

# Isolation and Identification of Headspace Volatiles from Brewed Coffee with an On-Column GC/MS Method

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Qualitative and quantitative analyses of headspace volatiles of roasted brewed coffee were conducted with use of a direct on-column injection technique. Qualitative analysis was done by gas chromatography/mass spectrometry (GC/MS). Quantitative analysis was performed by gas chromatography (GC) using an internal standard. Sixty-two volatile compounds were positively identified in the headspace of brewed coffee. The compounds identified included 23 furans, 10 pyrazines, 6 ketones, 5 aldehydes, 3 pyrroles, 3 thiophenes, and 8 miscellaneous compounds such as alcohols, sulfides, and pyridine. The major constituents were 2-methylbutanal (GC area % = 17.7), furan (13.8), and 3-methylbutanal (9.7). Some well-known coffee volatiles such as furfuryl mercaptan were not found in the headspace sample.

Coffee volatiles are among the most intensively studied flavor chemicals in foods and beverages. Over 700 constituents were reported by 1987, and it is expected that this number will reach 800 by the end of 1990. The major flavor chemicals identified by the early 1970s in coffee were aldehydes, ketones, and esters (Stoll et al., 1967). Recent reports on coffee flavors generally focus on chemicals with heteroatoms such as pyrazines, mercaptans, sulfides, disulfides, thiophenes, and thiazoles (Vitzthum and Werkhoff, 1976; Tressl and Silwar, 1981).

Establishing the composition of volatile chemicals in foods or beverages is very important in a study of food flavors. Consequently, many volatile flavor chemicals have been isolated by various techniques including steam distillation (Mussinan et al., 1973), simultaneous steam distillation-solvent extraction (Ohnishi and Shibamoto, 1984), simultaneous purging-solvent extraction (Umano and Shibamoto, 1987), purge and trap (Wada et al., 1987), and direct headspace collection (Hinshaw, 1988). However, all existing methods may cause compositional changes. Use of steam may alter some heat-labile components. Active surfaces of adsorbents may change the proportion of volatile constituents in a sample.

Direct injection of a headspace sample onto a GC column gives the most accurate composition of flavors. However, when a large volume of headspace gas is injected, the sample is diluted by the carrier gas between the injection chamber and the column, and consequently, band-broadening of the peaks occurs. This problem can be solved by injecting headspace gas directly into the interior of a capillary column (on-column injection). However, in this case, the sample is still delivered to the column in a volume too great (4-10 mL) and over a period too long (1-5 min) to obtain optimum narrow and sharp peaks. Cryofocusing the sample with liquid nitrogen at the head of the column during injection of the sample can greatly improve the chromatography (Takeoka and Jennings, 1984).

Surprisingly, there are virtually no reports on the analysis of food flavors with this simple method. In the present

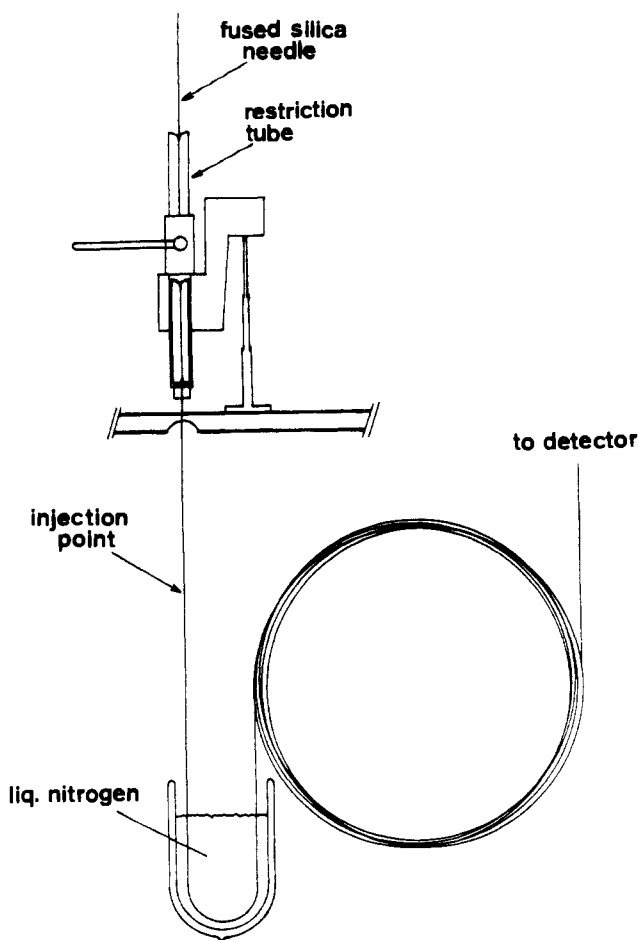


Figure 1. Diagram of on-column injection technique.

