CHEMIJA. 2012. Vol. 23. No. 3. P. 244–249

Fast determination of *Prangos uloptera* essential oil by nanoporous silica-polypyrrole SPME fiber

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A microwave-assisted SPME method with a new nanoporous polypyrrole / SBA-15 was successfully applied to the study of the essential oil composition of *Prangos uloptera* DC. The sample was irradiated by microwave radiation and its volatile components were collected by the fiber from the sample headspace and directly injected into a GC-MS injection port for analysis. A simplex method was used for optimization of three different parameters affecting the efficiency of the extraction. Under the optimized conditions (i. e. sample weight, 4 g, extraction time, 5 min and microwave power 450 W), the polypyrrole / SBA-15 nanonporous fiber could efficiently adsorb volatile components of *P. uloptera.* In comparison to the HD method, the proposed technique could equally monitor almost all the components of the sample, in an easier way, shorter time and requiring a much lower amount of the sample.

Key words: microwave-assisted hydrodistillation, solid phase microextraction, polypyrrole / SBA-15, essential oil

INTRODUCTION

Prangos uloptera DC (family: Apiaceae alt. Umbelliferae) is a perennial herb native to mountain slopes of the central and western Asian countries including Turkey, Iran, Iraq, Afghanistan and Uzbekistan. Prangos species, commonly known as 'Djashir' in Iran, are widely used in folk medicine as tonic, and for the treatment of flatulence, haemorrhoids, wounds and leukoplakia. Previous phytochemical studies on the aerial parts, fruits and roots of *P. uloptera* yielded various coumarins, monoterpenes and sesquiterpenes [1–5].

Among many different methods utilized for the extraction of the essential oil of plant materials, microextraction techniques have found extensive applications in recent years [6–10]. Both solid phase microextraction and solvent microextraction methods have been utilized for this purpose. Headspace solid-phase microextraction (HS-SPME) is a relatively new sampling and concentration technique for the extraction of plant essential oils [11–15]. HS–SPME followed by gas chromatography-mass spectrometry (GC-MS) has been proven to be a simple, sensitive and solvent-free method for the analysis of essential oil components. However, conventional HS-SPME still requires about 30 min for the extraction of essential oil compounds in medicinal plants. There has recently been widespread interest in the application of microwave heating to analysis of essential oils. The main advantage of microwave-assisted extraction (MAE) is the reduction of extraction time and organic solvent consumption. Recently, microwave distillation with concurrent solid-phase microextraction was first introduced for the successful isolation and concentration of essential oil components from medicinal plants [16]. The MAE-SPME technique combines the advantages of MAE and SPME, so it has high extraction efficiency, no need for any organic solvent, a small amount of sample and short extraction times.

The proposed fiber was selective towards some volatile organic compounds with extraction efficiencies better compared to a commercial PDMS fiber. Hexagonally ordered nanoporous silica (SBA-15), which possesses a large surface area and uniform tubular channels, was discovered by Zhao et al.

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in 1998 [17]. It has outstanding properties, such as highly ordered pore structures, large surface areas (up to 1 000 m^2/g), huge pore volume, high thermal stability and ability of functionalization by incorporation of organic groups. Increasing attention has been paid to SBA-15 supported nanocomposites because of their possible applications in catalysis [18], optical devices [19], electrochemical sensors [20] and miniaturized electronic devices [21].

Recently, our research group fabricated a novel SPME fiber, by coating highly porous polypyrrole / SBA-15 nanocomposits on a stainless steel wire [22].

The goal of the present study is to inspect the extraction efficiency of this new fiber for the extraction of *P. uloptera* volatile components in comparison to a commercial polydimethylsiloxane (PDMS) fiber. A comparative study is also made between microwave-assisted distillation headspace solid phase microextraction (MA-HS-SPME) and the traditional hydrodistilation (HD) method. A simplex method was used for rapid and efficient optimization of the conditions used for MA-HS-SPME.

EXPERIMENTAL

Plant material

The aerial parts of *P. uloptera* were harvested in July 2011 near the city of Kermanshah, in the west of Iran. The plants were identified and authenticated by Dr. Massomi (Department of Botany, Razi University, Kermanshah). The voucher number 2011-88 was specified by the Kermanshah University Herbarium. The plant materials were dried in air and stored in sealed bags in a cool place.

Chemicals and reagents

All chemicals and reagents were purchased from Merck (Darmstadt, Germany) and used as received. Tetraethyl orthosilicate (TEOS) as a silica source, poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (EO20-PO70-EO20 or Pluronic P123) as a surfactant were purchased from Sigma-Aldrich (Steinheim, Germany). Double distilled water was used throughout. The commercially available PDMS fiber (100 μm) was purchased from Supelco (Bellefonte, PA, USA).

