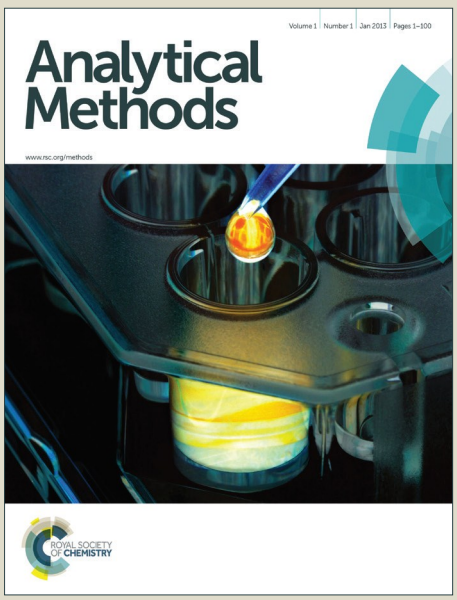
Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

Dendrimer grafted nanoporous silica as a new coating for headspace solid-phase microextraction fibers

Iman Saeedi[a], Payman Hashemi*[a], Zahra Ramezani[b,c], Alireza Badiei[d]

A dendrimer-like group (G1) was grafted onto Santa Barbara Amorphous-15(SBA-15) as a nanoporous silica support to be used as a highly porous coating material for headspace solid-phase microextraction (HS-SPME) fibers. The G1-dendrimer-SBA-15 particles were characterized by N_2 sorption and thermogravimetric analyses indicating that the particles had a lengthy morphology and a specific surface area of 200 m^2g^{-1}. The prepared nanomaterial was coated on a stainless steel wire for preparation of the SPME fiber. The prepared fiber was successfully applied for the extraction of target compounds in combination with gas chromatography-flame ionization detector. The selected extraction conditions, obtained with a simplex optimization method, were: sample volume 7.8 ml, extraction temperature 46.2 ^{0}C, extraction time 12.4 min, sonication time 6.4 min, pH 5.5 and salt concentration 7.2%. The repeatability for one fiber (n=6), expressed as relative standard deviation (RSD) was between 4.6% and 6.0% and the reproducibility for five prepared fibers was between 11.0% and 12.8% for the test compounds. In comparison with commercially available PDMS/DVB fibers, the new fiber is more robust and selective, highly porous and easily and inexpensively prepared. The capabilities of the proposed method are comparable or better than those of several other methods reported in the literature.

1. Introduction

Phenolic compounds are toxic and dangerous for human health and potentially carcinogenic. These compounds can influence the taste and odor of drinking water at very low concentrations. The European Union (EU) and the US Environmental Protection Agency (EPA) have included some phenols, especially chlorophenols, in their lists of priority pollutants.[1,2]

Phenolic compounds are produced in many industrial processes such as production of polymers, dyes, drugs, papers, pesticides and in the petrochemical industry.[3]Moreover chlorophenols have been extensively used for preservation of wood and disinfectants. Therefore, they have been generated in the environmental media.[4] They can also be produced from non-

[a]Department of Chemistry, Faculty of Science, Lorestan University, Khoramabad, Iran; E-Mail: payman_hashemi@yahoo.com
[b]Nanotechnology Research Center, Faculty of Pharmacy, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[c]Medicinal Chemistry Department, Faculty of Pharmacy, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[d]School of Chemistry, College of Science, University of Tehran, Tehran, Iran

chlorinated phenols during drinking water chlorination.[5] Therefore, there is an increasing demand for finding fast and simple phenolic compounds monitoring methods, and this has stimulated research activities in the field of sensor technology.

A number of different methods have been used for the determination of phenolic compounds such as spectrophotometry,[6] electrochemical methods,[7] liquid chromatography,[8] and gas chromatography (GC).[9] Among these mentioned methods, GC with flame ionization detector (FID), electron capture detector (ECD) or coupled with mass spectroscopy (MS) have been used more frequently due to the volatility of the phenolic compounds and the high separation efficiency of GC methods.[9] However, because of their low levels in environmental extracts which have often complex matrices, pretreatment (i.e. extraction and subsequent purification) of the samples is essential. As in many other fields of applications, liquid-liquid extraction (LLE) is still used for extracting liquid samples. However, the popularity of sorbent-based techniques such as solid-phase extraction (SPE) and solid-phase microextraction (SPME) have been increasing in recent years.[10]

SPME is an efficient and solvent-free sample preparation method, which integrates sampling, isolation and concentration into one step. It was first introduced in 1990 by Arthur and Pawliszyn.[11] This method has been considered as an efficient sample preparation technique in different fields of environmental science,[12] food analysis,[13] drug monitoring[14] and toxicology.[15]

Commercial SPME fibers often use fused-silica as the supporting substrate with a thin layer of sorbent material coated on it.[11] Silica based nanoporous materials such as MCM-41(mesoporous crystalline material-41),[16]SBA-15 (Santa Barbara Amorphous-15) [17] and LUS-1 (Laval University Silica-1) [18]are highly porous sorbents that have been recently used for the preparation of selective SPME fibers with high capacities. Preparation of such fibers are simple and cheap and the prepared fibers, with a metal support, are more stable than commercial fused silica fibers.[19]Functionalization of nanoporous silica with various groups provides SPME fibers with different selectivities towards desired groups of compounds.[16-19]

The purpose of this work was to synthesize, characterize and use a SBA-15 silica-supported dendrimer[20] for the preparation of new SPME fibers. For this purpose, the prepared nanoporous sorbent is coated on a stainless steel wire to be used as a selective and highly porous SPME fiber coating for the headspace (HS) extraction of volatile phenolic compounds.

