Journal of Chromatography A, 1218 (2011) 4599–4605

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Ultrasonic nebulization extraction-heating gas flow transfer-headspace single drop microextraction of essential oil from pericarp of *Zanthoxylum bungeanum* Maxim.

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ARTICLE INFO

Article history:
Received 9 November 2010
Received in revised form 22 February 2011
Accepted 13 May 2011
Available online 20 May 2011

Keywords:
Heating gas flow
Essential oil
Headspace single drop microextraction
Ultrasonic nebulization extraction

ABSTRACT

The ultrasonic nebulization extraction-heating gas flow transfer coupled with headspace single drop microextraction (UNE-HGFT-HS-SDME) was developed for the extraction of essential oil from *Zanthoxylum bungeanum* Maxim. The gas chromatography–mass spectrometry was applied to the determination of the constituents in the essential oil. The contents of the constituents from essential oil obtained by the proposed method were found to be more similar to those obtained by hydro-distillation (HD) than those obtained by ultrasonic nebulization extraction coupled with headspace single drop microextraction (UNE-HS-SDME). The heating gas flow was firstly used in the analysis of the essential oil to transfer the analytes from the headspace to the solvent microdrop. The relative standard deviations for determining the five major constituents were in the range from 1.5 to 6.7%. The proposed method is a fast, sensitive, low cost and small sample consumption method for the determination of the volatile and semivolatile constituents in the plant materials.

1. Introduction

The pericarp of *Zanthoxylum bungeanum* Maxim. is well used as a kind of spice in China [1–5] and the traditional Chinese medicine for its therapeutic properties [2,3,6,7]. It is effective for the treatment of inflammatory diseases, epigastric pain, stomachache, toothache, ascariosis, diarrhea and dysentery. In addition, the pericarp of *Z. bungeanum* Maxim. was also used as antimicrobial, insect repellent, antioxidant and feeding deterrent [1,4] and these functions resulted from its essential oil.

The sample preparation is a critical step for the analysis of essential oil in the plants. Hydro-distillation (HD) is a kind of the standard technique for sample preparation in China [8]. However, to surmount the drawbacks of the waste of time and consumption of sample, solid-phase extraction (SPE) was applied [9]. Although SPE surmounted the drawbacks of HD, the packing in SPE were relatively expensive. Solid-phase microextraction (SPME) system was simple and portable [10–14]. The researchers in some laboratories cannot afford the expensive fibers used in SPME. Single-drop microextraction (SDME) was then applied to the extraction of the volatile constituents in the matrices. Moreover, the advantages of a small amount of solvent, rapidity, simplicity and cheapness are obvious. SDME has been widely applied and divided into direct immersion (DI)-SDME [14–17] and headspace (HS)-SDME [18–20]. HS-SDME has been coupled with stirring extraction, ultrasonic extraction and microwave assisted extraction [14].

In the ultrasonic nebulization extraction (UNE) [21–25], the sample particles and extraction solvent in the bottom of sample device were irradiated by an ultrasonic irradiation, the frequency of which is approximately 1.7 MHz [26]. An ultrasonic fountain containing the target analytes existed in the nebulization device [22]. This method is suitable for the extraction of volatile compounds [22,25]. When the aerosol is full of the sample device in the UNE process, the analytes in the gaseous phase and the aqueous phase come to the partition equilibrium rapidly at the same time. The extraction efficiency of the semivolatile compounds was not so high as that of the volatile compounds. UNE-HS-SDME was used for the extraction of essential oil from plant materials in our laboratory [27,28]. The major constituents obtained by UNE-HS-SDME are basically similar to those obtained by HD. Compared with those obtained by HD, the contents of low boiling point constituents obtained by UNE-HS-SDME are higher and the contents of high boiling point constituents are lower. Therefore, an on-line method was developed in which purging carrier gas was heated and introduced into the extraction system [26]. The method would be appropriate for the extraction of volatile and semivolatile constituents at the same time.

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doi:10.1016/j.chroma.2011.05.047

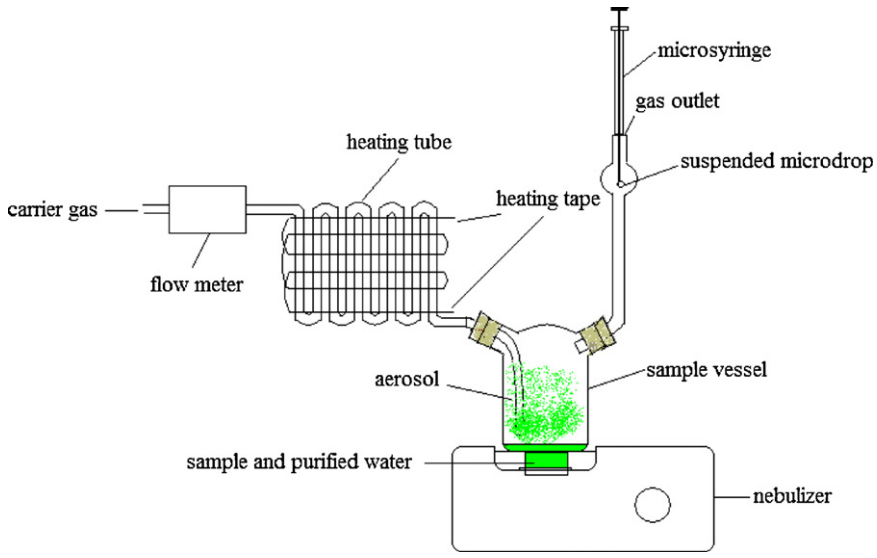

Fig. 1. UNE-HGFT-HS-SDME system.

