

Analysis of Flavor Composition of Coriander Seeds by Headspace Mulberry Paper Bag Micro-Solid Phase Extraction

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This paper reports the example of headspace mulberry paper bag micro solid phase extraction (HS-MPB- μ -SPE) as a new sampling method for the determination of volatile flavor composition of coriander seeds. Adsorption efficiencies between two configurations of mulberry paper bag were compared, and several parameters affecting the HS-MPB- μ -SPE were investigated and optimized. The optimized technique uses an adsorbent (Tenax TA, 0.1 mg) contained in a mulberry paper bag of front configuration where fine surface was outside, and minimal amount of organic solvent (0.6 mL). Linalool and γ -terpinene were found as abundant flavor compounds from coriander seeds. The limit of detection (LOD) and the limit of quantitation (LOQ) for linalool of major flavor in coriander seeds were 10.3 ng/mL and 34.4 ng/mL, respectively. The proposed method showed good reproducibility and good recovery. The HS-MPB- μ -SPE is very simple to use, inexpensive, requires small sample amounts and solvent consumption. Because the solvent for extraction is reduced to only a very small volume, there is minimal waste or exposure to toxic organic solvent and no further concentration step.

Key Words: Headspace, Mulberry paper bag, Micro solid phase extraction, GC/MS, Coriander flavor

Introduction

The main purpose of this study is to develop a novel, simple, sensitive, reproducible, convenient for the field work, and low cost method that are applicable for extracting and measuring flavor components from coriander seeds. Coriander (*Coriandrum sativum* L.) is an annual herb belongs to Apiaceae (or Umbelliferae) and its seeds and leaves primarily used as a flavoring agent and a garnish in the cuisines of Southeast Asia, China, India, and Central America. Fresh coriander leaves have a bold taste that combines a strong sage flavor with sharp citrus notes. Coriander leaves, when crushed, give off an unpleasant odor like squashed bugs. According to the literature,¹ bug-like smell is caused by the trans-tridec-2-enal content. However, coriander seeds have no sage-like flavor at all, but a much more pleasant aroma like a lemony citrus flavor when crushed.² The brown-grey seeds of coriander are almost ovate globular. Coriander seeds have slightly pungent, sweet and spicy top note. It is also described as warm, nutty, spicy, and orange flavored.

Analyses of volatile composition from coriander seeds are already studied by steam distillation and/or supercritical fluid extraction combined with gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS).³⁻⁶ Very recently, we reported a new headspace sampling method called headspace mulberry paper bag micro solid phase extraction (HS-MPB- μ -SPE).⁷⁻⁸ The technique used only an adsorbent (Tenax TA) contained in a mulberry paper bag, and minimal amount of organic solvent. Korean handmade mulberry paper, Hanji, is made by traditional papermaking process from the strong bast fiber obtained chiefly from the phloem of Dak tree (mulberry, *Broussonetia kazinoki* Siebold & Zucc., moraceae family).

Generally, the adsorption of volatile molecules by passing through mulberry paper from headspace to adsorbent particles can be conducted by one of two ways: the front configuration

from fine surface (outside) of mulberry paper to coarse backside (inside), and the reverse configuration from coarse backside (outside) to fine surface (inside). However, adsorption efficiencies between two configurations were not compared in our previous report.

In the present study, we found that the front configuration (where fine surface was outside) showed better efficiency than the reverse configuration. In the present initial work, the use of front configuration mode of Hanji bag in which contained Tenax TA adsorbent as a new headspace sampling for the characterization of flavor compounds from coriander seeds is proposed. Several parameters affecting the HS-MPB- μ -SPE combined with GC/MS for the analysis of flavor composition of coriander seeds were investigated and optimized.

Experimental

Materials and reagents. The dried samples of Chinese coriander seeds were purchased from the local super market of Dalian in China. Moroccan (Gaban Co. Ltd.) and Japanese (Asaoka spice Co.) coriander seeds were purchased in Tokyo, Japan. The dried coriander seeds were finely crushed to powders, and then used directly without any further treatment.

