Journal of Medicinal Plants and By-products (2021) 2: 161-167

Original Article

Analysis of *Grammosciadium platycarpum* Boiss. & Hausskn. Essential Oil Using of Three Dimensional Nanocomposite Based on MgAl Layered Double Hydroxide as a Fiber Coating of SPME

Marzieh Babashpour-Asl[1*] and Marzieh Piryaei[2]

[1]*Department of Horticulture, Maragheh Branch, Islamic Azad University, Maragheh, Iran*
[2]*Department of Chemistry, Faculty of Science, University of Maragheh, Maragheh, Iran*

Article History: Received: 27 July 2020/Accepted in revised form: 17 October 2020

Abstract

This study evaluates the reliability of polystyrene/MgAl-layered double hydroxide as a 3D new nanostructure solid phase microextraction fiber coating for extraction and determination the essential oil of *Grammosciadium platycarpum* Boiss. & Hausskn. growing wild in Maragheh region, East Azerbaijan province, Iran. The Headspace solid phase microextraction coupled with gas chromatography/mass spectrometric method was applied for analyzing of volatile oils. The Headspace solid phase microextraction parameters including the extraction temperature and time, sample weight, and water amount were optimized. The method was compared with traditional hydrodistillation. The analysis of the oils resulted in the identification of 31 compounds. Linalool (57.31 and 61.05%) and α-humulene (5.62 and 4.82%) were found to be the major components, in hydrodistillation and headspace solid phase microextraction methods, respectively. The novel 3D nanostructure fiber coating based on MgAl LDH had the advantages of the strong interaction between analyte and sorbent, simplicity, high thermal stability and more convenient handling than the other traditional SPME fibers. Although to date, SPME devices have been used mainly in laboratory applications, recent research has been directed towards remote monitoring, particularly for clinical, field environmental and industrial hygiene applications.

Keywords: Volatile Oil, Microextraction, LDH, Nanomaterial, *Grammosciadium* DC., GC/MS

Introduction

Distillation is a conventional extraction method for essential oils extracted from medicinal plants. However, it often needs a large amount of sample and is time-consuming and laborious. Nowadays, modern sample preparation in analytical chemistry is characterized by simplification, high enrichment and minimization of sample amount and solvent [1]. In recent years, headspace solid phase microextraction (HS-SPME) has gained wide acceptance as an effective extraction technique for a wide variety of samples [2-4]. HS-SPME has mainly been applied for studying the composition of the volatile fraction, in addition to or as an alternative to other sampling techniques. A review of 108 articles covering the use of HS-SPME in the field of aromatic and medicinal plants was presented by Belliardo *et al*. [5]. A number of SPME fibers with different polarity and coating thickness are commercially available and are used for extraction of the volatile compounds in medicinal plants [6-16]. From solid phase microextraction point of view, the fiber coating and the material of coating are very important [6,9,15,17,18]. For this purpose, new sorbents based on activated carbon [19], metal oxide nano particles [20], hexagonally ordered silica material [18], conducting polymers [9,17], molecular-imprinted polymers (MIPs) [21] and ionic liquid-modified silica [22] are recently appeared as alternatives to conventional SPME materials. Recently, there is a series of reports on the research of polymer/Layered double hydroxides nanocomposite as fiber coating. Layered double hydroxides (LDHs) are well characterized as anionic clays and utilized in wide range of technological applications such as catalysts, adsorbents, separation techniques and ion-exchangers [23,24]. The general chemical formula of LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^n)_{x/n}.\ mH_2O$, where, M^{2+} is a metal divalent cation (Co^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}), M^{3+} is a metal trivalent cation

*Corresponding author: Department of Horticulture, Maragheh Branch, Islamic Azad University, Maragheh, Iran
Email Address: babashpour@gmail.com

(Mn^{3+}, Ga^{3+}, Al^{3+}, In^{3+}) and A^{n-} is an interlayer anion (NO^{3-}, Cl^{-}, CO_3^{2-}, OH^{-}) [25].