In this article, based on UNE-HS-SDME coupled with heating purge gas transfer, a new extraction method was developed. The proposed method is suitable for the extraction of both the volatile and semivolatile constituents from plant materials. The proposed method was compared with UNE-HS-SDME, ultrasonic assisted extraction (UAE) and HD. Owing to the introduction of the heating gas, the contents of analytes obtained by the proposed method were similar to those obtained by HD. The extraction efficiency of the semivolatile compounds obtained by the proposed method was higher than that obtained by UNE-HS-SDME. The enrichment efficiency of the proposed method was much higher than that of UAE.

2. Materials and methods

2.1. Materials and reagents

The pericarps of *Z. bungeanum* Maxim. (samples 1–3) used in this work were purchased from a local market in Changchun, Jilin Province, China. Sample 1 was used in all other experiments besides the experiment mentioned in Section 4.3. The pericarp of *Z. bungeanum* Maxim. was crushed with a disintegrator (FW-100 Test Instrument Co., Ltd, Tianjin, China) and then filtered through 80 mesh sieve. The sample powders collected were stored in the desiccator before analysis.

The n-dodecane (99%), n-pentadecane (99%), n-heptadecane (99%) and 1-octanol (99%) were used as extraction solvent and purchased from Acros Company (NJ, USA). The n-decane was used as internal standard and purchased from Ourchem (Shanghai, China). The mixture of n-alkane standards (C-6–C-19) was purchased from Accustandard (New Haven, USA) and the other reagents were purchased from Beijing Chemical Factory (Beijing, China) and were of analytical grade.

2.2. Apparatus

The extraction and concentration system was assembled in our laboratory and the schematic diagram is shown in Fig. 1. An ultrasonic humidifier (Beijing Branson Ultrasound Co. Ltd., China) was used for ultrasonic nebulization purpose. The maximum output power and the frequency of vibration were 35 W and 1.7 MHz, respectively. The extraction vessel was a glass flask (100 mL, ID 10 cm) with three ports. One port on the bottom of the vessel sealed

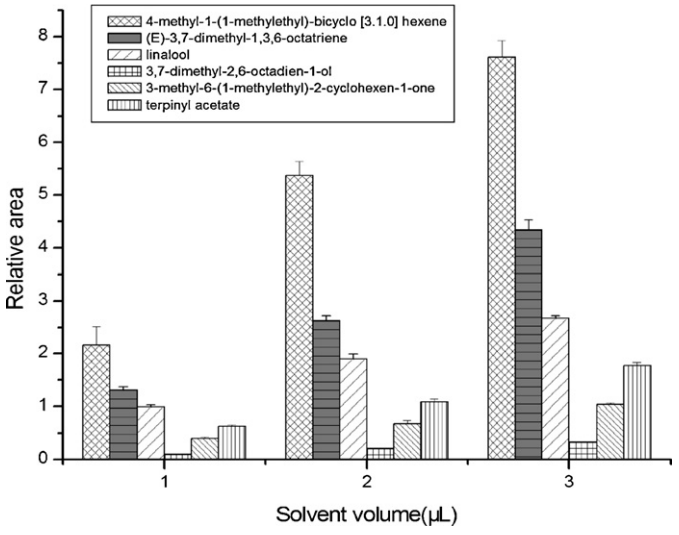

Fig. 2. Influence of microdrop volume of n-heptadecane on relative peak areas of analytes.

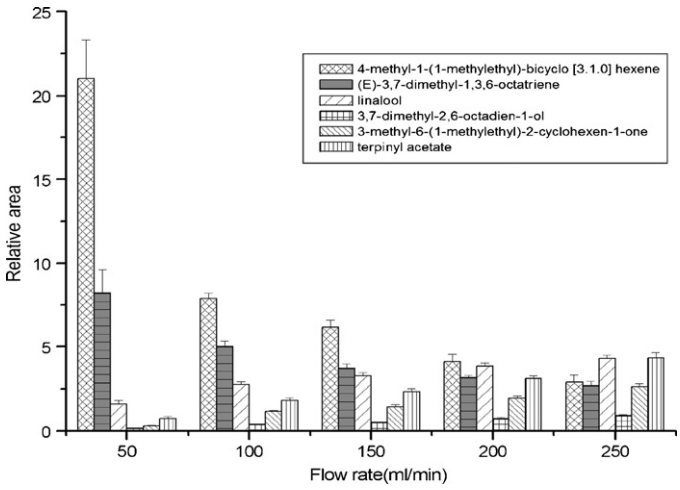

Fig. 3. Influence of flow rate of heating gas on relative peak areas of analytes.

