

Investigation of the Change in the Flavor of a Coffee Drink during Heat Processing

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Heat processing is responsible for the change in the flavor of a coffee drink. In this study, the application of gas chromatography–olfactometry of headspace samples (GCO-H) using the vapor fraction before and after heat processing of the coffee samples resulted in the detection of 12 odor-active peaks for which the flavor dilution (FD) factors changed. Eight potent odorants were identified from these peaks by gas chromatography–mass spectrometry (GC-MS). Among these components, methanethiol (putrid), acetic acid (sour), 3-methylbutanoic acid (sour), 2-furfuryl methyl disulfide (meaty), and 4-hydroxy-2,5-dimethyl-3(2H)-furanone (caramel-like) increased after heating of the coffee sample, whereas 2-furfurylthiol (roasty), methional (potato-like), and 3-mercapto-3-methylbutyl formate (roasty) decreased compared with the coffee sample before heat treatment. In addition, extensive studies have been carried out on the pH effects on the change in the concentration of 2-furfurylthiol during heat processing and in the pH range of 5–7; it was found that the concentration of this compound in the model solutions had significantly changed.

KEYWORDS: Coffee; heat processing; gas chromatography–olfactometry of headspace samples; 2-furfurylthiol

INTRODUCTION

Coffee is the one of the most widely consumed beverages in the world. The high acceptability of coffee is due to many factors, one of the most contributory factors being its flavor. The volatile compounds of coffee have been investigated by many researchers (1–6), and over 800 volatile compounds have been reported (7). Canned coffee drinks are very popular in Japan. During the manufacturing process of a canned coffee drink, the coffee flavor changes. Heat processing during sterilization especially affects the flavor of the coffee. It was reported that the decrease in the roasty odor after heating of the coffee drink was significantly caused by the decrease in the amount of three sulfur compounds (2-furfurylthiol, methional, and 3-mercapto-3-methylbutyl formate), and it was assumed that these odorants were changed by oxidation, thermal degradation, and/or hydrolysis (8). However, these sulfur odorants were part of the important components involved in changing the coffee flavor during heat processing. Therefore, the details of potent odorants with respect to the flavor change in the coffee drink have not yet been clarified.

2-Furfurylthiol is a significant odorant causing the sulfury–roasty odor quality in coffee drinks. However, this odorant is not stable and rapidly decreases when coffee drinks are processed or stored (8–11). Recent investigations indicated that the melanoidins in the coffee brew are involved in the loss of

2-furfurylthiol when brewed coffee is kept warm in a Thermos flask. On the other hand, adjustment of the pH of the coffee brew is one of the important techniques for the production of canned coffee drinks. This process is performed to prevent an increase in the sour taste and the cohesion of the coffee and milk components during sterilization (12). However, the pH effects on the thermal stability of 2-furfurylthiol during heat processing have not yet been clarified.

In the present paper, we report that changes in the potent odorants during heat processing of the coffee drinks were screened by gas chromatography–olfactometry of headspace samples (GCO-H) and identified using gas chromatography–mass spectrometry (GC-MS). Furthermore, the pH effects on the change in the concentration of 2-furfurylthiol during heat processing were also investigated.

MATERIALS AND METHODS

Materials. *Coffee Drinks.* The Arabica coffee beans were medium-roasted (luminosity value = 22.9), sealed under vacuum, and stored at –20 °C until used. Deionized hot water (~90 °C, 500 mL) was poured on the ground coffee powders (50 g) in a filter. The filtrate (~450 mL) was immediately cooled to ~20 °C in tap water, and then NaHCO₃ was added to a pH of 6.0; the mixture was canned without the deoxidization process. The canned coffee drink was sterilized at 121 °C for 10 min followed by immediate cooling to ~10 °C in tap water. Sterilization was performed in a retort pasteurizer (model PRS-02-II-VC; supplied from Nissen, Japan). The pH value after heat processing of the coffee drink was 5.2.

