Drying Technology, 23: 2185–2196, 2005

ISSN: 0737-3937 print/1532-2300 online
DOI: 10.1080/07373930500212669

Taylor & Francis
Taylor & Francis Group

Characteristic Evaluation for Volatile Components of Soluble Coffee Depending on Freeze-Drying Conditions

Yasuyuki Sagara[1], Koji Kaminishi[1], Eri Goto[1], Taketoshi Watanabe[2], Yuriko Imayoshi[2], and Hisakatsu Iwabuchi[2]
[1]Graduate School of Agricultural and Life Sciences, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
[2]San-Ei Gen F.F.I., Inc., Osaka, Japan

Abstract: Volatile aroma compounds of freeze-dried soluble coffee were investigated to evaluate the effects of freeze-drying temperature conditions on their intensities and aroma characteristics by employing both GC/MS and charm-analysis, which is a GC/Olfactometry (GC/O) method. The coffee solutions with 40% solid content were freeze-dried changing freezing and drying temperatures. According to the results, it was demonstrated that the compounds identified based on human olfactory sense were different from those detected by GC/MS, and that the GC/O analysis method enabled evaluation of the characteristics and intensity of each compound as well as aroma profiles under various freezing and drying temperatures. Subsequently, GC/O method was found to be effective to detect and identify the volatile compounds giving the aroma peculiar to freeze-dried coffee, and useful to obtain the fundamental information for designing the optimal aroma characteristics of final product to conform the consumer preference based on the characteristic changes in aroma affected by freeze-drying conditions.

Keywords: Volatile aroma compounds; GC/O analysis; Freezing and drying temperature conditions; Consumer's preference

INTRODUCTION

Freeze-drying has played an increasingly important role in the production of dehydrated foods whose quality depends mainly on flavor retention. Interest in the freeze-drying of liquid food materials in the past

Correspondence: Koji Kaminishi, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan; E-mail: aa47127@mail.ecc.u-tokyo.ac.jp

decade has led to a number of investigations into the factors affecting the retention of volatile organic compounds during the freeze drying of aqueous solutions. For example, Flink[1] described the relative retention of volatile compounds in freeze-dried sugar solutions as a function of the freezing rate and the operation pressure. These compounds are considered to be sensitive to both freezing and drying temperature conditions.

According to research by Thijssen and Rulkens,[2] slow freezing and quick drying were found to provide good retention of aroma compounds. The slow freezing produces large ice crystals excluding the solute, which brings about highly concentrated solutions. The prolonged drying makes the thermal denaturation to change the original flavor.

In previous research to investigate aroma retention in the freeze-dried product, the component analysis has been performed mainly with gas chromatograph mass spectrometer (GC/MS). However, this analysis method is invalid for compounds that are involved only slightly in the material, even though they give distinct aromas due to low threshold concentration to be detected. As some of those compounds may contribute to the aroma characteristic of the object material, it is necessary to identify and quantify them.

A novel method, gas chromatography olfactometry (GC/O) has recently been developed to detect the slight aroma compounds by utilizing human olfactory function. With this method, both the intensity and characteristic of each volatile compound can be investigated.

The objective of this research is to evaluate the effect of temperature conditions in freezing and drying processes on the characteristics and intensity of volatile aroma compounds in freeze-dried food by employing GC/O and GC/MS methods.

EXPERIMENT

Freezing and Freeze-Drying Operations

The concentrated coffee solution of 40% in solid content was used as a sample material to investigate the aroma retention, which is considered to be the most emphasized quality in the commercial freeze-dried coffee.

