

# Countercurrent Supercritical Fluid Extraction and Fractionation of Alcoholic Beverages

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A procedure for the recovery of aromatic extracts from distilled alcoholic beverages by means of a countercurrent supercritical fluid extraction (CC-SFE) on a pilot plant scale is studied. The beverage is directly in contact with the carbon dioxide current in a packed column, and the extracts are recovered in two different fractionation cells, where the depressurization occurs. The proposed method allows the selective extraction of aromatic components of the brandy flavor, rendering a high-value concentrated extract and a colored residue without brandy aroma. The content in ethanol of the aromatic extract can be modified by tuning the extraction/fractionation conditions, rendering from 15 to 95% recovery. The effect of the main variables, including extraction pressure and quality of extracting CO<sub>2</sub>, has been tested.

**Keywords:** *Countercurrent SFE; fractionation; alcoholic beverages; brandy*

## INTRODUCTION

The flavor of an alcoholic beverage is formed by a great number of different substances, including esters, aldehydes, ketones, higher alcohols, terpenes, lactones, etc. (1). The recovery of the aroma of beverages is of great commercial interest for the industry, and several techniques have been developed for this task, including distillation, pervaporation, adsorption, and supercritical fluid extraction (SFE) (2). The use of SFE has distinct advantages because of its variable selectivity, lack of toxic solvents, and ability to produce aromatic extracts of greater quality in shorter times (3).

SFE has been employed in the dealcoholization of alcoholic beverages, with several patent applications and references in the bibliography, covering wine (4) beer (5), and cider (6).

However, the extraction of the aromatic fraction of alcoholic drinks with supercritical CO<sub>2</sub> has been scarcely studied, and it has been applied to concentrates previously obtained by vacuum distillation of wine or beer (7). Vacuum evaporation has been employed to separate a fraction with the aroma substances from high-alcohol beverages and, subsequently, to extract the aroma from the distillate (8), with the goal of obtaining low-alcohol drinks, resulting in a slow and tedious process during which losses of volatile compounds occur. Other patent applications use SFE to obtain aroma from alcoholic beverages but without using a packed column for countercurrent extraction (9, 10). Therefore, the extraction efficiency was lower due to the smaller contact area between the drink and the CO<sub>2</sub> (extracting agent).

The present study describes a new procedure for the obtention of aromatic extracts from distilled alcoholic drinks by means of a countercurrent SFE in a pilot scale plant. The beverage is directly in contact with the carbon dioxide in a packed column, and the extracts are

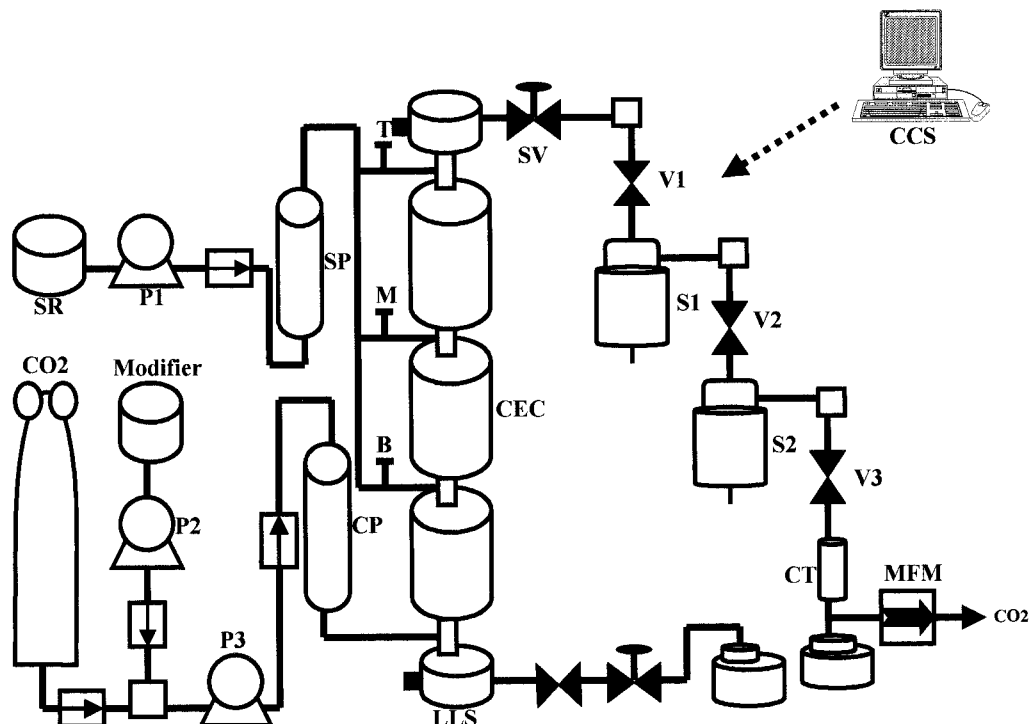
recovered in two different fractionation cells, where the depressurization occurs. Each fraction has a composition that can be modified depending on the operation conditions of the experiment. The effect of the main variables, including extraction pressure and quality of extracting CO<sub>2</sub>, has been tested. The presented method allows the selective extraction of aromatic components in brandy flavor, rendering a high-value concentrated extract.