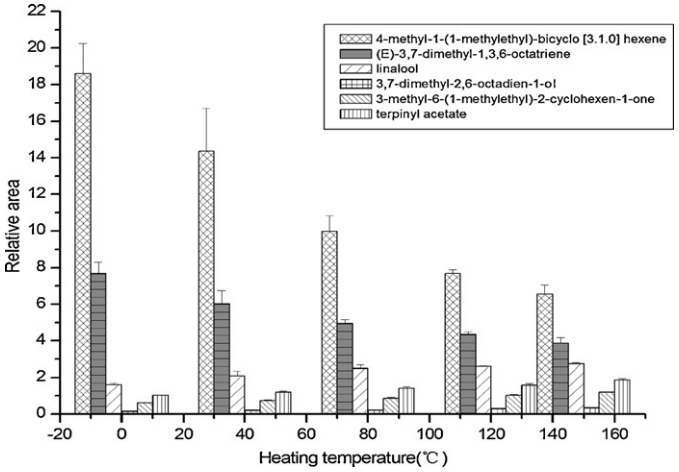

Fig. 4. Influence of the temperature of heating gas on relative peak areas of analytes.

with PVC film has the same size as the piezocrystal. The other two ports were positioned on the top of the vessel. One was used as gas inlet and the other was used as gas outlet. The gas inlet was connected with a gas flowmeter, a heating tube wound with a heating tape and a glass pipe inserting into the lower part of the vessel. The heating tape was connected with a thermocouple sensor (XMTD-2001 Xinghua AOTE temperature Instrument Co., Xinghua, China) which can detect and regulate the temperature. A 10 μL GC microsyringe (Zhenhaisan'ai Instrument Co. Ltd., Ningbo, China) was employed. In UAE, an ultrasonic generator (KQ2200E Kunshan ultrasonic Instrument Co. Ltd., Kunshan, China) was used. The maximum output power was 150 W and the ultrasonic frequency was 40 kHz.

2.3. UNE-HGFT-HS-SDME

100 mg of sample powders and 5 mL of water (extraction solvent) were mixed in the extraction vessel in Fig. 1. Nitrogen was used as carrier gas and heated in the heating tube. At the gas outlet, the needle of 10 μL microsyringe was clamped at a fixed position. 3 μL of n-heptadecane containing 0.04% n-decane (internal standard) was pushed out and suspended from the tip of the needle. The nebulizer was switched on and the heating carrier gas went through the extraction vessel at the same time. When the extraction was performed, the microdrop was withdrawn into the microsyringe. To ensure the homogeneity of the extract, the plunger of the microsyringe was moved up and down several times and then 0.6 μL extract in the microsyringe was injected into GC–MS system.

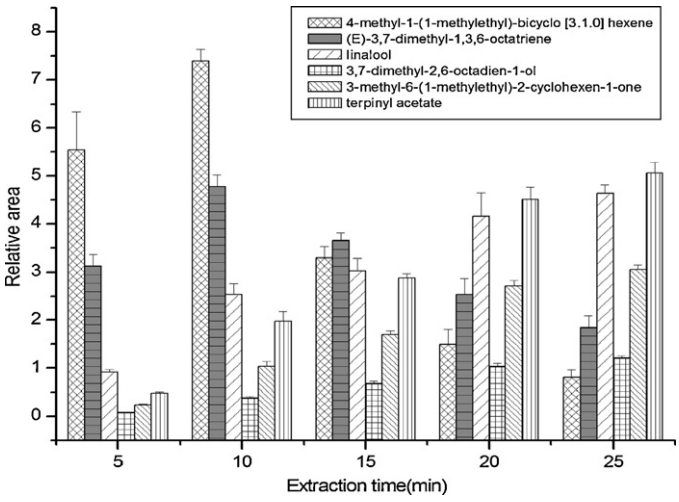

Fig. 5. Influence of extraction time on relative peak areas of analytes.

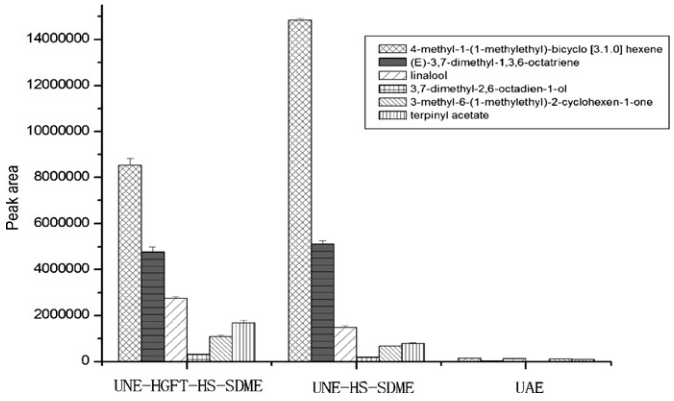

Fig. 6. Comparison of different methods.

2.4. HD

According to the Chinese Pharmacopoeia [8], 20 g of sample powders and 300 mL of water were added into a 500 mL round bottom flask wound with a heating jacket and heated at 100 °C for 4 h. The essential oil obtained was collected, dried with anhydrous sodium sulphate and then stored at 4 °C in the refrigerator before analysis.

2.5. UAE

100 mg of sample powders and 5 mL of ethanol were put into the sample vessel and extracted by UAE for 10 min. The suspension obtained was filtered through a 0.45 μm micropore filter membrane and 0.6 μL of the sample solution was injected into the GC–MS system for analysis.