2. Experimental

2.1. Reagents and Materials

Tetraethyl orthosilicate (TEOS, Merck) as silica source, poly(ethylene glycol)- block-poly(propylene glycol)- block-poly(ethylene glycol) (P123, Aldrich) as surfactant, 3-aminopropyltriethoxysilane solution (~65% in ethanol, APTES, Fluka) as amine compound,methyl acrylate, ethylenediamine, hydrochloric acid, sodium hydroxide, methanol, ethanol, and phenolic compounds (phenol, Ph; 4-chlorophenol, CP; 2,4-dichlorophenol, DCP) with maximum available purities were purchased from Merck. A mixture of these phenolics as standard solution (200 mg L^{-1}) was prepared in double distilled water and stored in the refrigerator. Working solutions were prepared by diluting the stock solutions with deionized water. The solutions were buffered in sodium hydrogen phosphate buffers (0.02 mol L^{-1}) for adjusting the pH.

2.2. Apparatus

Analysis of the studied phenolic compounds was performed with an Agilent 7890A GC system (Agilent Technologies, USA) equipped with a flame ionization detector (FID) and a split/splitless injector.

The column for the determination was a DB-17ms capillary column (Agilent Technologies, USA) (30 m × 0.32 mm id. × 0.25 μm film thickness). Ultrapure nitrogen (≥99.999%) was used as the carrier gas at 1 mL min^{-1}.

The injector was used in splitless mode at 260 ºC for the thermal desorption of the analytes from the SPME fiber. The detector temperature was fixed at 300 ºC. The initial column temperature was adjusted on 50 ºC and it was programmed at 10 ºC min^{-1} ramp to 250 ºC with holding at this temperature for 2 min.

The N_2 adsorption-desorption isotherm of SBA-G1 was performed on a high precision surface area and pore size analyzer (BELSORP-miniII- Microtrac-USA) at −196 ºC. Specific surface area, total pore volume and pore diameter of samples was obtained by Brunauer–Emmett–Teller (BET) method using BELSORP analysis software. Thermal analysis (TA) curve for SBA-G1 were performed on TGA Q50 (TA instruments-USA) in the temperature range from ambient to 700 ºC. The ramp rate used was 20 ºC min^{-1}.

The atomic force microscopy (AFM) image was obtained with an AFM instrument, model JPK Nanowizard II, Germany.

2.3. Synthesis of mesoporous SBA-15

SBA-15 was prepared in the presence of Pluronic P123 triblock copolymer as template.[21] P123 (4.0 g) (with thenominal chemical formula $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}$Hor $EO_{20}PO_{70}EO_{20}$) was dissolved inHCl (2 mol L^{-1}) solution. Subsequently, an amount of TEOS (tetraethyl orthosilicate) was added.

The resulting mixture was stirred for 8 h at 40 ^oC and then aged for 15 h at 100 ^oC. The synthesis mixture had the following molar composition: 1 TEOS : 0.0168 P123 : 5.854 HCl : 162.681 H_2O. The white product was filtered, washed, dried and calcined at 550 ^oC for 6 h in air atmosphere. The final product showed a BET surface area of 750 m^2/g and a pore diameter of 6.5 nm, based on adsorption-desorption of N_2 at -200 ^oC.

2.4. G-dendrimer supported on SBA-15

Calcined SBA-15 (15 g) was first dried at 100 °C under vacuum for 1 h to remove surface humidity. Then it was immersed into 100 mL of boiling anhydrous toluene. 3-aminopropyltriethoxysilane (9 mL) was added to this mixture and it was stirred and refluxed at 110 °C for 12 h. The white amine functionalized SBA-15 was separated by filtration, washed thoroughly with toluene and dried in ambient condition. Aminopropyl-functionalized SBA-15 and methyl acrylate (two fold of aminosilane mol number) were stirred at 40 °C in dry ethanol for 5 days. The mixture was cooled, filtered and washed with dry ethanol (3×50 mL). The residual solvent was removed in vacuum. The product was SBA-G(0.5). An excess amount of ethylenediamine (13 mL) was added to SBA-G(0.5) in dry ethanol and the mixture was stirred in 40 °C for 5 days. After cooling, filtration and washing the powder product SBA-G1 was obtained (Fig. 1).