Korean Hanji mulberry paper samples were obtained from local manufacturing company or stationer in Seoul. Chinese Xuan paper was purchased at the bookstore in Shanghai, China.

All working reference standards were of analytical grade and were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Tokyo Kasei (Nihonbashi, Tokyo, Japan). Petroleum ether, *n*-hexane and ethyl ether of chromatographic grade were obtained from Mallinckrodt Baker (Phillipsburg, NJ, USA). Tenax TA (particle size 221 ~ 173 μ m; 60/80 mesh) adsorbent was purchased from Supelco (Bellefonte, PA, USA). Prior to use, Tenax TA particles are pre-rinsed with petroleum ether and dried

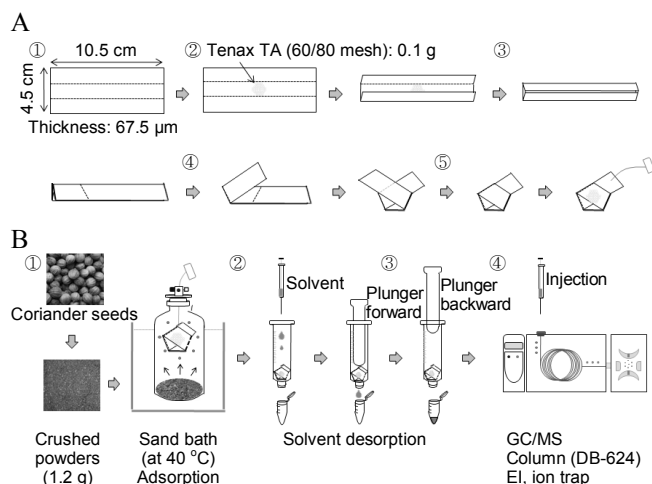


Figure 1. Schematic illustration showing how to fold a prototype mulberry paper bag for headspace μ -solid phase extraction. A, Folding method of mulberry paper bag. B, Procedure of HS-MPB μ -SPE and GC/MS.

at 150 °C for 60 min in order to remove impurities.

Headspace mulberry paper bag micro solid phase extraction (HS-MPB- μ -SPE). Schematic diagram of the experimental set-up of a prototype mulberry paper bag (MPB) is shown in Fig. 1. As seen in Fig. 1-A, preparation of a Tenax TA - MPB consists of five steps:

- 1) A small piece of individually cut mulberry paper (10.5 cm, length \times 4.5 cm, width) is used to make a MPB as a wrapper in which Tenax TA particles can be enclosed.
- 2) Purified Tenax TA adsorbent (*ca.* 100 mg) is obtained on a small sheet of mulberry paper.
- 3) Then a mulberry paper is folded twice upward and downward along lines made by folding, one folded part will be covered the other part to have them aligned. Tenax TA particles are wrapped inside three folding parts of a mulberry paper (10.5 cm, length \times 1.5 cm, width) that overlapped one another with transverse rectangular shape.
- 4) The both edges are folded and beveled to make sure Tenax TA is enclosed in a mulberry paper.
- 5) Then, a longer side edge is folded twice again obliquely, and inserted into a gap between two folded parts so as to across each other. The bag edges are closed themselves without further staples or sewing. A small label is attached to a small pentagonal-shaped bag (*ca.* 2.5 cm, I.D. \times 2 mm, thickness) of mulberry paper.