Figure 1 shows a programmed freezer utilized in freezing the samples. The coffee solution was put into a sample holder shown in Figure 2. The holder was acrylic cylinder of 60 mm in diameter and 20 mm in height, and it also contained the copper column of 5 mm in thickness at the bottom insulated at the top. Additionally, it was insulated at the top and around the side by Styrofoam to accomplish one dimensional freezing. The samples were frozen on the cooling copper plate whose upper surface could be controlled at a constant temperature

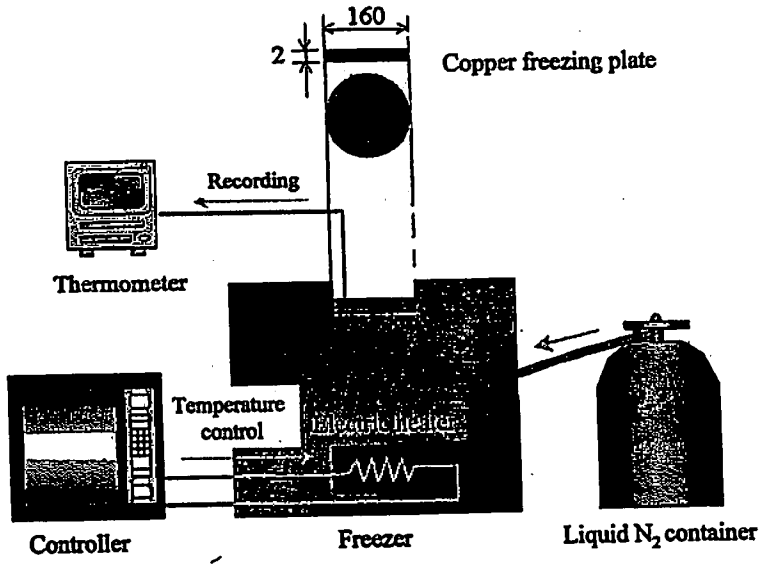

Figure 1. Programmed freezer.

ranging from 0 to −150°C. During the freezing process, temperature changes within the sample were measured with T-type thermocouple probes. Freezing was terminated when the temperature distribution reached equilibrium. The setting surface temperature of cooling copper plate was referred as the freezing temperature in the present research.

Figure 3 illustrates the schematic diagram of experimental freeze-dryer and measurement system. The chamber was a cylindrical, thermally insulated iron enclosure of 92.2 mm inside diameter and 470 mm length. It was equipped with a transparent door of 30 mm thickness, which permited visual observation of the sample during drying. The chamber was evacuated by a vacuum pump, and reached around 2 Pa in 5 min. Both

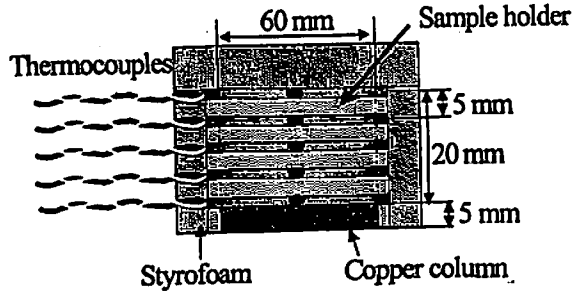

Figure 2. Sample holder.