## EXPERIMENTAL PROCEDURES

**Sample and Reagents.** The alcoholic beverage used in this work was a commercial brandy from a liquor store. Dichloromethane (HPLC grade) and *n*-pentane (95% purity) were obtained from Lab Scan Analytical Sciences (Dublin, Ireland), and ethanol (96%) was from Panreac (Barcelona, Spain). Both gases, CO<sub>2</sub> SFC (99.999998%) and CO<sub>2</sub>, N48 (99.9998%), were kindly supplied by AL Air Liquide España S.A. (Madrid, Spain).

**Instrumentation—Extraction Method.** An schematic diagram of the countercurrent (CC) SFE system employed in this study is shown in Figure 1. The CC-SFE liquid feed pilot plant has the following features: a CC extraction column with three levels of sample introduction (top, middle, and bottom as shown in Figure 1); two separator cells (270 mL capacity each), where a cascade decompression takes place; and a cryogenic trap at atmospheric pressure. Both CO<sub>2</sub> and sample were preheated at the exit of their respective pumps before introduction into the CC-SFE pilot plant. The plant has computerized PLC-based instrumentation and a control system, with several safety devices including valves and alarms. A 316 stainless steel extraction column (2 cm i.d.) packed with 316 stainless steel balls (5 mm i.d.) was used for all the experiments. The height of the extraction column was 180 cm (60 cm for each of the three parts of the column). The CO<sub>2</sub>, modifier, and liquid sample pumps were from Dosapro Milton Roy. During the extraction, a continuous flow of CO<sub>2</sub> was introduced into the column, through the bottom. When the operating pressure and temperature were reached, the liquid sample was pumped at the selected flow rate during the entire extraction time. The liquid sample introduction was carried out through the middle point of the packed column (see Figure

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**Figure 1.** Scheme of the CC-SFE pilot plant used in the present study. CCS, computerized control system; SR, sample reservoir; P1, liquid sample pump; P2, modifier pump; P3, CO<sub>2</sub> pump; SP, sample preheater; CP, CO<sub>2</sub> preheater; CEC, countercurrent extraction column; SV, security valve; S1, separator 1; S2, separator 2; LLS, liquid level sensor; MFM, mass flow meter; CT, cooling trap; V1, V2, V3, micrometering valves; T, top level of sample introduction; M, middle level of sample introduction; B, bottom level of sample introduction.

**Table 1. Conditions Used for the Experiments Performed at Pilot Plant Scale<sup>a</sup>**

expt	$F_{\text{liq}}$ (mL/h)	$F_{\text{CO}_2}$ (mL/h)	$T_{\text{ext}}$ (°C)	$T_{\text{sep1}}$ (°C)	$T_{\text{sep2}}$ (°C)	$P_{\text{ext}}$ (bar)	$P_{\text{sep1}}$ (bar)	$P_{\text{sep2}}$ (bar)
1	200	2700	40	40	25	100	90	20
2	200	2700	40	40	25	200	90	20
3	200	2700	40	40	25	200	150	30
4	200	2700	40	40	25	300	90	20
5	200	2700	40	40	25	300	150	30
6	200	2700	40	40	25	300	120	30

<sup>a</sup>  $F_{\text{liq}}$ , liquid sample flow rate;  $F_{\text{CO}_2}$ , CO<sub>2</sub> flow rate;  $T_{\text{ext}}$ , extraction temperature;  $T_{\text{sep1}}$ , temperature in separator 1;  $T_{\text{sep2}}$ , temperature in separator 2;  $P_{\text{ext}}$ , extraction pressure;  $P_{\text{sep1}}$ , pressure in separator 1;  $P_{\text{sep2}}$ , pressure in separator 2.