Chemicals. Methanethiol, 2-furfuryl methyl disulfide, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, and difurfuryl disulfide were obtained

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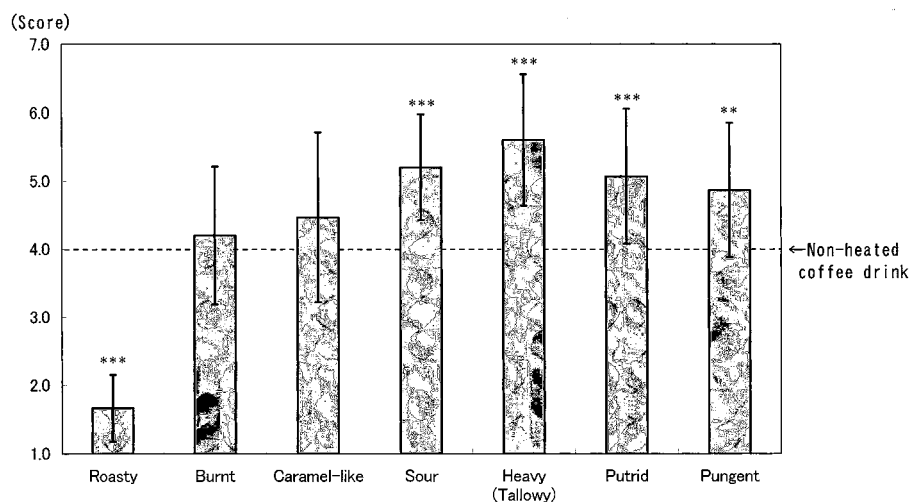


Figure 1. Odor attributes of after-heating coffee drink. For the nonheated coffee drink, all of the category scales were defined as 4. Significant difference from the control (nonheated coffee drink): **, $p < 0.01$; ***, $p < 0.001$.

from Sigma-Aldrich (Tokyo, Japan). 2-Furfurylthiol, methional, acetic acid, 3-methylbutanoic acid, furfural, furfuryl alcohol, and methyl octanoate were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). 3-Mercapto-3-methylbutyl formate was synthesized according to the literature (2).

Sensory Evaluation. The coffee drinks before and after heat processing were placed in glass beakers (~ 20 °C). The samples were sniffed by 15 panelists (12 males and 3 females, between the ages of 27 and 38). All panelists had previously received extensive training in descriptive sensory analysis of the coffee drinks and had experience in the sensory profiling of various food samples. The intensities of the attributes of the heated coffee drink was scored on a category scale of 1, 2, 3, ..., 7. For the unheated coffee drink, all of the category scales were defined as 4. The results obtained by the panelists were then averaged. The resulting data were evaluated by an analysis of variance.

Gas Chromatography—Olfactometry. GCO-H was performed with a Hewlett-Packard (HP) model 5890 series II gas chromatograph connected to the purge and trap system TCT/PTI (Chrompack). The empty glass tube in the desorption heating block of the purge and trap facility was deactivated by treatment with 5% 1,1,1,3,3,3-hexamethylidisilazane, which was dissolved in toluene. The gas chromatograph was equipped with a DB-Wax fused silica capillary column (30 m \times 0.25 mm i.d.; film thickness = 0.25 μ m; J&W Scientific) and a thermal conductivity detector (TCD). The column temperature was programmed from 40 to 210 °C at the rate of 3 °C/min in all runs. The flow rate of the helium carrier gas was 1.5 mL/min. A glass sniffing port was connected to the outlet of the TCD and was heated by a ribbon heater. Moist air was pumped into the sniffing port. The coffee drink (10 mL) was placed in a vessel (volume = 100 mL), sealed with a septum, and then held in a water bath at 40 °C for 10 min. The headspace volumes [20–0.1 mL corresponding to flavor dilution (FD) factors 1 to 200] were drawn by a gastight syringe and then injected into the purge system, which operated in the desorption mode for 5 min at a temperature of 150 °C. The carrier gas helium (flow = 10 mL/min) swept the headspace sample into the trap, which was cooled with liquid nitrogen at -150 °C. To start the GC run, the cold trap was heated rapidly to 200 °C, and this temperature was held for 5 min.

Enrichment of Odorants for Identification. The coffee drinks (~ 1 L, before and after the heat processing) were distilled under reduced pressure (40 °C, 20 mmHg). The steam distillate (~ 250 mL) was passed through a column packed with 10 g of Porapak Q (Waters). The adsorbed compounds were eluted with methylene chloride (100 mL). The eluate was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator to ~ 5 mL in volume. A further concentration was conducted with a nitrogen stream to ~ 100 μ L. The concentrate was used as the GC-MS sample for the identification experiments of the compounds in small amounts.