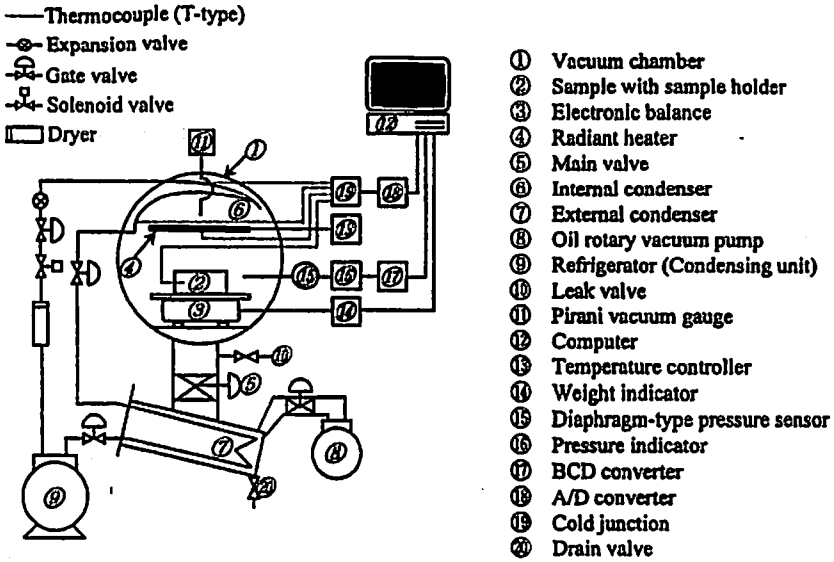

Figure 3. Experimental freeze-dryer.

internal and external condensers were utilized to capture the water-vapor sublimated from the sample. The refrigerator for these condensers was an air-cooled condensing unit with sufficient capacity to reduce the condenser-coil surface temperature to −45°C. By electrically heated plate located above the sample surface, radiant heat was one-dimensionally supplied to the sample insulated around the side. Then the sample surface temperature was controlled with the PID controller by regulating the electrical power to the radiant heater. The temperature distribution and weight of the sample as well as the operating conditions such as the chamber pressure, temperatures of the heater and condenser coil surfaces were monitored during the drying process. The drying process was terminated when the temperature distribution and weight of the sample got equilibrium.

To investigate the effects of the freeze-drying conditions on aroma retention, the samples were frozen on the copper freezing plate at −40, −60, and −120°C. The setting temperatures of the sample surface during drying process were 25, 45, 60, and 80°C, which were considered to be room temperature, the changing point of aroma, and that of nutrition and practical drying temperature, respectively. The original coffee solution before freeze-dried was used as a standard sample.

Extraction of Aroma Compounds in the Freeze-Dried Soluble Coffee

The dried samples were brought into dilute solutions of 6° in Brix with pure water, and then 2 mL of 0.03% dimethyl-phthalate solution was

admixed into 200 mL of this dilute solution as well as 150 mL of ethyl ether. After 15-min slow agitation at room temperature, the supernatant ether layer was separated, mixed with absolute sodium sulfate, and filtrated to obtain the samples for component analysis. Finally, GC/MS MS and GC/O analyses were performed with the obtained filtrate to investigate the intensity and characteristics of each volatile aroma compound.

GC/MS and GC/O Analyses

GC/MS analysis was performed with a mass selective detector model 5973 coupled to a gas chromatograph model 6890 (Hewlett Packard) by using the fused silica capillary column DB-WAX (J&W Scientific; 60 m × 0.25 mm). The temperature program was set at the initial temperature of 50°C for 2 min, followed by an increase of 3°C/min to 220°C. Figure 4 illustrates the schematic of charm-analysis system (DATU, Inc., Geneva, NY), which was one of the GC/O analysis developed by Acree et al.[3] to detect aromas in extracts of food and fragrance materials. It is the system that combines the human olfactory detectors to assess the activity of the odor carried by defined air streams with the gas chromatographic separation of volatile compounds. This method is effective to evaluate the intensity and characteristic of each volatile aroma compound contained in the sample.

At first, the filtrate including extracted aroma compounds was diluted to adjust serially the concentration ratio to 1, 1/3, and 1/9. The diluted solution was injected to the gas chromatograph to separate into individual volatile compounds. Each isolated compound was fed within the stream of purified and humidified air at a linear velocity through the sniffing port, so that a sensory panelist sniffed it in front of the olfactometer outlet to determine the detection time and characteristic