HS-MPB- μ -SPE procedure for GC/MS is illustrated in Fig. 1-B. In the extraction step, coriander seed powders (*ca.* 1.2 g) and a MPB containing Tenax TA are obtained in a vial (50 mL) and the vial is hermetically sealed with a polytetrafluoroethylene (PTFE, Teflon) mini-nut cap. Volatile aroma compounds emitted from coriander seed powders are extracted by exposure of a small MPB to the headspace for 60 min at 40 °C. After adsorption, a MPB is removed from a sample vial and inserted immediately into a clean glass syringe barrel (10 mL, 1.5 cm I.D. \times 9 cm long). And then, 0.6 mL of petroleum ether or other solvent is

added very slowly drop by drop, the plunger is moved slowly backward and forward four times to elute the volatile aroma compounds collected in a MPB. Aliquots (0.2 μ L) are analyzed by GC/MS without further treatment after the desorption step.

Gas chromatography conditions. GC analysis was carried out using Hewlett-Packard HP 5890 apparatus equipped with flame ionization detector (FID) and a 6% cyanopropylphenyl-94%-dimethylsiloxane copolymer (DB-624, 30 m length \times 0.25 mm I.D. \times 1.4 μ m film thickness, J & W Scientific, Folsom, CA, USA) capillary column. The oven temperature program was 50 °C (3 min) \sim 5 °C/min \sim 220 °C (10 min). Injector and detector temperatures were maintained 240 °C and 250 °C, respectively. Samples (0.2 μ L) were injected in the split mode (1:30), using 99.9% nitrogen as carrier gas at a constant flow rate (1.0 mL/min). Flow rates of hydrogen and air were kept at 30 mL/min and 300 mL/min, respectively. Data manipulation was accomplished by HP 3396A integrator.

Gas chromatography-mass spectrometry. Chromatographic separations were performed on a fused silica cross-linked 6% cyanopropylphenyl-94%-dimethylsiloxane copolymer (DB-624, 30 m length \times 0.25 mm I.D. \times 1.4 μ m film thickness, J & W Scientific, Folsom, CA, USA) capillary column. Flow rate of carrier gas (He, 99.999%) was 1.0 mL/min. GC/MS analysis was performed using a Trace GC 2000 and a GC-Q plus ion trap MSⁿ (Thermoquest-Finnigan, Austin, TX, USA) with electron impact (EI) ionization mode. The injected sample volume was 0.2 μ L. A split injection with a ratio of 1: 30 was used. The injector temperature was 240 °C. The oven temperature program was 50 °C (3 min) \sim 5 °C/min \sim 220 °C (10 min). Transfer line temperature was 230 °C. Operating conditions for the ion trap mass spectrometer were; ionization voltage, 70 eV; ion source temperature, 200 °C. The measuring mode was scanned from 50 to 500 mass ranges. Identifications of volatile aroma compounds were made by comparison of mass spectra and retention times of relevant chromatographic peaks obtained with those of authentic references and tentative identifications by comparison with corresponding spectra of the NIST and Wiley libraries.

Results and Discussion

Properties of mulberry paper and Tenax TA. Fig. 2-A shows scanning electron microscope (SEM) images of Jeonju Hanji mulberry paper which were randomly collected in this experiment. SEM images were observed by field emission-scanning electron microscope (Hitachi S-4200, electro gun; cold cathode field emission electron source, accelerating voltage; 0.5 \sim 30 kV, 0.1 kV/step, magnification; 100 \times and 1000 \times). Thickness and weight of Hanji mulberry papers used are summarized in Table 1. Bast fibers from the phloem of Korean mulberry tree have relatively long length (3 \sim 17 mm) and narrow wideness (13 \sim 42 μ m). Cellulose, lignin, and pentosan are known as chief constituents of its fiber. As seen in Fig. 2-A, there are a lot of fibers and micro-gaps between fibers. These micro-gaps have played an important role as possible pass ways to transport volatile molecules from outside of mulberry paper to inside and vice versa. According to the report, air or water vapor is possible to pass through Hanji mulberry papers (130 \sim 240 μ m, thickness), and amounts of their water vapor permeation were 38.1 \sim 38.8