Hydrodistillation (HD) apparatus and procedure

Air-dried aerial parts of *P. uloptera* (50 g) were ground and subjected to hydrodistillation for 1.5 h, using a Clevenger-type apparatus as recommended. Briefly, the plant was immersed in water and heated to boiling, then the essential oil was evaporated together with water vapor and finally collected in a condenser. The distillate was isolated and dried over anhydrous sodium sulfate. The oil was stored at 4 °C until analysis by GC-MS. The yield of the yellowish oil from the aerial parts of *P. uloptera* was 0.41% (w/w), based on the dry weight of the sample.

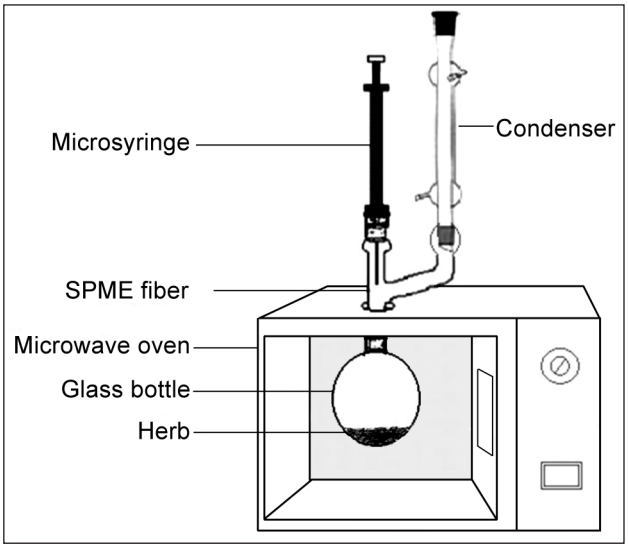

Fig. 1. The home-made apparatus of MA–HSME

MA-S-SPME of essential oil

The laboratory-made MA-HS-SPME apparatus is shown in Fig. 1. The microwave oven with a maximum delivered power of 900 W (model of GE614ST/GE614W, Samsung Company, Korea) was used as a heating device. In order to prevent from microwave leaking, an aluminum foil was tacked onto the inner wall and the outer wall of the microwave in the interface part [23–25].

MA-HS-SPME extraction was performed according to the following procedure. Weighed amount (4 g) of powdered herb was transferred into a 25 mL round bottom flask. After assembling a condenser, the SPME fiber was exposed to the sample headspace, the herb was heated by microwave power (450 W). After the extraction, the fiber was withdrawn from the bottle and inserted into the GC-MS injection port for analysis.

Gas chromatography-mass spectrometry

The GC-MS analysis was conducted using a gas chromatograph (Hewlett-Packard, USA, model HP 6890) coupled to a mass spectrometer with an electron impact ion source (Hewlett-Packard, model HP 5973). A HP-5 MS capillary column (30 m × 0.25 mm i. d., film thickness 0.25 μm) was used for separations. Helium, with a flow rate of 1.1 mL min^{-1}, was used as the carrier gas. The injection port, GC-MS interface, ion source and quadrupole temperatures were set at 260, 280, 230 and 150 °C, respectively. A split ratio of 50 was used for the ordinary injection of the essential oil samples. All injections of the SPME fibers were carried out on the splitless mode for 3.5 min. The column initial temperature was 50 °C. It was then raised to 180 °C with a rate of 15 °C min^{-1} and was held for 5 min. The temperature was then raised to 260 °C with a rate of 20 °C min^{-1} and was held for 5 min. Compounds were identified using the Wiley 7n (Wiley, New York, NY, USA) Mass Spectral Library.

Preparation of polypyrrole / SBA-15 nanocomposites

The polypyrrole / SBA-15 nanocomposite fiber was prepared as reported elsewhere. In short, polypyrrole / SBA-15 particles were prepared by a chemical polymerization method. To prepare the polypyrrole / SBA-15 nanocomposites, calcined SBA-15 was dried under vacuum at 250 °C for 6 h to remove air and water from the channels. Monomer pyrrole was adsorbed into the pores of SBA-15 through vapor at room temperature for 24 h. SBA-15-containing pyrrole was immersed in a 0.25 M aqueous solution of $FeCl_3 \cdot 6H_2O$ with stirring at room temperature for 24 h. Finally, the products were washed several times with deionized water and acetone, and then dried in a vacuum at 40 °C for 24 h [21].