2.6. UNE-HS-SDME

The UNE-HS-SDME was performed in a 100 mL sample vessel which was placed on the nebulizer. 100 mg of sample powders and 5 mL of water were put into the sample vessel. One of the upper two ports was sealed with plug and the 10 μL microsyringe was passed through the other. The nebulizer was turned on and the extraction was carried out for 5 min. Then the nebulizer was turned off and 3 μL of n-heptadecane containing 0.04% n-decane (internal standard) was pushed out and suspended from the top of the microsyringe. 10 min later, the microdrop was withdrawn and then 0.6 μL of the suspended solvent was injected into GC–MS system.

3. GC–MS analysis

The analysis of all extracts obtained was carried out on a GC–MS system (SHIMADZU, GC-MS-QP2010). Rxi-5MS (30.0 m × 250 μm; 0.25 μm film thickness) was used as the capillary column in GC–MS system. The conditions of temperature programming are as follows: the column temperature increased from 60 °C (3 min) to 80 °C (5 min) at 5 °C/min, and then increased to 260 °C (10 min) at 15 °C/min. The injector temperature and ion source temperature were maintained at 260 °C and 200 °C, respectively. Ionization voltage was 70 eV and the injection volume was 0.6 μL. Helium was used as carrier gas at a flow rate of 1 mL min^{-1} and the split ratio was 1:50 except for the detection by HD. When HD was applied the split ratio was 1:150. The constituents of the extract were identified

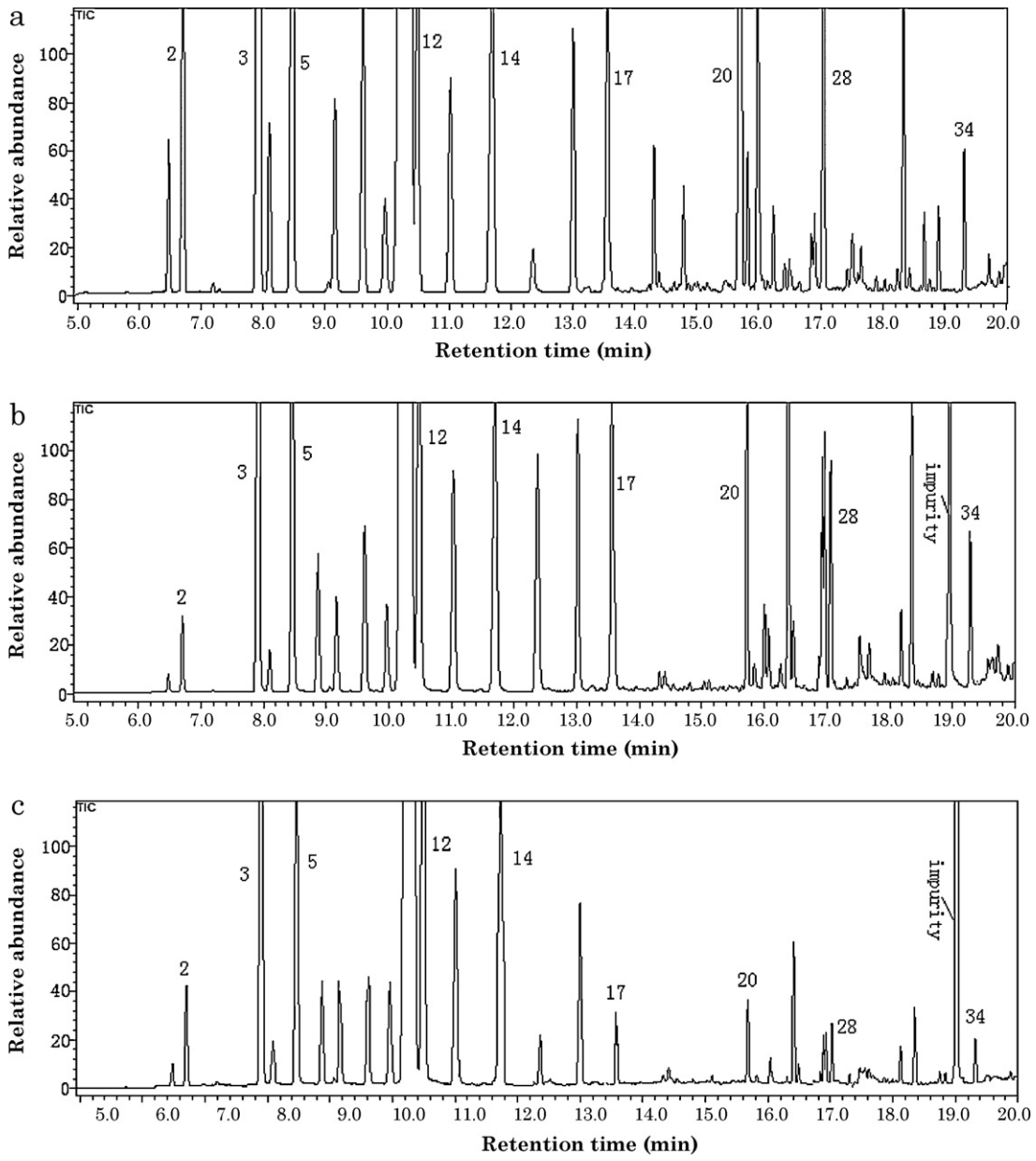

Fig. 7. Chromatograms of extracts obtained by HD (a), UNE-HGFT-HS-SDME (b) and UNE-HS-SDME (c).

by computer matching their mass spectral fragmentation patterns with those in NIST27 Library and comparing MS data with those reported in literature [29].