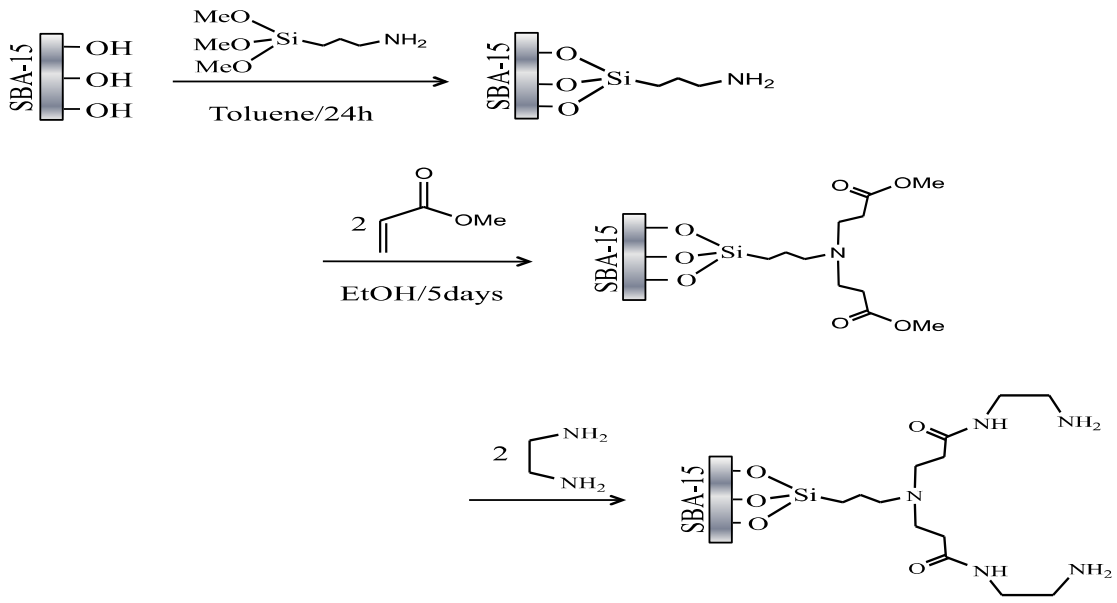


Fig. 1 Preparation of SBA-15 Silica-Supported dendrimer

2.5. Preparation of the HS-SPME fiber

A piece of stainless steel wire with 200 μm diameter was rinsed with methanol and dried at 60 ˚C. One centimeter of the wire was limed with epoxy glue (Razi Co., Iran) and the extra-fine powdered SBA-G1 material was immobilized on the wire.

The coated wire was heated at 65˚C for 24 h in an oven, which is slowly scrubbed to remove non-bonded particles and assembled to the SPME device. It was then inserted into the GC injection port to be cleaned and conditioned at 200˚C for 20 min in the nitrogen environment.

2.6. The HS-SPME procedure

A homemade manual SPME device was applied for holding and injection of the proposed fiber into the GC–FID injection port.

A 20 mL glass vial sealed with rubber septum was used as sample container. The bottle was sonicated in an ultrasonic bath during the extraction process. After a preset time, when the temperature reached a fixed value, the SPME device was fixed on top of the capped vial. Then the fabricated fiber was exposed to the sample headspace. After sample extraction, the fiber was withdrawn from the bottle and inserted into the GC–FID injection port for the thermal desorption and analysis.

2.7. Field samples

A tap water sample (Ahwaz, Iran), a water sample taken from an oil well of masjedsoleyman (no. 166) and three waste water samples were analysed by the proposed method in the present study. Some sewage water samples were also collected from Golestan hospital sewage (Ahwaz, Iran) and oil desalination units of Maroon 5 (Ahwaz, Iran) and Boniek (Gachsaran, Iran). All samples were collected in may 2014 and stored at 4 ºC before the analysis.

3. Results and discussion

3.1. Preparation and characterization of the fiber

G1-dendrimer was applied for functionalizing the SBA-15 to increase the selectivity and improving the sorption properties of SBA-15 as a coating material for SPME fibers. N_2 adsorption-desorption isotherm of SBA-G1 is shown in Fig. 2. The hysteresis loop type IV due to mesoporous structure of SBA-15 support is observed in this figure. The surface area for SBA-G1 was measured to be 200 m^2g^{-1} based on BET method. As expected for organic-functionalized material, the BET surface area, BJH pore sizes and pore volumes decrease relative to unfunctionalized SBA-15. The BJH pore radius value is 27 Å.

Thermal analysis curve for SBA-G1 is depicted in Fig. 3. The sample weight loss between 25 and 130 °C is attributed to desorption of water. The rest of the curve showed very slow, but continuous, weight loss. The next 18.28 % mass loss from 130 to 700 °C attributed to the pyrolysis of organic groups. The weight loss between 130 and 700 °C was used for calculation of dendrimer amount in sample which was about 0.65 mmol g^{-1}.

