odourants in roasted coffee by stable isotope dilution assays. *Flavour Fragance J.* **1995**, *10*, 1–7.
- Shimoda, M.; Ishikawa, H.; Kawano, T.; Osajima, Y. Extraction of volatile compounds from aqueous solution using micro bubble, gaseous, supercritical and liquid carbon dioxide. J. Food Sci. 1994, 59, 231–233.
- Spendley, W.; Hext, G. R.; Himsworth, F. R. Sequential application of simplex designs in optimisation and evolutionary operation. *Technometrics* **1962**, *4*, 441–461.
- Stoll, M.; Winter, M.; Gautschi, F.; Flament, I.; Willhalm, B. Research in aromas of coffee I. *Helv. Chim. Acta* **1967**, *50*, 628–694.
- Tressl, R.; Silwar, R. Investigation of sulfur-containing components in roasted coffee. J. Agric. Food Chem. 1981, 29, 1078–1082.
- Udaya Sankar, K. Supercritical fluid CO2 technology for extraction of spices and other high value bio-active compounds. In *Supercritical Fluid Processing of Food and Biomaterials;* Rizvi, S. S. H., Ed.; Blackie Academic & Professional: Glasgow, U.K., 1994.

Received for review January 5, 1998. Revised manuscript received June 1, 1998. Accepted August 12, 1998.

JF9800155