4. Results and discussion

4.1. Optimization of extraction conditions

In order to obtain the high extraction efficiency, several experimental parameters were investigated. The kind of suspended solvent, microdrop volume, flow rate of heating gas, temperature of heating gas and extraction time were evaluated.

4.1.1. Influence of suspended solvent

There are some requirements for the satisfactory suspended solvents. They should have high purity, low toxicity, high boiling point, high extraction ability and different retention time from the target analytes. The solvents, including n-dodecane (b.p. 216 °C), n-pentadecane (b.p. 270 °C), n-heptadecane (b.p. 302 °C) and 1-octanol (b.p. 195 °C) were examined. The retention times of n-dodecane, n-pentadecane and 1-octanol coincided with those of the target analytes. When n-heptadecane as the highest boiling point solvent was used, extraction efficiency was highest. As a result, n-heptadecane containing 0.04% n-decane (internal standard) was chosen as the suspended solvent for the research.

4.1.2. Influence of solvent microdrop volume

The effect of solvent microdrop volume on the chromatographic peak areas of analytes is shown in Fig. 2. It is illustrated that the peak areas of all the analytes increase with the increase of solvent microdrop volume from 1 μL to 3 μL. When solvent microdrop volume was larger than 3 μL, the microdrop seemed to be unstable and trend to drop down during the process of extraction. The relative peak areas of the analytes obtained with 3 μL solvent microdrop

Table 1
The constituents extracted from sample 1 by HD, UNE-HGFT-HS-SDME and UNE-HS-SDME.

Peak no.	RT (min)	Compounds	RI	Relative content (%)		
				HD	UNE-HGFT-HS-SDME	UNE-HS-SDME
1	6.470	3-Thujene	927	1.09	0.15	0.27
2	6.702	α-Pinene	935	4.23	1.08	1.50
3	7.945	4-Methylene-1-(1-methylethyl)-bicyclo[3.1.0]hexane	974	15.12	11.69	19.27
4	8.099	β-Pinene	978	1.37	0.64	0.44
5	8.471	β-Myrcene	988	6.80	5.20	7.61
6	9.156	α-Phellandrene	1006	2.03	1.12	1.76
7	9.611	α-Terpinene	1018	3.45	2.08	1.80
8	9.964	p-Cymene	1027	1.16	1.17	1.40
9	10.237	Limonene	1033	13.33	15.31	22.74
10	10.327	β-Phellandrene	1035	2.07	6.94	5.32
11	10.379	Eucalyptol	1036	3.48	7.46	8.34
12	10.493	(*E*)-3,7-Dimethyl-1,3,6-octatriene	1039	4.69	6.70	9.22
13	11.022	(*Z*)-3,7-Dimethyl-1,3,6-octatriene	1050	2.58	3.17	3.80
14	11.698	γ-Terpinene	1064	5.49	5.02	7.67
15	12.356	Cis-β-terpineol	1077	0.52	3.25	0.28
16	13.007	4-Carene	1089	2.57	3.14	3.09
17	13.563	Linalool	1099	3.85	4.00	0.85
18	14.312	Trans-1-methyl-4-(1-methylethyl)-2-cyclohexen-1-ol	1130	1.07	0.40	–
19	14.791	5-Methyl-2-(1-methylethyl)-cyclohexanol	1150	0.73	0.22	–
20	15.792	4-Methyl-1-(1-methylethyl)-3-cyclohexen-1-ol	1189	8.97	3.74	1.01
21	15.823	p-Menth-2-ene	1191	0.91	0.19	–
22	15.989	α-Terpinenol	1197	2.90	0.61	0.29
23	16.242	Piperitol	1211	0.57	–	–
24	16.422	1α,2α,5α-2-Methyl-5-(1-methylethyl)-bicyclo[3.1.0]hexan-2-ol	1222	0.39	6.52	2.23
25	16.500	3,7-Dimethyl-2,6-octadine-1-ol	1227	0.24	0.44	–
26	16.859	Cumaldehyde	1250	0.48	1.45	0.08
27	16.908	1,6-Octadien-3-ol,3,7-dimethyl acetate	1253	0.39	1.53	0.32
28	17.051	3-Methyl-6-(1-methylethyl)-2-cyclohexen-1-one	1261	3.59	1.57	0.34
29	17.515	p-Allylanisole	1289	0.51	0.62	–
30	18.344	Terpinyl acetate	1352	2.47	2.49	0.83
31	18.436	Neryl acetate	1359	0.12	–	–
32	18.676	Geranyl acetate	1378	0.42	0.11	–
33	18.908	γ-Elemene	1395	0.47	–	–
34	19.322	Caryophyllene	1434	0.88	1.16	0.40
35	19.724	α-Bioabolene	1471	0.25	0.35	0.02
		Content of fraction oxycompounds (%)		30.70	34.60	14.57
		Total content fraction of determined compounds (%)		99.29	99.52	99.68

were three times large as those obtained with 1 μL. In this study, 3 μL was chosen as the solvent microdrop volume.