The genus *Grammosciadium* DC. from the Apiaceae family consists of 9 species [26-29], three of them grow in Iran, which are characterized by setaceous leaf lobes, the persistent and often prominent sepals [30]. It is endemic to Irano-Turanian phytogeographic region [31]. *G. platycarpum* is a perennial plant growing up to 40 cm high, which is found in sandy mountain areas of Iran [32]. *Grammosciadium* species has been rarely documented in folk medicine. The dried leaves of *G. platycarpum* are used as spice for meals. This species which is named 'Jafari koohi', 'Shevid Koohi' and 'Samoureh', are also traditionally used for hyperlipidemia and cooked as edible foods in Iran [30,33-35]. It has a pleasant test and odor and is sold under the Azeri name 'Surulu' as a vegetable and food additive in Maragheh region during the spring [36]. There have been a number of studies on the chemical compositions of the volatile oils obtained from various species of the genus *Grammosciadium*, including *Grammosciadium scabridum* Boiss. [37], *G. platycarpum* [26,29,30,33], *G. daucoides* DC. [29,38], *G. pterocarpum* Boiss. [32], and *G. scabridum* Boiss. [39] growing in different countries. In this research we focused on investigation new application of layered double hydroxide nanostructured for essential oil extraction. So, a new three dimensionally (3D) polystyrene nanocomposite based on MgAl layered double hydroxide (PS/MgAl-LDH) sorbent, was synthesized and used as a novel coating for SPME fiber. The aim of this research was to develop a HS-SPME method using of proposed fiber in combination with GC/MS that can be utilized for the analysis of the essential oil of *G. platycarpum*. To the best of our knowledge, no related publications are available for the purpose.

Experimental

Plant Material

Aerial parts of *G. platycarpum* Boiss. & Hausskn. were collected during the flowering stage from Sahand region (37° 30' 0.2", 46° 17'49.2"; 1870 m, 15 km from Maragheh to Ashan village), East Azerbaijan province, Iran in May 2017. A voucher specimen (TUM-FPh-142) for these collections has been deposited at the Herbarium of the Faculty of Pharmacy, Tabriz University of Medical Sciences.

Chemicals and Ragents

Styrene monomer, Magnesium chloride ($MgCl_2$), aluminum chloride ($AlCl_3$), Sodium hydroxide (NaOH) with maximum available purities were purchased from Merck and used as received. All chemical solvents were obtained from the Fluka or Merck companies.

Hydrodistillation (HD) Procedure

After grinding 50 g of the air-dried aerial parts of *G. platycarpum*, the plant sample was subjected to hydrodistillation for 3 h with the help of a Clevenger-type apparatus according to the recommended guidelines. Upon immersion of the plant into water and its heating to the boiling point, the evaporated volatile oil was collected in a condenser together with water vapor. The isolated distillate was dried over anhydrous sodium sulfate. A dry weight of 0.85% (w/w) of the yellowish oil of the plant aerial parts was yielded, which was then stored at 4 °C to be later evaluated through GC/MS analysis.

Apparatus and GC–MS Analysis

A Hewlett-Packard Agilent 7890A series GC equipped with a split/splitless injector and an Agilent 5975 C mass-selective detector system were utilized for determination. The MS was operated in the EI mode (70 eV). Helium (99.999%) was employed as a carrier gas, and its flow-rate was adjusted to 1.1 mL/min. The separation of essential oils was performed on a 30 m×0.25 mm HP-5 MS column with 0.25 µm film thickness. The column was held at 50 °C and increased to 180 °C at a rate of 15 °C min^{-1} and then it was raised to 260 °C at 20 °C min^{-1} and kept at this temperature for 5 minutes. The injector temperature was set at 260 °C, and all injections were carried out on the splitless mode for 2 minutes. The GC-MS interface, ion source and quadrupole temperatures were set at 280, 230 and 150 °C, respectively. Compounds were identified using the Wiley 7N (Wiley, New York, NY, USA) Mass Spectral Library. A homemade SPME device was used for holding and the injection of the proposed fiber into the GC-MS injection port. The fiber was conditioned in the injection port of a GC for 1 h.

Synthesis of Polystyrene/MgAl-LDH Nanocomposite

Polystyrene (PS) spheres (ranging from 150 to 1000 nm) was prepared following the procedure of Kotera *et al*. [40] by 'emulsifier-free' emulsion polymerization. Monomer styrene was distilled before use to remove any traces of inhibitor. The PS particles initially suspended in water (10 wt%) were packed into three-dimensional colloidal crystals by centrifugation at 4000 rpm during 5 h. After drying at room temperature, 1 g of iridescent crystal was immersed in 6 mL of a 1 M solution of metal salts containing magnesium chloride (0.67 M) and aluminum chloride (0.33 M), and was formed by a mixture water-ethanol (50/50, v/v). The filled samples were dried and then soaked in 2 M sodium hydroxide aqueous solution in order to achieve the template LDH precipitation. The excess of solution was removed by a slight filtration in Buchner funnel; finally, the samples were washed with water, and then dried for a day. Subsequently, the polystyrene beads were removed by heating at 400 °C during one day. The calcined samples

were finally immersed in 5 mL of deionized water at room temperature for a day [41].