Scanning electron microscopic image of SBA-15 shows its highly porous structure.[23] An optical microscopic image of the fiber with a stainless steel core is presented in Fig. 4a. Fig. 4b shows an AFM imageof the sorbent particles. The uniform coating of SBA-G1 on the fiber and the nano-sizes of the particles is evident. Moreover, no significant in homogeneity of the coating was detected with the method used for the fiber coating. Measure of the thickness of the fiber was calculated from the difference between the diameters of the coated and uncoated stainless steel fiber to be about 50 μm.

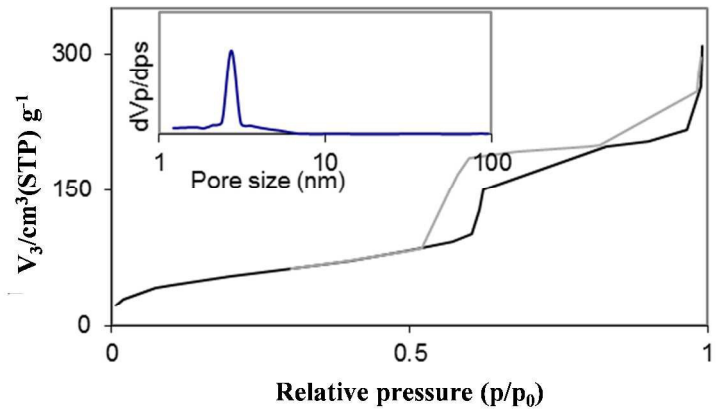


Fig. 2 Nitrogen adsorption-desorption isotherm and pore size distribution diagram for SBA-G1. V_a and *ps* are the volume adsorbed and pore size of the sorbent, respectively.

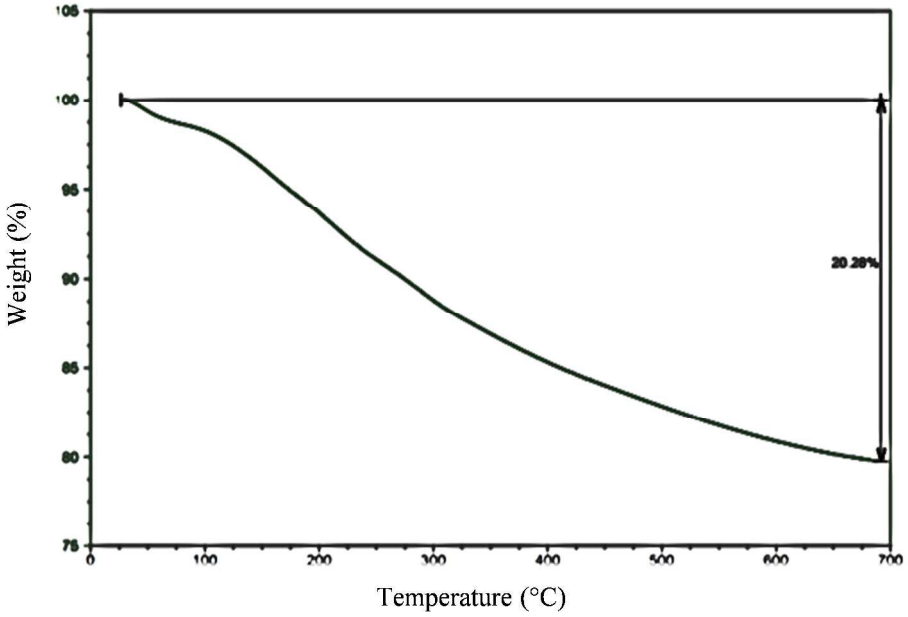


Fig. 3 Termogravimetric analysis curve for SBA-G1.