4.1.3. Influence of flow rate of heating gas

The purging gas can play a significant role in the transfer of the analytes from the gas phase to the organic phase (suspended solvent). The flow rate of the heating gas was controlled in the range of 50–250 mL min^{-1} and the effect of the flow rate on the relative peak areas was examined. The results are shown in Fig. 3. It can be seen that when the flow rate of the heating gas increases, the relative peak areas of 4-methyl-1-(1-methylethyl)-bicyclo[3.1.0]hexane (b.p. 154.6 °C) and (*E*)-3,7-dimethyl-1,3,6-octatriene (b.p. 177 °C) decrease and those of linalool (b.p. 198 °C), 3,7-dimethyl-2,6-octadien-1-ol (b.p. 225 °C), 3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one (b.p. 232–235 °C) and terpinyl acetate (b.p. 240 °C) increase. The volatility of linalool, 3,7-dimethyl-2,6-octadien-1-ol, 3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one and terpinyl acetate is lower than that of 4-methyl-1-(1-methylethyl)-bicyclo[3.1.0]hexane and (*E*)-3, 7-dimethyl-1, 3, 6-octatriene. The reason may be that the transfer rates of the volatile and semivolatile compounds are different. The semivolatile compounds are more easily transferred from gas phase into the organic phase and more difficultly from organic phase into gas phase than the volatile compounds. A compromise flow rate, 100 mL min^{-1} was selected.

4.1.4. Influence of temperature of the heating gas

The temperature of heating gas has effect on the relative peak areas. The influence of the temperature of the heating gas ranging from 0 °C to 150 °C was tested. As shown in Fig. 4, the relative peak areas of 4-methyl-1-(1-methylethyl)-bicyclo[3.1.0]hexane and (*E*)-3,7-dimethyl-1,3,6-octatriene decrease slightly with the increase of the temperature and those of linalool, 3,7-dimethyl-2,6-octadien-1-ol, 3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one and terpinyl acetate increase. Generally, because the partition coefficient of analytes decreases with the increase of temperature, the increase of temperature should be beneficial to the increase of the amount of analytes in gas phase. Therefore, the increase of temperature should be beneficial to the transfer of the analytes from the aqueous phase (sample solution) into the gas phase, and not beneficial to the transfer of the analytes from the gas phase into the organic phase (suspended solvent). The former is beneficial to the increase of the analytical signals but the latter is not. When the temperature increases, the effect of temperature on the transfer of the volatile analytes, such as 4-methyl-1-(1-methylethyl)-bicyclo[3.1.0]hexane and (*E*)-3,7-dimethyl-1,3,6-octatriene, from the gas phase into the organic phase should be more significant, and that on the semivolatile analytes, such as linalool, 3,7-dimethyl-2,6-octadien-1-ol, 3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one and terpinyl acetate, from the aqueous phase into the gas phase should be more significant. The temperature of the heating gas was selected as 120 °C by a compromise.

4.1.5. Influence of extraction time

The effect of extraction time on extraction yield was studied when the sample amount was 100 mg, the microdrop volume was 3 μL, the heating temperature was 120 °C and the flow rate of purg-

Table 2
The compounds extracted from sample 2 and sample 3 by HD and UNE-HGFT-HS-SDME.

Peak no.	RI	Compounds	Relative content (%)			
			Sample 2		Sample 3	
			HD	UNE-HGFT-HS-SDME	HD	UNE-HGFT-HS-SDME
1	927	3-Thujene	0.56	0.08	0.88	0.12
2	935	α-Pinene	3.31	0.55	3.90	0.95
3	974	4-Methylene-1-(1-methylethyl)-bicyclo[3.1.0]hexane	7.41	5.33	17.23	11.38
4	978	β-Pinene	0.69	0.23	1.50	0.52
5	988	β-Myrcene	6.11	5.31	5.41	4.03
6	1006	α-Phellandrene	1.32	0.86	1.57	0.96
7	1018	α-Terpinene	1.23	0.52	2.46	1.08
8	1027	p-Cymene	1.35	1.44	1.41	1.52
9	1033	Limonene	14.75	16.44	10.58	13.50
10	1035	β-Phellandrene	8.86	10.17	12.65	17.80
11	1036	Eucalyptol	6.55	9.67	1.34	5.48
12	1039	(*E*)-3,7-Dimethyl-1,3,6-octatriene	16.12	19.16	5.86	9.62
13	1050	(*Z*)-3,7-Dimethyl-1,3,6-octatriene	5.60	6.78	2.72	3.71
14	1064	γ-Terpinene	2.22	1.62	3.51	3.21
15	1077	Cis-β-terpineol	0.31	1.63	1.86	2.22
16	1089	4-Carene	1.07	1.58	2.12	2.99
17	1099	Linalool	2.93	3.30	5.36	4.82
18	1130	Trans-1-methyl-4-(1-methylethyl)-2-cyclohexen-1-ol	0.57	0.10	0.80	0.20
19	1134	2,6-Dimethyl-2,4,6-octriene	0.57	1.08	–	–
20	1147	Trans-pinocarveol	1.00	1.01	–	–
21	1150	5-Methyl-2-(1-methylethyl)-cyclohexanol	0.39	–	0.58	0.12
22	1189	4-Methyl-1-(1-methylethyl)-3-cyclohexen-1-ol	4.07	1.29	5.32	1.93
23	1191	p-Menth-2-ene	0.45	0.14	0.67	0.17
24	1197	α-Terpinenol	2.40	1.20	2.06	0.72
25	1211	Piperitol	0.33	0.26	0.47	0.20
26	1222	1α,2α,5α-2-Methyl-5-(1-methylethyl)-bicyclo[3.1.0]hexan-2-ol	0.09	0.97	0.07	3.62
27	1227	3,7-Dimethyl-2,6-octadine-1-ol	0.09	0.26	0.07	0.18
28	1250	Cumaldehyde	–	–	0.19	0.31
29	1253	1,6-Octadien-3-ol,3,7-dimethyl acetate	0.94	2.26	0.54	1.31
30	1261	3-Methyl-6-(1-methylethyl)-2-cyclohexen-1-one	2.41	1.24	4.09	2.05
31	1289	p-Allylanisole	0.67	0.52	0.32	0.68
32	1352	Terpinyl acetate	2.49	2.67	2.03	2.38
33	1359	Neryl acetate	0.17	–	0.12	–
34	1378	Geranyl acetate	0.77	0.24	0.50	0.16
35	1395	γ-Elemene	0.24	–	0.17	–
36	1434	Caryophyllene	0.39	0.77	0.78	1.02
37	1471	α-Bioabolene	0.25	0.66	0.21	0.70
		Content of fraction oxycompounds (%)	26.18	26.62	25.72	26.38
		Total content fraction of determined compounds (%)	99.14	99.44	99.35	99.66