1), located over the inlet of the CO<sub>2</sub>, creating a countercurrent between the flow of sample (downward) and the CO<sub>2</sub> flow (upward).

After the initial tests, six experiments were performed at pilot plant scale with each kind of gas, CO<sub>2</sub> SFC and CO<sub>2</sub> N48, as shown in Table 1. The ratio between CO<sub>2</sub> flow rate and sample flow rate was kept constant at 13.5 solvent-to-feed ratio. All temperatures were also maintained throughout the experiments to constant values ranging from 25 to 40 °C, to prevent damage to the aromatic volatile compounds. The total extraction time was 80 min for each experiment. Samples from separator 2 were taken every 20 min until the total time was completed.

**Analysis by Gas Chromatography (GC).** To estimate the quantity of volatile components extracted, the sum of areas of the GC analysis of supercritical fluid extracts of brandy was used. A Perkin-Elmer Autosystem XL gas chromatograph (Perkin-Elmer, Norwalk CT) equipped with a programmed split/splitless injector (PSS) and a flame ionization detector (FID) was used to perform all of the GC analyses. The system was coupled to a Perkin-Elmer chromatography software system (Turbochrom). A 30 m × 0.25 mm i.d. fused silica capillary column (Quadrex Corp., New Haven, CT) coated with a 0.25 μm layer of SE-30 (100% methyl silicone) was employed.

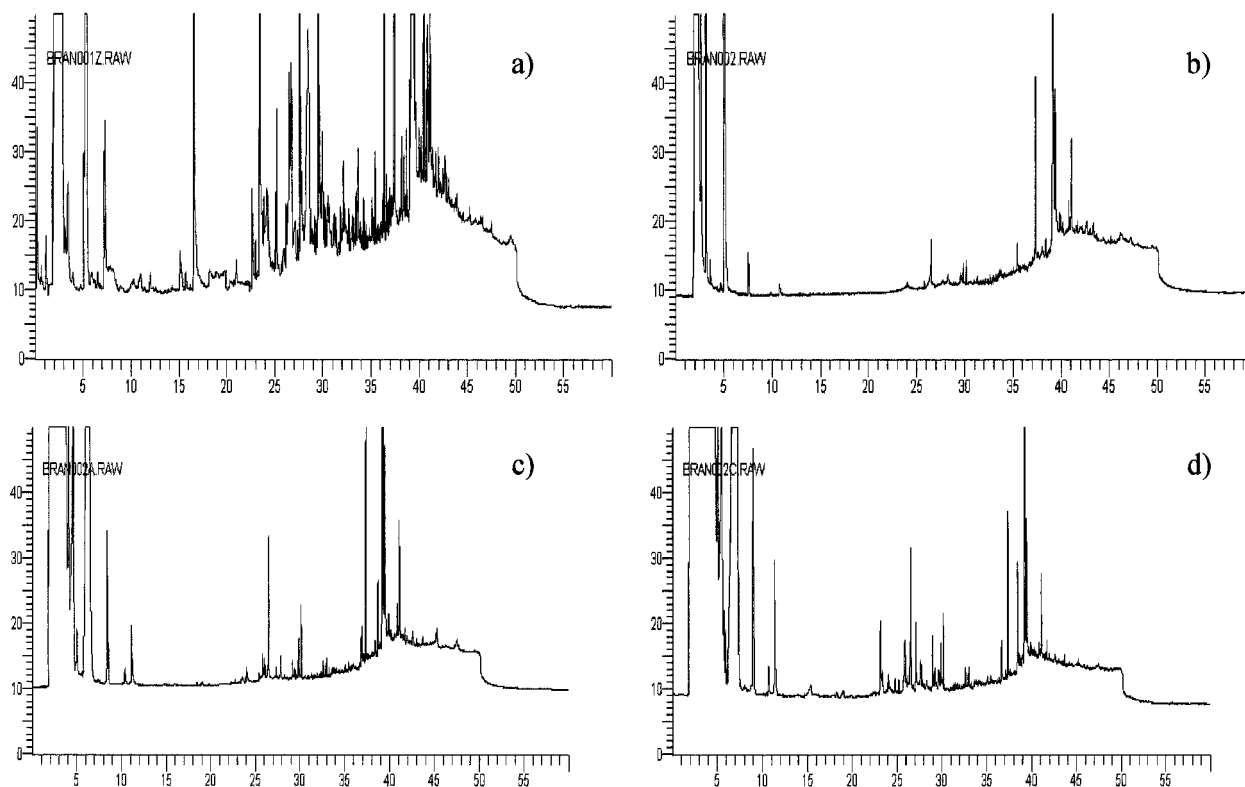
The operating conditions were as follows: injector temperature, 250 °C; detector temperature, 275 °C; oven temperature program, 40 °C (6 min at constant temperature), raised to 75 °C at 2 °C min<sup>-1</sup> and then to 270 °C (10 min at constant temperature) at 15 °C min<sup>-1</sup>. Helium at 1 bar was used as carrier gas with a flow rate of 1.3 mL/min. The split was 5 mL/min. Sample injection volume was 2 μL for both SFE extracts and liquid-liquid extracts.