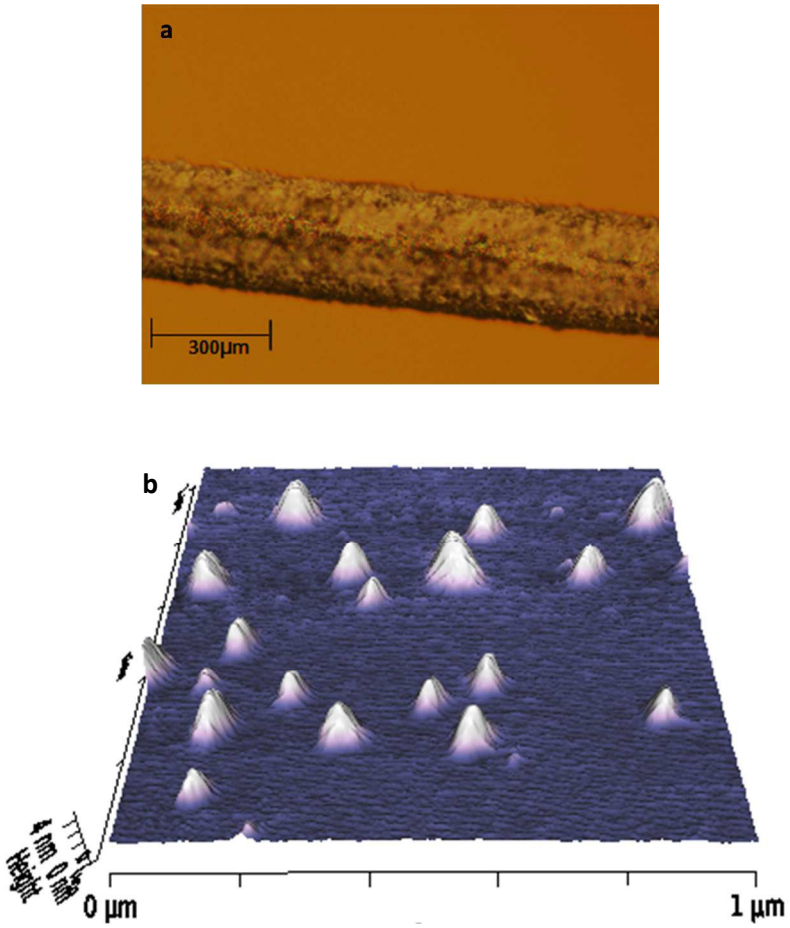


Fig. 4a. Opticalmicroscopic image of a fabricated SPME fiber (Olympus SZX-16 optical microscope). b. Atomic force micrograph of the surface of the SPME fiber.

3.2. The HS-SPME-GC-FID analysis

The efficiency of the prepared SBA-G1 fiber was tested for the extraction of some phenolic compounds by a HS-SPME method.

Some Preliminary experiments showed that the prepared fiber can efficiently adsorb phenolic compounds especially Ph, DCP and CP. Before optimization of the extraction parameters, complete desorption of the collected analytes in the GC injection port, and their proper separation over the column were optimized. For this purpose, different injector temperatures and desorption times were tested. It was found that a temperature of 260 ºC applied for 200 s, was most appropriate for the efficient desorption of the analytes from the SBA-G1 fiber without damaging the fiber or any significant memory effect.

Different temperature programs were tested for an appropriate separation of the target compounds. The program mentioned in the experimental section was selected as optimum.

3.3. Optimization of the extraction parameters

A simplex method was used for optimization of the HS-SPME conditions for determination of Ph, DCP and CP in water. In order to evaluate the work, the geometric mean[22] of peak areas for the compounds under study was considered as the experimental response to be optimized.

The optimization of extraction temperature, sonication time, collection time, sample volume and salt concentration on the extraction of phenolic compounds was performed using a simplex optimization method.[24] The conditions selected for this optimization and the responses obtained under each condition have been summarized in Table 1. The maximum efficiency was obtained for experiment no. 9. Therefore, the conditions of this experiment were selected as optimum.

Fig. 5 shows a chromatogram of a sewage water sample and a standard mixture of the three phenolic compounds (20 mg L^{-1}) under the optimum conditions.

Table 1 The conditions selected for the simplex optimization of the extraction of Ph, DCP and CP phenolic compounds by the proposed method.

Exp.no.	Sample volume (mL)[a]	Sonication time (min)	Extrn. time (min)	Extrn. temp. (◦C)	Salt concn. (%w/v)	pH	Response[b]
1	10	5	10	40	5	6	15895006
2	5	5	10	40	5	6	21457260
3	10	2	10	40	5	6	10961043
4	10	5	15	40	5	6	16332713
5	10	5	10	50	5	6	22162980
6	10	5	10	40	10	6	20698105
7	10	5	10	40	5	5	19355979
8	8.3	8	12	44	6.6	5.6	31899660
9	7.8	6	12.4	44.6	7.2	5.5	32550342
10	7	6.4	8.5	46.2	8	5.4	27327195
11	6	6.8	11	48.1	9	6.5	22920206
12	4.7	7.4	11.3	51	3.6	5.6	19791973

[a] The sample was a 20 mg L^{-1} solution of the phenolic compounds mixture in water.
[b] Geometric mean of the target peaks was considered as response.