ing gas was 100 mL min^{-1}. The effect of the extraction time on the relative peak areas is shown in Fig. 5. It can be seen that the relative peak areas of 4-methyl-1-(1-methylethyl)-bicyclo[3.1.0]hexane and (*E*)-3,7-dimethyl-1,3,6-octatriene increase with the increase of the extraction time from 5 min to 10 min, but decrease when the time is longer than 10 min. The decrease of analytical responses may be due to the back-extraction and flowing away by the purging gas when the time further increases. It is found that the peak areas of linalool, 3,7-dimethyl-2,6-octadien-1-ol, 3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one and terpinyl acetate increase when the extraction time increases straightly. Therefore, the extraction time of 10 min was employed in this study.

4.2. Validation of enrichment performance

The proposed method was compared with UNE-HS-SDME and UAE. Fig. 6 shows the relative peak areas for all analytes obtained by the three methods. It can be found that the peak areas obtained by the proposed method were much larger than those obtained by UAE. Though enrichment factor for the volatile analytes obtained by the proposed method was not as high as that obtained by UNE-HS-SDME, the enrichment factor for the semivolatile analytes obtained by the proposed method was obviously higher than that obtained by UNE-HS-SDME. The proposed method is suitable for extracting the semivolatile analytes because the analytes are transferred from the headspace to the solvent microdrop more easily in the presence of heating flow. The proposed method should be suitable for the extraction of both the volatile and semivolatile analytes.

4.3. Sample analysis

The constituents of the pericarp of *Z. bungeanum* Maxim. were extracted by HD and the proposed method and then analyzed by GC–MS. The gas chromatograms of extracts from pericarp of *Z. bungeanum* Maxim. obtained by the three extraction methods are shown in Fig. 7. The compounds in essential oil, their retention time (RT) and linear retention index (RI), the content of each constituent, total content fraction of determined compounds and the content fraction of oxycompounds are listed in Table 1. The total content fraction of determined compounds and the content fraction of oxycompounds represent the percentages of qualified compounds and oxycompounds in the total compounds, respectively. It can be seen from Fig. 7 and Table 1 that the kinds of the compounds obtained by HD and the proposed method are much the same. The total content fraction of determined compounds obtained by HD and UNE-HGFT-HS-SDME are 99.29% and 99.52%, respectively. The content fraction of the major constituents obtained by the proposed method is similar to that obtained by HD, but much different from that obtained by UNE-HS-SDME. It illustrated that the proposed method is more suitable for the extraction

of the essential oil from the plant materials. The RSDs for determining 4-methyl-1-(1-methylethyl)-bicyclo[3.1.0]hexene, (*E*)-3,7-dimethyl-1,3,6-octatriene, linalool, 3,7-dimethyl-2,6-octadien-1-ol, 3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one and terpinyl acetate are 1.5%, 3.6%, 5.0%, 4.4%, 6.7%, 6.1% respectively. To validate the feasibility of the proposed method, the other two different kinds of *Z. bungeanum* Maxim. from different cultivated areas were also studied in this study. The obtained results by HD and UNE-HGFT-HS-SDME are listed in Table 2. The contents of constituents of the essential oil in *Z. bungeanum* Maxim. obtained by UNE-HGFT-HS-SDME and HD are similar to each other. The results indicated that the proposed method is suitable to extract the volatile and semivolatile constituents from the plant materials.

5. Conclusion

In the UNE-HS-SDME, the target analytes transferred from the solid phase (sample powders) to the liquid phase (extraction solvent) and then to the headspace aerosol. The aerosol was transferred into the gas phase by ultrasonic fountain and then dropped into the bottom of the vessel by gravity time by time. The analytes was transferred into the gas phase in the process. The distribution equilibrium of analytes in the gas phase and the aqueous phase was reached rapidly. The concentration of the semivolatile compounds in the gas phase should be low at low temperature. However, the introduction of heated carrier gas can result in the increase of the temperature of the system. The high temperature is beneficial to the increase of concentration of semivolatile compounds in the gas phase and the heated gas could bring both the volatile and semivolatile components to the suspended solvent immediately. Because the gas was heated, the loss of cooling components was reduced and the concentration of the volatile components and semivolatile components in the suspended solvent increased. Thus the extraction of analytes was more effective.