**Liquid-Liquid Extraction.** In a separation funnel, the commercial brandy (20 mL) was extracted either with dichloromethane or with *n*-pentane (30 mL) for 30 min at room temperature. The organic layer was separated, and 2 μL was injected to be analyzed by GC at conditions previously described.

**Aroma Analysis by Headspace Solid-Phase Microextraction (HS-SPME/GC).** The aroma of the commercial brandy was analyzed using HS-SPME. An SPME holder (Supelco, Bellefonte, PA) equipped with a fused-silica fiber coated with a thin (100 μm) layer of poly(dimethylsiloxane) was chosen to extract the aroma compounds. Three milliliters of commercial brandy was placed in a 6 mL vial, which was closed with Parafilm. The fiber was exposed to the headspace of the sample at 60 °C for 15 min. The poly(dimethylsiloxane) fiber used to perform the HS-SPME was thermally desorbed by heating the injector to 200 °C for 10 min (splitless). The chromatographic conditions used were as described above.

**Ethanol Analysis by GC.** To evaluate the ethanol content of the extracts, a calibration curve was prepared with ethanol blank solutions (from 10 to 100% ethanol content). The chromatographic conditions were as follows: injector temperature, 190 °C; detector temperature, 250 °C; oven temperature, isothermal at 40 °C. Helium at 1 bar was used as a carrier gas. The split was 40 mL/min, and the sample volume injected was 1 μL.

**Sensory Evaluation.** One of the responses used to evaluate the quality of the supercritical fluid extracts was the resemblance, based on a human olfaction test, of their aroma to that of a commercial brandy. Aromatic extracts were evaluated with a panel of six experts panelist (four males and two females, 26–50-year-old individuals) who judged the similarity of the



**Figure 2.** Chromatographic profiles, corresponding to separator 2, obtained at conditions of experiment 5, high-quality gas: (a) 20 min extraction; (b) 40 min extraction; (c) 60 min extraction; (d) 80 min extraction.

aromas. The scale used for sensorial evaluation was not structured (11) to mark the similarity between the aroma of the extracts and that of a commercial brandy; that is, it only had two extreme points, and the right end represented the aroma of a commercial brandy. Thus, the higher the score, the higher the similarity between the aroma of the supercritical extracts and the aroma of the commercial brandy, and the distance (in centimeters) to the left end was considered for the statistical analysis of the data. The residue at the bottom of the column was not evaluated due its previously determined lack of aroma.