Preparation of the SPME Fiber

A piece of stainless steel wire with a 200µm diameter was cleaned twice with methanol in an ultrasonic bath for 20 minutes and dried at 70 °C. One centimeter of the wire was limed with epoxy glue and the PS/MgAl-LDH nanocomposite was immobilized onto the wire. The coated wire was heated to 50 °C for 48 h in an oven, gently scrubbed to remove non-bonded particles and assembled to the SPME holder device. Finally, prepared SPME fiber was inserted into the GC injection port to be cleaned and conditioned at 260 °C for 1 h in a helium environment. The thickness of the uniform coating layer was calculated from the difference between the coated and uncoated stainless steel wire and come out to be about 20µm.

The Headspace Solid Phase Microextraction (HS-SPME) Procedure

SPME was performed with the prepared 3D-LDH fiber, mounted in its SPME device (Figure 1). During the headspace extraction, the aqueous samples were continuously stirred with a magnetic stir bar. The extraction temperature was controlled using a thermostated water bath. Thermal desorption of retained compounds on fiber was carried out at 275 °C while the split valve of injector on the GC kept closed at different period of times. After reaching the extraction time, the SPME probe containing analytes from the sample, was withdrawn from the vial and inserted into the GC injection port for thermal desorption.

Results

Optimization of the HS-SPME Apparatus

Before optimization of the extraction parameters, complete desorption of the collected analytes in the GC/MS injection port, and their proper separation over the column were optimized. For this purpose, different injector temperatures and desorption times were tested. The upper temperature that can be used for desorption of the analytes from a fiber is limited by the thermal stability of its coating. For the 3D-LDH SPME fiber, desorption temperatures ranged between 200 and 280 °C. A temperature of 260 °C was found to be appropriate for the efficient desorption of analytes from the proposed fiber without damaging its coating (Fig. 2). Desorption times from 60 to 200 sec. were investigated at this temperature and 150 sec. was selected for a complete desorption with no memory effect (Fig. 3).

Extraction Temperature Effect

A varied extraction temperature of 40-100 °C was considered as shown in Figure 4. Either the total or individual peak areas were found to be enhance with the temperatures of up to 80 °C, which then led to a leveling-off state. The significant impact of the extraction temperature on the extraction process was evidenced due to its effect on the compound distribution between the headspace and the fiber/sample. These results made us choose the final temperature of 80 °C for this work.

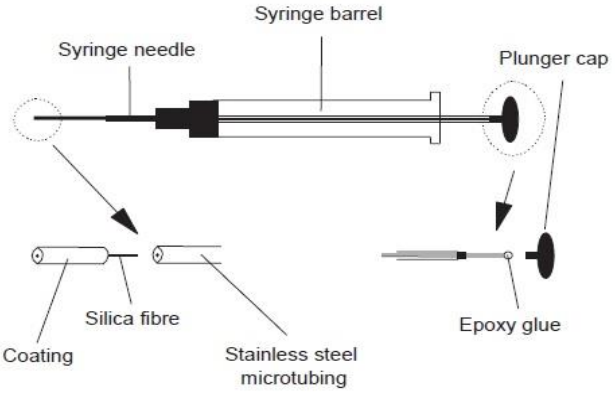

Fig. 1 The custom-made SPME device based on the Hamilton 7000 series syringe [42].

Extraction Time Effect

The extraction time varying from 10 to 35 minutes was investigated and the results are shown in Figure 5. The profile for the total and individual peaks area shows highest peak area at 20 minutes for the target compounds.

Sample Weight Effect

Increasing the sample weight generally leads to elevated analyte signals; however, extraction efficiency may be influenced by its large amounts. This does not mean that better results can be achieved by larger amounts of a sample. In the present work, a range of 0.5 to 3 g of the sample weight was utilized. The results of their effects on the total and individual peak areas of the 4 studied compounds are presented in Figure 6. As expected, the mentioned peak areas leveled off with the amounts of more than 1.5 g after augmenting up to this amount.