The results obtained from this study indicated that the proposed method surmounted the drawbacks of UNE-HS-SDME. The contents of analytes obtained by the proposed method were similar to those obtained by HD, the results were greatly better than those obtained by UNE-HS-SDME and the extraction efficiency of terpinyl acetate was significantly improved. Furthermore, the extraction and enrichment could be performed in a single step. Compared with HD, the proposed method requires shorter time and smaller amount of sample. The UNE-HGFT-HS-SDME should be an alternative method to extract the volatile and semivolatile compounds in other samples besides the spices.

References

[1] J.H. Zhang, L.F. Jiang, Bioresour. Technol. 99 (2008) 8995.
[2] W.S. Bowers, F. Ortego, X.Q. You, P.H. Evans, J. Nat. Prod. 56 (1993) 935.
[3] X.G. Yang, J. Agric. Food Chem. 56 (2008) 1689.
[4] C.C. Chyau, J.L. Mau, C.M. Wu, J. Agric. Food Chem. 44 (1996) 1096.
[5] F.X. Yang, Y.Q. Su, X.H. Li, Q. Zhang, R.C. Sun, J. Agric. Food Chem. 56 (2008) 7891.
[6] Z.L. Liu, S.S. Chu, G.H. Jiang, J. Agric. Food Chem. 57 (2009) 10130.
[7] Y. Tezuka, S. Irikawa, T. Kaneka, A.H. Banskota, T. Nagaoka, Q.B. Xiong, K. Hase, S. Kadota, J. Ethnopharmacol. 77 (2001) 209.
[8] The State Pharmacopoeia Commision of P.R. China, The Pharmacopoeia of People's Republic of China 2005, Chemical Industry Publishing House, Beijing, 2005, p. 57.
[9] J. Muñoz, J.R. Baena, M. Gallego, M. Valcárcel, J. Chromatogr. A 1023 (2004) 175.
[10] J.F. Cavalli, X. Fernandez, L.L. Cuvelier, A.M. Loiseau, J. Agric. Food Chem. 51 (2003) 7709.
[11] M. Fabre, V. Aubry, E. Guixhard, J. Agric. Food Chem. 50 (2002) 1497.
[12] C.H. Deng, Y. Mao, F.L. Hu, X.M. Zhang, J. Chromatogr. A 1152 (2007) 193.
[13] H. Farahani, M.R. Ganjali, R. Dinarvand, P. Norouzi, J. Agric. Food Chem. 57 (2009) 2633.
[14] L. Xu, C. Basheer, H.K. Lee, J. Chromatogr. A 1152 (2007) 184.
[15] K. Demmestere, J. Dewulf, B.D. Witte, H.V. Langenhove, J. Chromatogr. A 1153 (2007) 130.
[16] Q. Xiao, B. Hu, C.H. Yu, L.B. Xia, Z.C. Jiang, Talanta 69 (2006) 848.
[17] M.C. López-Blanco, S. Blanco-Cid, B. Cancho-Grande, J. Simal-Gándara, J. Chromatogr. A 984 (2003) 245.
[18] S.P. Huang, S.D. Huang, J. Chromatogr. A 1176 (2007) 19.
[19] Y.C. Fiamegos, C.D. Stalikas, Anal. Chim. Acta 609 (2008) 175.
[20] R. Batlle, P. Lópze, C. Nerín, C. Crescenzi, J. Chromatogr. A 1185 (2008) 155.
[21] B. Avvaru, M.N. Patil, P.R. Gogate, A.B. Pandit, Ultrasonics 44 (2006) 146.
[22] K. Yasuda, Y. Bando, S. Yamaguchi, M. Nakamura, A. Oda, Y. Kawase, Ultrason. Sonochem. 12 (2005) 37.
[23] H. Takaya, S. Nii, F. Kawaizumi, K. Takahashi, Ultrason. Sonochem. 12 (2005) 483.
[24] N. Jalbani, T.G. Kazi, B.M. Arain, M.K. Jamali, H.I. Afridi, R.A. Sarfraz, Talanta 70 (2006) 307.
[25] L. Wang, D. Li, L.Ch. Bao, J.Y. You, Z.M. Wang, Y.H. Shi, H.Q. Zhang, Ultrason. Sonochem. 15 (2008) 738.
[26] L. Wang, Y. Liang, Z.M. Wang, C.L. Qu, D. Lin, Y.H. Shi, H.Q. Zhang, Talanta 80 (2009) 864.
[27] L. Wang, Z.M. Wang, H.H. Zhang, X.Y. Li, H.Q. Zhang, Anal. Chim. Acta 647 (2009) 72.
[28] L. Wang, Z.M. Wang, X.Y. Li, H.H. Zhang, X. Zhou, H.Q. Zhang, Chromatographia 71 (2010) 455.
[29] Z.M. Wang, L. Ding, T.C. Li, X. Zhou, L. Wang, H.Q. Zhang, L. Liu, Y. Li, Z.H. Liu, H.J. Wang, H. Zeng, H. He, J. Chromatogr. A 1102 (2006) 11.