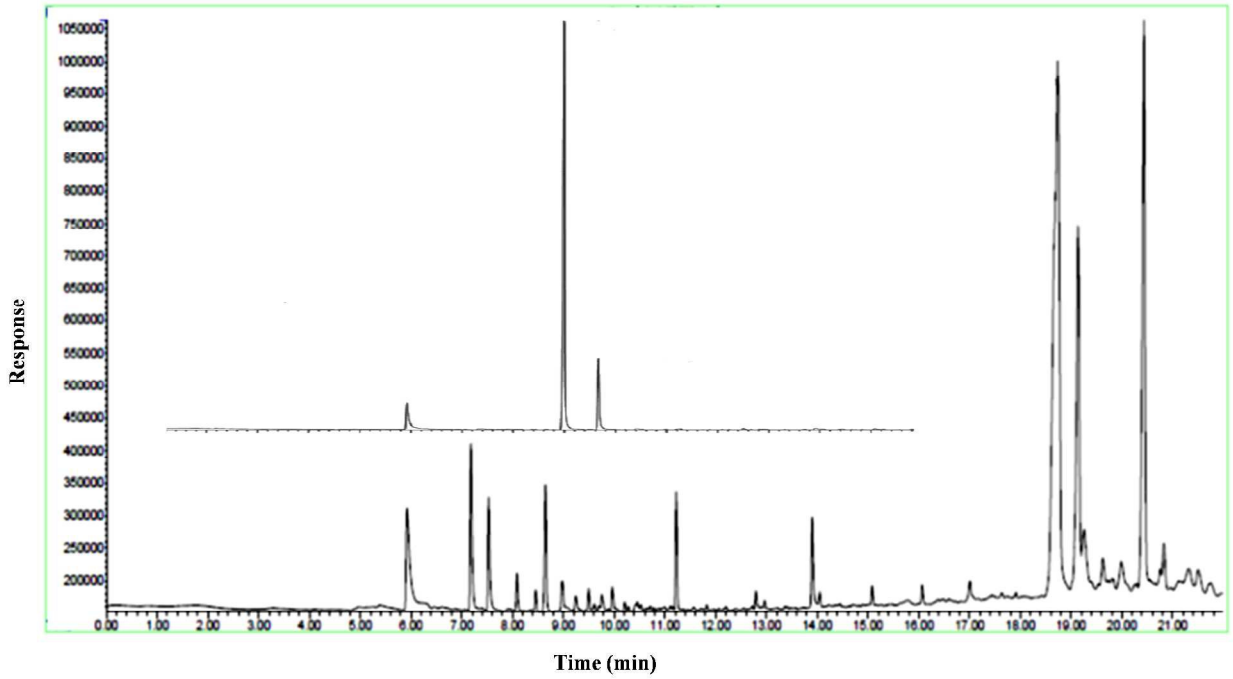


Fig. 5 GC-FID chromatograms of a sewage water sample from Boniek, Gachsaran (down) and a standard mixture of three phenolic compounds, 20 mg L^{-1} (up) under the optimized conditions (Ph, t_R=5.9 min; DCP, t_R = 8.9 min; CP, t_R = 9.8 min).

3.4. Comparison of the SBA-G1 and commercial PDMS/DVB fiber

The extraction efficiency of the proposed fiber was compared with that of a commercial PDMS/DVB fiber for the extraction of phenolic compounds. The SBA-G1 fiber contains polar amino groups, therefore it has a high tendency towards the adsorption of polar phenolic compounds. Fig. 6 shows that the peak heights of all the studied phenolic compounds are higher for the SBA-G1 fiber. This indicates an average of about three times better efficiency for the new fiber.

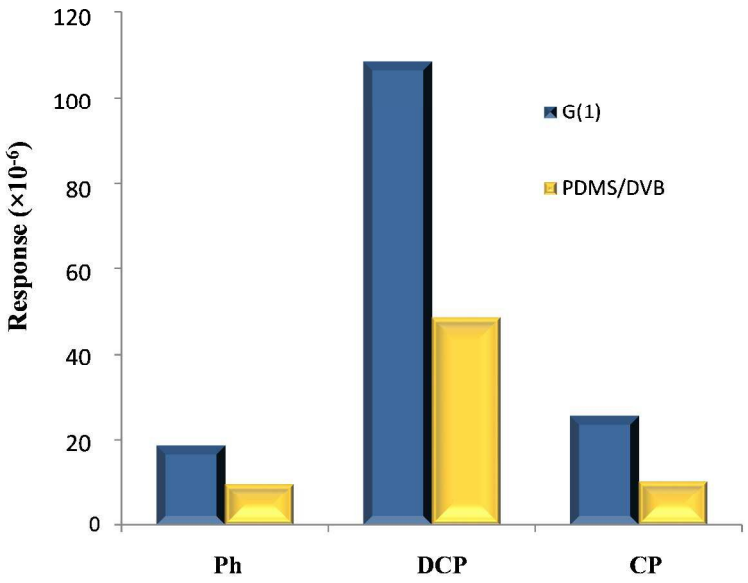


Fig.6 Comparison of SBA-G1 and PDMS/DVB fibers for the extraction of Ph, DCP and CP phenolic compounds (40 mg L^{-1}). Experimental conditions are as in experiment number 9 in Table 1.

3.5. Method evaluation

Analytical parameters of the quantitation of phenolic compounds including dynamic linear range, intercept, slope and correlation coefficient of calibration graph, repeatability (RSD%), fiber-to-fiber reproducibility, and detection limit with the proposed method are listed in Table 2. The linear range of the considered method was tested by extracting different aqueous standards with increasing concentrations. As shown in Table 2, the linear ranges were up to 70 μg mL^{-1} for Ph and CP and up to 80 μg ml^{-1} for DCP with R^2 values larger than 0.991. Limit of detections (LOD), calculated for 3σ, have been shown in Table 3. The results of table 2 indicate that the detection limits and the linear ranges found in the present work are better than those found in other researches which used the same method for fiber coating.[23,25] The linear ranges in this work are wider than aforementioned studies.[23,25,26]

3.6. Application to field samples

The SBA-G1 fiber was applied to the determination of Ph; DCP and CP in several water samples. The samples were a tap water sample (Ahwaz, iran), a water sample from oil well no.166 of Masjedsoleyman, Iran and three effluent samples from Golestan hospital sewage, Maroon 5 oil desalting unit (Ahwaz) and Boniek oil desalting unit (Gachsaran). Table 3 shows the satisfied results obtained for the field samples.

