Dispersive liquid–liquid microextraction with deep eutectic solvent coupled with GC-MS for the determination of chiral carvone in herbaceous plants

Yuluan Wu [a], Ming Liang [a], Yanping Xian [*a], Rongqiao Chen [a], Junpeng Hu [a], Hang Dai [a], Chenghao Liu [a], Xiangchang Hou [a]

[a] Guangzhou Quality Supervision and Testing Institute, Research Center of Risk Dynamic Detection and Early Warning for Food Safety of Guangzhou City, Key Laboratory of Detection Technology for Food Safety of Guangzhou City, Guangzhou NQI-Quality Safety Science and Technology Collaborative Innovation Center, Guangzhou 511447, China

*Corresponding authors: Yanping Xian

zjyxyp2015@163.com

Current address: No. 1-2, Zhujiang Road, Panyu District, Guangzhou, China

Tel: +86-20-83183575; Fax: +86-20-83183575

Table S1. Composition of the DESs.

No.	HBA	HBD	Water	Molar ratio
DES1	choline chloride	formic acid	/	1:2~1:3
DES2	choline chloride	phosphoric acid	/	1:2
DES3	choline chloride	lactic acid	/	1:2
DES4	choline chloride	glucose	water	2:1:1
DES5	choline chloride	diethylene glycol	/	1:2
DES6	choline chloride	glycerol	/	1:2
DES7	choline chloride	diethylamine	/	1:2

Table S2. Response surface experimental factors and level design.

Level	Factors		
	Liquid-solid ratio/mL·g^{-1}	Extraction time/min	Extraction temperature/℃
-1 (Low)	15	20	40
0 (Center)	20	30	50
1 (High)	25	40	60

Table S3. Response surface experiment results.

No.	Liquid-solid ratio /mL·g^{-1}	Extraction time/min	Extraction temperature/℃	Recovery (%)	
				L-carvone	*D*-carvone
1	20	30	50	94.6	95.5
2	15	30	40	72.8	70.5
3	15	30	60	63.8	69.3
4	25	20	50	100.4	99.6
5	20	20	60	74.1	76.1
6	15	40	50	79.8	81.2
7	20	40	60	67.9	70.5
8	20	30	50	93.4	91.4
9	20	30	50	92.1	95.7
10	20	40	40	65.9	63.9
11	25	40	50	83.2	84.1
12	20	30	50	95.3	91.8
13	20	30	50	87.9	85.9
14	20	20	40	73.5	69.8
15	15	20	50	77.4	78.3
16	25	30	60	81.1	79.5
17	25	30	40	76.9	76.1

Table S4. ANOVA for response surface quadratic model of *L*-carvone.

Source	Sum of squares	df	Mean suqare	F-value	P-value Prob>F	Significance
Model	1948.10	9	216.46	34.17	<0.0001	significant
A	285.60	1	285.60	45.08	0.0003	
B	102.25	1	102.25	16.14	0.0051	
C	0.61	1	0.61	0.095	0.7663	
AB	96.04	1	96.04	15.16	0.0059	
AC	43.56	1	43.56	6.88	0.0343	
BC	0.49	1	0.49	0.077	0.7890	
A2	18.22	1	18.22	2.88	0.1338	
B2	121.87	1	121.87	19.24	0.0032	
C2	1206.84	1	1206.84	190.50	<0.0001	
Residual	44.35	7	6.34			
Lack of fit	10.09	3	3.36	0.39	0.7656	Not significant
Pure error	34.25	4	8.56			
Corrected total	1992.44	16				
SD	2.52	R2	0.9777			
CV%	3.10	Adj-R2	0.9491			
		Pred-R2	0.8921			

Note: Significant difference P<0.05, highly significant difference P<0.01

Table S5. ANOVA for response surface quadratic model of *D*-carvone.

Source	Sum of squares	df	Mean suqare	F-value	P-value	Significance
Model	1776.46	9	197.38	15.92	0.0007	significant
A	200.00	1	200.00	16.13	0.0051	
B	72.60	1	72.60	5.85	0.0461	
C	28.50	1	28.50	2.30	0.1733	
AB	84.64	1	84.64	6.82	0.0348	
AC	5.29	1	5.29	0.43	0.5345	
BC	0.023	1	0.023	1.814E-003	0.9672	
A2	6.50	1	6.50	0.52	0.4926	
B2	106.00	1	106.00	8.55	0.0222	
C2	1212.19	1	1212.19	97.74	<0.0001	
Residual	86.81	7	12.40			
Lack of fit	23.28	3	7.76	0.49	0.7087	Not significant
Pure error	63.53	4	15.88			
Corrected total	1863.28	16				
SD	3.52	R2	0.9534			
CV	4.34	Adj-R2	0.8935			
		Pred-R2	0.7468			

Note: Significant difference P<0.05, highly significant difference P<0.01

Table S6 Comparison with other methods reported in the literature for the detection of carvone

Analytes	Matrix	Instrumental method	Pre-treatment method	Linear range	LOD	Recoveries	Precision	Reference
Carvone and nitrendipine	Skin diffusate and microemulsions	UFLC	Direct measurement after dilution	0.125-30μg/mL	0.075μg/mL	90-105%	<10%	1
Carvone, cineole, perillaldehyde, perillyl alcohol and sobrerol	The diet of laboratory animals	HPLC	Extracted by 90% methanol in water	1-150 μg/mL	2 μg/g	97.9±2.6%	5.5-23.3%	2
Piperine, embeline, and carvone	Ayurvedic formulation catpusphadhya churna	HPTLC	Extracted by methanol using a Soxhlet apparatus.	1-9 ng/spot	0.2 ng/spot	100.09	/	3
Carvone, menthol, thymol, carvacrol and methyl salicylate	Chicken breast	GC-MS/MS	QuEChERS	2-100 mg/L	LOQ: 2.9 μg/kg	80-102%	<15%	4
Ratios of *d,l*-Carvone	Caraway seeds and speamint leaves	HPLC	Extracted with supercritical fluid of carbon dioxide	Caraway seeds contain only *d*-carvone and speamint leaves contain both *d*-carvone (7%) and *l*-carvone (93%)				5
Chiral terpenoids	Essential oil of *Mentha spicata*	GC-FID and GC-MS	Hydrodistilled to extract essential oils	(S)-(+)-Carvone has been identified as the major compound in *M. spicata* essential oils				6
Compositional analysis	Spearmint (*Mentha spicata*) essential oil	GC-MS	Isolation of the essential oil by hydrodistillation	The five most abundant constituents of the Iranian spearmint essential oil are (+)-carvone (73.20%), limonen (14.63%), b-bourbonene (1.13%), cineole (1.10%) and 3-terpinolenone (0.82%).				7
Compositional analysis	Celery (*Apium graveolens*) leaf and root	GC-MS	Extracted with liquid carbon dioxide	The main constituents in the oil of roots were limonene, carvone and 3n-butylphthalide. The essential oil of leaves contained higher amount of limonene, and very small amount of carvone.				8
D and *L*-Carvone	Herbaceous plants	GC-MS	Extract by DES	0.5-50.0 mg/kg	8.0 mg/kg	83.5%-101.3%	3.2-6.1%	This work

UFLC: ultra fast liquid chromatographic
HPTLC: High performance thin layer chromatography

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