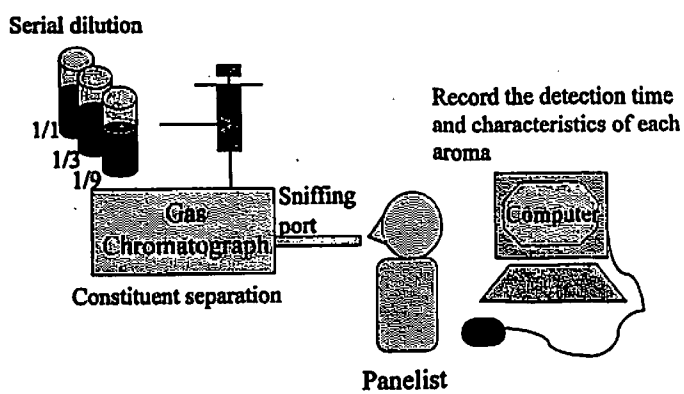

Figure 4. Schematic of charm-analysis system.

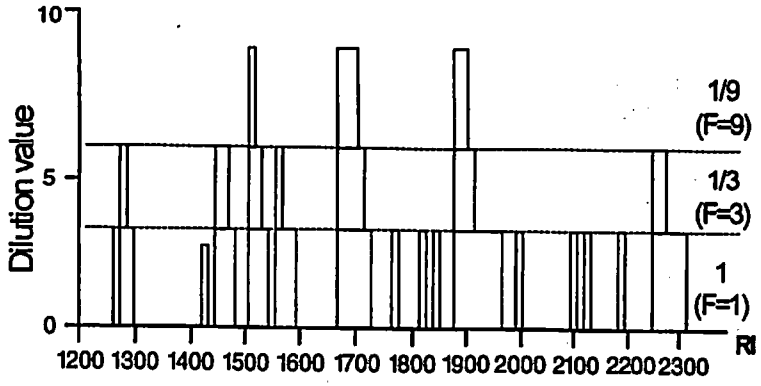

Figure 5. Aroma chromatogram obtained by charm-analysis.

of each sniffed aroma. These data were recorded in the personal computer. To describe the characteristic, each detected aroma was associated with the appropriate term among 11 predesignated characteristic indices. Furthermore, charm-analysis yielded the chromatogram, called an aroma chromatogram, as shown in Figure 5. The abscissa and ordinate indicate the retention index (*RI*) showing a ratio of the retention time (*RT*) of analyte to that of a standard, and dilution value as titer, respectively. This chromatogram could be obtained by repeating the olfactory response exam three times with different concentration ratios and cumulating the results. Based on this result, each aroma intensity, called charm value (*CV*), was calculated with integration of each peak area as shown in following equation

$$CV = \int_{\text{peak}} F^{n-1} di \qquad (1)$$

where F, n, and di mean dilution factor, number of dilution, and the detection time ($RI_{\text{end}} - RI_{\text{begin}}$), respectively. Each compound was identified by comparison with reference materials in mass spectrum and *RI*.

RESULTS AND DISCUSSION

Freezing Curves

Figure 6 shows the typical freezing curves for 40% coffee solution frozen with the copper plate at −40°C. Not withstanding discrepancy between the setting and monitored value in the beginning, the surface temperature of the cooling copper plate could be well controlled and kept at the constant one. The solidification stage finished after about 33 min from the beginning of freezing process. The freezing curves at the center and upper

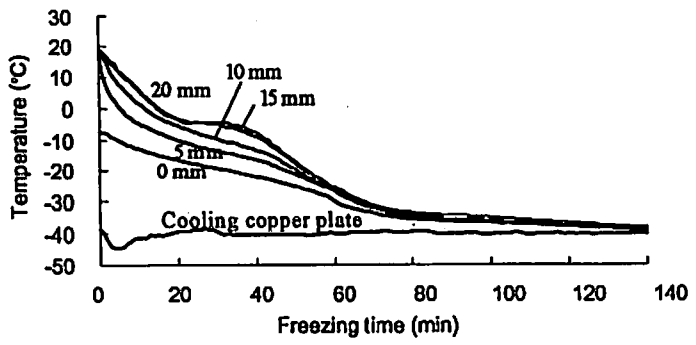

Figure 6. Freezing curve of 40% coffee solution frozen on the cooling copper plate of −40°C.

surface of the sample required about 450 and 1150 s to pass through the zone of maximum ice crystal formation from 0 to −5°C, respectively. The freezing process was terminated when the temperature distribution in the sample reached an equilibrium state at the final temperature of around −38°C, which required 140 min.