4. Conclusion

The new SBA-G1 fiber was successfully applied for the determination of phenolic compounds in water samples by a HS-SPME-GC method. The prepared SBA-G1 fiber, in comparison with commercial fibers, showed several advantages such as its inexpensive and easy preparation, robustness, porous structure and strong adhesion of the coating to the stainless steel wire.In comparison with other works (Table 4), the proposed fiber showed a wider linear range, lower detection limits and better repeatabilities (lower RSD%).

Acknowledgements

The financial support of the Ahwaz Jundishapur University of Medical Sciences and the Lorestan University are gratefully acknowledged. Also, A. Zaiadi is acknowledged for GC studies.

Table 2 Analytical parameters for the HS-SPME-GC-FID of the phenolic compounds extracted by the SBA-G1 fiber.

Sample	Linear range ($\mu g\ ml^{-1}$)	Slope	Intercept	R^2	LOD ($\mu g\ ml^{-1}$)	RSD[a] (%) (N=6)	
						One fiber	Fiber-to-fiber
Ph	0.02-70	3.8×10^5	2.2×10^6	0.991	0.0063	4.6	12.8
DCP	0.001-80	2.0×10^6	1.0×10^7	0.994	0.0004	6.0	11.9
CP	0.008-70	5.8×10^5	2.0×10^6	0.994	0.0024	5.6	11.0

[a] For solution containing 40 $\mu g.ml^{-1}$ Ph, DCP, CP

Table 3 Comparison of analytical parameters of the proposed HS-SPME-GC-FID method with some other works.

Analytical parameters	Present work[a]	Ref.23[b]	Ref. 25[c]	Ref.26[d]
Detection limit ($ng\ mL^{-1}$)	0.4-6.3	1-13	1.5-68	0.02-0.05
Linear range ($\mu g\ mL^{-1)}$	0.001-80	10-200	10-800	0.0005-0.2
RSD(%)	4.6-6.0	6.5-9.8	8.4-15	6.8-9.2

[a] SBA-G1 fiber and FID detection
[b] HPTES-SBA-15 fiber and MS detection
[c] CMK-3 fiber and MS detection
[d] TMSPA/OH-PDMS fiber and MS detection

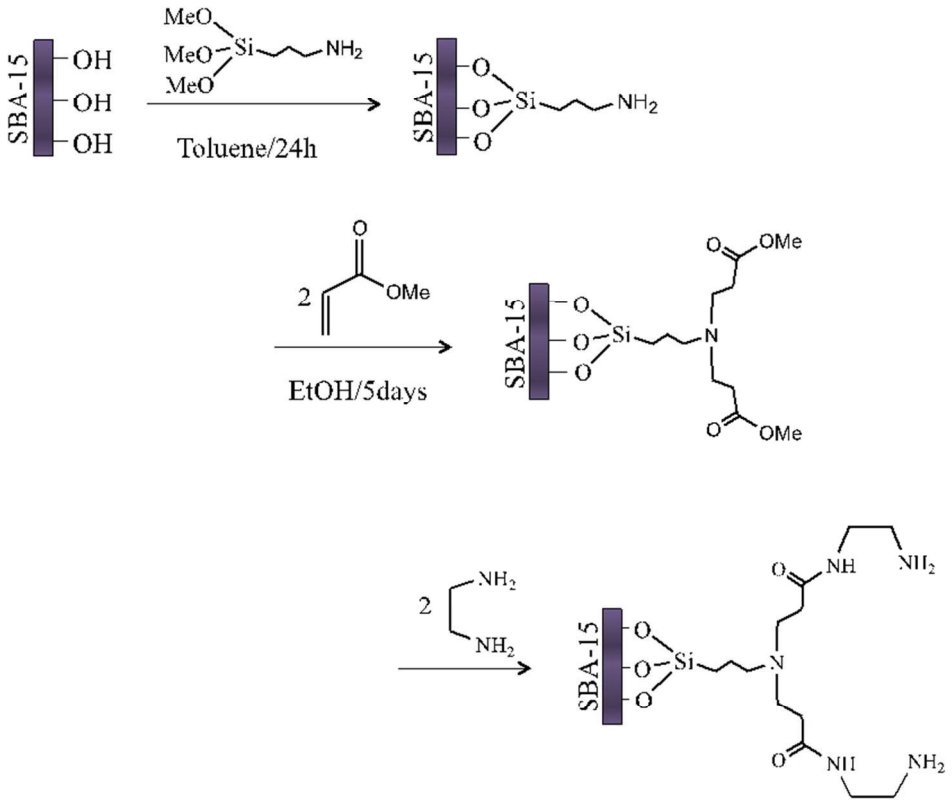
Table 4 The results obtained for the analysis of the water and sewage water samples by the proposed method, before and after addition of 10 mg L^{-1} Ph, DCP and CP under the optimized conditions.