RESULTS AND DISCUSSION

In the present study, the volatile constituents in *P. uloptera* were transferred to the headspace by a heating source, and the analytes in the headspace were simultaneously extracted and concentrated on the SPME fiber. Isolation, extraction, and concentration of the volatile components were performed in one single step. The microwave power, irradiation time, extraction time and sample mass that can affect the extraction efficiency of MA-HS-SPME were studied.

Optimization of MA-HS-SPME

A simplex method was used for optimization of effective parameters on the extraction efficiency in the MA-HS-SPME method. Use of a simplex method can significantly reduce the number of experiments required for achievement of the maximum extraction efficiency. The relative areas of four main peaks in the GC-MS chromatogram (α-Pinene, β-Phellanderne, Terpinolene and Bornyl acetate) were monitored during the optimization. In the simplex method, (n + 1) initial experiments were designed (n is the number of effective parameters on the extraction efficiency in the HSME method), the conditions corresponding to the worst response were reflected, and the reflection process was repeated until no further improvement in the response was observed. Some of the reflections were modified when appropriate [26].

Table 1. **Experimental conditions used and results obtained for the MA-HS-SPME experiments performed in the simplex optimization procedure**

Exp. No.	Sample weight, g	Extraction time, min	Microwave power, W
1	3	4	180
2	4	4	300
3	3	4	300
4	3	5	300
5	3	4.5	450
6 (Refl.)[b]	4	5	450
7 (Refl.)	2.5	6	450
8 (Refl.)	3	3.5	700
9 (Refl.)	3	5	450
10 (Refl.)	3	4.5	180

[a] Total relative peak area for α-Pinene, β-Phellanderne, Terpinolene and Bornyl acetate.
[b] Reflection.

The conditions used for the initial experiments and the subsequently designed experiments for MA-HS-SPME are summarized in Table 1. The experimental conditions were obtained by use of a modified reflection method. The modifications were usually performed in accordance with practical limitation of some factors [26]. The results clearly indicate the positive effects of the sample weight, microwave irradiation power and extraction time on the extraction efficiency of MA-HS-SPME methods.

As shown in Fig. 2, the maximum response was obtained for experiment No. 6. Therefore, the MA-HS-SPME extraction was required only for about 4 g of the sample and was performed in about 5 min.

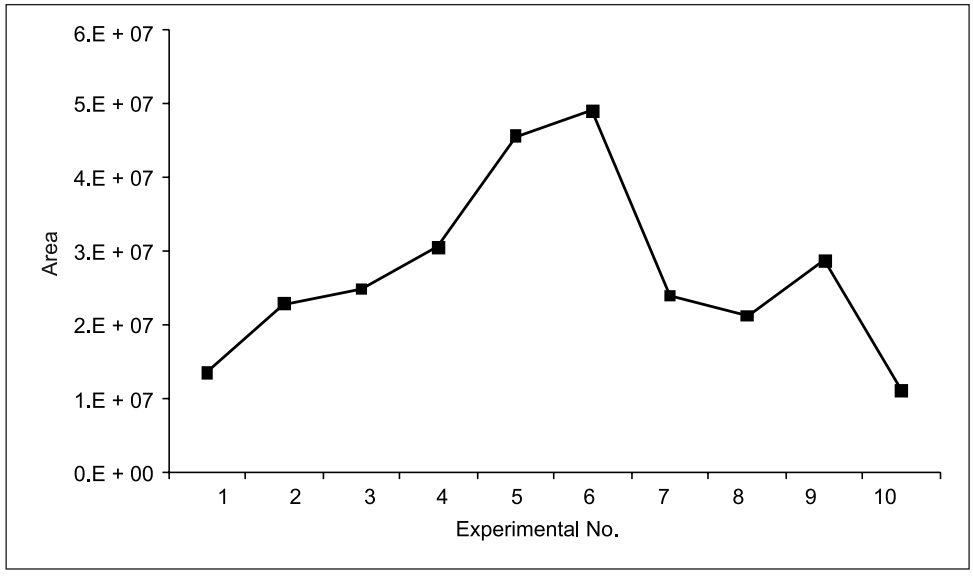

Fig. 2. The response (sum area of four main peaks of *Prangos uloptera* samples) for the designed experiments mentioned in Table 1