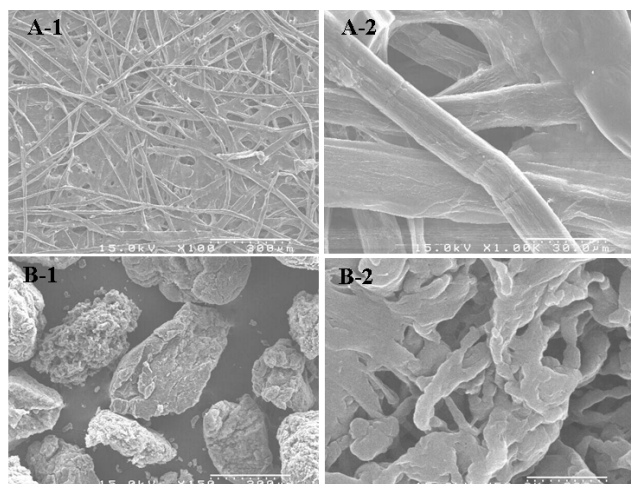


Figure 2. SEM images of mulberry papers and Tenax. A, Jeonju Hanji; (Magnification: 1, 100 \times ; 2, 1000 \times) B, Tenax TA. (Magnification: 1, 150 \times ; 2, 50,000 \times).

Table 1. Thickness and weight of Hanji mulberry papers (mean \pm SD, $n = 3$)

Hanji mulberry paper sample	Thickness (μm)	Weight (g/m^2)
Jeonju Hanji	67.5 (± 1.69)	28.7 (± 0.32)
Poongsan Hanji	79.2 (± 1.66)	31.5 (± 0.35)
Poongsan Hwaseonji	47.5 (± 1.66)	26.9 (± 0.35)
Xuan paper (Qintan tree paper)	55.0 (± 1.93)	21.9 (± 0.99)

$\text{g}/\text{m}^2\cdot\text{h}$.⁹ Thus, window papers or wall papers made from Hanji mulberry paper control indoor humidity by water vapor permeation.⁹⁻¹⁰ Interestingly, Hanji mulberry papers reduce considerable amounts of carbon dioxide, carbon monoxide, formaldehyde, and toluene in the indoor air by passing these gases through micro-gaps between fibers of mulberry papers.⁹

Scanning electron micrographs (magnification: 150 \times and 50,000 \times) of Tenax TA (particle size 221 \sim 173 μm ; 60/80 mesh) used in this study are shown in Fig. 2-B. The shape of Tenax TA particle is granular and available in a wide range of mesh sizes. Tenax TA is one of the hydrophobic commercial adsorbents. Tenax TA is a macroporous, semi-crystalline polymer manufactured from 2,6-diphenyl-*p*-phenylene oxide (DPPO). Pore sizes have been classified by IUPAC as macropores (> 50 nm diameter), mesopore (greater than 2 nm but less than 50 nm diameter), and micropores (< 2 nm diameter). Average pore size and pore volume of Tenax TA (60/80 mesh) are 200 nm and 2.4 mL/g, respectively. It has a relatively low density (0.25 g/mL) and a low surface area (about 35 m^2/g). The relatively inert nature, high thermal stability (limit temperature; 350 $^\circ\text{C}$) and rapid desorption kinetics of Tenax TA make it a very suitable adsorbent for the cold trap of thermal desorbers or for collecting of many volatile molecules from headspace of low concentrations. The tubes used to hold the adsorbent for thermal desorption are usually made of stainless steel or precision-bore borosilicate glass. In this study, mulberry paper has replaced of stainless steel or glass for headspace adsorption and solvent desorption.