Drying Characteristics

A typical freeze-drying characteristics for coffee solution and corresponding drying conditions are shown in Figure 7. The sample surface temperature increased until it approached the control temperature of 45°C and then remained constant. The temperature in the frozen part of the sample appeared to maintain a constant value of about −20°C, and then began to rise toward the surface temperature indicating the passage of retreating sublimation front. The drying rate increased until it reached the maximum value, and followed by the gradual decrease indicating an increasing resistance of the dried layer.

Detected Compounds

Figure 8 shows gas and aroma chromatograms of the freeze-dried coffee sample frozen at −40°C and dried at 80°C, obtained by GC/MS and GC/O, respectively.

According to the gas chromatogram, several compounds were identified for freeze-dried coffee samples, including furfural, acetic acid, furfuryl alcohol, and so on. However, there is no telling which compounds contribute to the aroma characteristic of the sample. Besides, in spite of high relevance to the characteristic, there remained some compounds that could not be identified by GC/MS.

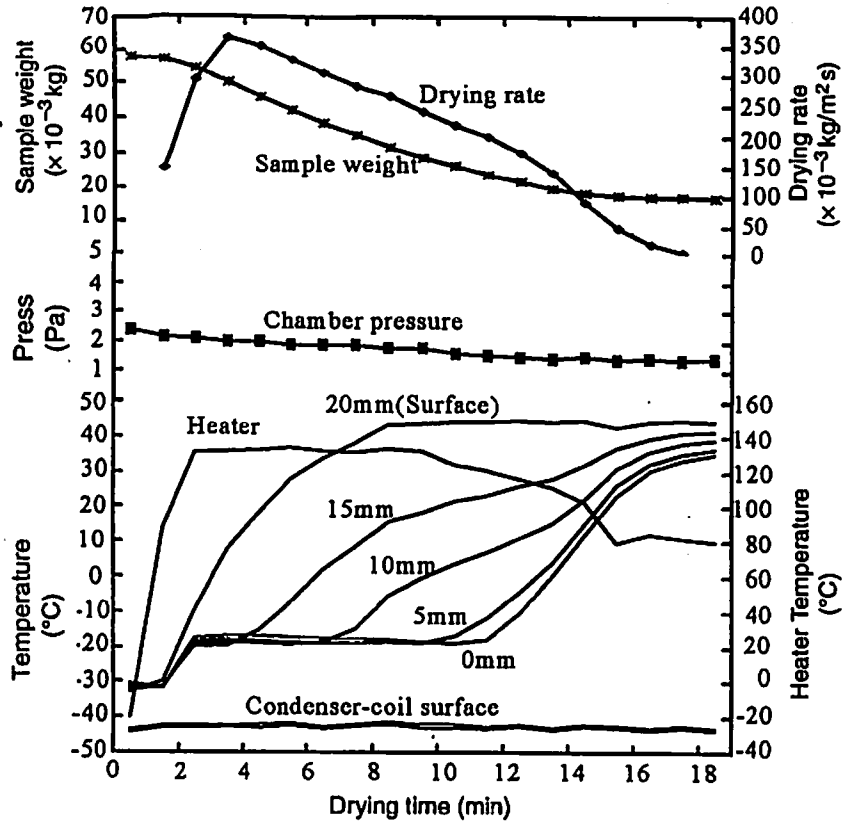

Figure 7. Drying characteristics of 40% coffee solution freeze-dried by keeping the surface temperature at 45°C.