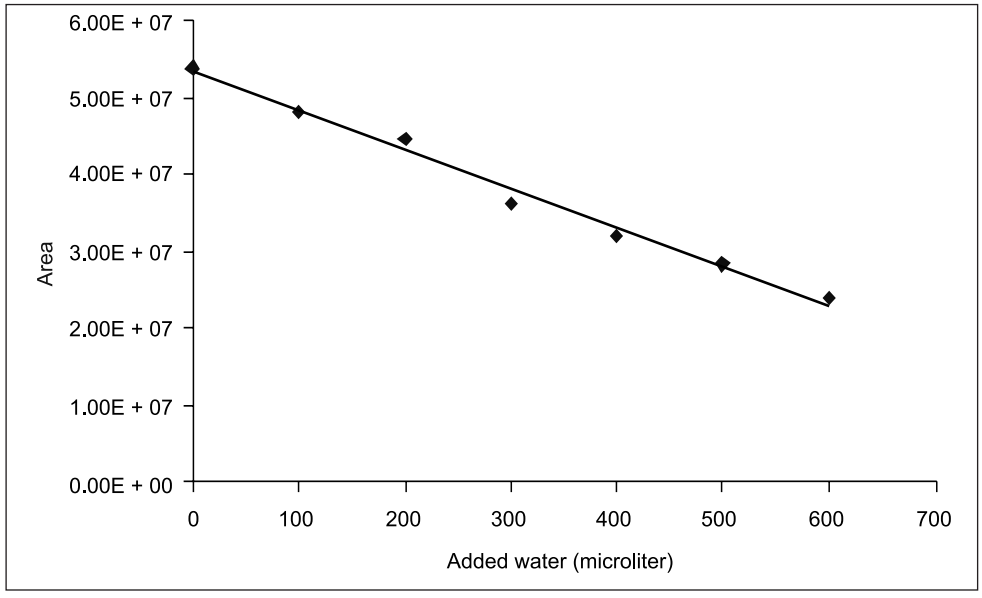

Fig. 3. Effect of water addition on the extraction efficiency of the SPME method

Effect of water addition

It has been reported that the humidity or addition of water to the samples may have significant influence on the extraction in the SPME experiment [27]. Since in this study the dried *P. uloptera* plants were used as the samples, the effect of humidity was studied by addition of different amounts of water to the samples in the optimized conditions. As shown in Fig. 3, addition of water had negative influence on the response. From these results, it can be concluded that the water vapor in the gaseous samples decreases the amount of analytes extracted effectively. It means that the water molecules can deactivate the fiber surface by blocking the active sites; therefore, the proposed fiber is a good adsorptive fiber for sampling from the dry samples.

MA-HS-SPME and HD of *P. uloptera*

The components of *P. uloptera* oil and their percentages obtained by calculation of the peak area relative to the total peak area for the conventional hydrodistillation and MA-HS-SPME method are presented in Table 2.

Almost the same number of components (sixty) was found in HD and MA-HS-SPME. Using a regression line method for comparison of the results indicated a linear correlation between the data of the nanoporous fiber, then the

Table 2. **The identified components and their percentages obtained with the SPME and HD methods**

	Compounds	RI[a]	(HD) area, %[b]	PDMS area, %	(SBA15/PPy) area, %[c]
1	α-Thujene	929	0.27	0.29	0.30
2	α-Pinene	940	15.37	14.26	15.24
3	Camphene	950	2.71	2.82	3.1
4	Sabinene	972	0.36	0.40	0.42
5	β-Pinene	977	1.49	1.81	1.76
6	β-Myrcene	993	9.10	9.8	10.16
7	δ-3-Carene	1 011	26.26	26.12	26.42
8	p-Cymene	1 027	8.60	8.53	8.21
9	z-Phellandrene	1 035	7.62	8.01	8.16
10	cis-Ocimene	1 040	0.09	0.11	0.10
11	trans-Ocimene	1 050	0.35	0.33	0.34
12	γ-Terpinene	1 061	1.26	1.12	0.92
13	Terpinolene	1 090	1.98	1.84	1.75
14	Isopentyl-isovalerate	1 103	0.40	0.61	0.32
15	p-Menth-1,3,8-triene	1 108	0.43	0.36	0.30
16	cis-β-Dihydro-terpineol	1 131	0.06	0.03	0.03
17	Hexyl-methyl propanoate	1 136	0.25	0.24	0.26
18	Camphor	1 147	0.30	0.26	0.28