Optimization of headspace mulberry paper bag-micro solid phase extraction (HS-MPB- μ -SPE). Linalool is considered as a

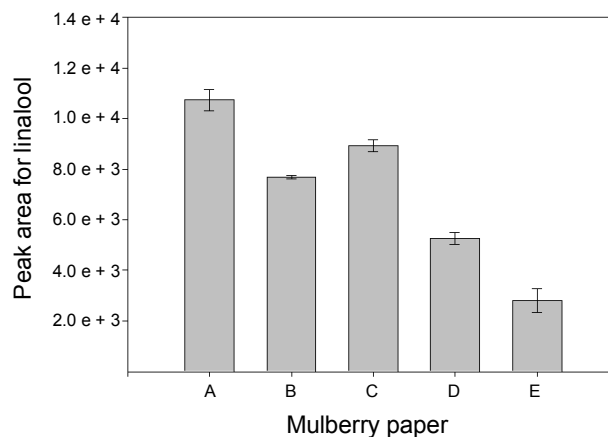


Figure 3. Comparison of the efficiency of HS-MPB- μ -SPE and GC-FID by different mulberry papers. A, Jeonju Hanji (front configuration: fine surface); B, Jeonju Hanji (reverse configuration: coarse backside); C, Poongsan Hwaseonji; D, Poongsan Hanji, Xuan paper.

representative constituent of coriander seed flavors. The optimization of HS-MPB- μ -SPE was performed by GC-FID using stock solution of linalool as model compounds at a concentration of 1.0 mg/mL in petroleum ether. The chromatographic peak area of linalool was considered as analytical signal for optimization. Once the optimization has been completed, optimum value of a variable is fixed for further studies.

HS-MPB- μ -SPE procedure described in materials and methods section was carried out using four different Hanji mulberry papers listed in Table 1. The mulberry paper showed no adsorption peaks of volatile compounds from coriander samples when control experiments carried out using only MPB without the Tenax TA. Therefore MPB itself has not adsorption properties. The peak areas for linalool (1 $\mu\text{g}/\mu\text{L}$) were compared. Jeonju Hanji (67.5 μm , thickness) among four papers showed best efficiency (highest peak area), as shown in Fig. 3. A sheet of Jeonju Hanji mulberry paper is made up of the relatively fine surface and the coarse backside. The adsorption of volatile molecules by passing through mulberry paper from headspace to adsorbent particles can be conducted by one of two ways: the front configuration from fine surface (outside) to coarse backside (inside), and the reverse configuration from coarse backside (outside) to fine surface (inside). Adsorption efficiencies of linalool between two configurations were compared. Interestingly, the front configuration (where fine surface was outside) showed better efficiency than the reverse configuration (Fig. 3 A and B). In case of thinner Poongsan Hwaseonji (47.5 μm , thickness) for painting and calligraphy has a disadvantage too thin to avoid the tearing during the extraction process. Meanwhile, lighter and thinner Chinese Xuan paper (55.0 μm , thickness) showed lower peak area among four papers investigated. The Chinese Xuan paper made from Qintan tree bark is also well known as a painting paper in East Asian countries. Therefore, Jeonju Hanji mulberry paper was chosen to make a MPB for further studies, then paper was configured with caution so that Tenax TA particles are placed on the coarse backside of before wrapping.

According to our very recent study,^{7,8} Tenax TA was chosen as an adsorbent that must be included in the design of mulberry

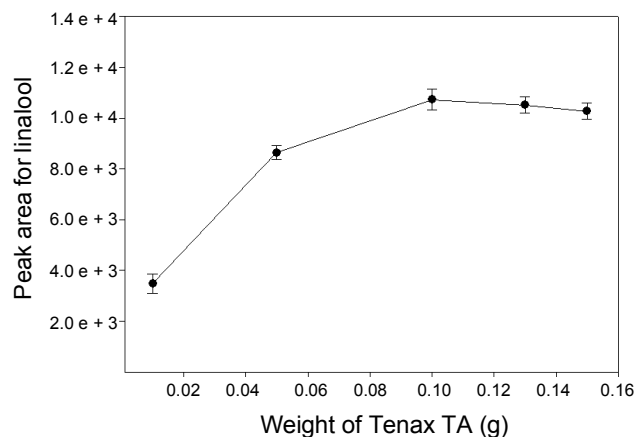


Figure 4. Influence of sample size on efficiencies of HS-MPB- μ -SPE and GC/MS.