## RESULTS AND DISCUSSION

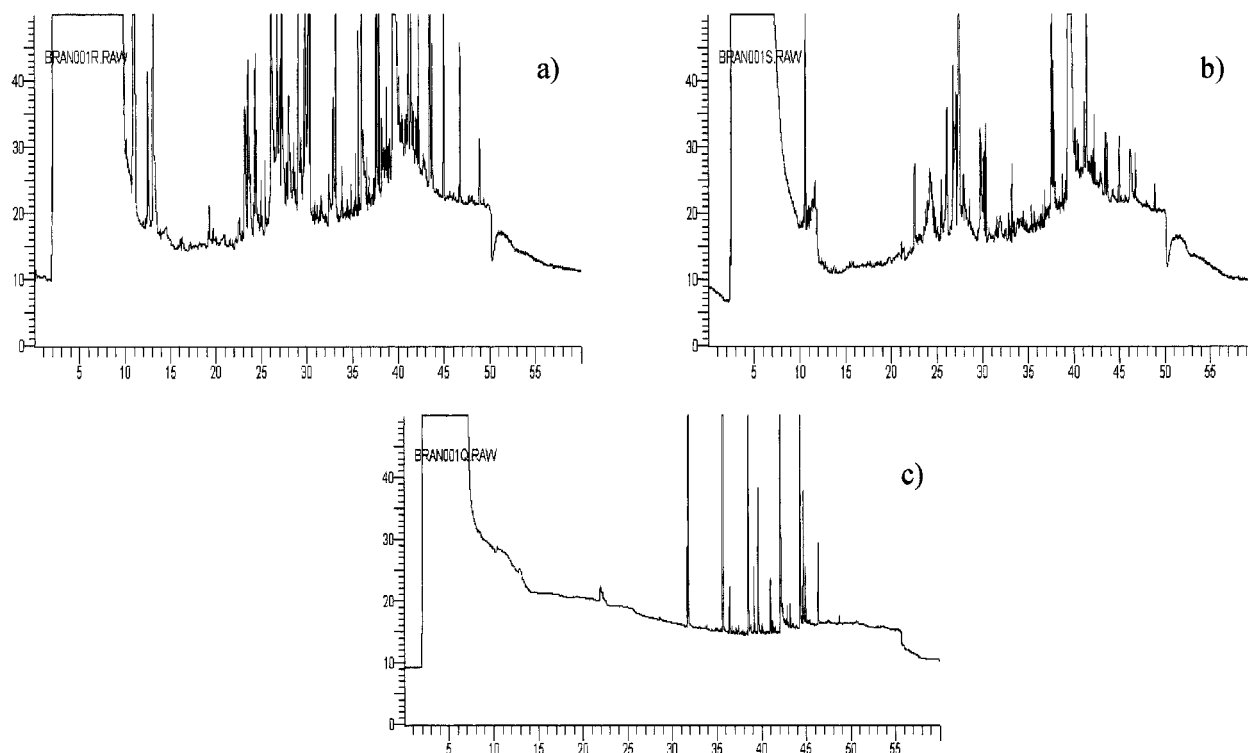
Different extraction and fractionation conditions were selected to perform the CC-SFE experiments at pilot plant scale, as shown in Table 1. This study attempted a screening of different variables involved in the SFE and fractionation process of a commercial brandy to obtain aroma extracts with great resemblance to the original brandy aroma. As described under Experimental Procedures, and considering this study as a first approach to this complex process, solvent and feed flow rates were maintained throughout the experiments to a constant value equal to a 13.5 solvent-to-feed ratio at conditions that allow the semicontinuous operation of the extraction plant without flooding the column or the fractionation cells. The sample was introduced into the CC column through the middle point. Temperatures were also maintained at low values ( $\leq 40$  °C) to avoid sample degradation. The extraction process was performed for 80 min, and samples were collected in the second separator every 20 min to evaluate and select the optimal extraction time for future work. Extraction conditions tested ranged from a maximum extraction density of 0.91 g/mL (300 bar and 40 °C) to a minimum of 0.63 g/mL (100 bar and 40 °C) followed by fractional separation in two separation vessels. Separation condi-

tions selected covered a density range between 0.5 and 0.78 g/mL in the first separator, whereas a total decompression stage was achieved in the second separator. Another variable that has been included in the study was the quality of the CO<sub>2</sub> used to perform the experiments, with high- (99.999998% CO<sub>2</sub>, SFC) and low-quality (99.9998% CO<sub>2</sub>, N48) gases selected.

The extracts were evaluated in terms of their ethanol content, sum of areas obtained by GC, and sensory analysis. Also, byproducts of extracted samples (raffinates or residues) were described in terms of ethanol content, although they lack aroma in the sensory analysis and their analysis by GC showed a very small response (no significant peaks of volatile compounds apart from ethanol).