However, the aroma chromatogram demonstrated several peaks of various aroma characteristics. Based on the accumulated data of volatile aroma compounds obtained by the previous GC/O analysis, the corresponding odorant could be identified for each characteristic. As a result, furfuryl thiol and cyclotene were also found as compounds having aroma peculiar to coffee as well as 3-mercapto-3-methylbutyl formate and 3-isobutyl-2-methoxypyrazine, although the concentrations of these compounds were only very slight in the sample. Additionally, ethional, which generated the aroma like soy sauce, furaneol and sotolone, which provided a smoky sweet aroma, were commonly detected for all samples.

Hence, it was found that the compounds identified by the chemical analysis with GC/MS did not coincide with those detected with human olfactory sense, and that GC/O analysis was the useful method to detect and identify the volatile compounds giving aromas peculiar to coffee.

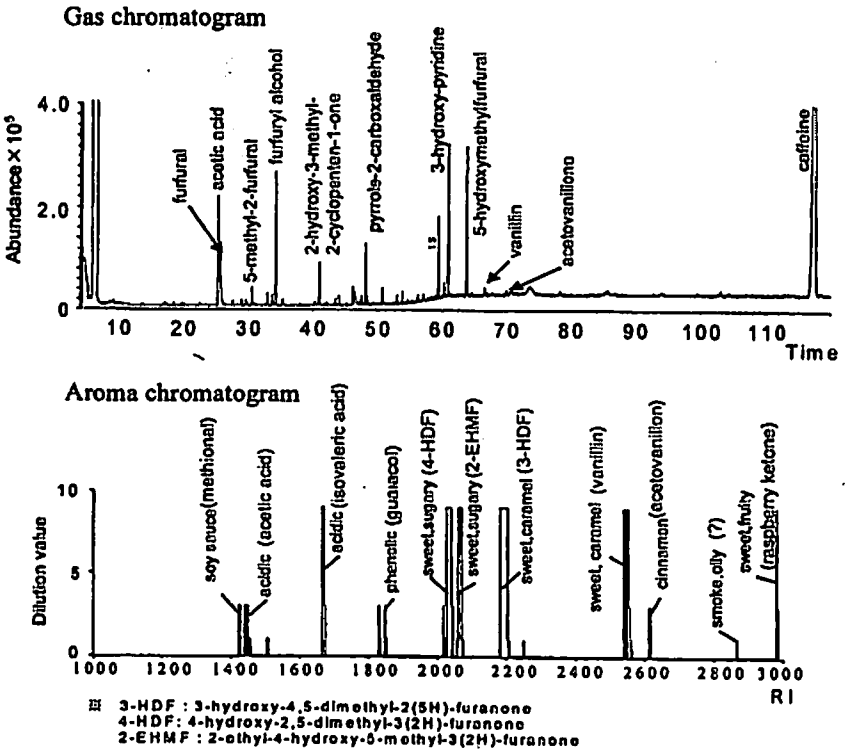

Figure 8. Gas and aroma chromatograms of freeze-dried soluble coffee frozen at −40°C and dried at 80°C, obtained by GC/MS (A) and GC/O (B) methods.

Temperature Dependence of Aroma Intensity

Figure 9 indicates a result to show the effects of freezing and drying temperature conditions on charm-value of the identified volatile compounds. In this figure, the values of the original coffee solution were presented for purpose of comparison. The figure demonstrated that charm-value of methional increased with drying at higher temperature as well as freezing at lower temperature, which indicated the increase of the aroma like soy sauce.