paper bag. Effect of Tenax TA (60/80 mesh) adsorbent mass on the peak area for linalool (1 μ g/ μ L in petroleum ether) was investigated in the range of 10 mg ~ 150 mg. 100 mg of Tenax TA showed highest peak area, as shown in Fig. 4. And it was also found that about 150 mg of Tenax TA is maximum mass which is containable within a sheet of Jeonju Hanji mulberry paper with defined size (10.5 cm \times 4.5 cm). For these reasons, weight of Tenax TA to make a mulberry paper bag was fixed to 100 mg for further experiments.

The effect of the extraction temperature on the efficiency of HS-MPB- μ -SPE was tested in the range from 30 $^{\circ}$ C to 80 $^{\circ}$ C. The highest peak area of linalool was obtained at 40 $^{\circ}$ C. When the extraction time varied from 30 min to 90 min at 40 $^{\circ}$ C, the equilibrium condition for the adsorption process of linalool was obtained after 60 min. For further experiments, 40 $^{\circ}$ C extraction temperature and 60 min extraction time were used.

Selection of desorption solvent should be considered because Tenax TA is incompatible with many solvent systems. For example, in the case of chloroform, Tenax TA in a MPB was dissolved by chloroform and unable to extract practically.⁷ A series of experiments were carried out to investigate the relative extraction efficiencies of petroleum ether, ethyl ether and *n*-hexane. Their efficiencies were compared based on the GC-FID peak area after HS-MPB- μ -SPE process for linalool. Petroleum ether showed the best extraction efficiency and therefore it was selected as the optimum solvent.

Influence of different volumes (400 μ L ~ 900 μ L) of solvent was evaluated. The extraction of linalool was almost satisfactory when a 600 μ L volume of petroleum ether were employed. Relatively cleaner extracts were obtained using 600 μ L of petroleum ether. All petroleum ether was absorbed by mulberry paper bag when 400 μ L was used. The results showed decreasing of peak area when the volume of solvent is increased over 700 μ L to 900 μ L. This result suggests the signal could be decreased with the dilution of analyte.

Since only sub-mL of solvent is used, there is minimal waste or exposure to toxic organic solvent. In addition, this method allowed combining of extraction, enrichment, and clean-up in a single step.

The effect of the sample size in HS-MPB- μ -SPE and GC/MS

Table 2. Comparison of concentration factors (CF) of characteristic components from coriander seeds sample by HS-MPB- μ -SPE

Compound	mol.wt	b.p ($^{\circ}$ C)	Concentration factor (CF)
			HS-MPB- μ -SPE (Tenax TA, 0.1 g) (mean \pm SD, n = 3)
α -Pinene	136.23	155	0.70 (\pm 0.05)
β -Myrcene	136.23	165	1.18 (\pm 0.03)
Limonene	136.23	176	2.39 (\pm 0.27)
ρ -Cymene	134.22	177	2.49 (\pm 0.38)
γ -Terpinene	136.23	183	5.47 (\pm 0.79)
Terpinolene	136.23	184	1.86 (\pm 0.03)
Linalool	154.25	198	6.60 (\pm 0.44)
Camphor	152.23	209	1.78 (\pm 0.08)

of linalool was evaluated by extracting different amounts of the same coriander seeds sample. The peak area of linalool increased by increasing the sample size in the range of 0.9 ~ 1.2 g. However, almost constant plateau was observed in the range of 1.2 ~ 1.5 g. Therefore, 1.2 g was selected as sample size in HS-MPB- μ -SPE and GC/MS.