study, headspace volatiles of brewed coffee were analyzed with this on-column injection/cryofocusing method.

## EXPERIMENTAL SECTION

**Materials.** Commercially roasted coffee beans (Columbian Arabica) were purchased from a local market. All authentic chemicals were obtained from reliable commercial sources.

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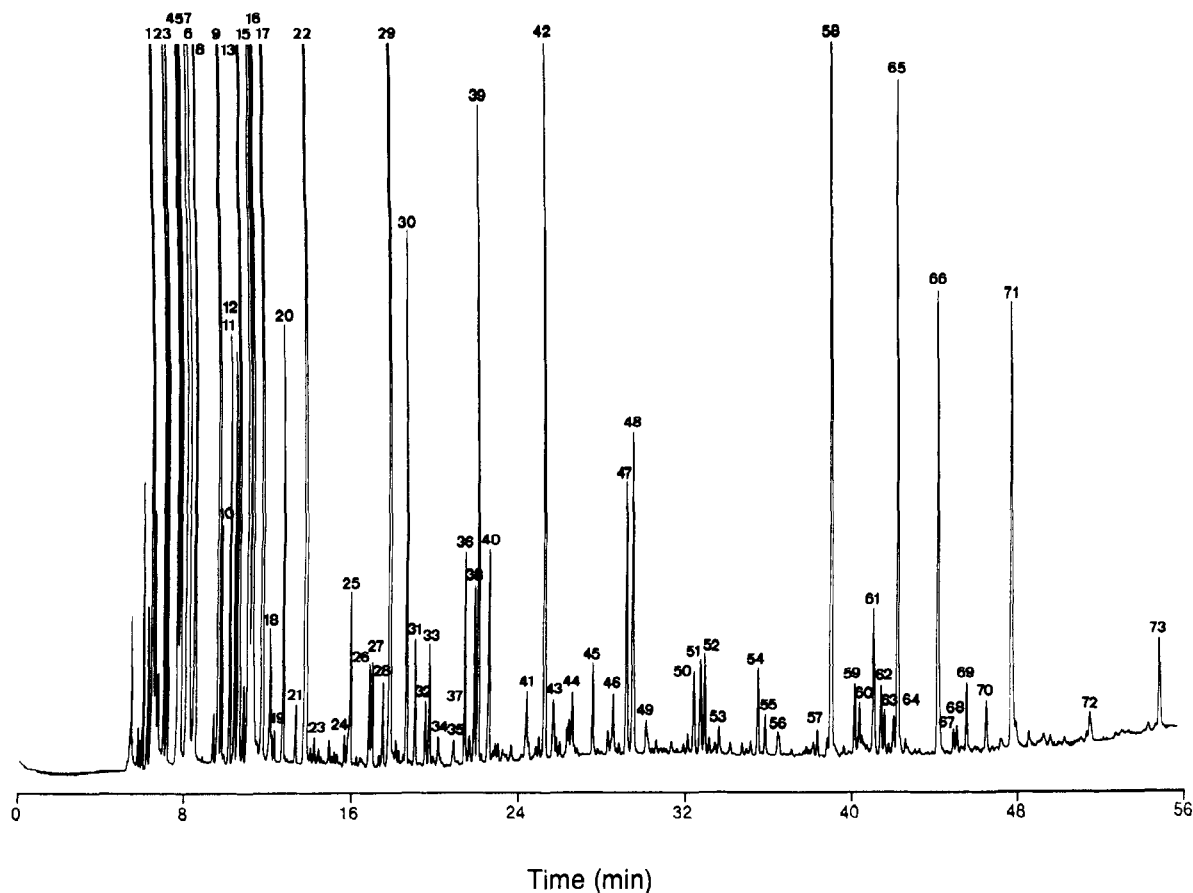


Figure 2. Typical gas chromatogram of headspace sample from brewed coffee.