Model Experiments on the Thermal Stability of 2-Furfurylthiol in Aqueous Solution. At a concentration of 1 ppm, 2-furfurylthiol was

dissolved in citric/ Na_2HPO_4 buffer solutions of pH 3.0, 4.0, 5.0, 5.4, 6.0, 6.4, and 7.0 (mixed 1/10 M citric acid and 1/5 M Na_2HPO_4). Half of each solution was canned without the deoxidization process and treated by heat processing (121 °C, 10 min; the instrument was described above), followed by immediate cooling to ~ 10 °C in tap water, and the other half of the solution was not heated. 2-Furfurylthiol in the treated and untreated solutions (100 mL) were isolated by extraction with methylene chloride (50 mL \times 2). After drying over anhydrous sodium sulfate, the solvent was evaporated to ~ 5 mL in volume. A further concentration was conducted with a nitrogen stream to ~ 100 μ L. The internal standard solution (20 μ L) prepared from methyl octanoate (53.3 mg) in methylene chloride (10 mL) was added to the concentrate before the solvent was removed by the evaporator. Quantification of 2-furfurylthiol was performed by GC, and the residual ratios (percent) were calculated from the measured values of 2-furfurylthiol in the thermally treated and nontreated solutions.

Gas Chromatography. An HP 5890 series II gas chromatograph equipped with a flame ionization detector (FID) was used. A fused silica column (60 m \times 0.25 mm i.d.; coated with a 0.25 μ m film of DB-Wax; J&W Scientific) was used. The column temperature was programmed from 80 to 210 °C at the rate of 3 °C/min for all runs. The injector and detector temperatures were both 250 °C. The flow rate of the nitrogen carrier gas was 1.2 mL/min, and the split ratio was 1:28.

Gas Chromatography—Mass Spectrometry. An HP 5890 series II gas chromatograph coupled to an HP model 5972 series mass spectrometer was used. The column was a 60 m \times 0.25 mm i.d. DB-Wax fused silica capillary column (J&W Scientific) with a film thickness of 0.25 μ m. The column temperature was programmed from 40 to 210 °C at the rate of 3 °C/min. The injector temperature was 250 °C. The flow rate of the helium carrier gas was 1 mL/min, and samples (0.2 μ L) were applied using the splitless injection technique. The mass spectrometer was used under the following conditions: ionization voltage, 70 eV (EI); ion source temperature, 150 °C.

Headspace GC-MS. The instrument used for the GCO-H was modified. The column length was changed to 60 m, and the end of the column was coupled to the mass spectrometer (HP 5972). The flow rate of the helium carrier gas and temperature program were as previously described for the GCO-H analysis, and the MS conditions were as previously described for the GC-MS analysis.

Identification of Components. The identification of the components was made by comparison of their Kovats GC retention indices, mass spectra, and odor quality to those of authentic compounds.

RESULTS AND DISCUSSION

Sensory Evaluation. After heat processing, the flavor of the coffee drink had changed. **Figure 1** shows the odor attributes of the coffee drink sample after heating. The after-heating coffee