Figures 10 and 11 showed the aroma profiles, radar charts expressed with 11 axes to indicate the summation of charm-value for each aroma characteristic. They were used to investigate the relationship between temperature conditions and the overall aroma characteristic in the sample frozen at −60°C and that dried at 80°C, respectively. According to Figure 10, as mentioned above, the charm-values of the aroma like soy sauce showed a tendency to increase significantly with the increase of drying temperature, while those of the aromas expressed as honey,

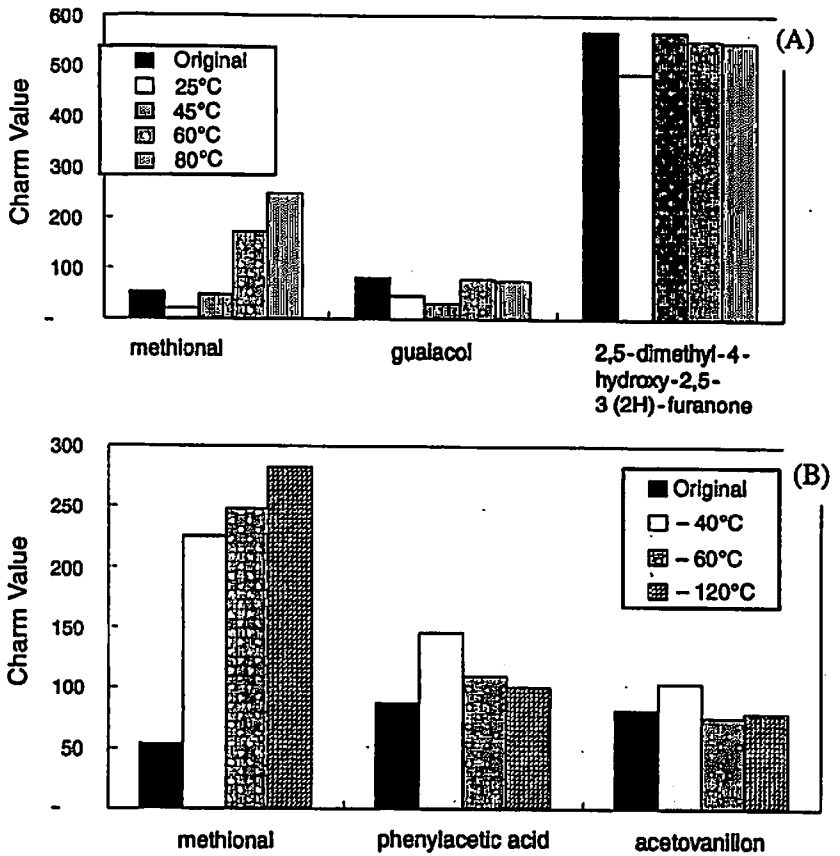

Figure 9. Effects of freezing and drying temperatures on the charm-values of aroma compounds A, samples frozen at −60°C, B, samples dried at 80°C.

fruity-juicy, and spicy-caramel-sweet-sugary decreased. Additionally, aromas expressed as cinnamon and nutty-smoke-oily were found to weaken suddenly in the range above 60°C.

Figure 11 showed that the aroma like soy sauce increased in freezing at lower temperature, and that the same tendency was observed in aromas expressed as fruity-juicy and green-black, current-earthy. In contrast, higher freezing temperature was found to increase the aromas of honey, acidic, and cinnamon.

Subsequently, it was demonstrated that GC/O analysis was the effective method to evaluate the characteristics and intensities of aroma volatile compounds in freeze-dried coffee depending on temperature variations during freezing and drying, which was one of the most essential data to determine the optimum condition in freeze-drying process.