Added Eater Effect

Since in this study the dried *G. platycarpum* plants were used as the samples, the effect of humidity was studied by the addition of different amounts of water to the samples in the optimized conditions. As shown in Figure 7, addition of water had a negative influence on the response. 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 dried samples.

Comparison of HD and HS-SPME using nanostructure PS/MgAl-LDH Fiber coating methods Almost the same

number of components (31) were found in the HD and HS-SPME methods (Table 1). Linalool (57.31 and 61.05%) and α-humulene (5.62 and 4.82%) were found to be the major components, in HD and HS-SPME methods, respectively.

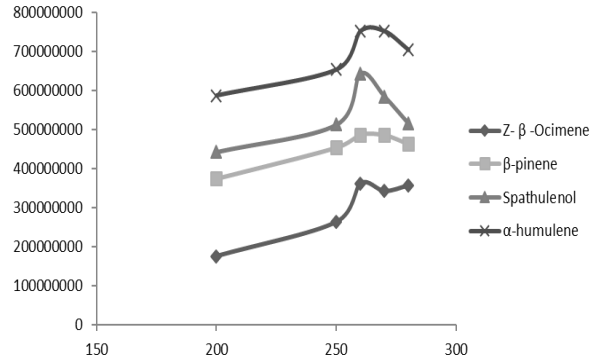

Fig. 2 Effect of the desorption temperature on the extraction efficacy of essential oils of *G. platycarpum* Boiss. & Hausskn.

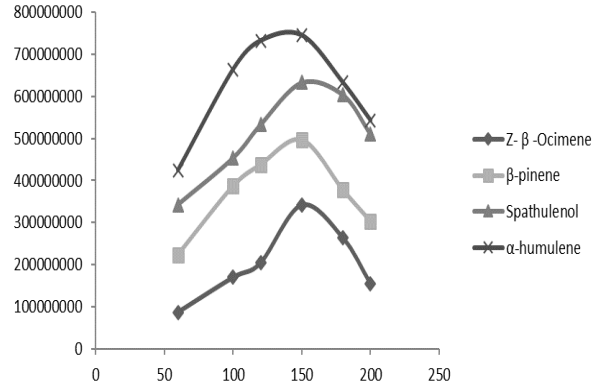

Fig. 3 Effect of the desorption time on the extraction efficacy of essential oils of *G. platycarpum* Boiss. & Hausskn.

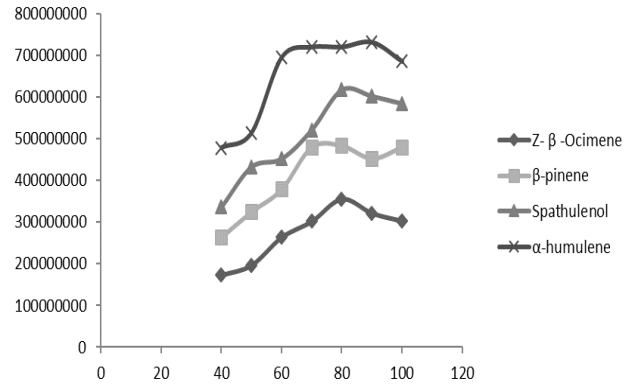

Fig. 4 Effect of the extraction temperature on the extraction efficacy of essential oils of *G. platycarpum* Boiss. & Hausskn.

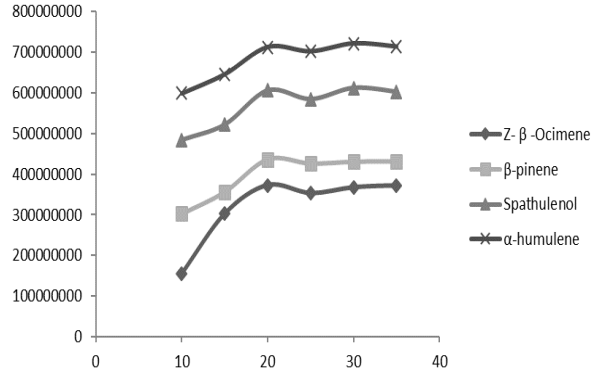

Fig. 5 Effect of the extraction time on the extraction efficacy of essential oils of *G. platycarpum* Boiss. & Hausskn.