Evaluation of the method performance. The optimized conditions were adopted in the validation of method. Ten points of concentration were tested in three replicates to plot calibration curve, these concentrations covered the concentration ranges expected for linalool in coriander seeds. Good linearity ($y = 78.29x - 1053$) with squared correlation coefficient of $r^2 = 0.9956$ was obtained in the range of 34.4 ng/mL ~ 750.0 μ g/mL of linalool by HS-MPB- μ -SPE and GC/MS. The limit of detection (LOD) and the limit of quantitation (LOQ) for linalool were very low of 10.3 ng/mL and 34.4 ng/mL, respectively. LOD and LOQ were calculated by $3 s/m$ and $10 s/m$, respectively. Where, s is the standard deviation of the blank and m is the slope obtained in the calibration curve for linalool. Under the optimized conditions described above, the reproducibility of the proposed HS-MPB- μ -SPE method was 3.44% ~ 4.46% (RSD). In order to check the accuracy of the method, the technique of standard addition methods were used. Known quantities of linalool were spiked at five levels and in triplicate. The recovery for linalool was 93.68%.

Concentration factor. The overall extraction efficiency was evaluated by the relative concentration factor (CF) of the several characteristic components of coriander seeds. The CF was expressed by the following formula:

$$CF = [C_1] / [C_0]$$

where, $[C_1]$ is the concentration of analytes measured by HS-MPB- μ -SPE technique and $[C_0]$ is the initial concentration in the headspace. The CF values can be calculated by the ratio between the peak area (A_1) of the analytes by HS-MPB- μ -SPE-GC-FID and the corresponding peak area (A_0) obtained by static HS-GC-FID. Thus, the CF values can be expressed in terms of GC-FID signals:

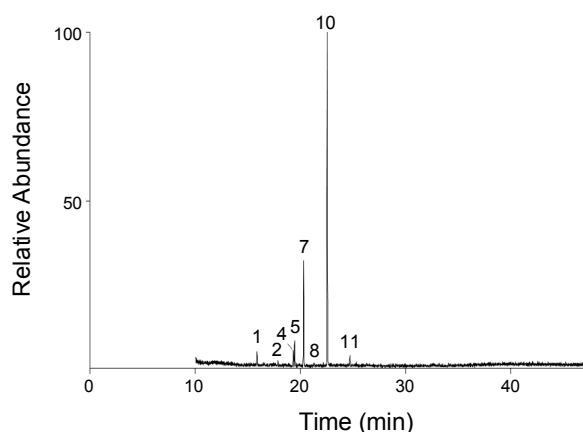
$$CF = [A_1] / [A_0]$$

In this case, $[A_0]$ was determined by injection of the sample headspace into the injection port of the GC-FID using a 10 mL

Table 3. Comparison of flavor compositions obtained by HS-MPB- μ -SPE from different coriander seeds

Peak No.	Compounds	Group	t_R	Mr	Normalized peak area (%) from coriander seeds mean value (n = 3)			Characteristic mass spectral ions (EI) m/z (relative abundance %)
					Chinese	Japanese	Moroccan	
1	α -Pinene	I	17.09	136	2.93	2.49	1.10	91(100), 77(60), 51(42), 93(31), 65(18), 105(14), 119(11)
2	β -Myrcene	I	19.09	136	0.36	0.61	0.43	91(100), 77(62), 93(45), 51(44), 65(14), 94(6), 121(4)
4	Limonene	I	20.60	136	2.30	2.26	2.48	67(100), 91(76), 77(60), 93(37), 94(10), 135(4)
5	ρ -Cymene	I	20.74	134	3.19	4.42	4.02	119(100), 91(62), 117(40), 115(20), 134(15), 77(14), 105(6)
7	γ -Terpinene	I	21.59	136	17.02	23.06	20.08	91(100), 77(52), 93(32), 51(18), 105(8), 119(8), 136(4)
8	Terpinolene	I	22.62	136	0.49	0.39	0.36	91(100), 77(92), 121(54), 136(42), 65(38), 93(34), 105(14)
10	Linalool	III	23.84	154	70.63	65.03	68.05	91(100), 77(64), 93(60), 67(50), 137(17), 121(15), 138(2)
11	Camphor	V	26.11	152	3.08	1.74	3.48	95(100), 67(99), 79(86), 108(36), 109(24), 137(12), 152(6), 123(4)

I: Monoterpenes, II: sesquiterpenes, III: alcohol, IV: ester, V: ketone, VI: others.