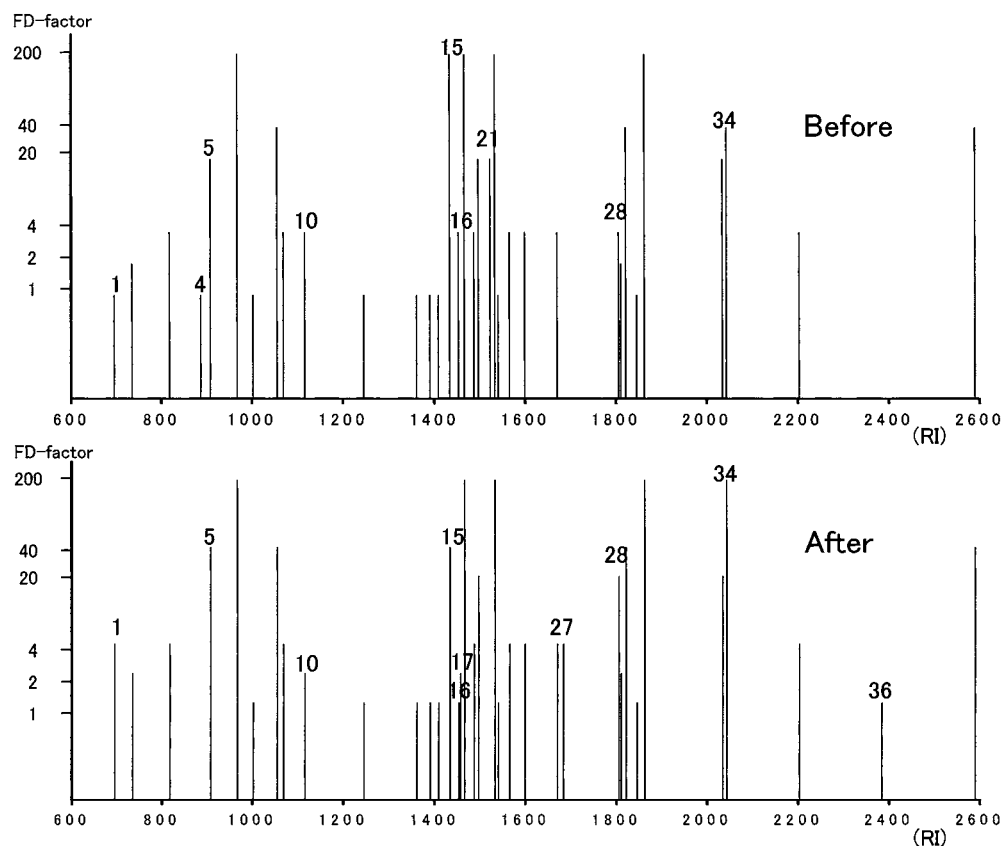


Figure 2. Flavor dilution chromatograms (DB-Wax stationary phase column) of coffee drinks before (top) and after (bottom) heat processing. Numbers indicate the positions at which an odor was perceived at the sniffing port.

Table 1. Potent Odorants of Coffee Drinks Showing Differences in Their FD Factors before and after Heat Processing

no. ^a	RI ^b	RI ^c	compound	odor quality ^f	FD factor ^g	
					before heating	after heating
1a	696	690	methanethiol ^d	putrid	1	4
1b	696		unknown	pungent	1	4
4	887		unknown	roasty	1	nd
5	908		unknown	pungent	20	40
10	1116		unknown	roasty	4	2
15	1434	1435	2-furfurylthiol ^e	roasty	200	40
16	1453	1448	methional ^e	potato-like	4	1
17	1454	1447	acetic acid ^e	sour	nd	2
21	1523	1521	3-mercapto-3-methylbutyl formate ^e	roasty	20	nd
27	1684	1676	3-methylbutanoic acid ^e	sour	nd	4
28	1806	1813	2-furfuryl methyl disulfide ^e	meaty	4	20
34	2043	2040	4-hydroxy-2,5-dimethyl-3(2H)-furanone ^e	caramel-like	40	200
36	2384		unknown	sour	nd	1

^a Numbering refers to **Figure 2**. ^b Retention index on DB-Wax column (30 m × 0.25 mm i.d.; coated with a 0.25 μm film) observed for GCO-H. ^c Retention index on DB-Wax column (60 m × 0.25 mm i.d.; coated with a 0.25 μm film) observed for GC-MS. ^d Identified by headspace-GC-MS. ^e Identified by GC-MS using enrichment of odorants samples. ^f Odor quality assigned during GCO-H. ^g Relationship between FD factor and headspace volume is given under Materials and Methods.

drink had a more pungent, putrid, heavy (tallowy), sour, and caramel-like odor compared to the nonheated coffee drink. The characteristic roasty odor of the fresh coffee drink was found to have significantly decreased due to the heat processing.