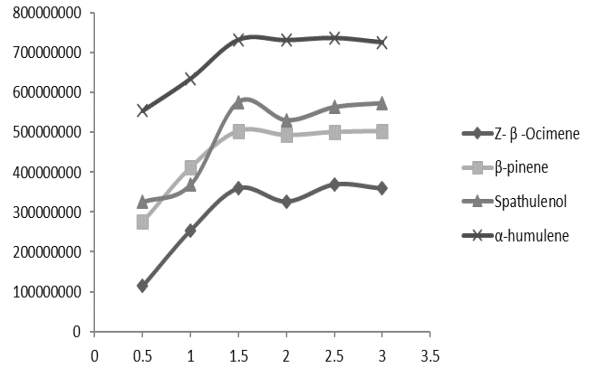

Fig. 6 Effect of the sample weight on the extraction efficacy of essential oils of *G. platycarpum* Boiss. & Hausskn.

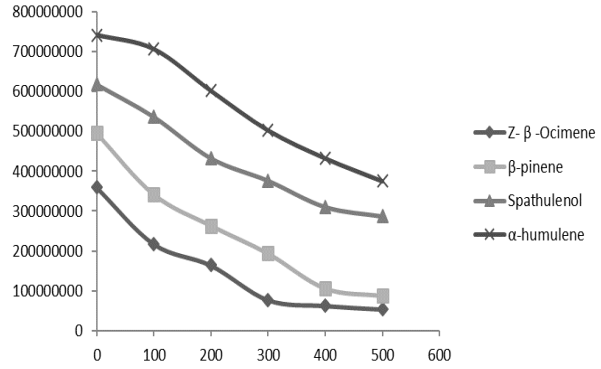

Fig. 7 Effect of the added water on the extraction efficacy of essential oils of *G. platycarpum* Boiss. & Hausskn.

Discussion

In this study, the volatile constituents of *G. platycarpum* were transferred to the headspace, 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 use of headspace is usually preferred because of completely limiting the extent of damage to the fiber caused by the sample matrix. It is well-documented that the extraction ability of a fiber is

strongly influenced by the mass transfer from the matrix to the vapor phase that conditions headspace composition and the mass transfer from the vapor phase to the fiber coating. It is therefore reasonable to evaluate the effect of parameters affecting these equilibrium conditions, because the equilibrium for all components of a complex matrix, as a medicinal or aromatic plant, can be very difficult to achieve because of their different volatility and polarity (25). For optimization of the microextraction conditions by the 3D-LDH SPME fiber, a one-at-the-time optimization strategy was used. The optimized parameters were the extraction temperature and time, sample weight and water amount. In the optimization protocols, the peak area of seven major compounds present in the medicinal plant that was identified by HD method was used for optimization procedure.

A review of the chemical constituents of *Grammosciadium* showed that the phytochemical composition of the genus has been addressed by a few studies in the past. Sonboli *et al*. [30] reported that the essential oil from the whole aerial parts of *G. platycarpum* is consisted mainly of linalool (79.0-81.8%) and limonene (5.8-10.0%). Also, Sonboli *et al*. [32] analyzed the volatile constituents of the aerial parts of *G. scabridum*. This oil was characterized by high amounts of δ-terpinene (73.5%), p-cymene (14.2%), and (E)-β-farnesene (5.3%). Nickavar *et al*. [38] reported that the major components of the hydrodistilled essential oils obtained from dried leaves and fruits of *G. platycarpum* were linalool (26.1 and 53.9 %), (E,E)-α-farnesene (24.1 and 20.4%) and (Z) -β- santalol (10.6 and 10.9%), respectively.

Moreover, α-farnesene, the major compound of *G. platycarpum* was also reported as the predominant compound by Nickavar *et al*. [43]. There are some differences between this research and the previous investigation on the essential oil of *G. platycarpum*. In our study, the major composition data of the essential oils from *G. platycarpum* Boiss. & Hausskn. was in agreement with the results from previous studies in Iran and Azerbaijan where linalool was the major component [1,2,30,39].