Figure 2 shows the chromatographic profiles obtained at conditions of experiment 5, high-quality carbon dioxide, for a series of extracts collected every 20 min for a total extraction time of 80 min. Observing the profiles and considering the total area of the chromatograms, it can easily be determined that after 1 h, almost all of the aroma is extracted. Considering all of the experiments done, the 20 min overtime corresponds to <30% of the total area of the chromatograms with respect to the total aroma extracted. Therefore, no more time is needed to obtain a representative aroma of the samples, and 60 min was selected as the extraction time for future experiments.

Table 2 shows the results obtained for the different extraction conditions tested using the two different CO<sub>2</sub> qualities. Ethanol content was calculated on the basis of chromatographic data using a calibration curve obtained experimentally for ethanol percentages ranging from 10 to 100% ( $y = 189412x + 865725$ ,  $R^2 = 0.8945$ ); even though these data cannot be considered



**Figure 3.** GC profiles of brandy extracts obtained after liquid–liquid extraction with (a) dichloromethane and (b) *n*-pentane. (c) SPME-GC of brandy extract obtained at conditions described under Experimental Procedures.

**Table 2.** Results Obtained for the Different Extraction Conditions Tested Using the Two Different CO<sub>2</sub> Qualities

expt	gas type	ethanol content (%) S1	ethanol content (%) S2	ethanol content (%) R	sum areas S1	sum areas S2	score S1	SD	score S2	SD
1	SFC	50.6	72.3	19.3	297447	1840109	15.0	1.4	21.0	1.4
2	SFC	60.3	66.7	25.3	185778	1974999	21.0	1.4	19.5	2.1
3	SFC	43.2	61.0		251877	574070	19.5	0.7	20.0	1.4
4	SFC	47.8	60.7	15	3237288	11454178	19.0	1.4	19.5	3.5
5	SFC	48.8	56.4	21.6	1666149	11488330	17.0	2.8	17.5	0.7
6	SFC	86.3	80.8	32.6	418849	4014483	16.5	0.7	19.0	1.4
1	N48	57.1	83.7		665779	4055491	15.5	3.5	20.5	2.1
2	N48	42.5	85.2	39.8	128178	1228649	19.5	0.7	16.5	0.7
3	N48	52.9	94.7	17.6	743990	6383650	11.5	6.4	17.5	0.7
4	N48	38.8	71.4	17.3	1329198	5669585	15.5	7.8	20.5	0.7
5	N48	45.1	77.1	57.6	361441	933003	15.5	10.6	20.0	1.4
6	N48	73.3	69.6	8.5	102467	1281017	17.5	4.9	19.5	2.1

as quantitative, it is enough for comparison among the different experiments and the different separators.

From the ethanol content it can be clearly seen that the residue contains almost no ethanol or much lower percentages than those found in both separators 1 and 2. The residues obtained after CC-SFE extraction are mainly aqueous and odorless and have an important color concentration. Conversely, extracts obtained in both separators are alcoholic, have an important aroma concentration, and are colorless. As a general trend, extracts obtained in separator 2 had a higher ethanol concentration than those in separator 1, being in some experiments double the percentage in separator 1. This ethanol concentration can be varied in each separator depending on the SFE conditions.

In terms of sum of areas obtained by GC, a multifactor analysis of variance was performed to evaluate the differences among experiments, gases, and separators. The means comparison criterium used was the least significant difference (LSD), and the statistical analysis was done using Statgraphics Plus v. 3.1 software (Statistical Graphics Corp., Manugistics Inc., Rockville,

MD, 1997). As a dependent variable (response), the sum of areas obtained by GC was selected, whereas the factors considered were the experimental run at different extraction conditions, the separator cell, and the gas type. Only differences between separators 1 and 2 can be considered to be significant with a *p* value of 0.014, whereas no significant differences at a 95% confidence level can be found among the different experiments (*p* value = 0.17) and the two types of gases tested (*p* value = 0.21). Even if the global differences among the extracts obtained at the six experimental conditions tested cannot be considered to be statistically significant, some important individual differences can be found by comparing the data shown in Table 2. The results suggested a higher aroma extraction when the strongest extraction conditions (experiments 4 and 5) were considered, but no absolute conclusions could be obtained. Nevertheless, these results provoked interest in further studies in this field, probably extending the set of conditions applied and using experimental design methods to evaluate the influence of more factors and

interactions. These studies are being conducted at present in our laboratory.