Table 2. **Continued**

	Compounds	RI[a]	(HD) area, %[b]	PDMS area, %	(SBA15/PPy) area, %[c]
19	Camphen-hydrate	1 153	0.30	0.33	0.41
20	iso-Pulegol	1 161	0.28	0.25	0.20
21	Borneol	1 167	0.20	0.12	0.16
22	Terpinen-4-ol	1 177	0.29	0.28	0.24
23	p-Methyl-acetophenone	1 187	0.70	0.74	0. 63
24	Verbenone	1 192	0.23	0.28	0.31
25	Decanal	1 201	0.13	0.14	0.11
26	p-Cymene-9-ol	1 205	0.36	0.28	0.32
27	Carvone	1 222	0.15	0.18	0.18
28	Geraniol	1 243	0.87	0.65	0.51
29	trans-Chrysanthenyl acetate	1 261	0.73	0.66	0.72
30	Bornyl acetate	1 286	2.35	2.13	2.36
31	Thymol	1 292	0.45	0.41	0.36
32	Pinocarvyl acetate	1 310	0.42	0.36	0.55
33	(2E,4E)-Decadienal	1 315	0.28	0.23	0.19
34	Octyl methyl propanoate	1 332	0.34	0.36	0.24
35	Trans- carvyl acetate	1 337	0.40	0.48	0.52
36	Butyl benzoate	1 341	0.25	0.28	0.23
37	Eugenol	1 351	0.57	0.48	0.46
38	Phenyl acetonitril	1 365	0.74	0.66	0.68
39	Geranyl acetate	1 379	0.19	0.21	0.23
40	Isolongifolene	1 389	0.28	0.27	0.28
41	Caryophyllene	1 413	0.34	0.30	0.26
42	Germacrene D	1 475	0.32	0.28	0.24
43	β-Ionone	1 480	0.31	0.26	0.24
44	γ-Muurolene	1 488	0.17	0.21	0.15
45	γ-Cadinene	1 508	0.40	0.36	0.43
46	β-Bisabolene	1 512	1.76	1.62	1.55
47	Germacrene B	1 551	0.66	0.52	0.64
48	Isocaryophyllene oxide	1 556	0.09	1.02	1.12
49	Viridiflorol	1 593	0.59	0.67	0.68
50	Cedrol	1 598	0.86	0.77	0.75
51	1,10-DI-EPI-cubenol	1 671	0.31	0.28	0.32
52	Cedr-8(15)-en-9-alpha-ol	1 641	0.10	0.08	0.09
53	Cadalene	1 647	0.33	0.42	0.37
54	Valerianol	1 655	0.16	0.11	0.13
55	Valeranone	1 672	0.13	0.15	0.12
56	α-Bisabolol	1 680	0.24	0.29	0.30
57	Cedren-13-ol(8)	1 686	0.05	0.09	0.08
58	(E,E)-Farnesol	1 722	0.08	0.10	0.08
59	β-Bisabolen-12-ol	1 759	0.09	0.08	0.05
60	γ-Eudesmol acetate	1 773	4.11	4.23	4.12

[a] Retention indices using a DB5-MS column.

[b] Relative area (peak area relative to total peak area) for hydrodistillation method.

[c] Relative area (peak area relative to total peak area) for PDMS fiber.

[d] Relative area (peak area relative to total peak area) for polypyrrole / SBA-15 fiber.

commercial fiber, with the HD results. Therefore, the nanoporous fiber can provide similar information to those of the HD method by using much lower amounts of the sample and in much shorter time.

The hydrodistillation method required long time (2 h) to isolate the volatile oil from *P. uloptera* In the MA-HS-SPME method, the isolation of volatile compounds in the herb was rapidly completed, and then the isolated volatile compounds were simultaneously extracted and concentrated by fiber (total time 5 min). Therefore, MA-HS-SPME is an easy, rapid, low-cost, and solvent-free method for the determination of the volatile oil in *P. uloptera*.

CONCLUSIONS

A polypyrrole / SBA-15 SPME fiber was introduced and evaluated for the extraction of volatile components of *P. uloptera*. The presented experimental results clearly demonstrate that polypyrrole / SBA-15 fibers are suitable for MA-HS-SPME of essential oil analyses. In comparison to the HD method, the proposed technique could equally monitor almost all the components of the sample, in an easier way, shorter time and requiring a much lower amount of the sample. This simplex method was shown to be a rapid and efficient means of the optimization of microextraction conditions by performing just a few experiments.

Received 20 April 2012
Accepted 30 April 2012

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PRANGOS ULOPTERA ETERINIŲ ALIEJŲ GREITAS NUSTATYMAS NAUDOJANT NANOPORINGĄ SILICIO DIOKSIDO-POLIPIROLO PLUOŠTĄ

S a n t r a u k a

Pasiūlytas greitas *Prangos uloptera* eterinių aliejų nustatymo būdas. Tiriamasis pavyzdėlis yra švitinamas mikrobangomis, o lakūs komponentai sorbuojami nanoporingu polipirolo/SBA-15 pluoštu ir po to tiesiogiai įvedami į dujų chromatografą – masių spektrometrą. Optimizuoti pasiūlyto būdo parametrai.