Table 1 Constituents of the essential oil of *G. platycarpum* Boiss. & Hausskn. by hy drodistillation and HS-SPME methods

No.	Compounds	RI [a]	(HD) Area% [b]	(HS-SPME) Area% [c]	Repeatability R.S.D.% [d]	Reproducibility R.S.D%
1	α-Thujene	929	0.12	0.08	11.2	13.4
2	α-Pinene	937	0.07	0.11	10.5	12.7
3	Camphene	955	0.05	0.05	11.8	10.8
4	Sabinene	975	0.14	0.06	14.5	14.7
5	β-pinene	978	2.68	2.52	8.3	13.5
6	Myrcene	996	1.10	0.17	10.7	15.8
7	α-Terpinene	1021	0.72	0.55	8.6	11.5
8	p-cymene	1025	0.08	0.03	8.4	10.2
9	1,8-cineole	1030	0.27	0.31	11.3	14.6
10	Z- β -Ocimene	1039	1.25	1.05	12.6	11.7
11	γ-Terpinene	1062	0.63	0.41	11.4	10.6
12	Terpinolene	1080	0.08	0.05	10.8	14.5
13	Cis Linalool oxide	1075	0.12	0.07	13.0	11.7
14	linalool	1100	57.31	61.05	9.5	14.1
15	α-Terpineol	1191	2.59	2.33	11.8	12.9
16	Geraniol	1253	1.31	0.14	9.6	13.1
17	Bornyl acetate	1283	0.11	0.05	7.4	12.7
18	α-Copaene	1375	0.06	0.03	10.6	12.1
19	E-caryophyllene	1421	2.21	1.75	11.8	15.1
20	Z-β-Farnesene	1441	1.23	1.18	12.2	14.6
21	α-humulene	1452	5.62	4.82	12.7	14.5
22	(9-epi-E) Caryophyllen	1465	1.25	0.52	10.7	15.3
23	γ –Gurjunene	1472	1.09	1.12	12.3	12.8
24	Bicyclogermacrene	1490	0.05	0.11	14.1	10.9
25	E,E-α-Farnesene	1502	3.05	2.14	10.6	12.5
26	β-bisabolene	1509	0.36	0.05	8.5	14.3
27	γ-cadinene	1522	1.15	0.08	11.7	12.5
28	γ-Elemol	1545	2.12	3.05	10.3	15.1
29	Spathulenol	1575	3.04	2.81	13.2	13.6
30	Caryophyllene oxide	1583	0.12	0.03	6.7	12.4
31	Humulene epoxide	1606	2.37	2.81	12.9	13.8

a) Retention indices using a HP-5MS 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 HS-SPME method.

d) RSD values for HS-SPME method (n = 4).

The majority of some common compounds in the essential oils may supply some contributions to the chemotaxonomy of the family patterns [44].

According to the results of present contribution, the nanoporous fiber coating can provide similar information to those of the HD method by using much lower amounts of the sample and in a much shorter time. The proposed SPME fiber is mechanically stable and there is no need to use different fibers in analysis. The HD method required long time (3 h) to isolate the volatile oil from *G. platycarpum.* In the 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. Therefore, HS-SPME is an easy, rapid, low cost, and solvent-free method for the determination of volatile components in the *G. platycarpum*.

Conclusion

The objective of this research was to determine the volatile compounds in *G. platycarpum* by a HS-SPME method and applying a PS/MgAl-LDH as a 3D nanostructure for SPME fiber coating. The presented experimental results clearly demonstrated that the novel fiber was suitable for HS-SPME of essential oils analyses. The fiber was mechanically stable, exhibited relatively high thermal stability and good repeatability. The construction of the fiber was very simple. The enhanced sorbent capacity was originated from the properties of the nanostructures, including porous structure, large surface area, and homogeneous honeycomb morphology. In comparison with an HD method, the proposed technique could equally monitor almost all the components of the sample, in an easier way, shorter time, and a much lower amount of sample was needed.

Acknowledgements

This study was funded by Department of Horticulture, Maragheh Branch, Islamic Azad University, Maragheh, Iran**.**

Conflicts of Interest

The authors have declared no conflicts of interest.