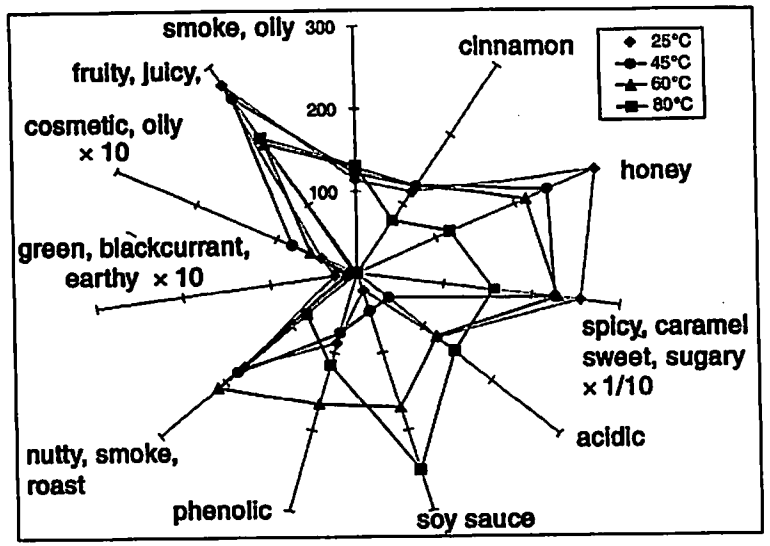

Figure 10. Aroma profiles obtained at various drying temperatures in the samples frozen at −60°C.

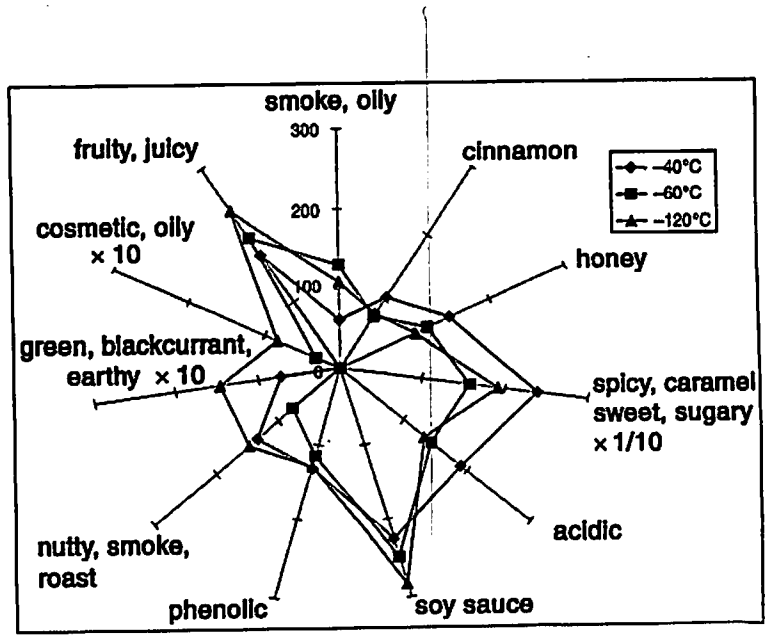

Figure 11. Aroma profiles obtained at various freezing temperatures in the samples dried at 80°C.

CONCLUSION

Several kinds of volatile aroma compounds giving the distinct aromas peculiar to coffee were identified with GC/Olfactometry analysis. Additionally the aroma characteristics and intensity of each compound in freeze-dried soluble coffee were elucidated based on the freezing and drying temperature conditions. The results demonstrated that this analysis method is found to be effective to obtain the fundamental information for designing the optimal aroma characteristics of final product conform to the consumer preference.The optimal design takes into account the characteristic changes in aroma affected by freeze-drying conditions.

REFERENCES

1. Flink, J.; Karel, M. Retention of organic volatiles in freeze-dried solutions of carbohydrates. Journal of Agricultural Food Chemistry **1970**, *18* (2), 295–302.
2. Thijssen, H.A.C.; Rulkens, W.H. Retention on aromas in drying food liquids. De Ingenieur, Chemische Technik **1968**, *80*, 45–56 (Niederlande).
3. Acree, T.E.; Barnard. J.; Cunningham D.G. A procedure for the sensory analysis of gas chromatographic effluents. Food Chemistry **1984**, *14*, 273–286.
4. Sagara, Y.; Ichiba, J. Measurement of transport properties for the dried layer of coffee solution undergoing freeze drying. Drying Technology **1994**, *12* (5), 1081–1103.