Changes in the Odor Activities of the Coffee Drink Caused by the Heat Processing. The coffee drink has a characteristic flavor that was changed by the heat processing. GCO-H was performed to assess the potency of the volatiles before and after the heat processing in relation to the sensory profiles of the samples. GCO-H of these samples revealed 34 and 35 odor-active peaks with flavor dilution (FD) factors in the range of 1–200 for the before- and after-heating coffee drinks, respec-

tively (**Figure 2**). The components responsible for the 12 peaks for which the FD factors had changed were identified by comparison of their Kovats indices, mass spectra, and odor quality to those of authentic compounds. The odors of these peaks were sniffed by the GCO-H, and these results are summarized in **Table 1**. Eight compounds were identified from the 12 peaks by GC-MS. Among these potent odor-producing compounds, methanethiol (**1a**) was identified by headspace GC-MS. However, a pungent odorant (**1b**) eluted at the same time as methanethiol could not be identified. The headspace samples often contain odorants in such small levels that they give no detector response. No mass spectrum with headspace GC-MS

Table 2. Residual Ratios^a of 2-Furfurylthiol after Heating of Model Solutions at Different Temperatures and pH Values

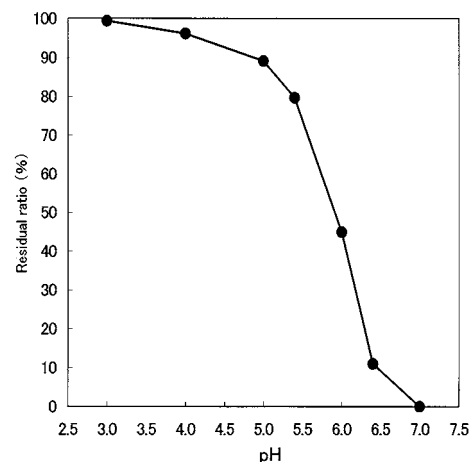
pH	121 °C, 10 min	123 °C, 20 min
6.8	5.5	5.3
6.0	48.3	43.4

^a Residual ratios are denoted by percentage.

was obtained for compounds **15–17**, **21**, **27**, **28**, and **34**. These odorants were identified by GC-MS using enrichment of the odorant samples that were separated by steam distillation under reduced pressure and then concentrated by the adsorptive column method. Methanethiol (**1a**) and unknown compounds (peaks 1 and 5) were responsible for the putrid and pungent odor of the after-heating coffee drink. Acetic acid (**17**), 3-methylbutanoic acid (**27**), and an unknown compound (peak 36) increased after heat processing. They seemed to be mainly responsible for the sour odor in the heated coffee drink. Furthermore, 2-furfuryl methyl disulfide (**28**) and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**34**) increased during the heat processing. These compounds were assumed to be responsible for the heavy (tallowy) and caramel-like odor. On the other hand, the comparative GCO-H data indicated a correspondence between the change in the FD factors and the decreased roasty odor in the odor profile analysis, because the decrease in the FD factors (peaks 4, 10, 15, 16, and 21), which related the roasty odor, were found in the after-heating coffee drink compared with the before-heating processed coffee drink. This finding was in agreement with our previous study, and it was assumed that these odorants were changed by oxidation, thermal degradation, and/or hydrolysis during the heat processing (8). However, there is a limit in the comparison of individual odorants with odor attributes because the factors of synergistic and antagonistic effects between the odorants and other constituents in the coffee drinks are not considered.

On the basis of these results, the important components involved in changing the coffee drink odor during heat processing were screened. However, it is known that FD factors in general contain some errors (13), and the static headspace sampling technique has the problem that the high water solubility and high boiling point compounds suffer losses. Therefore, to reveal the change in the absolute amount of these compounds, which were contained in the coffee drinks consisting of complex mixtures of food matrices, a further study would be required.

Thermal Stability of 2-Furfurylthiol in Aqueous Solutions. 2-Furfurylthiol (**15**), which is assumed to be a key contributor to the roasty odor, showed a much higher FD factor in the before-heating processed coffee drink, and the FD factor of the after-heating coffee drink decreased to one-fifth of its initial FD factor (Figure 2). However, the residual ratio of 2-furfurylthiol (~20%), which was calculated from the measured values of the GC-O experiment before and after heat processing of the coffee drinks, was much higher than that of the model experiment (3.6%: pH 6.8, 123 °C for 20 min) in our previous study (8). It was thought that the differences in the residual ratios were affected by the different temperatures (121 °C for 10 min and 123 °C for 20 min) and pH (pH 6.0 and 6.8) conditions. Therefore, the following model experiment was done to clarify the residual ratios of 2-furfurylthiol affected by the different conditions. The results shown in Table 2 indicate that more pronounced differences in the residual ratios occurred at the different pH conditions compared with the different time and temperature conditions. Furthermore, an additional experiment focused on the effect of pH on the thermal stability in