References

1. Zhang C, Qi M, Shao Q, Zhou S, Fu R. Analysis of the volatile compounds in *Ligusticum chuanxiong* Hort. using HS-SPME–GC-MS. J Pharmaceut Biomed Anal. 2007;44:464-470.
2. Bicchi C, Drigo S, Rubiolo P. Influence of fibre coating in headspace solid-phase microextraction–gas chromatographic analysis of aromatic and medicinal plants. J Chromatogr. A. 2000;892:469-485.
3. Kataoka H, Lord HL, Pawliszyn J. Applications of solid-phase microextraction in food analysis. J Chromatogr A. 2000;880:35-62.
4. Ulrich S. Solid-phase microextraction in biomedical analysis. J Chromatogr A. 2000;902:167-194.
5. Belliardo F, Bicchi C, Cordero C, Liberto E, Rubiolo P, Sgorbini B. Headspace-solid-phase microextraction in the analysis of the volatile fraction of aromatic and medicinal plants. J Chromatogr Sci. 2006;44:416-29.
6. Arthur C, Pawliszyn J. Solid phase microextraction with thermal desorption using fused silica optical fibers. Anal Chem. 1990;62:2145-2148.
7. Auxilio A, Andrews P, Junk P, Spiccia L. The adsorption behavior of CI Acid Blue 9 onto calcined Mg–Al layered double hydroxides. Dyes Pigm. 2009;81:103-112.
8. Du Y, Hu G, O'Hare D. Nucleation and growth of oriented layered hydroxides on polymer resin beads. J Mat Chem. 2009;19:1160-1165.
9. Gholivand MB, Abolghasemi MM, Fattahpour P. Highly porous silica- polyaniline nanocomposite as a novel solid- phase microextraction fiber coating. J Sep Sci. 2012;35:101-106.
10. He S, Zhao Y, Wei M, Evans DG, Duan X. Fabrication of hierarchical layered double hydroxide framework on aluminum foam as a structured adsorbent for water treatment. Ind Eng Chem Res. 2012;51:285-291.
11. Hendi R, Piryaei M, Babashpour-Asl M, Abolghasemi MM. Nanoporous Silica-Polypyrrole/SBA-15 as Fiber Coated in the Solid-Phase Microextraction for Determination of *Salvia hydrangea* DC. Essen Oil. Pharm. Sci. 2018;24:235-239.
12. Hosseinzadeh Z, Piryaei M, Babashpour-Asl M, Abolghasemi MM. ZnO polythiophene SBA-15 nanoparticles as a solid-phase microextraction fiber for fast determination essential oils of *Matricaria chamomilla*. Nanochem. Res. 2018;3:124-130.
13. Lazaridis N, Pandi T, Matis K. Chromium (VI) removal from aqueous solutions by Mg− Al− CO3 hydrotalcite: sorption− desorption kinetic and equilibrium studies. Ind. Eng. Chem. Res. 2004;43:2209-2215.
14. Nemati Kharajuo M, Piryaei M, Babashpour Asl M, Abolghasemi MM. Fast analysis of volatile compounds from *Lippia citriodora* with nanoporous aluminum wire as solid-phase microextraction fibres. Nat Prod Res. 2017;31:351-354.
15. Yang R, Xie W. Determination of cannabinoids in biological samples using a new solid phase micro-extraction membrane and liquid chromatography–mass spectrometry. Forensic Sci. Int. 2006;162:135-139.
16. Zhang T, Chen X, Li Y, Liang P. Application of headspace liquid-phase microextraction to the analysis of

volatile halocarbons in water. Chromatographia. 2006;63:633-637.