By analyzing the scores given by the panelists to the different extracts obtained at the extraction conditions shown in Table 1, it can easily be seen that most of the extracts obtained a high score, meaning that they have a high resemblance to the original aroma of brandy. Statistical studies showed no significant differences (95% confidence level) among experiments, gas type, and separators. However, appreciable differences can be observed in terms of separators, which is in accordance with the chemical data obtained by GC.

From data analysis it can be concluded that it is possible to obtain high-quality extracts, with aroma close to that of the original brandy and with ethanol concentration ranging from 40 to 85%, whereas the residue contained less alcohol and no appreciable aroma. As can be seen in Table 2, the content in ethanol of the aromatic extracts can be modified by tuning the extraction/fractionation conditions, rendering from 15 to 95% recovery.

For comparison with the extracts obtained by CC-SFE, different conventional extraction techniques have been used, including liquid-liquid extraction with *n*-pentane and dichloromethane and solid-phase microextraction. Brandy was extracted at the conditions described under Experimental Procedures, and the corresponding chromatograms are shown in Figure 3. The profile shown in Figure 2a, corresponding to the CC-SFE extraction at conditions of experiment 5 with CO<sub>2</sub> of SFC grade, is similar to that corresponding to the brandy extract after liquid-liquid extraction with dichloromethane (Figure 3a). This is easily explained by considering the similarities in terms of polarity among the different solvents; therefore, the types of compounds extracted must be very alike. Most of these compounds also match those analyzed using SPME-GC, which corroborates the hypothesis about their nature taking into account the type of nonpolar fiber used to extract these compounds.

In conclusion, further studies will be needed to clearly observe the effects of the different experimental conditions in both ethanol concentration and aroma extraction. Results shown in the present paper demonstrate the interest of the technique as a method for processing alcoholic beverages with the objective of obtaining high-quality aroma extracts with tunable characteristics in

terms of alcoholic content that make them adequate to be used in different food matrices.

Studies for the optimization of the extraction conditions as well as the optimization of the CC conditions are being conducted at present in our laboratory.

#### LITERATURE CITED

- (1) *Volatile Compounds in Food and Beverages*, Maarse, H., Ed.; Dekker: New York, 1991.
- (2) Karlsson, H. O. E.; Tragardh, G. Aroma recovery during beverage processing. *J. Food Eng.* **1997**, *34*, 159–178.
- (3) Carnacini, A.; Marignetti, N.; Antonelli, A.; Natali, N.; Migazzi, S. Alcohol removal and aroma recovery from wine by permoseparation, dialysis, and extraction with CO<sub>2</sub>. *Ind. Bevande* **1989**, *18*, 257–264.
- (4) Gamse, T.; Rogler, I.; Marr, R. Supercritical CO<sub>2</sub> extraction for utilisation of excess wine of poor quality. *J. Supercrit. Fluids* **1999**, *14*, 123–128.
- (5) Stein, W. Reduction of the alcohol content of beer—comparison of methods. *Voedingsmiddelen Technol.* **1993**, *26*, 30–32.
- (6) Medina, I.; Martinez, J. L. Dealcoholisation of cider by supercritical extraction with carbon dioxide. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 14–18.
- (7) Seidlitz, H.; Lack, E.; Lackner, H. Process for the reduction of the alcohol content of alcoholic beverages. Eur. Patent Appl. EP0397642A1, AT89-1104, 1990 (Schoeller-Bleckmann, Ternitz, Austria).
- (8) Hochberg, U.; Trefzer, J.; Zander, J. Process for preparation of a comparatively low-alcohol drink from a drink with a relatively high alcohol content. German Fed. Republic Patent Appl. DE 3819527, 1989 (Gea Wiegand, Ettlingen, Germany).
- (9) Berger, F.; Sagi, F.; Cerles, B. Method for extracting aroma from alcoholic drinks obtained from fruit or similar products. Fr. Patent Appl. FR2505616A1, 1983 (Rhône-Poulenc SA).
- (10) Sugiyama, K. Extraction of flavour component of sake. Jpn. Patent Appl. JP 1117761A, 1989 (Morinaga & Co. Ltd).
- (11) Amerine, M. A.; Pangborn, R. M.; Roessler, E. B. *Principles of Sensory Evaluation of Foods*; Academic Press: New York, 1965.

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