**Figure 5.** Typical total ion chromatograms obtained by HS-MPB- μ -SPE-GC/MS from Chinese coriander seeds sample.

Hamilton 1010RN gas tight syringe (Supelco). These comparative experiments were carried out using coriander seeds sample (1.2 g) in a 50 mL vial instead of standards to ensure that matrix effects are identical to those encountered during actual sampling. Experimental CF values for several characteristic compounds of coriander seeds are given in Table 2. CF values (mean value of three replicates) by HS-MPB- μ -SPE varied between 0.70 and 6.60.

Application of HS-MPB- μ -SPE for the analyses of coriander seeds. The HS-MPB- μ -SPE technique without further cleanup steps was successfully applied to the analyses of the real samples. Three coriander seeds samples were analyzed by HS-MPB- μ -SPE and compared with another extraction method of HS-SPME. Fig. 5 shows typical total ion chromatogram (TIC) obtained by HS-MPB- μ -SPE for the volatile flavor components from coriander seeds samples. The peak numbers shown in Fig. 5 correspond to those indicated in Table 3. Linalool and γ -terpinene were most abundant flavors of coriander seeds. Amounts of linalool were 364.0 ng/g for Chinese coriander seeds, 301.4

ng/g for Japanese, and 405.9 ng/g for Moroccan, respectively.

Conclusions

HS-MPB- μ -SPE using Tenax TA prior to GC/MS was newly developed for the determination of flavor components from coriander seeds. The new HS-MPB- μ -SPE technique is very simple to use, inexpensive, rapid, sensitive, and reproducible. The HS-MPB- μ -SPE can reduce significantly solvent consumption and sample size in the sample preparation. Because the solvent for extraction is reduced to only a very small volume (0.6 mL), there is minimal waste or exposure to toxic organic solvent. In addition, this method allowed combining of extraction, enrichment, and clean-up in a single step. HS-MPB- μ -SPE and GC/MS is a promising technique of the measurement of volatile flavor compounds from spices.

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References

1. PDR for Herbal Medicines, 3rd ed. Thomson PDR, Montvale, NJ 2004.
2. Sellar, W. *The Directory of Essential Oils*; C. W. Daniel Co. Ltd.: Cambridge, 2001; p 56.
3. Anitescu, G.; Doneanu, C.; Radulescu, V. *Flavour Fragr. J.* **1997**, *12*, 173.
4. Grosso, C.; Ferraro, V.; Figueiredo, A. C.; Barroso, J. G.; Coelho, J. A.; Palavra, A. M. *Food Chem.* **2008**, *111*, 197.
5. Eyres, G.; Marriott, P. J.; Dufour, J. P. *J. Chromatogr. A* **2007**, *1150*, 70.
6. Eyres, G.; Dufour, J. P.; Hallifax, G.; Sotheeswaran, S.; Marriott, P. J. *J. Sep. Sci.* **2005**, *28*, 1061.
7. Yoon, O. K.; Lee, D. S. *Bull. Korean Chem. Soc.* **2009**, *30*, 35.
8. Won, M. M.; Cha, E. J.; Yoon, O. K.; Kim, N. S.; Kim, K.; Lee, D. S. *Anal. Chim. Acta* **2009**, *631*, 54.
9. Lee, J. W.; Hwang, H. Y. *J. Architect. Inst. Korea: Plan. Des.* **2007**, *23*, 211.
10. Lee, J. W.; Lim, J. M. *Korean J. Air-cond. Refrig. Eng.* **2004**, *16*, 599.