Sample	Befor the addition[a]			After the addition[a]		
	Ph	DCP	CP	Ph	DCP	CP
Tap water (Ahwaz)	N.D[b]	N.D	N.D	10.31(0.4)	10.27(0.38)	9.88(0.29)
Water from oil well No.166	2.72(0.22)	0.10(0.013)	0.64(0.066)	11.62(0.38)	11.32(1.22)	11.11(0.26)
Golestan hospital sewage	1.25(0.09)	N.D	N.D	10.97(1.06)	9.81(0.83)	10.56(0.84)
Maroon 5 oil desalination unit	2.72(0.21)	N.D	N.D	13.49(0.8)	10.88(0.57)	10.87(0.59)
Boniek oil desalination unit	4.39(0.56)	0.1(0.01)	N.D	16.02(0.71)	11.07(1.02)	10.87(0.59)

[a] The figures within parentheses are standard deviations for three replicates.
[b] N.D., stands for not detected

References

1 J. W. Moore and S. Ramamoorthy, *Acta Hydrochim. Hydrobio.*, 1986, **14**, 198.
2 C. M. Santana, Z. S. Ferrera, M. E. Torres Padrón and J. S. Rodríguez, *Molecules,* 2009, **14**, 298.
3 D. Martínez, E. Pocurull, R. M. Marcé, F. Borrull and M. Calull, *J. Chromatogr. A,*1996, **734**, 367.
4 G. Ohlenbusch, M. U. Kumke and F. H. Frimmel, *Sci. Total Environ.,*2000, **253**, 63.
5 A. B. McKague, *J. Chromatogr. A,* 1981, **208**, 287.
6 K. O. Lupetti, F. R. P. Rocha and O. Fatibello-Filho, *Talanta,*2004, **62**, 463.
7 Z. Liu, Y. Liu, H. Yang, Y. Yang, G. Shen and R. Yu, *Anal. Chim. Acta*,2005, **533**, 3.
8 H. Bagheri, A. Mohammadi and A. Salemi, *Anal. Chim. Acta*, 2004, **513**, 445.
9 T. Heberer and H.-J. Stan, *Anal. Chim. Acta*, 1997, **341**, 21.
10 I. Rodríguez, M. P. Llompart and R. Cela, *J. Chromatogr. A,* 2000, **885**, 291.
11 C. L. Arthur and J. Pawliszyn, *Anal. Chem.,*1990, **62**, 2145.
12 J. L. Martínez Vidal, P. Plaza-Bolaños, R. Romero-González and A. Garrido Frenich, *J. Chromatogr. A,* 2009, **1216**, 6767.
13 H. H. Jeleń, M. Majcher and M. Dziadas, *Anal. Chim. Acta*, 2012, **738**, 13.
14 H. Kataoka, *Anal. Bioanal. Chem.,* 2010, **396**, 339.
15 F. Pragst, *Anal. Bioanal. Chem.,* 2007, **388**, 1393.
16 J.-g. Hou, Q. Ma, X.-z. Du, H.-l. Deng and J.-z. Gao, *Talanta,* 2004, **62**, 241.
17 M. Anbia and S. Irannejad, *Anal. Methods.,*2013, **5**, 1596.
18 P. Hashemi, A. Badiei, M. Shamizadeh, G. M. Ziarani and A. R. Ghiasvand, *J. Chin. Chem. Soc.,*2012, **59**, 727.
19 M. A. Farajzadeh and N. A. Rahmani, *Talanta,* 2005, **65**, 700.
20 D. A. Tomalia and Y. Cheng, *Dendrimer-based drug delivery systems: from theory to practice*. John Wiley & Sons, 2012, Vol. **18**.
21 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc., 1*998, **120**, 6024.
22 D. W. Mitchell, *The Mathematical Gazette,* 2004, **88**, 142.
23 P. Hashemi, M. Shamizadeh, A. Badiei, P. Z. Poor, A. R. Ghiasvand and A. Yarahmadi, *Anal. Chim. Acta*, 2009, **646**, 1.
24 P. Hashemi, A. Yarahmadi, K. Azizi and B. Sabouri, *Chromatographia.,*2008, **67**, 253.
25 A. Rahimi, P. Hashemi, A. Badiei, P. Arab and A. R. Ghiasvand, *Anal. Chim. Acta*, 2011, **695**, 58.
26 H. Bagheri, E. Babanezhad and F. Khalilian, *Anal. Chim. Acta*, 2008, **616**, 49.



Preparation of SBA-15 Silica-Supported dendrimer
235x190mm (96 x 96 DPI)