Table I. Volatile Constituents Identified in Headspace Gas of Brewed Coffee

peak in Figure 2	compound	peak area, %	I <sup>a</sup>	RSD <sup>b</sup>	peak in Figure 2	compound	peak area, %	I <sup>a</sup>	RSD <sup>b</sup>
1	2-butene	5.2	674	6.7	38	1-methylpyrrole	0.24	1140	5.1
2	1,3-pentadiene (isomer)	1.0	728	5.3	39	unknown	0.95	1143	5.4
3	1,3-pentadiene (isomer)	0.79	737	3.3	40	5-methyl-2-vinylfuran	0.37	1152	4.3
4	acetaldehyde	2.5	769	3.9	41	3-methyl-2-vinylfuran	0.13	1183	9.6
5	dimethyl sulfide	4.0	777	5.0	42	pyridine	0.91	1193	11.6
6	furan	13.8	797	3.2	43	unknown	0.13	1204	11.4
7	2-methylpropanal	5.5	801	4.0	44	pyrazine	0.10	1219	5.9
8	methyl acetate	1.7	810	3.1	45	2-(methoxymethyl)furan	0.12	1241	7.5
9	3-methylfuran	9.7	851	5.1	46	5-methyl-2(E)-propenylfuran	0.08	1257	10.2
10	unknown	0.27	856	2.9	47	2-methyltetrahydrofuran-3-one	0.33	1270	9.0
11	unknown	0.47	868	4.8	48	2-methylpyrazine	0.44	1274	13.1
12	2-methylfuran	0.48	876	6.0	49	5-methyltetrahydrofuran-2-one	0.07	1288	7.4
13	2-butanone	3.1	881	4.9	IS	heptan-3-ol		1306	
14	methanol	0.09	888	5.1	50	2,5-dimethylpyrazine	0.11	1332	13.6
15	2-methylbutanal	17.7	896	2.4	51	2,6-dimethylpyrazine	0.14	1338	11.1
16	3-methylbutanal	9.69	900	2.1	52	2-ethylpyrazine	0.13	1343	9.6
17	dichloromethane (solvent)	4.0	914	7.2	53	2-methyl-2-cyclopentenone	0.03	1357	11.6
18	ethanol	0.17	926	6.6	54	2-ethyl-6-methylpyrazine	0.09	1393	7.2
19	unknown	0.04	932	6.3	55	2-ethyl-5-methylpyrazine	0.05	1399	5.0
20	2,5-dimethylfuran	0.54	943	4.1	56	2,3,5-trimethylpyrazine	0.04	1413	14.6
21	2-ethylfuran	0.07	960	3.8	57	2,5-dimethyl-3-ethylpyrazine	0.03	1455	18.4
22	2,3-butanedione	2.2	971	3.5	58	furfural	1.3	1468	12.0
23	unknown	0.04	982	6.5	59	furfuryl methyl sulfide	0.09	1492	10.8
24	3-ethylfuran	0.04	1021	8.6	60	furfuryl methanoate	0.06	1497	13.7
25	thiophene	0.28	1023	8.0	61	2-acetylfuran	0.20	1512	16.2
26	toluene	0.16	1042	8.9	62	benzaldehyde	0.11	1520	11.9
27	4-methylpentane-2,3-dione	0.14	1046	7.3	63	1-(2-furyl)propan-2-one	0.06	1524	11.1
28	2,3,5-trimethylfuran	0.11	1056	5.6	64	unknown	0.05	1534	12.2
29	pentane-2,3-dione	3.6	1062	4.7	65	furfuryl acetate	0.92	1539	12.4
30	dimethyl disulfide	0.67	1078	4.8	66	5-methyl-2-furfural	0.69	1582	15.3
31	2-vinylfuran	0.17	1085	4.2	67	2-acetylpyrazine	0.03	1599	9.7
32	2-methylthiophene	0.09	1094	7.2	68	furfuryl propionate	0.04	1603	11.1
33	2-methylbut-2-en-1-ol	0.16	1098	3.4	69	2,2'-methylenebisfuran	0.11	1615	13.1
34	3-methylthiophene	0.04	1106	16.0	70	1-methyl-2-formylpyrrole	0.07	1637	15.2
35	unknown	0.04	1121	5.1	71	furfuryl alcohol	0.66	1666	11.1
36	2,4-dimethylpentan-3-one	0.25	1132	6.1	72	isobutylpyrrole	0.09	1759	12.3
37	unknown	0.03	1134	8.4					

<sup>a</sup> Kovats index on DB-WAX. <sup>b</sup> Relative standard deviation (SD/mean × 100) of 10 replications.