**Figure 3.** Residual ratios of 2-furfurylthiol after model solutions (121 °C, 10 min) were heated at various pH values.**Table 3.** Quantitative Data (Relative Amounts)^a for 2-Furfurylthiol and Degradation Products after Heating of Model Solutions at Different pH Values

compound	pH						
	3.0	4.0	5.0	5.4	6.0	6.4	7.0
2-furfurylthiol	0.46	0.44	0.41	0.37	0.21	0.05	<0.01
difurfuryl disulfide	<0.01	0.01	0.03	0.07	0.13	0.14	0.17
furfural	<0.01	0.01	0.01	0.01	0.02	0.02	0.03
furfuryl alcohol	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01

^a Relative amounts of compounds are shown as the ratio of the peak area of each compound to the peak area of an internal standard (methyl octanoate) on the GC.

aqueous solution. Figure 3 shows the residual ratios of 2-furfurylthiol in aqueous model solutions at various pH values. The data clearly indicate that the stability of 2-furfurylthiol during heat processing has a close correlation with the pH of the aqueous solutions. The residual ratios of 2-furfurylthiol in the after-heating model solutions decreased with increasing pH. Especially, in the pH range of 5.0–7.0, the residual ratios sharply decreased with an increase in the pH. This finding can account for the residual ratios of the 2-furfurylthiol difference between pH 6.0 and 6.8. In the after-heating model solutions, difurfuryl disulfide, furfural, and furfuryl alcohol were detected by GC as the volatile degradation products of 2-furfurylthiol. Among these compounds, difurfuryl disulfide was the major degradation product, and its amount in the after-heating model solutions increased with increasing pH (Table 3). It is well-known that 2-furfurylthiol easily oxidizes to disulfide (14, 15). The oxidation mechanism of thiols may be either polar, radical, or both (16). However, the total amount of the volatile degradation products of 2-furfurylthiol detected by GC analysis was less than the amount of 2-furfurylthiol lost during heat processing. It can be assumed that the volatile and nonvolatile degradation products were produced at the same time according to a Fenton-type reaction (11). In general, the canned coffee drinks are sterilized after the pH range has been adjusted to between 5 and 7 to prevent an increase in the sour taste and the cohesion of the coffee and milk components (12). However, as for the concentration of 2-furfurylthiol in the after-heating model solutions, it was found that the significant difference were brought about by the condition of pH (in the range of 5–7) of aqueous solutions. Therefore, the sulfury-roasty flavor of canned coffee drinks would be expected to change with the difference in only a few pH values during heat processing.

The concentration of 2-furfurylthiol in the coffee drinks was much lower than in the model solutions in these experiments; moreover, the coffee drinks consist of complex mixtures of food matrices. Therefore, it is thought that the change in the flavor of the coffee drink during heat processing is associated with the various reactions [for example, thiols binding to coffee melanoidins (9, 10) and the Fenton-type reaction (11)], together with pH-dependent degradation.

Conclusions. The application of GCO-H using the before- and after-heating processed coffee drinks resulted in the detection of 12 odor-active peaks for which the FD factor changed. Methanethiol, acetic acid, 2-furfurylthiol, methional, 3-mercapto-3-methylbutyl formate, 3-methylbutanoic acid, 2-furfuryl methyl disulfide, and 4-hydroxy-2,5-dimethyl-3(2H)-furanone seemed to be mainly responsible for the flavor change in the after-heating coffee drink. pH effects on the change in the concentration of 2-furfurylthiol during heat processing were demonstrated. In the pH range of 5–7, which is used for the manufacturing process of the canned coffee drink, the concentration of this compound in the model solutions was significantly reduced by the heat processing.

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Received for review October 7, 2002. Revised manuscript received January 11, 2003. Accepted January 12, 2003.

JF021025F