17. Gholivand MB, Abolghasemi MM. Inside needle capillary adsorption trap device for headspace solid-phase dynamic extraction based on polyaniline/hexagonally ordered silica nanocomposite. J Sep Sci. 2012;35:695-701.
18. Gholivand MB, Abolghasemi MM, Fattahpour P. Polypyrrole/hexagonally ordered silica nanocomposite as a novel fiber coating for solid-phase microextraction. Anal Chim Acta. 2011;704:174-179.
19. Zhong LS, Hu JS, Liang HP, Cao AM, Song WG, Wan LJ. Self- Assembled 3D flowerlike iron oxide nanostructures and their application in water treatment. Adv Mater. 2006;18:2426-2431.
20. Mehdinia A, Mousavi MF, Shamsipur M. Nano-structured lead dioxide as a novel stationary phase for solid-phase microextraction. J Chromatogr A. 2006;1134:24-31.
21. Djozan D, Ebrahimi B. Preparation of new solid phase micro extraction fiber on the basis of atrazine-molecular imprinted polymer: application for GC and GC/MS screening of triazine herbicides in water, rice and onion. Anal Chim Acta. 2008;616:152-159.
22. Abolghasemi M, Karimi B, Yousefi V. Periodic mesoporous organosilica with ionic liquid framework as a novel fiber coating for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons. Anal Chim Acta. 2013;804:280-286.
23. Abolghasemi M, Yousefi V. Three dimensionally honeycomb layered double hydroxides framework as a novel fiber coating for headspace solid-phase microextraction of phenolic compounds. J Chromatogr A. 2014;1345:9-16.
24. Costa FR, Leuteritz A, Wagenknecht U, Jehnichen D, Haeussler L, Heinrich G. Intercalation of Mg-Al layered double hydroxide by anionic surfactants: preparation and characterization. Appl Clay Sci. 2008;38:153-164.
25. Suresh K, Kumar RV, Pugazhenthi G. Processing and characterization of polystyrene nanocomposites based on CoAl layered double hydroxide. Adv Mater Dev. 2016;1:351-361.
26. Bani B, Mavi Ö, Adigüzel N. Morphological and Anatomical Notes on a Local Endemic Species: *Grammosciadium confertum* Hub.-Mor. & Lamond(Umbelliferae). Biol Dev Conserv. 2011;4:1-6.
27. Hedge I, Lamond J. eds. *Grammosciadium* DC. Flora of Turkey and East Aegean Islands 4. ed. P. Davis. Edinburgh Univeristy Press: Edinburgh. 1972.
28. Pimenov, M. and M. Leonov, The Asian Umbelliferae biodiversity database (ASIUM) with particular reference to South-West Asian taxa. Turk J. Bot. 2004;28:139-145.
29. Vinogradova V. The new data on the genus *Grammosciadium* and the systematic position of *Fuernrohria setifolia* (Apiaceae). Bot Zhur. 1995;80:91-99.
30. Sonboli A, Eftekhar F, Yousefzadi M, Kanani MR. Antibacterial activity and chemical composition of the essential oil of *G. platycarpum* Boiss. from Iran. Z. Naturforsch. C. 2005;60:30-34.
31. Takhtajan AL, Crovello TJ, Cronquist A. Floristic regions of the world. Berkeley: University of California Press. 1986.
32. Sonboli A, Salehi P, Kanani MR, Ebrahimi SN. Antibacterial and antioxidant activity and essential oil composition of *Grammosciadium scabridum* Boiss. from Iran. Z. Naturforsch. C. 2005;60:534-538.
33. Ahvazi M, Khalighi-Sigaroodi F, Charkhchiyan M, Mojab F, Mozaffarian V, Zakeri H. Introduction of medicinal plants species with the most traditional usage in Alamut region. Iran. J Pharm Res. 2012;11:185.
34. Babashpour-Asl M, Talebpour A, Alijanpour R. Introducing of medicinal plants in Maragheh, Eastern Azerbaijan province (northwestern Iran). J Med Plants Res. 2012;6:4208-20.
35. Mozaffarian V. Dictionary of Iranian plant names. Tehran: Farhang Mo'aser. 2003.
36. Nazemiyeh H, Delazar A, Movahedin N, Jodari M, Imani Y, Ghahramani M, Nahar L, Sarker S. Free radical scavengers from the aerial parts of *G. platycarpum* Boiss. & Hausskn.(Apiaceae) and GC-MS analysis of the essential oils from its fruits. Rev Bras Farmacogn. 2009;19:914-918.
37. Shikhiev AS, Abbasov R, Malinovskaya T. Essential oils from two species of *Grammosciadium* genus from the Umbelliferae family. Khim Prir Soedin. 1979;3:410-411.
38. Nickavar B, Kamalinejad M, Mohandesi S. Comparison of the components of the essential oils from leaves and fruits of *Grammosciadium platycarpum*. Chem Nat Compd. 2006;42:686-688.
39. Küçükboyacı N, Demirci B, Adıgüzel N, Bani B, Hüsnü K, Başer C. Volatile compounds from the aerial part and fruits of *Grammosciadium pterocarpum* Boiss. growing in Turkey. J Essen Oil Res. 2015;27:177-181.
40. Kotera A, Furusawa K, Kudō K. Colloid chemical studies of polystyrene latices polymerized without any surface-active agents. Prog Colloid Polym Sci. 1970;240:837-842.
41. Géraud E, Prévot V, Leroux F. Synthesis and characterization of macroporous MgAl LDH using polystyrene spheres as template. J Phys Chem Solids. 2006;67:903-908.
42. Pawliszyn J. Handbook of solid phase microextraction. Elsevier. 2011.
43. Nickavar B, Mojab F, Kamalinejad M. Chemical composition of the leaf and fruit oils from *Grammosciadium platycarpum*. Planta Med. 2008;74:PB88.
44. Yüc E, Paksoy MY, Bagci E. Essential oil composition of two *Grammosciadium* DC Species, *G. platycarpum* (Boiss et Hausskn) Schischk and *G. macrodon* Boiss (Apiaceae), from Turkey. Trop Pharm Res. 2016;15:411-414.