**Sample Preparations.** Roasted ground beans (8 g) and 60 mL of deionized boiling water were placed into a 300-mL Erlenmeyer flask. A 200- $\mu$ L portion of heptan-3-ol solution (100  $\mu$ g/mL of water) was added to the coffee solution as an internal standard for GC analysis. The flask was sealed with a Teflon plug equipped with a Teflon stopcock. The coffee solution was stirred for 1 min with a magnetic stirrer, and then the flask was heat at 60 °C in a water bath for 20 min. A sample of headspace gas (4 mL) was drawn into a 20-mL gas-tight syringe equipped with a fused silica capillary column needle.

**Gas Chromatography.** A headspace sample was injected directly into a fused silica capillary column with an on-column injector (J&W Scientific, Folsom, CA) installed on a Hewlett-Packard Model 5890A gas chromatograph (GCT). The sample was cryofocused about 20 cm from the end of the column with liquid nitrogen for 5 min as shown in Figure 1. After removal of the liquid nitrogen, the oven temperature was held at 40 °C for 6 min and programmed to 190 °C at 3 °C/min. The GCT was equipped with a 60 m  $\times$  0.25 mm (i.d.) DB-WAX bonded-phase fused silica capillary column (J&W Scientific) and a flame ionization detector (FID). The linear flow rate of helium carrier gas was 30 cm/s. The detector temperature was 260 °C.

**Gas Chromatography/Mass Spectrometry.** A gas chromatograph (HP 5890A) with on-column injector interfaced to a VG Trio-2 mass spectrometer was used to obtain mass spectra of gas chromatographic components of the coffee headspace sample. The ionization voltage was 70 eV, and the ion source temperature was 140 °C.

**Identification of the Coffee Headspace Constituents.** Identification of the coffee headspace constituents was made by comparison of their GC Kovats indices (*I*) and mass spectra to those of authentic samples.

## RESULTS AND DISCUSSION

A typical gas chromatogram of the headspace from brewed coffee is shown in Figure 2. The mixture of chemicals from a headspace is generally different from that of the samples obtained by organic solvent extraction (Stoll et al., 1967; Shibamoto et al., 1981). Many furan derivatives, which are known sugar degradation products (Hodge, 1967), have been reported in coffee samples prepared by solvent extraction. For example, 16 furan derivatives were reported in a dichloromethane extract of roasted coffee beans (Shibamoto et al., 1981). In contrast, 23 furans were identified in the present study, but their total GC area percent was less than that of a solvent extract. Furan was a major constituent of the headspace sample (13.8%) in the present study but was not reported in the sample prepared by dichloromethane extraction. Among furans, furfuryl alcohol appears to be the compound with the lowest vapor pressure in a headspace over brewed coffee. Many pyrazines recognized as the volatiles contributing to roasted or toasted aromas of cooked foods (Seifert et al., 1972; Parliment and Epstein, 1973) were identified in the present study. On the other hand, furfuryl mercaptan, which gives fresh roasted coffee aroma in a dilute aqueous solution (Arctander, 1969), was not found in the present study. This may be due to its very low concentration in coffee.

The reproducibility of the experimental procedure was examined with 10 replications. The reproducibility was

determined on the basis of the peak area ratio of a component and the internal standard (heptan-3-ol) and listed as a relative standard deviation (RSD). The RSD of components with *I* smaller than 1000 gave satisfactory values (less than 6.7%). However, the RSD of components with *I* greater than 1000 had relatively high values (10–15%) with some exceptions. The consistent injection of less volatile compounds is extremely difficult due to their condensation and/or adsorption on surfaces of the system. The present method is a quite simple technique and is much less time-consuming than other methods such as a purge and trap method.

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